UNIT 12
Aldehydes, Ketones and Carboxylic Acids

Points to Remember

Nomenclature

Aldehydes and Ketones

Common names: replace -e from alkyl group by aldehyde or ketone e.g. CH_3– CHO is acetaldehyde

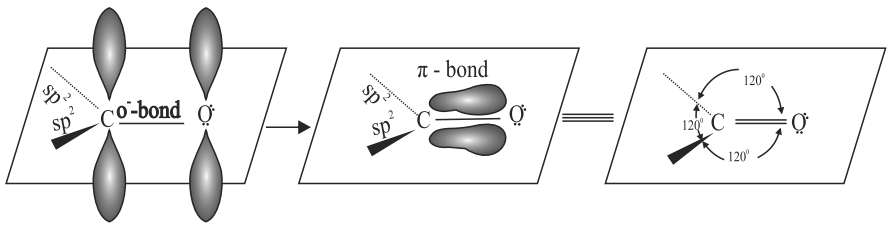
IUPAC names: replace -e by -al for aldehydes and - one for ketones e.g. CH_3–CHO is ethanal and CH_3–$COCH_3$ is propanone.

Carboxylic Acids

Common names: end with-oic acid e.g. CH_3CH_2COOH is propanoic acid

IUPAC names: replace -e in corresponding alkanes by -oic acid e.g. CH_3CH_2COOH is propanoic acid.

Structure of Carbonyl group



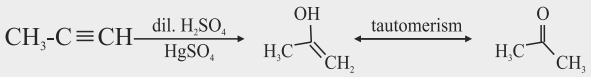
Carbonyl carbon is sp^2 Hybridised and planar in shape, with one sigma and one π bond between C=O

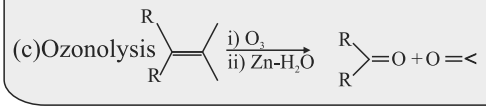
General Methods:

(a) **Contolled oxidation/dehydrogenation of primary and secondary aicohols**

Primary alcohol gives aldehyde, secondary gives ketones, tertiary undergoes dehydration

(b) **Hydration of Alkynes**



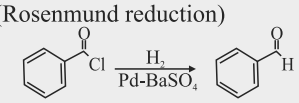


Preparation of Aldehydes, Ketones and Carboxylic Acids

Aldehydes:

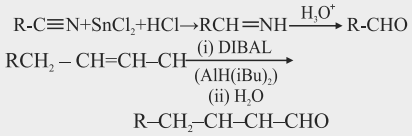
(a) From acyl chloride (acid chloride)

(Rosenmund reduction)

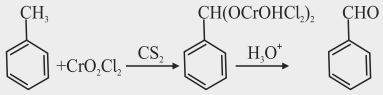


(b) From nitriles and esters

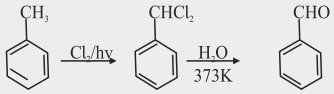
(Stephen reaction)



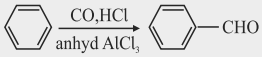
(c) From hydrocarbons (Etard Reaction)



(d) (Side chain chlorination)



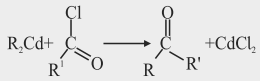
(e) (Gatterman-Koch reaction)



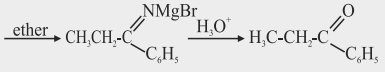
Ketones:

(a) From acyl chlorides

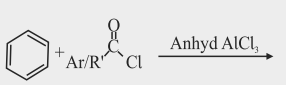
2 R-MgX + $CdCl_2 \rightarrow R_2Cd + Mg(X)Cl$



(b) from nitriles $CH_3CH_2CN + C_6H_5MgBr$

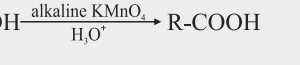


(c) From benzene (Friedel-craft acylation)

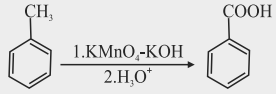


Carboxylic Acids:

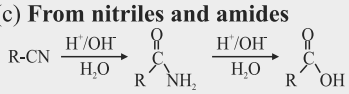
(a) **From Primary alcohol/aldehyde**



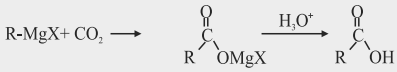
(b) **From alkylbenzene**



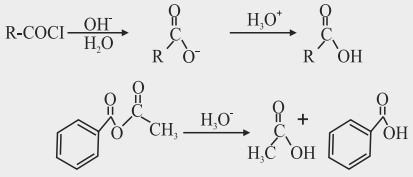
(c) **From nitriles and amides**



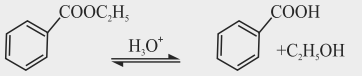
(d) **From Grignard reagent**



(e) **From acyl halides and anhydrides**

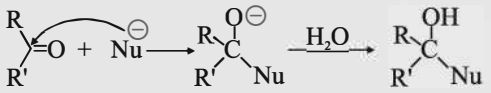


(f) **From esters**



Reactions of Aldehydes, Ketones and Carboxylic Acids

Aldehyde and Ketones
Nucleophilic Addition reaction



(a) $\rangle C=O + HCN \longrightarrow$ Cyanohydrin (b) $\rangle C=O + NaHSO_3 \longrightarrow$

(c) $RCHO + R'OH \longrightarrow R-C(O^-)(OH)-OR^1 \xrightarrow{R'OH} R-CH(OR')_2$ Acetal (d) $\rangle C=O + NH_2-Z \longrightarrow$ (Ammonia derivatives) $\longrightarrow -C=NZ + H_2O$

1. Reduction: Aldehydes and ketones converts to primary and secondary alcohols respectively in presence of $NaBh_4/LiAlh_4$. $NaBh_4$ selectively reduces aldehydes and ketones only in presence of other carbonyl containing functional groups including carboxylic acids, esters etc.

   Clemmensen reduction:

   $\rangle C=O \xrightarrow[HCl]{Zn-Hg} \rangle CH_2$

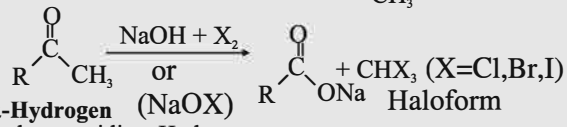
   Wolf - Kishner Reduction:

   $\rangle C=O \xrightarrow{H_2N-NH_2} \rangle C=NNH_2 \xrightarrow[\text{Ethylene glycol}]{KOH} \rangle CH_2$

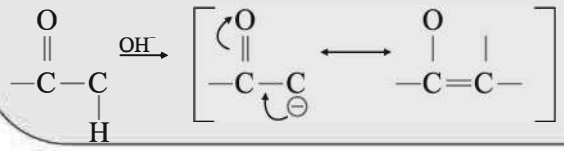
2. Oxidation:
   (a) Tollens' Test.
   $R\text{-}CHO + 2\,[Ag(NH_3)_2]^+ + OH^- \longrightarrow RCOO^- + 2\,Ag$ (silvery mirror) $+ 2\,H_2O + 4\,NH_3$

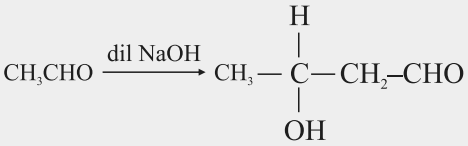
   (b) Fehling's Test
   $R\text{-}CHO + 2\,Cu^{2+} + 5\,OH^- \longrightarrow R\text{-}COO^- + Cu_2O$ (Red ppt) $+ 3\,H_2O$

   (c) Haloform reaction: given by methyl ketones 

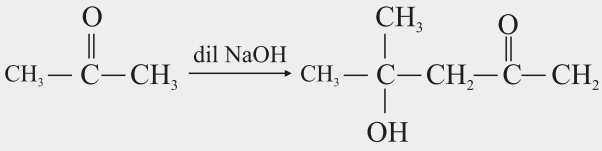


3. **Reaction due to α-Hydrogen**
   Aldol condensation due to acidic a-Hydrogen





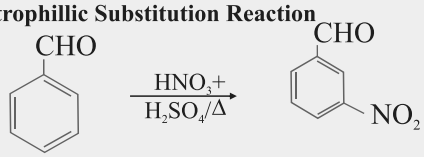
β-hydroxy aldehyde



β-hydroxy ketone.

4. **Cannizzaro Reaction**
Aldehyde don't have α-Hydrogen

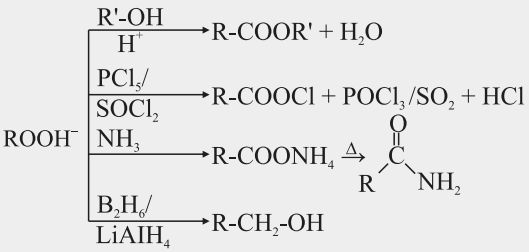
5. **Electrophillic Substitution Reaction**

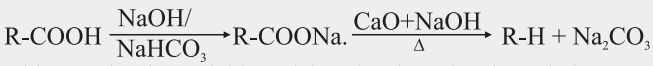


Carboxylic Acids

Acidic nature : $R\text{-}COOH + NaHCO_3 \rightarrow RCOONa + H_2O + CO_2$ (Brisk effervescence)
(Chemical test for carboxylic acid)

Formation of carboxylic acid derivatives:

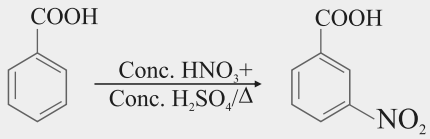




This reaction is useful in redcing the size of carbon chain

Hell-Volhard Zelinsky reaction: $R\text{-}CH_2\text{-}COOH \xrightarrow[ii)\ H_3O^+]{i)\ X_2/\ Red\ P} R\text{-}\underset{X}{\overset{H}{C}}\text{-}COOH$
substitution takes place at α carbon

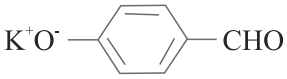
Electrophillic Substitution Reaction

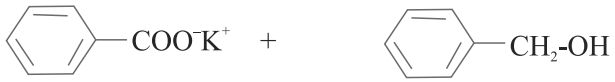


OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. Which product is formed when benzaldehyde is treated with concentrated KOH solution?

