

OPEN STUDENT FOUNDATION

STD:12th Chemistry

Date : 05/03/24

PRACTICE TEST-15

Section A

● Write the answer of the following questions. [Each carries 2 Marks]

[10]

1. Explain Stephen reaction in brief.
2. Write a note on solubility of aldehydes and ketones.
3. Write a note on silver mirror test.
4. Explain reduction reaction of carboxylic acids.
5. Explain with chemical reactions, the formation of acyl chlorides from carboxylic acids.

Section B

● Write the answer of the following questions. [Each carries 3 Marks]

[9]

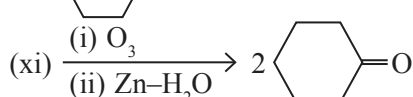
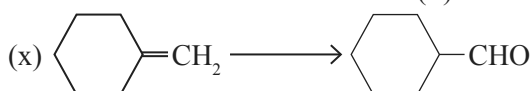
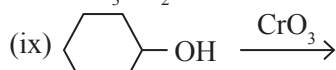
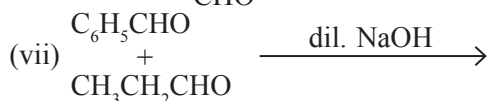
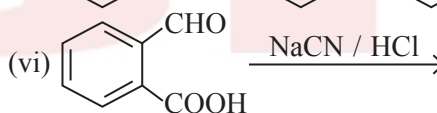
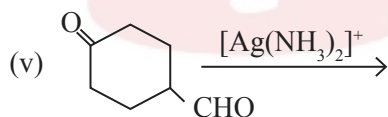
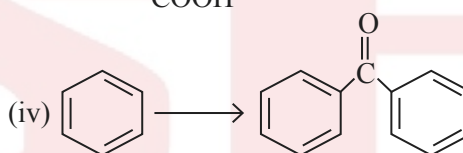
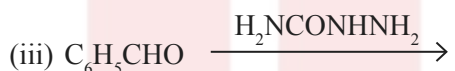
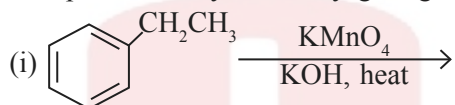
6. Explain the effect of substituents on the acidity of carboxylic acids.
7. Give plausible explanation for each of the following :
 - (i) Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.
 - (ii) There are two $-NH_2$ groups in semicarbazide. However, only one 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.
8. An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.

Section C

● Write the answer of the following questions. [Each carries 4 Marks]

[12]

9. Write detailed note on the addition reaction of aldehydes and ketones with ammonia derivatives .
10. Complete each synthesis by giving missing starting material, reagent or products.



11. How will you prepare the following compounds from benzene ? You may use any inorganic reagent and any organic reagent having not more than one carbon atom :
- (i) Methyl benzoate
(ii) *m*-Nitrobenzoic acid
(iii) *p*-Nitrobenzoic acid
(iv) Phenylacetic acid
(v) *p*-Nitrobenzaldehyde.

Section D

- Write the answer of the following questions. [Each carries 5 Marks] [5]

12. How will you bring about the following conversions in not more than two steps?
- (i) Propanone to Propene
(ii) Benzoic acid to Benzaldehyde
(iii) Ethanol to 3-Hydroxybutanal
(iv) Benzene to *m*-Nitroacetophenone
(v) Benzaldehyde to Benzophenone
(vi) Bromobenzene to 1-Phenylethanol
(vii) Benzaldehyde to 3-Phenylpropan-1-ol
(viii) Benzaldehyde to α -Hydroxyphenylacetic acid
(ix) Benzoic acid to *m*- Nitrobenzyl alcohol


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Section A

- Write the answer of the following questions. [Each carries 2 Marks]

[10]

1. Explain Stephen reaction in brief.

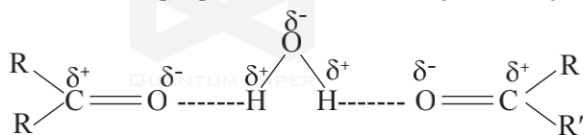
⇨ Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.



⇨ This reaction is called stephen reaction.

2. Write a note on solubility of aldehydes and ketones.

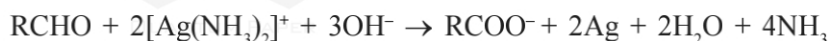
⇨ The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportion, because they form hydrogen bond with water.



⇨ However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain. All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform, etc. The lower Aldehydes have sharp pungent odours.

