CBSE Test Paper - 04

Class - 12 Chemistry (Aldehydes, Ketones and Carboxylic Acids)

1. Compound 'A' undergoes formation of cyanohydrins which on hydrolysis gives lactic acid ($CH_3CHOHCOOH$). Therefore, compound 'A' is
   a. acetone
   b. benzaldehyde
   c. acetaldehyde
   d. formaldehyde
2. Which sequence of steps below describes the best synthesis of 5 – oxohexanoic acid starting with 1 – methylcyclopentan – 1 – ol.
   a. 1. H_2SO_4 and heat
      2. O_3
      3. $(CH_3)_2S$
      4. PCC
   b. 1. Conc. $KMnO_4$
      2. Dry gaseous HBr
      3. mg/ether
      4. CO_2
   c. 1. Conc. $KMnO_4$
      2. CH_3MgBr/ether
      3. H_3O^+
   d. 1. H_2SO_4 and heat
      2. Conc. $KMnO_4$
3. Esters react with DIBAL – H to produce
   a. Ketones
   b. Carboxylic acids
   c. Aldehydes
   d. None of these
4. Arrange the following alcohols, hydrocarbon and ether in order of their increasing

boiling points Pentan – 1 – ol, n – butane, pentanal, ethoxyethane.

a. n – Butane, ethoxyethane, pentanal and pentan – 1 – ol
b. ethoxyethane, pentanal and pentan – 1 – ol, n – Butane
c. pentan – 1 – ol , n – Butane, ethoxyethane, pentanal
d. pentanal and pentan – 1 – ol, n – Butane, ethoxyethane

5. For making distinction between 2 – pentanone and 3 – pentanone the reagent to be employed is
   a. $K_2Cr_2O_7$ / H_2SO_4
   b. SeO_2
   c. Zn – Hg/HCl
   d. Iodine/NaOH
6. Write the structure of alkenes that on ozonolysis will give ketone only.
7. Predict the products formed when cyclohexanecarbaldehyde reacts with PhMgBr and then H_3O^+.
8. What is vinegar?
9. Write the steps for the conversion of Methanal to Ethanal.
10. Write the names of the reagents and equations in the conversion of
    i. phenol to salicylaldehyde.
    ii. anisole to p-methoxyacetophenone.
11. Arrange the following compound in increasing order of their acid strengths:
    CH_3CH_2COOH, $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$
12. How would you bring about the following conversions?
    i. Propanal to butanone
    ii. Benzaldehyde to benzophenone
    iii. Benzoyl chloride to benzonitrile
13. How do you perform the conversion: Acetaldehyde to Acetamide?
14. Highly branched carboxylic acids are less acidic than unbranched acids. Why?

15. Give plausible explanation for each of the following:
    i. Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6 trimethylcyclohexanone does not.
    ii. There are two - groups in semicarbazide. However, only one is involved in the formation of semicarbazones.
    iii. During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

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Solutions

1. (c) acetaldehyde

   Explanation: Cyanohydrin formation from aldehydes or ketones followed by complete hydrolysis is used to produce alpha hydroxycarboxylic acids.

   $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$

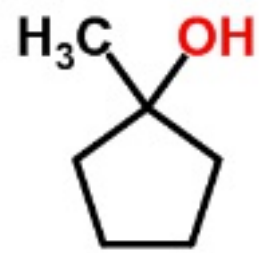
   $CH_3CH(OH)CN + H_3O^+ \rightarrow CH_3CH(OH)COOH$

   and on complete hydrolysis CN converts to COOH.

2. (d)

   1. H_2SO_4 and heat
   2. Conc. $KMnO_4$

   Explanation: 5 – oxohexanoic acid starting with 1 – methylcyclopentan – 1 – ol can be synthesized using conc H_2SO_4 which will cause dehydration forming alkene which with $KMnO_4$ opens the ring and forms 1 – methylcyclopentan – 1 – ol.

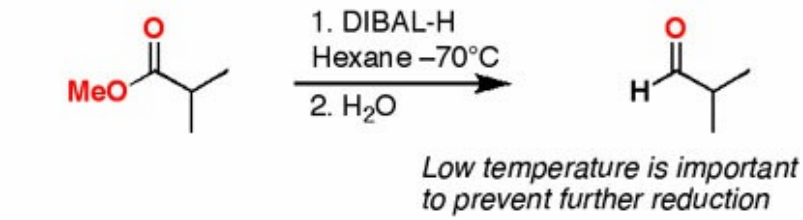
   this 1-methylcyclopentan-1-ol reacts with conc H_2SO_4 to form 1-methylcyclopent-1-ene which on reaction with conc $KMnO_4$ cause oxidative ozonolysis of alkene and forms 5 – oxohexanoic acid.

3. (c) Aldehydes

   Explanation: Esters are reduced to aldehydes selectively with DIBAL-H. DIBAL-H is bulky and electrophilic reducing agent.