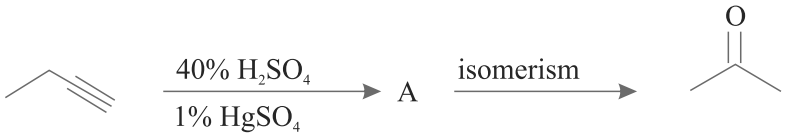
(a) 

(b) 

(c) 

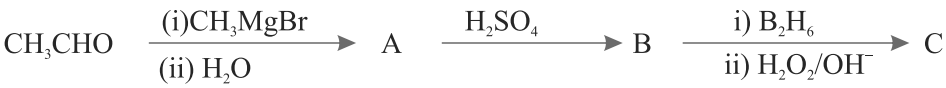
(d) 

2. 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
(d) Prop-1-en-2-ol, tautomerism

3. Compound A and C in the following reaction are:-



(a) Identical (b) Position isomer
(c) Functional group isomer (d) Optical isomer

4. Toluene 

the product 'C' is:-

(a) $C_6H_5CH_2OH$ (b) C_6H_5CHO

(c) C_6H_5COOH (d) $C_6H_5CH_3$

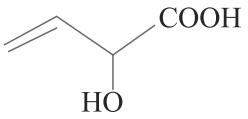
5. Among the following which has the lowest pk_a value:-

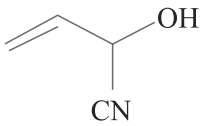
(a) CH_3COOH (b) HCOOH

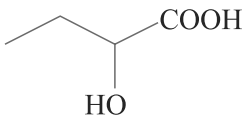
(c) $(CH_3)_2CHCOOH$ (d) CH_3CH_3OH

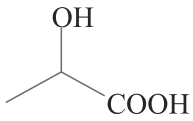
6. $CH_3CHO + HCHO \xrightarrow[\text{Heat}]{\text{dil.NaOH}} A \xrightarrow[H_3O^+]{HCN} B$

The structure of 'B' is:-

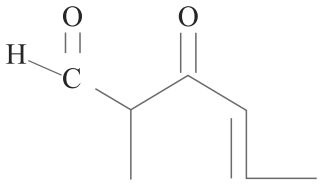
(a) 

(b) 

(c) 

(d) 

7. The IUPAC name of compound is:



(a) 2-Formylhex-2-ene-3-one

(b) 5-Methyl-4-oxohex-2-en-5-al

(c) 3-Keto-2-methylhex-5-enal

(d) 3-Keto-2-methylhex-4-enal

8. Which of the following reactions will not result in the formation of carbon-carbon bond?

(a) Cannizzaro reaction (b) Wurtz reaction

(c) Friedel Crafts reaction (d) Reimer-Tiemann reaction

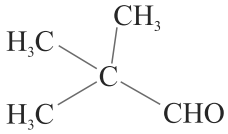
9. Reduction of aldehydes and ketones into hydrocarbon using zinc amalgam and conc. HCl is called.....

(a) Dow process (b) Cope reduction

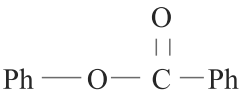
(c) Wolf-Kishner reduction (d) Clemmensons Reduction

10. Which of the following compound do not undergo aldol condensation?

(a) CH_3CH_2CHO (b) CH_3CHO

(c) CH_3COCH_3 (d) 

11. The treatment of following compound with NaOH yields.....as major product.



(i) Phenol (ii) Sodium phenoxide

(iii) Sodium benzoate (iv) Benzophenone

(a) I,II (b) III only

(c) I,III (d) IV only

12. Which of the following will undergo Cannizzaro reaction?

(a) Acetophenone (b) Propanone

(c) 2,2-Dimethylpropanal

(d) Both acetophenone and 2,2-Dimethylpropanal

13. Which of the following neither gives Fehling's test nor iodoform test?

(a) Benzaldehyde (b) Ethanal

(c) Propanone (d) Acetophenone

14. Which reagent(s) is/are best for following conversion?

CH_3-CH=CH-CN $\rightarrow$ CH_3-CH=CH_3-CHO

(a) H_2, Pd-$BaSO_4$ (b) DiBAL-H

(c) H_2/Ni (d) $NaBH_4$

15. Benzophenone can be obtained by the reaction of -

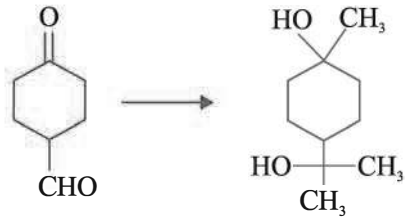
(a) Benzoyl chloride + Benzene + anhy. $AlCl_3$

(b) Benzoyl chloride + Diphenyl anion

(c) Benzoyl chloride + Phenyl magnesium chloride

(d) Benzene + carbon monoxide+$ZnCl_2$

16. Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution?
    (a) Butan-l-ol
    (b) Butan-2-ol
    (c) Both of these
    (d) None of these
17. Reaction of alkene **X** with with O_3 followed by H_2O_2/ Zn forms propanone and ethanal. Alkene **X** is-
    (a) Pent-3-ene
    (b) Pent-2-ene
    (c) 2-Methylbut-2-ene
    (d) 2,2-Dimethylprop-1-ene
18. The correct sequence of the following conversion is



    (a) CH_3MgBr, $[Ag(NH_3)_2]^+OH$, H^+/CH_3OH
    (b) $[Ag(NH_3)_2]OH$, CH_3MgBr, H^+/CH_3OH
    (c) $[Ag(NH_3)_2]^+OH$, H^+/CH_3OH, CH_3MgBr
    (d) CH_3MgBr, H^+/CH_3OH, $[Ag(NH_3)_2]OH$
19. When 2-hydroxybenzoic acid is distilled with zinc dust it gives
    (a) Phenol
    (b) Benzoic Acid
    (c) Benzaldehyde
    (d) A polymeric product
20. Tollens' reagent forms silvery mirror when it reacts with:
    (a) CH_3CHO
    (b) CH_3COOH
    (c) CH_3COCH_3
    (d) CH_3OH

II FILL IN THE BLANKS

1. Tollens' reagent is chemically known as .....
2. Reaction of phthalic acid with ammonia followed by strong heating gives.....
3. Acetyl chloride may be converted into acetaldehyde by .....reduction.
4. Groups like nitro- and chloro- .....acidity of aromatic carboxylic acids.
5. Phenol and benzoic acid can be distinguished by the reaction with.....
6. On reaction of propanal with Fehling's reagent red precipitate of ..... is formed.
7. Reaction of Grignard reagent with .....results into formation of primary alcohols.
8. Lower aldehydes are soluble in water due to.....interactions with water molecules.
9. DIBAL-H is used to reduce nitriles or esters to corresponding.....
10. Reaction of ethyl magnesium bromide with carbon dioxide followed by acidification gives .....

III ASSERTION REASON TYPE QUESTIONS

The question given below consist of an Assertion and Reason. Use the following key to choose the appropriate answer.

(a) Assertion and reason both are correct and reason is the correct explanation of the assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

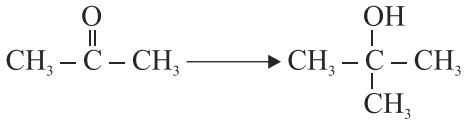
(c) Assertion is correct statement but reason is wrong statement.

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

1. **ASSERTION:** Reaction of Pentanoic acid with Cl_2/ Red P followed by water gives 2-chloropentanoic acid.
   REASON: The substitution takes places at α-carbon.
2. **ASSERTION:** Carboxylic acids have higher boiling point than aldehydes and ketones of comparable molar masses.
   REASON: Due to strong intermolecular H-bonding in carboxylic acids.
3. **ASSERTION:** Nitration of benzoic acid gives *m*-nitrobenzoic acid.
   REASON: Carboxyl group increases electron density on ring.
4. **ASSERTION:** Benzaldehyde undergoes Cannizzaro reaction.
   REASON: It contains one α-hydrogen.
5. **ASSERTION :** Formaldehyde is a planar molecule.
   REASON : It contains sp^2 hybridised carbon atom.
6. **ASSERTION :** Compounds containing -CHO group are easily oxidised to corresponding carboxylic acids.
   REASON : Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$.
7. **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.
8. **ASSERTION :** Aromatic aldehydes and formaldehyde undergo Cannizaro reaction.
   REASON : Aromatic aldehydes are almost as reactive as formaldehyde.
9. **ASSERTION :** Aldehydes and ketones, both reacts with Tollens' reagent to form silvery mirror.
   REASON : Both, aldehydes and ketones contain a carbonyl group.
10. **ASSERTION:** Ketones are oxidised under drastic conditions.
    REASON: Oxidation of ketones gives carboxylic acids having carbons lesser than parent molecule.