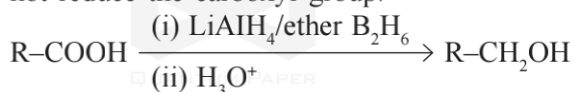
3. Write a note on silver mirror test.

⇨ 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.



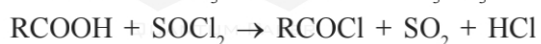
4. Explain reduction reaction of carboxylic acids.

⇨ Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride or better with diborane. Diborane does not easily reduce functional groups such as ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.



5. Explain with chemical reactions, the formation of acyl chlorides from carboxylic acids.

⇨ The hydroxyl group of carboxylic acids, behaves like that of alcohols and is easily replaced by chlorine atom on treating with PCl_5 , PCl_3 or SOCl_2 . Thionyl chloride (SOCl_2) is preferred because the other two products are gaseous and escape the reaction mixture making the purification of the products easier.



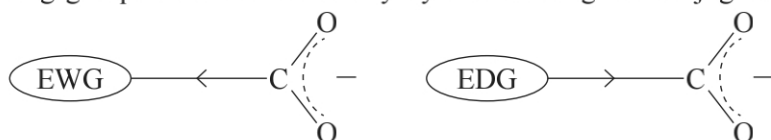
Section B

- Write the answer of the following questions. [Each carries 3 Marks]

[9]

6. Explain the 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.



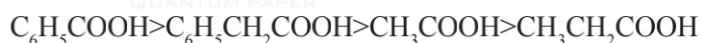
Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid

Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid

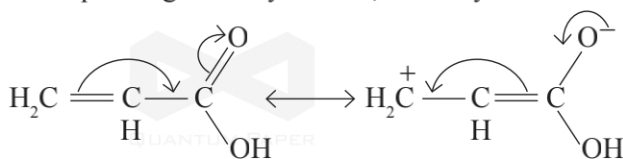
- ⇒ The effect of the following groups in increasing acidity order is



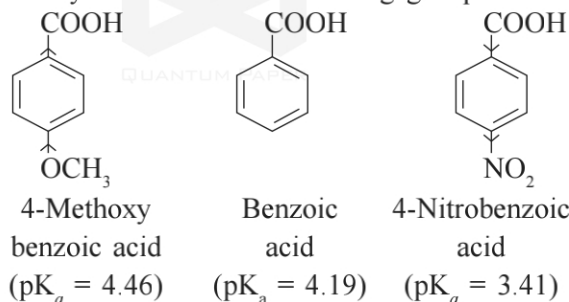
- ⇒ Thus, the following acids are arranged in order of decreasing acidity (based on pK_a values) :



- ⇒ Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid, contrary to the decrease expected due to resonance effect shown below:



- ⇒ This is because of greater electronegativity of sp^2 hybridised carbon to which carboxyl carbon is attached. The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.



7. Give plausible explanation for each of the following :

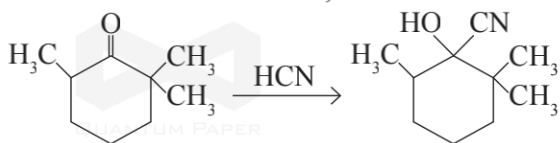
- Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.
- There are two $-\text{NH}_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazones
- During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

- ⇒ (i) Cyanohydrins are formed by cyclohexanones according to the following equation.

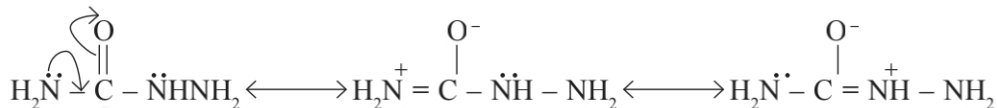


Cyclohexanone Cyanohydrin

In this case, there will not be any steric hindrance, hence the nucleophile CN^- can easily attack. However, in the case of 2, 2, 6-trimethylcyclohexanone, methyl groups at α -positions offer steric hindrances and as a result, CN^- cannot attack effectively.

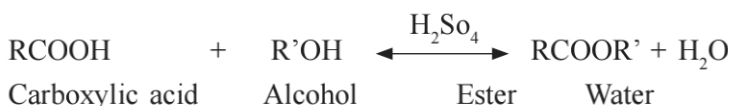


- ⇨ (ii) Semicarbazide undergoes resonance involving only one of the two $-\text{NH}_2$ groups, which is attached directly to the carbonyl-carbon atom.