Example 1: Reduction of esters to aldehydes



Low temperature is important to prevent further reduction

4. (a) n – Butane, ethoxyethane, pentanal and pentan – 1 – ol

   Explanation: Alcohols are involved in hydrogen bonding with each other i .e. intermolecular hydrogen bonding and thus have a higher boiling point compared to aldehydes or ketones and ethers.

   Aldehydes and ketones due to their polar CO bond have higher boiling point compared to ethers.

   Alkanes being non-polar have the least boiling point.

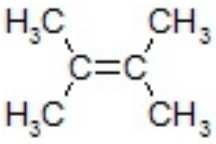
5. (d) Iodine/NaOH

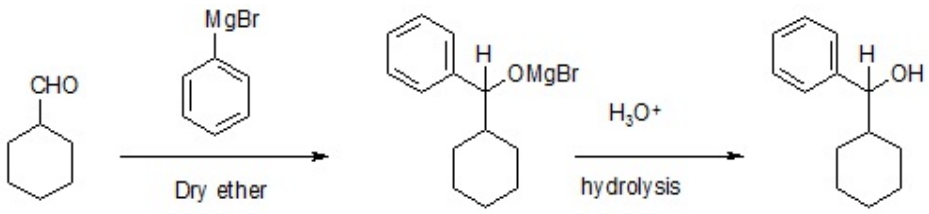
   Explanation: 2-pentanone ($CH_3COCH_2CH_2CH_3$) will give iodoform test (reaction with I_2 + NaOH) because of presence CH_3CO- group and yellow precipitate will be formed but 3-pentanone ($CH_3CH_2COCH_2CH_3$) does not have CH_3CO- group hence will not give iodoform test.

   $CH_3COCH_2CH_2CH_3 + I_2 + NaOH \rightarrow CHI_3$ (yellow precipitate) + $CH_3CH_2CH_2COO^-Na^+$

   $CH_3CH_2COCH_2CH_3 + I_2 + NaOH \rightarrow$ No reaction

6. All substituted alkenes on ozonolysis give ketones. For example 2,3-Dimethylbut-2-ene



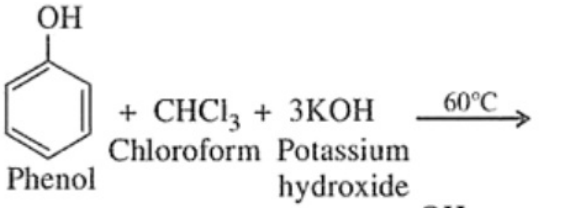
7. 

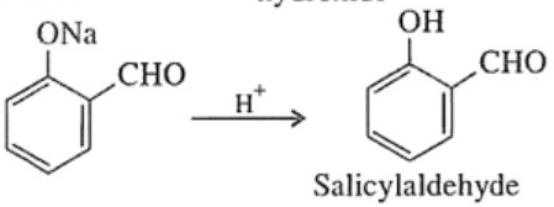
8. An 8-10% solution of acetic acid in water is called vinegar.

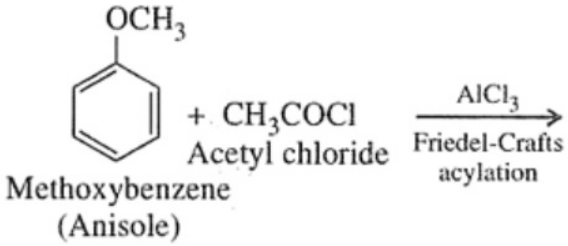
9. Methanal to Ethanal

$$\text{H -CHO + } CH_3MgBr \rightarrow H - \underset{H}{\overset{OMgBr}{\overset{|}{\underset{|}{C}}}} - CH_3 \xrightarrow{H^+/H_2O} CH_3\text{ - CHO}$$

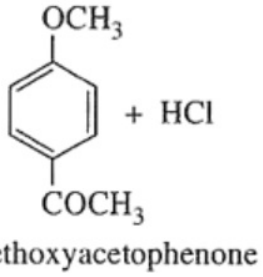
10. i.







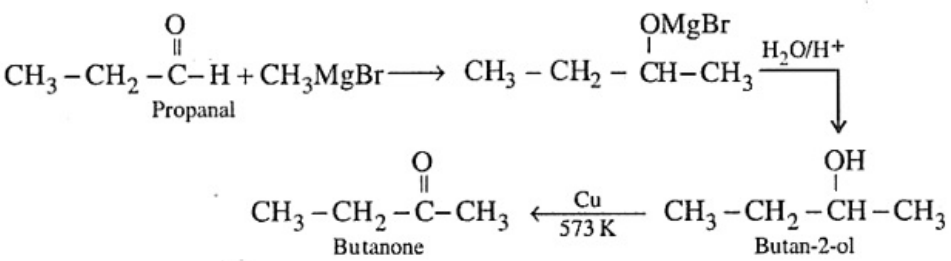
ii.