IV ONE WORD ANSWER TYPE QUESTIONS

1. Name the product formed by addition of one equivalent of monohydric alcohol to aldehydes.
2. Name the product formed by the reaction of benzene with CO, HCl in presence of anhyd. $AlCl_3$
3. Which reagent is used to convert carboxylic acid to corresponding alcohol?
4. Which reaction is carried out to reduce the number of carbons from carboxylic acids?
5. Which ester will be formed by the reaction of methanol and propanoic acid?
6. Write the major product formed by the reaction of benzaldehyde and acetophenone.
7. Which reagent will be best to convert ketone to corresponding alcohol in presence of carboxylic acid?
8. Which reagent converts carboxylic acids into corresponding anhydrides?
9. Name the carboxylic acid formed by reaction of cyclohexene with $KMnO_4$-H_2SO_4 and heating.
10. Which out of each pair is expected to be stronger acid ?
    (a) CH_3COOH or HCOOH
    (b) $CH_2(Cl)COOH$ or $CH_2(Br)COOH$
11. Name the test which can be used to distinguish between pentan-2-one and pentan-3-one .
12. Predict the products when cyclohexancarbaldehyde reacts with zinc analgam and HCl.
13. Write the catalyst used in Rosenmund's reduction
14. Name the reagent used in following reaction



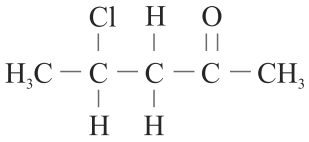
15. Out of CH_3CHO and CH_3COCH_3 which one is more reactive towards HCN.

VERY SHORT ANSWER TYPE QUESTIONS (1 Marks)

1. Arrange the following compounds in increasing order of their acidic strengths:
$(CH_3)_2CHCOOH, CH_3CH_2CH(Br)COOH, CH_3CH(Br)CH_2COOH$

Ans. $(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

2. Draw the structure of the compound whose IUPAC name is 4-chloropentan-2-one.

Ans.


3. Which type of aldehyde can undergo Cannizzaro reaction?

Ans. Aromatic and aliphatic aldehydes which do not contain α-hydrogen.

4. Name the aldehyde which does not give Fehling's test.

Ans. Benzaldehyde.

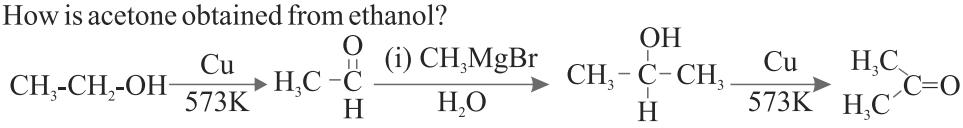
5. Arrange the following in order of their increasing reactivity towards HCN:
$CH_3CHO, CH_3COCH_3, HCHO, C_2H_5COCH_3$

Ans. $C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

6. Arrange the following compounds in increasing order of their boiling point:
$CH_3CHO, CH_3CH_2OH, CH_3OCH_3, CH_3CH_2CH_3$

Ans. $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

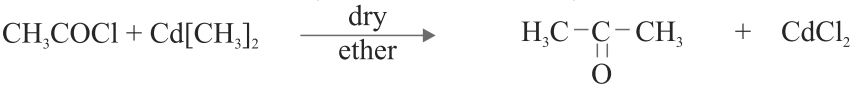
8. How is acetone obtained from ethanol?

Ans.


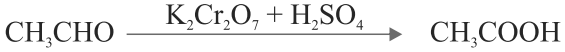
9. Why do aldehydes and ketones have lower boiling point than alcohols?

Ans. Due to presence of associated molecules with H-bonding in alcohols.

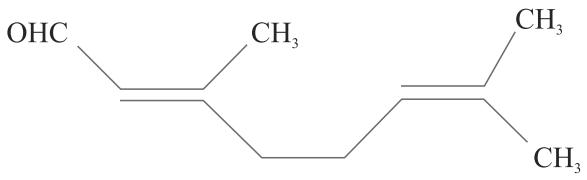
10. Write reaction between acetyl chloride and dimethyl cadmium.

Ans.


11. What happens when CH_3CHO is treated with $K_2Cr_2O_7$ in presence of H_2SO_4?

Ans.


12. Write IUPAC name of following compound:



Ans. 3,7-Dimethylocta-2,6-dien-1-al

13. Give balanced equation and name of products when CH_3COOH is treated with PCl_5?

Ans. $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

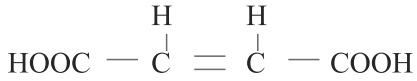
14. What product is obtained when ethyl benzene is oxidized with alkaline $KMnO_4$ followed by acidification.

Ans. Benzoic acid (C_6H_5COOH) is obtained.

15. CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN. Give reason.

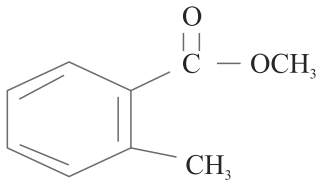
Ans. Due to presence of two -CH_3 group in CH_3COCH_3 which shows more +I effect and steric hindrance than CH_3CHO.

16. Write IUPAC names of the following compound:



Ans. But-2-ene-1,4-dioic acid

17. Write the IUPAC name of following molecule:



Ans. 2-Methylmethylbenzoate

18. Why does benzoic acid does not undergo Friedel-Crafts reaction?

Ans. -COOH group in is an electron withdrawing group, which deactivates the benzene ring strongly and hence electrophilic substitution becomes difficult.

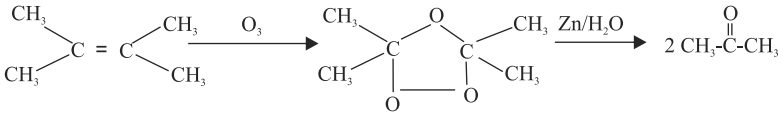
19. Benzaldehyde gives a positive test with Tollens' reagent but not with Fehling's and Benedict's solutions. Why ?

Ans. It is due to stronger oxidising nature of Tollens' reagent as compared to Fehling's and Benedict's solution and cannot oxidise benzaldehyde to benzoic acid. In general, all these three can oxidise aliphatic aldehydes.

20. Write the chemical equation for Wolf-Kishner Reduction.

Ans. $CH_3CHO \xrightarrow{NH_2NH_2} CH_3\text{-}C{=}N\text{-}NH_2 \xrightarrow[\text{Ethylene glycol}]{KOH/} CH_3\text{-}CH_3 + N_2$

21. Name alkene which on ozonolysis give acetone as a product

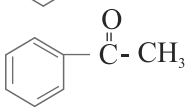


2, 3-Dimethylbut-2-ene

22. Give reason why hydrazones of RCHO and ketone are not produced in strongly acidic medium ?

Ans. In acidic medium, $\ddot{N}H_2\ddot{N}H_2$ get protonated and will not act as $Nu^{\ominus}$.

23. Complete the reaction

Ans. 

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

1. How will you convert:

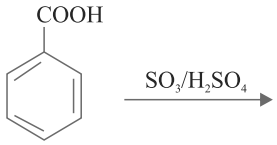
   (i) $C_2H_2 \rightarrow CH_3COOH$

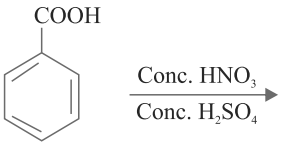
   (ii) $C_6H_5CONH_2 \rightarrow C_6H_5COOH$

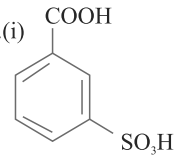
Ans. (i) $C_2H_2 \xrightarrow[HgSO_4]{H_2SO_4} CH_3CHO \xrightarrow[dil.\ H_2SO_4]{KMnO_4} CH_3COOH$

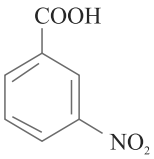
(ii) $C_6H_5CONH_2 \xrightarrow[\Delta]{OH^-/H^+} C_6H_5COOH + NH_3 + NaCl$

2. Complete the following:

(i) 

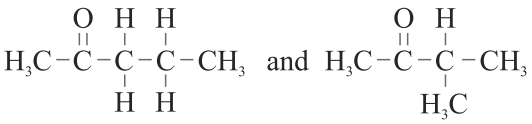
(ii) 

Ans.(i) 

(ii) 

3. An organic compound 'X' has molecular formula $C_6H_{10}O$. It does not reduce Fehling's solution but forms a bisulphite compound. It also gives positive Iodoform test. What are possible structure of 'X'? Explain.

Ans. 'X' gives positive test with Iodoform. It is methyl ketone.



are possible structures of the compound.

4. Give the chemical test to distinguish between:

   (i) CH_3CHO and $H_3C-\overset{\overset{O}{\|}}{C}-CH_3$

   (ii) CH_3CHO and C_6H_5CHO

Ans. (i) CH_3CHO produce silver mirror with Tollens' reagent.

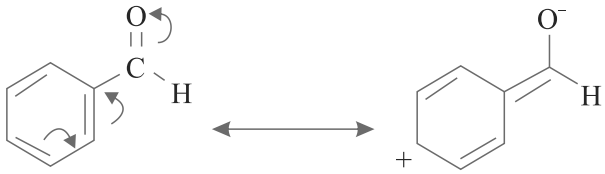
$CH_3CHO + 2AgNO_3 + 2NH_4OH \rightarrow CH_3COOH + 2Ag + 2NH_4NO_3 + 2H_2O$

(ii) CH_3CHO gives brick red ppt. in Fehling test

$CH_3CHO + 2CuSO_4 + 4NaOH \rightarrow CH_3COOH + \underset{\text{Brick red ppt.}}{Cu_2O} + Na_4SO_4 + 2H_2O$

5. Is benzaldehyde more reactive or less reactive towards nucleophilic addition reactions than propanal ? Explain your answer.

Ans. Carbon atom of carbonyl is C_6H_5CHO is less reactive than that of propanal. C_6H_5CHO is less polar due to resonance.