Therefore, the electron density on $-\text{NH}_2$ group involved in the resonance also decreases. As a result, it cannot act as a nucleophile. Since the other $-\text{NH}_2$ 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.



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 should be removed.

8. An organic compound (A) (molecular formula $\text{C}_8\text{H}_{16}\text{O}_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.

- ⇨ A is an organic compound with a molecular formula $\text{C}_8\text{H}_{16}\text{O}_2$. This gives a carboxylic acid (B) and alcohol (C) on hydrolysis with dilute sulphuric acid. Thus, compound A must be an ester.

- ⇨ Further, oxidation of alcohol (C) with chromic acid gives acid B. Thus, B and C must contain an equal number of carbon atoms.

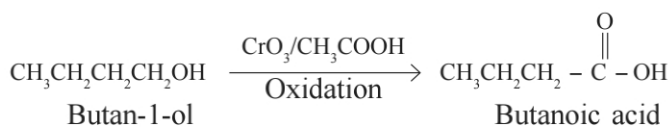
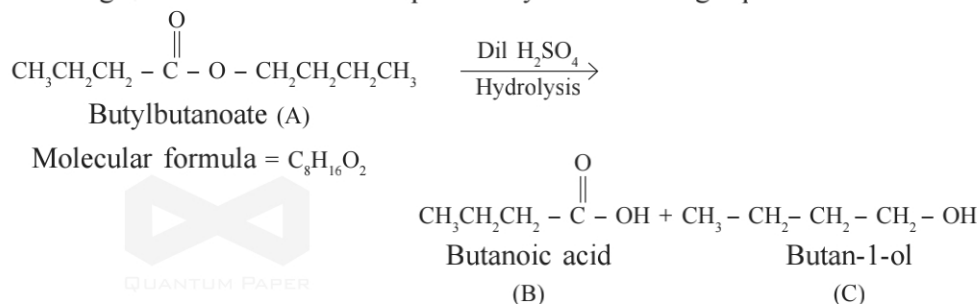
- ⇨ A total of 8 carbon atoms are present in compound A, each of B and C contain 4 carbon atoms.

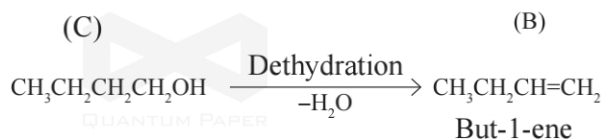
- ⇨ Again, alcohol C gives but-1-ene on dehydration. Therefore, C is of straight-chain and hence, it is butan-1-ol.

- ⇨ On oxidation, Butan-1-ol gives butanoic acid. Hence, acid B is butanoic acid.

- ⇨ Hence, the ester with molecular formula $\text{C}_8\text{H}_{16}\text{O}_2$ is butylbutanoate.

- ⇨ All the given reactions can be explained by the following equations.





Section C

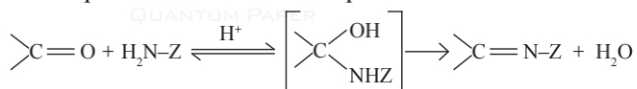
● Write the answer of the following questions. [Each carries 4 Marks]

[12]

9. Write detailed note on the addition reaction of aldehydes and ketones with ammonia derivatives .

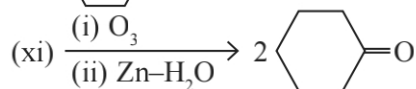
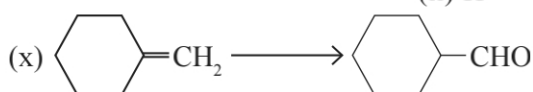
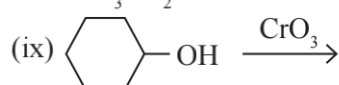
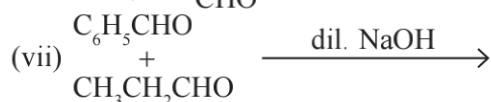
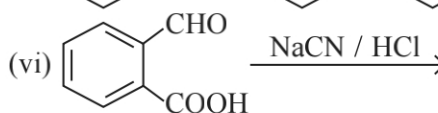
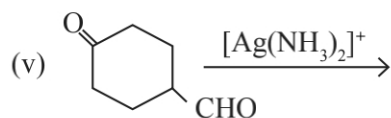
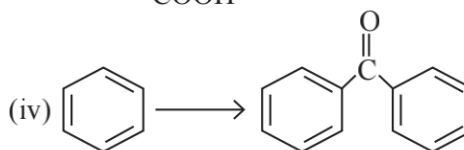
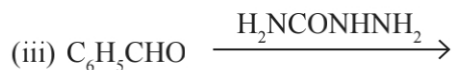
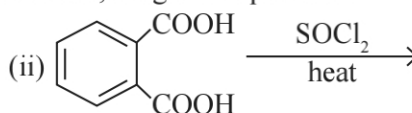
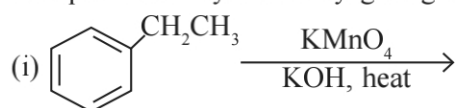
⇒ Addition of ammonia and its derivatives: Nucleophiles, such as ammonia and its derivatives $\text{H}_2\text{N}-\text{Z}$ add to the carbonyl group of aldehydes and ketones. The reaction is reversible and catalysed by acid.