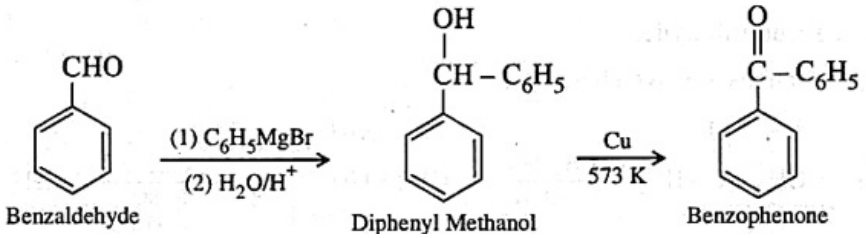
p-Methoxyacetophenone

11. Electronegative substituents increase acidity of the carboxylic acids by inductive electron withdrawal and the closer the substituent is to the carboxyl group the greater is its effect. Hence, the order of acidity is $CH_3CH_2COOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$.

12. The following steps are involved in the conversions:
    i. Propanal to butanone



    ii. Benzaldehyde to Benzophenone



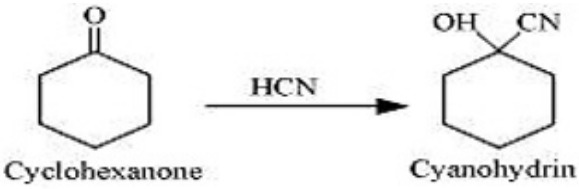
iii. Benzoyl Chloride to Benzonitrile

$$\underset{Benzoyl\ chloride}{C_6H_5COCl} \xrightarrow[Heat]{NH_3} \underset{Benzamide}{C_6H_5CONH_2} \xrightarrow[heat]{P_2O_5} \underset{Benzonitrile}{C_6H_5C \equiv N}$$

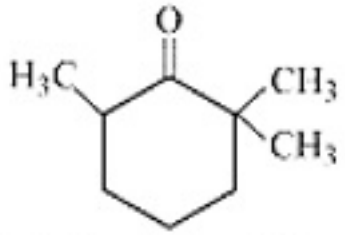
13. $$CH_3CHO \xrightarrow[KMnO_4]{(O)} CH_3COOH \xrightarrow{NH_3} CH_3COO^-\overset{+}{N}H_4 \xrightarrow[-H_2O]{\triangle} CH_3 - \overset{O}{\overset{\|}{C}} - NH_2$$

14. The carboxylate ion **($RCOO^-$)** of branched chain acids is shielded from solvent molecules and therefore, cannot be stabilized by solvation as effectively as the carboxylate ion of unbranched acids.

15. i. Cyclohexanones form cyanohydrins according to the following equation.



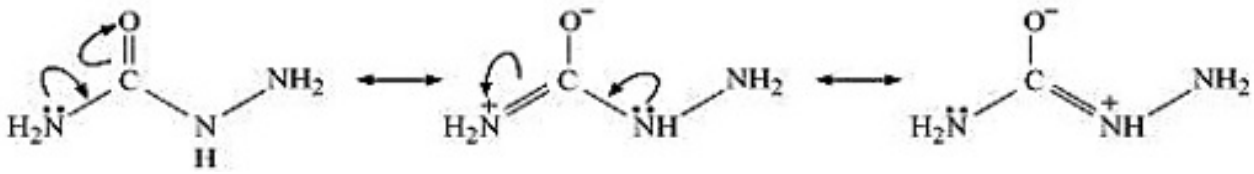
In this case, the nucleophile **CN^-** can easily attack without any steric hindrance. However, in the case of 2, 2, 6 trimethylcydohexanone, methyl groups at 2,2,6 positions offer steric hindrances and as a result, **CN^-** cannot attack effectively.



2, 2, 6 – Trimethylcyclohexanone

For this reason, it does not form a cyanohydrin.

ii. Semicarbazide undergoes resonance involving only one of the two - NH_2 groups, which is attached directly to the carbonyl-carbon atom.



Therefore, the electron density on - NH_2group involved in the resonance also decreases. As a result, it cannot act as a nucleophile. Since the other - NH_2 group is not involved in resonance; it can act as a nucleophile and can attack carbonyl-carbon atoms of aldehydes and ketones to produce semicarbazones.

iii. Ester along with water is formed reversibly from a carboxylic acid and an alcohol in presence of an acid.

$$\underset{Carboxylic\,acid}{RCOOH} + \underset{Alcohol}{R'OH} \overset{H^+}{\longleftrightarrow} \underset{Ester}{RCOOR'} + \underset{water}{H_2O}$$

If either water or ester is not removed as soon as it is formed, then it reacts to give back the reactants as the reaction is reversible. Therefore, to shift the equilibrium in the forward direction i.e., to produce more ester, either of the two products should be removed (Le-Chateliers Principle).