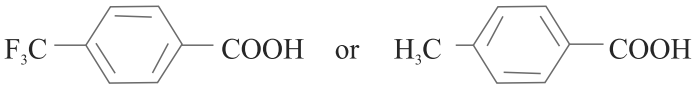


6. Which acid of each pair shown here would you expect to be stronger ?

(i) CH_3CO_2H or CH_2FCO_2H

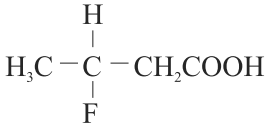
(ii) CH_2FCO_2H or CH_3ClCO_2H

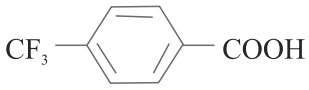
(iii) $CH_2FCH_2CH_2CO_2H$ or $CH_3CHFCH_2CO_2H$

(iv) 

Ans. (i) FCH_2COOH

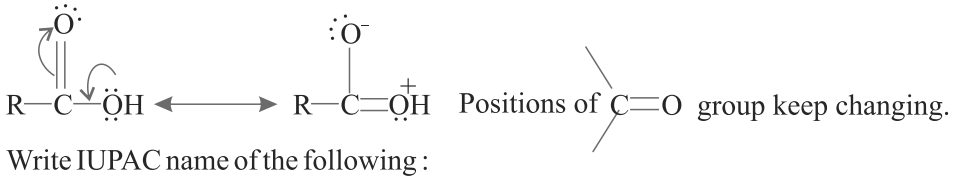
(ii) CH_2FCOOH

(iii) 

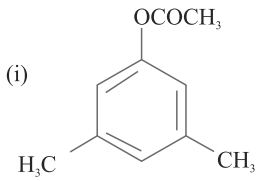
(iv) 

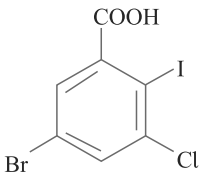
7. Carboxylic acids do not give reactions of aldehydes and ketones why?

Ans. It is due to resonance



8. Write IUPAC name of the following :

(i) 

(ii) 

Ans. (i) 3,5-dimethylphenylethanoate.

(ii) 5-Bromo-3-chloro-2-iodobenzoic acid.

9. Give chemical test to distinguish between following pair of compounds:

(i) C_2H_5OH and CH_3CHO

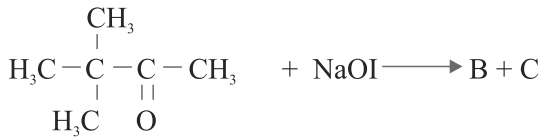
(ii) $C_6H_5COCH_3$ and $C_6H_5CH_2CHO$

Ans. (i) CH_3CHO gives silvery mirror with Tollens' reagent while C_2H_5OH does not.

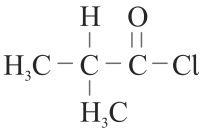
(ii) Acetophenone will give yellow ppt. of iodoform while $C_6H_5CH_2CHO$ will not.

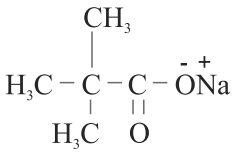
10. Complete the following reactions by identifying A, B and C :

(i) $A + Hydrogen(g) \xrightarrow{Pd/BaSO_4} (CH_3)_2CHCHO$

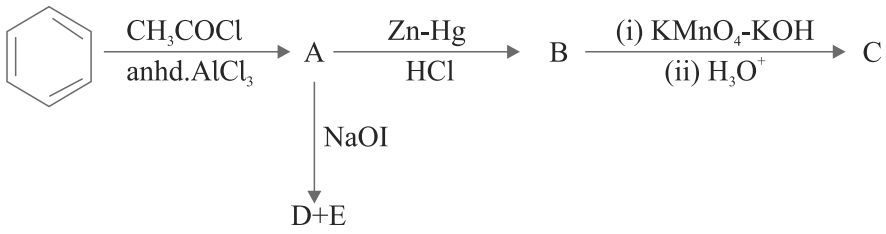
(ii)  $+ NaOI \longrightarrow B + C$

Ans.

(i) 'A' is 

(ii) 'B' is CHI_3 and 'C' is 

11. Write the structures of A,B,C,D and E in the following reactions:



Ans. A=$C_3H_5COCH_3$

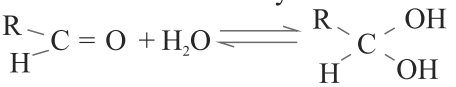
B=$C_6H_5CH_2CH_2$

C=C_6H_5COOH

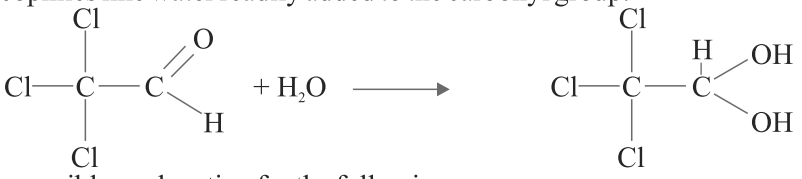
D=C_6H_5COONa

E=CHI_3

12. Aldehydes usually do not form stable hydrates but chloral normally exists as chloral hydrate. Give reason.

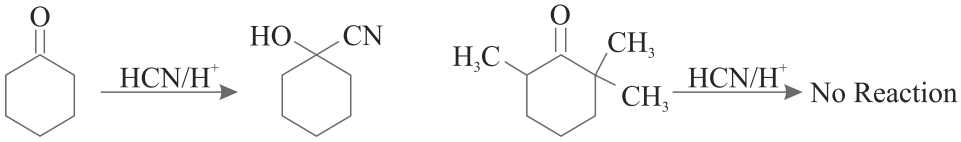


Ans. In case of aldehyde reaction is reversible.
In case of $CC1_3CHO$, Cl atoms increases positive charge on carbonyl carbon. Therefore, weak nucleophiles like water readily added to the carbonyl group.

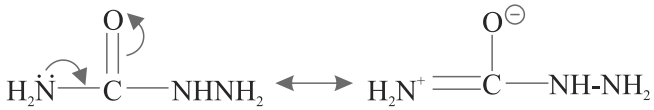


13. Give possible explanation for the following:
    (i) Cyclohexanone forms cyanohydrins in good yield but 2,2,6-trimethyl cyclohexanone does not.
    (ii) There are two - NH_2 groups in semicarbazide. However,only one is involved in formation of semicarbozone.

Ans. (i) Due to steric hindrance for CN^- at C=O due to 3-methyl groups at α-position.



(ii) Only one -NH_2 group attached to C=O is involved in resonance. As result electron density on these -NH_2 group decreases and hence does not act as nucleophile.



14. Convert the following in not more than two steps:
    (i) Benzoic acid to Benzadehyde
    (ii) Propanone to Propene

Ans. (i) $C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow[Pd\text{-}BaSO_4]{H_2} C_6H_5CHO$

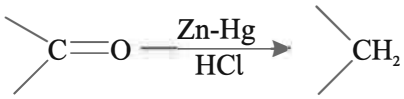
(ii) $CH_3COCH_3 \xrightarrow{NaBH_4} CH_3\text{–}\underset{\displaystyle OH}{\underset{|}{CH}}\text{–}CH_3 \xrightarrow{conc.\ H_2SO_4} CH_3\text{-}CH{=}CH_2$

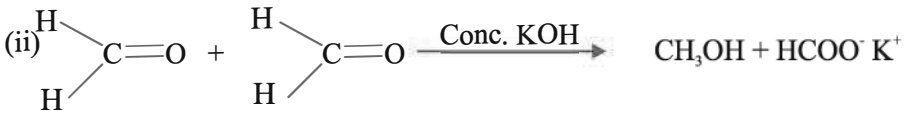
15. Write the reactions involved in the following reactions:

(i) Clemmensen reduction

(ii) Cannizzoro reaction

Ans.

(i) 

(ii) 

16. Convert the following

(i) Ethylbenzene to Benzoic acid

(ii) Ethanal to But-2-enal

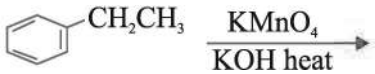
Ans.

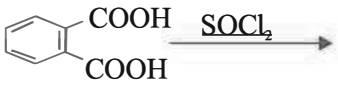
(i) $C_6H_5C_2H_5 \xrightarrow{K_2Cr_2O_7/H^+} C_6H_5COOH$

(ii) $2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CHCH_2CHO \xrightarrow{\text{heat}} CH_3\text{-}CH{=}CH\text{-}CHO$

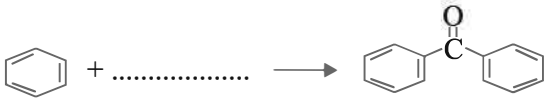
(OH)

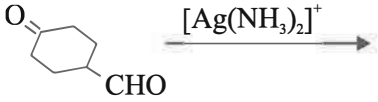
17. Predict the organic products of the following reactions:

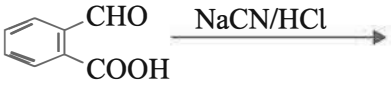
(i) 

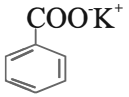
(ii) 

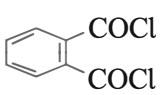
(iii) 

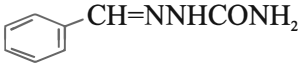
(iv) 

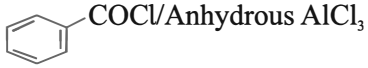
(v) 

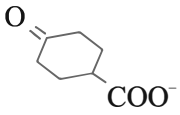
(vi) 

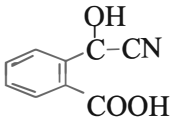
Ans. (i) 

(ii) 

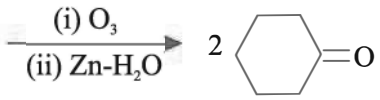
(iii) 

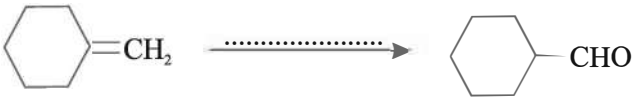
(iv) 

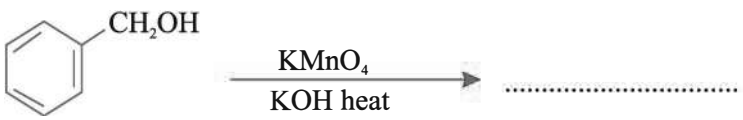
(v) 

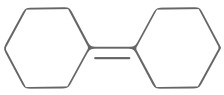
(vi) 

18. Complete the following as missing starting material, reagent or products:

(i)..... 

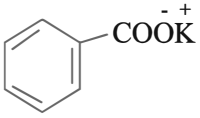
(ii) 

(iii) 

Ans.(i)  (ozonolysis)

1,2-Dicyclohexylethene

(ii) B_2H_6/THF,H_2O_2/(Hydroboration) OH^-, then PCC

(iii)  (Oxidation)

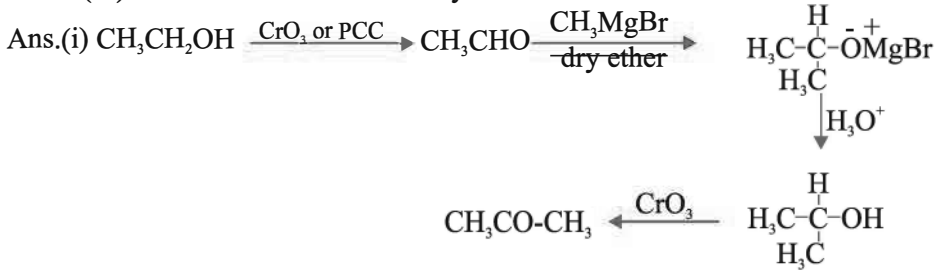
Patassium benzoate

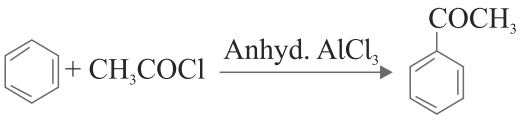
19. Mention the reactions involved for the following conversion.

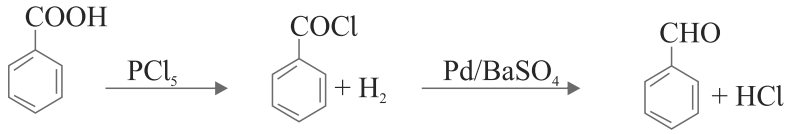
(i) Ethanol→Acetone

(ii) Benzene→Acetophenone

(iii) Benzoic acid → Benzaldehyde

Ans.(i) 

(ii) 

(iii) 

20. Give reason for the following:

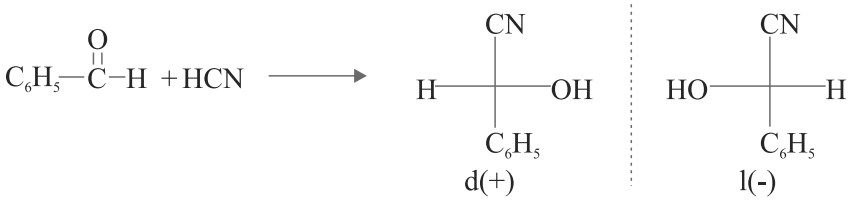
(i) Why are carboxylic acid more acidic than alcohol or phenols although all of then have H– atom attached to oxygen atom (—O—H)?

(ii) Treatment of C_6H_5CHO with HCN gives a mixture of two isomers which cannot be separated even by fractional distillation.

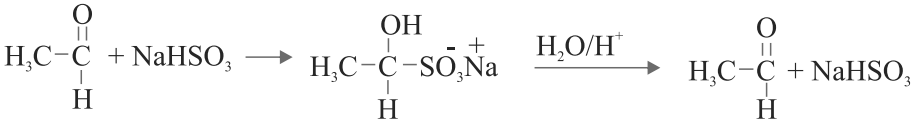
(iii) Sodium bisulphite is used for purification of ketones and aldehydes.

Ans. (i) Then is resonance in carboxylate ion, negative charge disperse over oxygen atom. But there is no resonance in alcohol(R–OH). Also in phenol less dispersal of negative change in phenolate ion as compare to carboxylate.

(ii) Due to two optical isomers fractional distillation is not possible.



(iii) Due to formation of addition compound of aldehydes and ketones with $NaHSO_3$ whereas impurities do not.



21. Write chemical tests to distinguish between following pair of compounds:

(i) CH_3CHO and C_6H_5CHO

(ii) C_6H_5-OH and CH_3COOH

(iii) Pentanal and Pentan-2-one

Ans. (i) CH_3CHO gives brick red ppt. with Fehling while C_6H_5CHO does not.

(ii) Phenol does not give brisk effervescence but CH_3COOH gives this test with $NaHCO_3$.

(iii) Pentanal forms silver mirror but Pentan-2-one does not. Or pentan-2-one give positive do form test

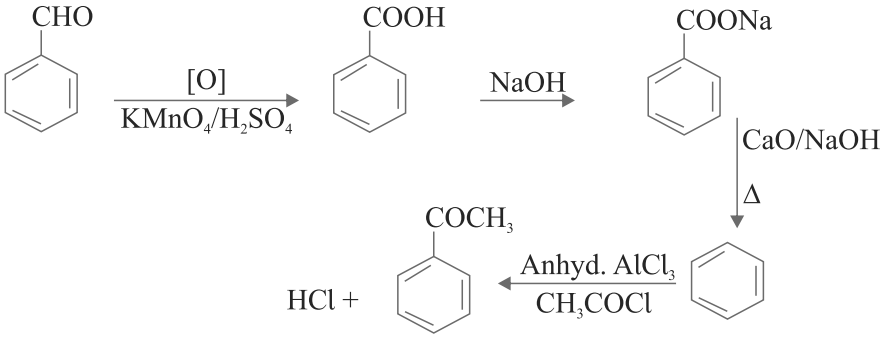
22. Convert the following:

(i) Benzaldehyde to Acetophenone

(ii) Malonic acid to Acetic acid

(iii) Acetaldehyde to Butan-2-ol

Ans. (i)



(ii) $H_2C(COOH)_2 \xrightarrow{heat} CH_3COOH + CO_2$

(iii) $2CH_3CHO \xrightarrow{OH^-} CH_3-CH(OH)-CH_2-CHO \xrightarrow[H_2SO_4/\Delta]{Conc.} H_3C-C(H)=C(H)-CHO \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$ (Butanol)

LONG ANSWER TYPE QUESTIONS (5 Marks)

1. Write chemical reaction to perform the following conversion:

(i) Butan-1-ol to Butanoic acid

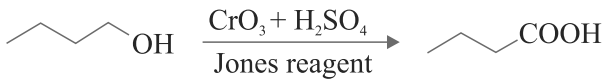
(ii) Benzyl alcohol to Phenylethanoic acid

(iii) 3-Nitrobromobenzene to 3-Nitrobenzoic acid

(iv) 4-Methylacetophenone to Terephthalic acid

(v) Cyclohexene to Hexane-1,6 dioic acid

Ans. (i)



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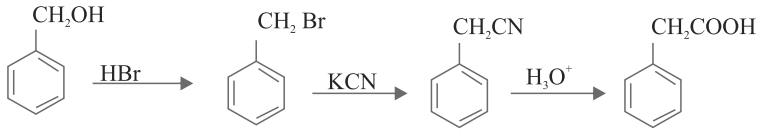

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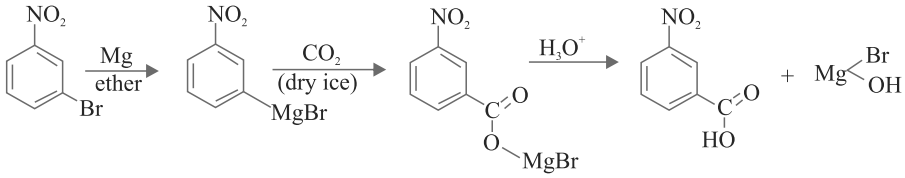

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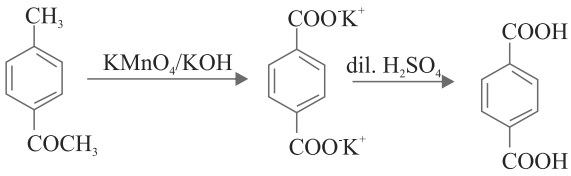

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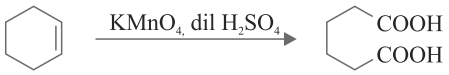
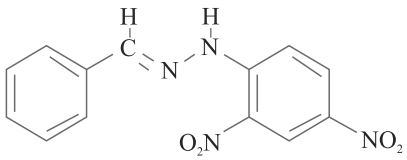


2. Draw the structure of the following derivatives:
   (i) 2,4-Dinitrophenylhydrazone of C_6H_5CHO
   (ii) Cyclopropanone oxime
   (iii) Acetaldehyde Dimethylacetal
   (iv) Semicarbazone of Cyclobutanone
   (v) Ethylene ketal of Hexan-3-one
   (vi) Methylhemiacetal of formaldehyde

Ans. (i)



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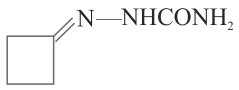
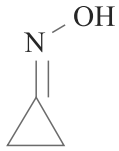
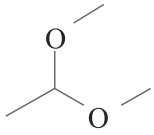
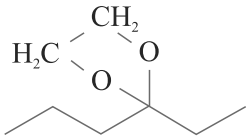
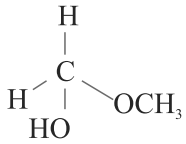


(ii) 

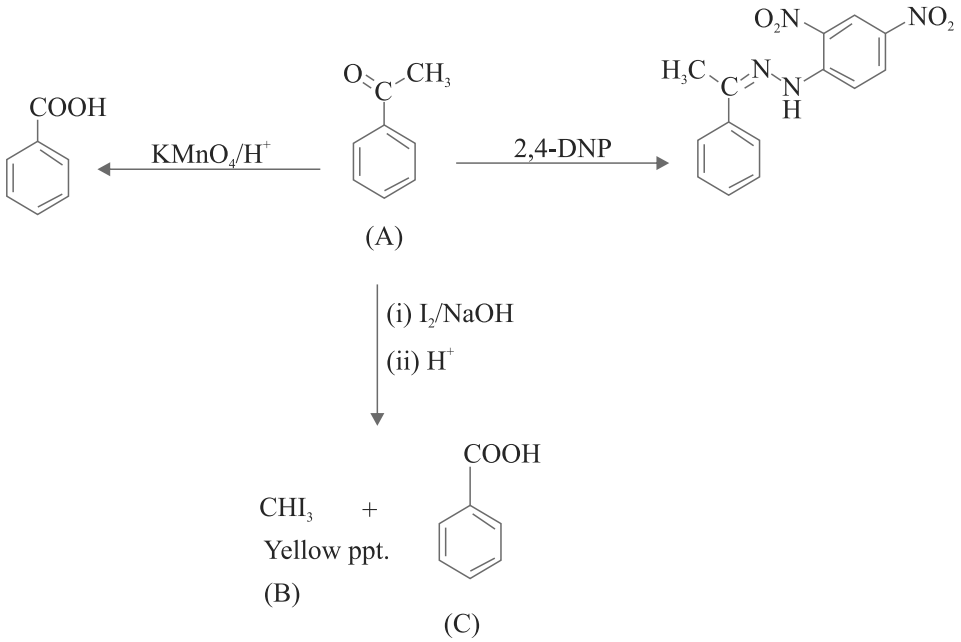
(iii) 

(v) 

(vi) 

3. An aromatic compound 'A' (Molecular formula C_8H_8O) 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 $C_7H_6O_2$), 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:



4. Give reason for the following:

(i) C_6H_5COOH is weaker acid than formic acid.

(ii) HCOOH and CH_3CHO can not be distinguished by Tollens' reagent.

(iii) R-COOH do not give characteristic reaction with >C=O.

(iv) Carboxylic acids are stronger acids than phenols.

(v) Acid amides are weakly basic in nature.

Ans. (i) In C_6H_5COOH, carboxylate ion is resonance stabilised

(ii) Presence of -CHO group in both.

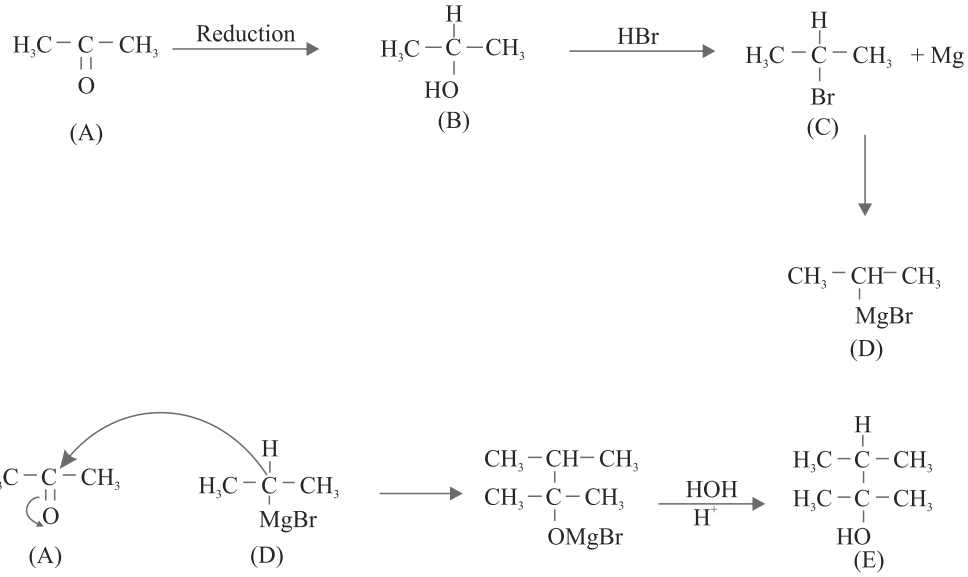
(iii) >C=O group is sterically hindered in carboxylic acid.

(iv) Dispersal of negative charge on carboxylate ions is more than phenoxide ion.

(v) Acid amides are weak basic due to involvent lone pair in conjugation with give of electrons on nitrogen atom.

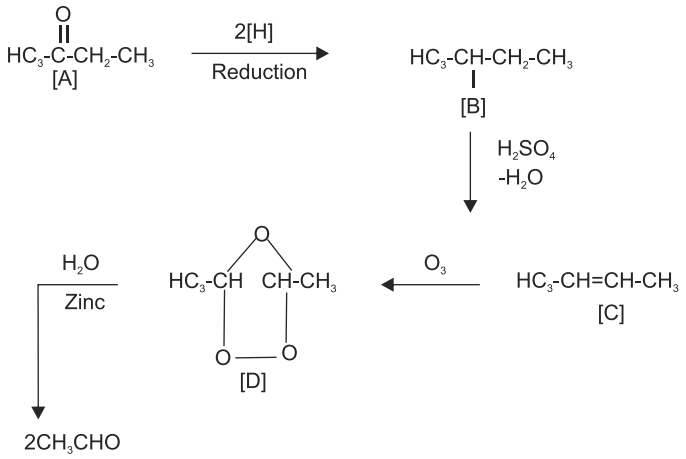
5. An organic compound 'A' (C_3H_6O) is resistant to oxidation but forms compound 'B' (C_3H_8O) on reduction. 'B' reacts with HBr to form the compound 'C'. 'C' with Mg forms Grignard's reagent 'D'which reacts with 'A' to form a product which on hydrolysis gives 'E'. Identify 'A'to 'E'.

Ans. 'A' must be ketone.



6. A ketone [A] which undergoes haloform reaction gives compound [B] on reduction. [B] on heating with H_2SO_4 gives compound [C] which forms monozonide [D] by reacting with ozone. [D] on hydrolysis in the presence of Zinc dust gives acetaldehyde. Identify [A], [B], [C], [D]. Write the reaction involved.

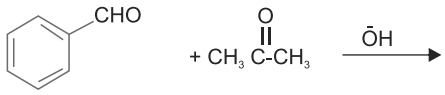
Ans.

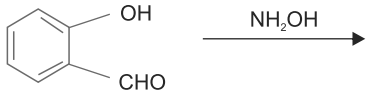


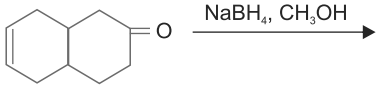
7. Complete the following reaction

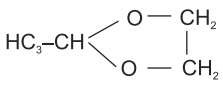
(a) $CH_3CHO + HOCH_2CH_2OH \longrightarrow$

(b) $C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4}$

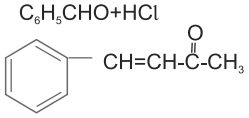
(c) 

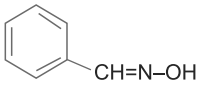
(d) 

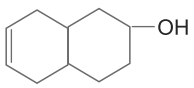
(e) 

Ans. (a) 

(b) $C_6H_5CHO + HCl$

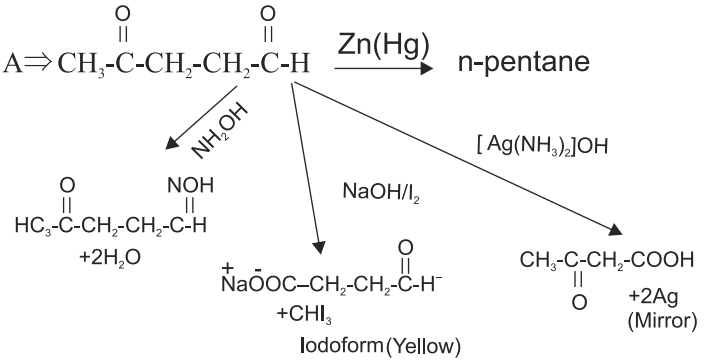
(c) 

(d) 

(e) 

8. An organic compound [A] with molecular formula $C_5H_8O_2$ is reduced to n-pentane on treatment with Zn-mg/HCl. The compound [A] forms a dioxime with hydroxyle amine and gives a positive iodo form test and Tollen's test. Identify the compound [A] and deduce its structure.

Ans.



(9). Complete the missing products

(a) $HCHO \xrightarrow{H_2/Ni} [A] \xrightarrow{PCl_5} [B] \xrightarrow{KCN} [C] \xrightarrow{H_3O^+} [D]$

(b) $CH{\equiv}CH \xrightarrow[H_2SO_4/HgSO_4]{H_2O} [A] \xrightarrow{[O]} [B] \xrightarrow{SOCl_2} [C]$

(c) $CH_2{=}CH_2 \xrightarrow{HBr} [A] \xrightarrow{KCN} [B] \xrightarrow{H_2O/H^+} [C] \xrightarrow{LiAlH_4} [D]$

Ans. (a) A= CH_3OH, B= CH_3Cl, C= CH_3CN, D= CH_3COOH
(b) A= CH_3CHO, B= CH_3COOH, C= CH_3COCl
(c) A= CH_3CH_2-Br, B= CH_3CH_2-CN, C= CH_3CH_2COOH,
D= $CH_3CH_2CH_2OH$

10. [A], [B] and [C] are three non-cyclic functional isomer of a carbonyl compound with molecular formula C_4H_8O. Isomer [A] and [C] gives positive Tollen's test whereas Isomer [B] does not give Tollens' test but give positive iodoform test. Isomer [A], [B] on reduction with Zn[Hg]/conc. HCl give same product [D]. Identify A, B, C, D.

Ans. A= $CH_3CH_2CH_2CHO$ Butan-1-al

B= $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CHO$ Butan-2-one

C= $CH_3-\underset{\underset{CH_3}{|}}{C}-CHO$ 2- Methylpropanal

D= $CH_3-CH_2-CH_2-CH_3$ Butane

CASE-STUDY BASED QUESTIONS

1. **Read the passage and answer the following questions:**

Carboxylic acids are compounds with excellent chemical and physical properties, the most particular characteristics of this type of organic compounds, is their high solubility in polar solvents, as water, or alcohols, methanol, ethanol, etc. Chemical structure contains a carbonyl function (-C=O) and an hydroxyl group (OH), these groups interact easily with polar compounds, forming bridges of H, obtaining high boiling points. The carbonyl group (C=O) is considered a one of the most functional groups involved in many important reactions. The carboxylic acids are the most important functional group that present C=O.

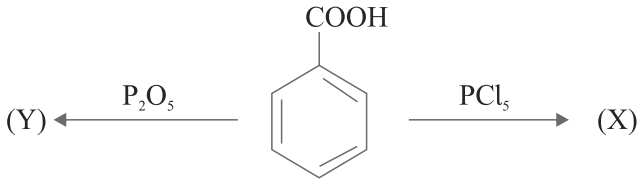
This type of organic compounds can be obtained by different routes, some carboxylic acids, such as citric acid, lactic acid or fumaric acid are produced from by fermentation, most of these type of carboxylic acids are applied in the food industry. Historically, some carboxylic acids were produced by sugar fermentation. Synthetics route, there are different synthesis reactions such as reactions of oxidation from alcohols in the presence of strong oxidants such as $KMnO_4$, oxidation of aromatic compounds among other routes.

For example, citric acid is a carboxylic acid, can be obtained by different routes, synthetic, enzymatic and naturally occurring, is considered harmless and cheap, used in the food industry, because is non-toxic, has a thermal stability to the 175°C. Bian et al., in 2017, reported the use of citric acid impregnated in porous material for the synthesis of Ni particles. They showed, that the presence of citric acid, is important in the dispersion of the Ni particles when are incorporate in porous materials, thus inhibiting the agglomeration.

Derivatives of carboxylic acid, as alkyl halides, esters, and amides, present different and important application in diverse areas. In the case of esters, these are obtained from the reaction between carboxylic acids and alcohols in presence of an acid catalyst usually H_2SO_4 with heat, this type of reaction is known as esterification. In the case of the amides, it is obtained in the presence of an amine, may be primary and secondary, with a carboxylic acid, in this reaction also can be used a catalyst and heat to accelerate the reaction.

Reference : Aide Sienz-Galindo, Lluvia I. Lopez-Lopez, Fabiola N. de la Cruz- Duran, Adali O.Castafieda-Facio, Leticia A. Ramirez-Mendoza, Karla C. Cordova-Cisneros and Denisse de Loera-Carrera (March 15th 2018). **Applications of Carboxylic Acids in Organic Synthesis, Nanotechnology and Polymers, Carboxylic Acid-Key Role in Life Sciences**, Georgiana Ileana Badea and Gabriel Lucian Radu, *IntechOpen*, DOI: 1 0.5772/intechopen.74654.

(A) Identify A and B in following reaction:



(B) Assertion: Carboxylic acids are highly acidic.
Reason: Carboxylate ion is resonance stabilised.

(a) Assertion and reason both are correct and reason is the correct explanation of the assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

(c) Assertion is correct statement but reason is wrong statement.

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

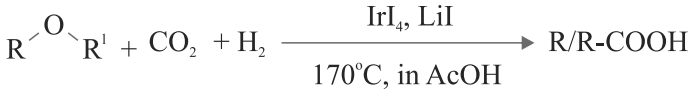
(C) What happens when phthalic acid reacts with ammonia followed by strong heating?

(D) How acetyl chloride may be converted to ethanoic acid?

2. **Read the passage and answer the following questions:**

'Tetrahydrofuran (THF) is a bulk chemical, which can be obtained from various feedstocks including biomass. In addition, the C5 carboxylic acids are much more expensive than THF. Therefore, we adopted THF as model ether to study the catalytic system (Table 1). The reaction could be efficiently accelerated by IrI_4 catalyst and LiI promoter in AcOH solvent at 170 °C, and the yield of C5 carboxylic acids reached 70% after 16 h (entry1). The products contained two isomers, i.e., pentanoic acid and 2-methylbutanoic acid, and their molar ratio was 58:42. A little C6 carboxylic acids were also formed in the reaction. The rest of the THF substrate was converted to butane.

In addition, trace of methane was also detected. We also tried different Ir catalyst precursors, such as $Ir(CO)(PPh_3)_2C1$, $Ir(CO)_2(acac)$, and $IrCl_3$, the results indicated that they were not as efficient as IrI_4 . We set the reaction time at 8 h and tested other catalytic systems. The IrI_4 catalyst was essential to the reaction because no target product was observed without it. The Rh catalyst was effective for synthesis of carboxylic acids via olefin and/or alcohol hydrocarboxylation with CO_2 and H_2. Whereas in this work no product was obtained when RhI_3

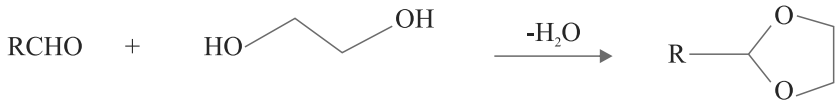


(A) How ethers can be distinguished from carboxylic acid?

(B) Propanol on reaction with.....and.....gives propanal and propane respectively.

3. **Read the passage and answer the following questions:**

The acetal is the most common protecting group for aldehydes and 1,3-dioxolanes are the most commonly encountered type of acetal, usually prepared by reaction of the aldehyde with ethylene glycol with azeotropic removal of water (eq1). Regeneration of the carbonyl is normally out with aqueous acid.

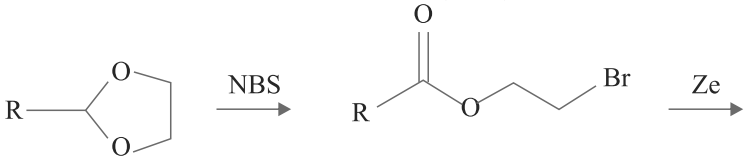


(1)

We have been concerned with the general problem of converting dioxolanes into Carboxylic acids without employing acid to first remove the protective group (eq 2). The non-acidic alternative to eq 2 would allow the introduction of acid groups into a molecule containing.

(2)

various acid-sensitive functionalities. Our solution to this problem is outlined in eq 3. Prugh and McCarthy in 1966 showed that cyclic acetals are converted into bromo esters when treated with N-bromosuccinimide (NBS). Indeed, a



(3)

variety of dioxolanes give good yields of the corresponding 2-bromoethyl esters when refluxed with NBS in CCl_4. For example, 3-phenyl-1,3-dioxolane gives a 98% yield Of 2-bromocthyl benzoate (88% after distillation).

The transformation of eq 3 is completed by a zinc-induced elimination which yields the acid upon workup. Despite the precedent for this second step, a variety of reaction conditions failed to give any acid from 2-bromoethyl benzoate.

Zinc in refluxing THF gave no reaction. Even zinc which had activated with copper sulfate was ineffective and ultraactive zinc from the potassium metal or sodium naphthalenide reduction of zinc chloride also failed to promote elimination. Zinc in refluxing methanol or ethanol gives 42-46% benzoic acid plus 47-52% of transesterification product. Ester interchange can be avoided by using zinc in refluxing THF to give a 44% yield of benzoic acid and a recovery of starting material. Addition of catalytic sodium iodide improves the yield of benzoic acid from this reaction to with only of starting material recovered.

Reference : Lawrence C. Anderson, Harold W. Pinnick, **Preparation of carboxylic acids from protected aldehydes** *J. Org. Chem.* **1978**, 43, 17, 3417-3418 **https://doi.org/10.1021/io00411a044**

(A) The formation of acetal from aldehyde is an example of ..... reaction.

(B) Which of the following reagent(s) can be used to convert butan-1-ol to butanoic acid?

(a) 1. $KMnO_4$ — KOH 2. H^+

(b) CrO_3 — H_2SO_4

(c) Both i) and ii)

(d) None of these

(C) Write the structure of the product formed when propanal reacts with methanol.

(D) What happens when propanal reacts with ethyl magnesium iodide followed by reaction with dilute acid?

4. **Read the passage and answer the following questions:**

Nucleophilic additions to a carbonyl group leading to tetrahedral species which are products or intermediates in a mechanistic sequence occupy a central place in biochemistry as well as in organic chemistry. It has been shown recently that the structural pathway for the nucleophilic addition of an amino group to carbonyl can be mapped on the basis of crystal structure data. However, from structural data alone no direct information about the energy variation along the reaction pathway can Obtained. Furthermore, it was not entirely clear to what extent steric requirements of substituents on the nucleophile and the carbonyl group. as well as crystal packing effects, influence the arrangement of the reactive centers. An an attempt to till these gaps we have carried out calculations on the reaction path of the simple model system.

$CH_2=O+H^- \rightarrow CH_3O^-$

corresponding to nucleophilic addition of hydride anion to formaldehyde to produce methanolate anion. A calculation has also been made for the system consisting of an ammonia and a formaldehyde molecule at a of 20 nm.

Reference : H. B. Buergi, J. M. Lehn, G. Wipft, **Ab initio study of nucleophilic addition to a carbonyl group**, *J. Am. Chem. Soc.* 1974, 96, 6, 1956-1957, Publication Date: March 1, 1974 https://doi.org/10.1021/ja00813a062

(A) Which of the following nucleophilic addition reaction generates chiral carbon?

(a) Benzaldehyde + KOH

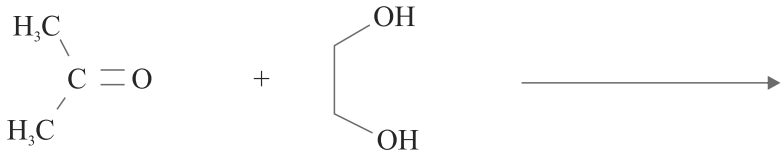
(b) Benzaldehyde + ammonia

(c) Propanone + KOH

(d) Propanone + ammonia

(B) Write the major product on reaction of acetophenone with CH_3-NH_2?

(C) Complete the reaction:



(D) Which will undergo reaction with 2,4-dinitrophenylhydrazine at fastest rate?

(a) Acetophenone (b) Propanone

(c) Benzaldehyde (d) Propanal

ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. (b) 2. (d) 3. (b). 4. (b) 5. (b) 6. (a) 7. (d) 8. (a) 9. (d) 10. (d) 11. (c) 12. (c) 13. (a) 14. (b). 15. (a) 16. (b) 17. (c) 18.(c) 19.(b) 20.(a)

II FILL IN THE BLANKS

1.	Ammoniacal silver nitrate	2.	Phthalimide	3.	Rosenmund
4.	Increases	5.	$NaHCO_3$	6.	Cu_2O
7.	Methanal/Formaldehyde	8.	H-bonding.	9.	Aldehydes
10.	Propanoic acid				

III ASSERTION REASON TYPE QUESTIONS

III. 1. (a) 2. (a) 3. (c) 4. (c) 5. (a) 6. (b) 7. (d) 8. (c) 9. (d) 10. (b)

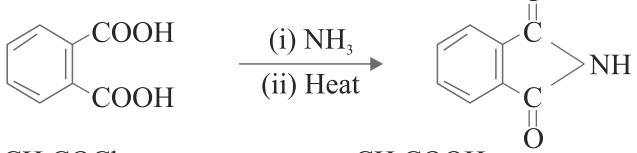
IV ONE WORD ANSWER TYPE QUESTIONS

1.	Hemiacetal	2.	Benzaldehyde	3.	$LiA1H_4$ or B_2H_6
4.	Decarboxylation	5.	Methyl propanoate		
6.	1,3-Diphenylprop-2-en-l-one or Benzalacetophenone				
7.	$NaBH_4$	8.	P_2O_5 or H^+/Δ	9.	Hexane-1,6-dioic acid
10.	a) HCOOH, (b) $CH_2(Cl)COOH$			11.	Iodoform Test
12.	Methycyclohexane	13.	$Pd/BaSO_4$	14.	$CH_3MgBr/H_2O/H+$
15.	CH_3CHO				

CASE STUDY BASED QUESTIONS

1. (A) $X=C_6H_5COCl$ $Y=(C_6H_5CO)_2O$

(B) (a)

(C) 

(D) $CH_3COCl \xrightarrow[H_2O/H^+]{} CH_3COOH$

2. (A) With $NaHCO_3$ carboxylic acids give brisk effervescence, whereas ethers cannot.

(B) PCC

PASSAGE :3

3. (A) Nucleophilic addition reaction

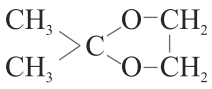
(B) (c)

(C) $CH_3CH_2CH(OCH_3)_2$

(D) $(C_2H_5)_2CHOH$

4. (A) (c)

(B) $C_6H_5-\underset{\underset{CH_3}{|}}{C}-=N\text{-}CH_3$

(C) 

(D) (d)

UNIT TEST-1

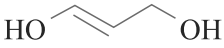
Aldehydes, ketones and carboxylic acid

Maximum Marks : 20 **Time : 1 Hrs.**

1. Identify the correct product in following reaction:

(a) 

(b) 

(c) 

(d) 

2. Which of the following reagent(s) is most suitable for following conversion?

Propanone → Propane

(a) PCC (b) $LiAlH_4$

(c) (i). $KMnO_4$-KOH (ii). H^+ (d) Zn(Hg) /HCl

3. The highest pK_a value is observed in-

(a) Phenol (b) Benzoic acid

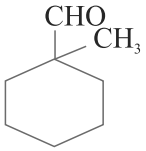
(c) 4-Nitrobenzoic acid (d) Ethanoic acid

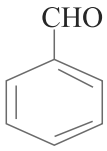
4. Which of the following undergoes nucleophilic addition reaction at fastest rate?

(a) Benzaldehyde (b) Acetophenone

(c) Methanal (d) Ethanal

5. Cannizzaro reaction is not shown by-

(a) 

(b) 

(c) HCHO (d) CH_3CHO

6. Give a chemical test to distinguish between following compounds: 2

(a) Benzaldehyde and Acetophenone

(b) Benzoic acid and Phenol

7. How butanoic acid can be synthesised using appropriate: 2

(a) Grignard reagent

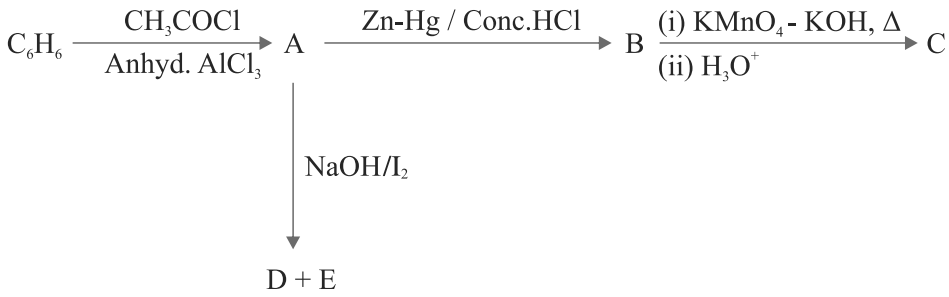
(b) Amide

8. Arrange following in ascending order of given properties: 2

   (a) Ethanal, Ethanol, Methoxymethane, Propane (boiling point)

   (b) Propanal, Benzaldehyde, Acetophenone (reactivity towards nucleophilic addition reaction)

9. Complete the reaction sequence by writing structures of A-E. Also name the reaction involved in the conversion of A to B. 2



10. Explain following: 3

   (a) α- hydrogens in aldehydes and ketones are acidic in nature.

   (b) There are two $-NH_2$ groups in semicarbazide. However only one involves in the formation of semicarbazone.

   (c) Propanone is less reactive than propanal towards nucleophilic addition reactions.

11. How will you carry out following conversions? 3

   (a) Bromobenzene to 1-Phenylethanol

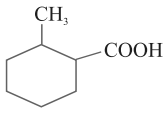
   (b) Benzoic acid to *m*- Nitrobenzyl alcohol

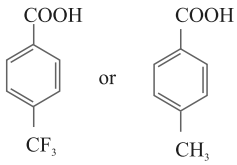
   (c) Propanone to Propene

UNIT TEST- 2

Aldehydes, ketones and carboxylic acid

Maximum Marks : 20 **Time : 1 Hrs.**

1. Give the IUPAC of 

2. Which acid will be more acidic 
 1

3. Write product of CH_3CHO with hydrazine. 1

4. Which will have higher boiling point CH_3CHO or CH_3COOH. 1

5. How many mole of hydrazine will be used with one mole of benzaldehyde 1

6. Write chemical distinguish test to seperate following. 1
   (a) Pentan-2-one and Pentan-3-one
   (b) Benzophenone and Benzoic acid

7. Write short not on 1
   (a) Hell-Volhard-Zelinsky Reaction
   (b) Etard Reaction

8. How will you synthesise (i) Acetone from propene. (ii) Salicylic acid from benzene. 2

9. Arrange the following compound in increasing order of their properties.
   (a) CH_3COOH, $C_6H_5COCH_3$, CH_3CHO (Reactivity towards nucleophilic addition reaction)
   (b) Cl-CH_2-COOH, F-CH_2-COOH, CH_3-CH_2-COOH (acidic character)
   (c) CH_3CHO, CH_3CH_3, CH_3COOH, CH_3CH_2OH (boiling point)

10. Give reason. 3
    (a) Cyclohexanone forms cyanohydrin in good yield but 2,2,6- trimethyl cyclohexanone does not.
    (b) There are two-NH_2 group in semicarbazide howere only one is involved in the formation of semicarbazone.

11. (a) Convert the following 3
    (i) Benzaldehyde to 3-Phenylpropan-1-ol
    (ii) Benzole acid to m-Nitrobenzyl alcohol
    (b) An organic compound with molecular formula $C_5H_{10}O$ from 2,4-DNP derivatives, reduce Tollens' reajent and undergoes Cannizarro's reaction. on vigrous oxidation it gives 1,2- Benzenedicarboxylic acid. Identify the compound.