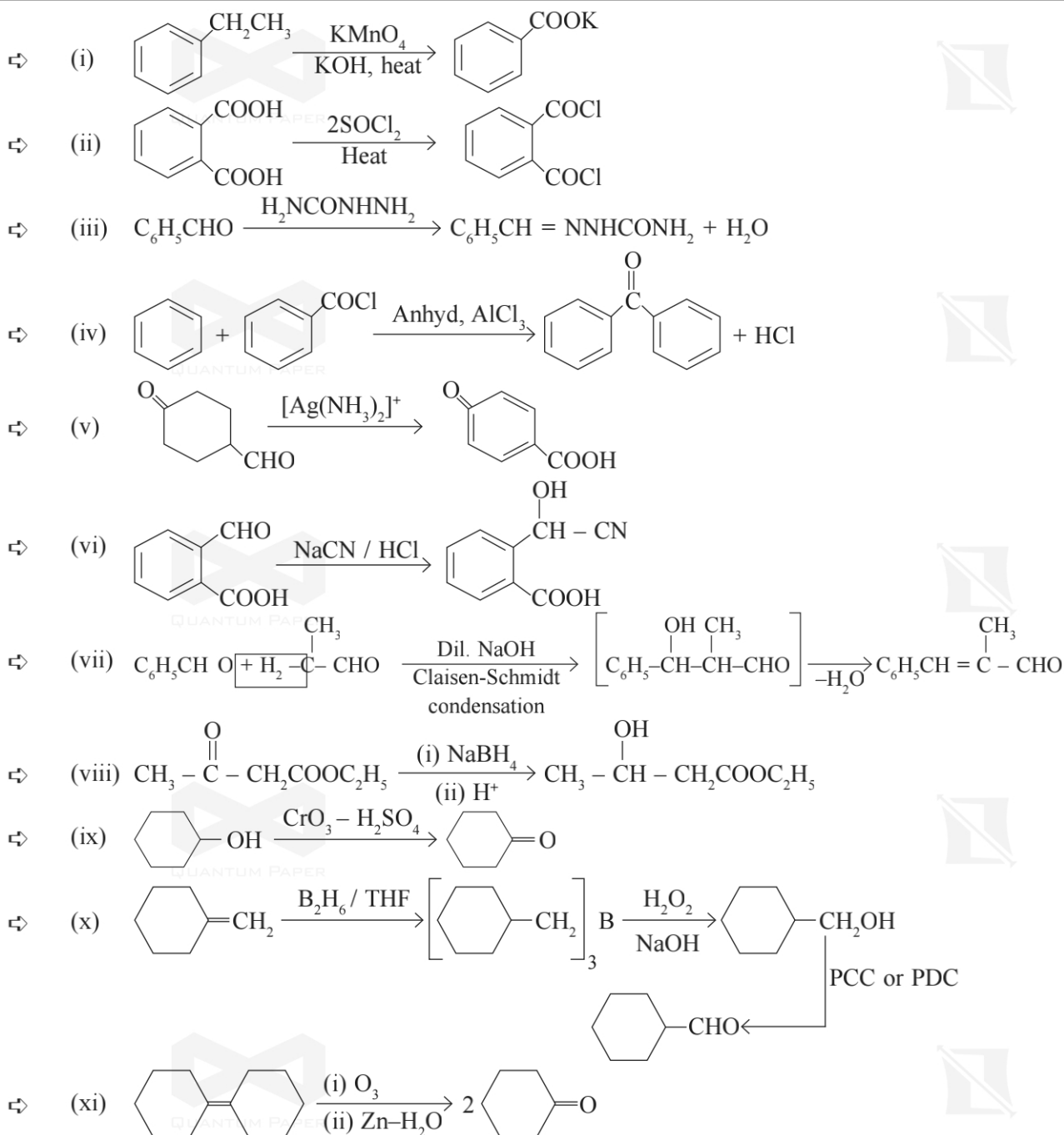
⇒ The equilibrium favours the product formation due to rapid dehydration of the intermediate to form $>\text{C}=\text{N}-\text{Z}$.



Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	$>\text{C}=\text{NH}$	Imine
-R	Amine	$>\text{C}=\text{NR}$	Substituted imine (Schiff's base)
-OH	Hydroxylamine	$>\text{C}=\text{N}-\text{OH}$	Oxime
$-\text{NH}_2$	Hydrazine	$>\text{C}=\text{N}-\text{NH}_2$	Hydrazone
$-\text{HN}-\text{C}_6\text{H}_5$	Phenylhydrazine	$>\text{C}=\text{N}-\text{NH}-\text{C}_6\text{H}_5$	Phenylhydrazone
$-\text{HN}-\text{C}_6\text{H}_3(\text{NO}_2)_2$	2,4-Dinitrophenylhydrazine	$>\text{C}=\text{N}-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$	2,4 Dinitrophenylhydrazone
$-\text{NH}-\text{C}(=\text{O})-\text{NH}_2$	Semicarbazide	$>\text{C}=\text{N}-\text{NH}-\text{C}(=\text{O})-\text{NH}_2$	Semicarbazone

10. Complete each synthesis by giving missing starting material, reagent or products.





11. How will you prepare the following compounds from benzene ? You may use any inorganic reagent and any organic reagent having not more than one carbon atom :

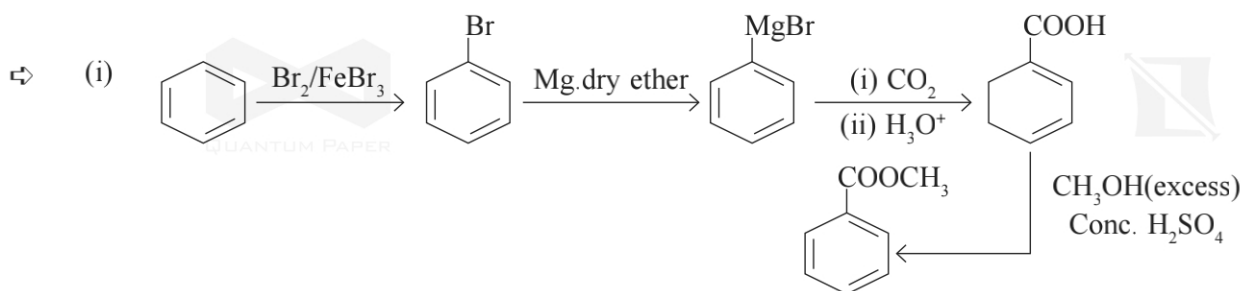
(i) Methyl benzoate

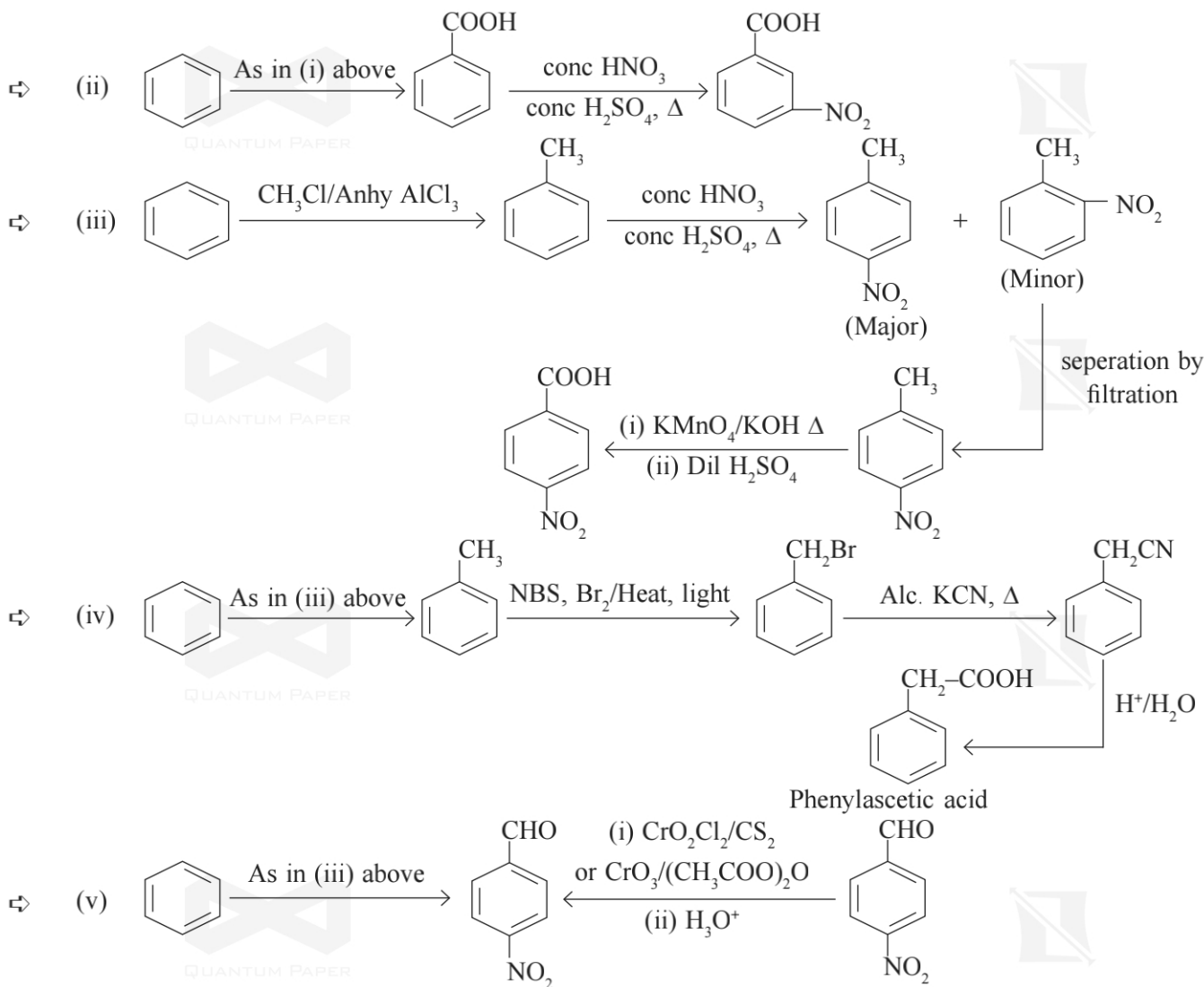
(ii) *m*-Nitrobenzoic acid

(iii) *p*-Nitrobenzoic acid

(iv) Phenylacetic acid

(v) *p*-Nitrobenzaldehyde.





Section D

● Write the answer of the following questions. [Each carries 5 Marks]

[5]

12. How will you bring about the following conversions in not more than two steps?

(i) Propanone to Propene

(ii) Benzoic acid to Benzaldehyde

(iii) Ethanol to 3-Hydroxybutanal

(iv) Benzene to *m*-Nitroacetophenone

(v) Benzaldehyde to Benzophenone

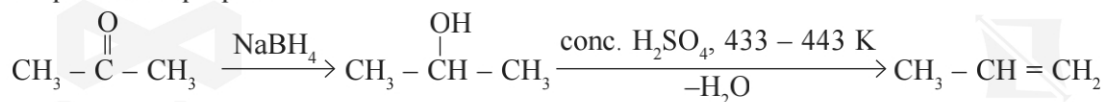
(vi) Bromobenzene to 1-Phenylethanol

(vii) Benzaldehyde to 3-Phenylpropan-1-ol

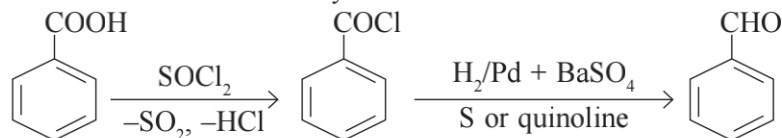
(viii) Benzaldehyde to α -Hydroxyphenylacetic acid

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

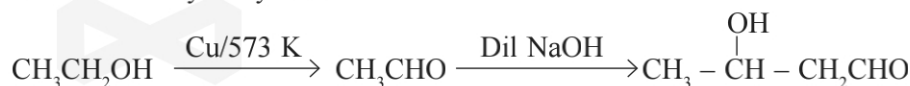
(i) Propanone to propene :



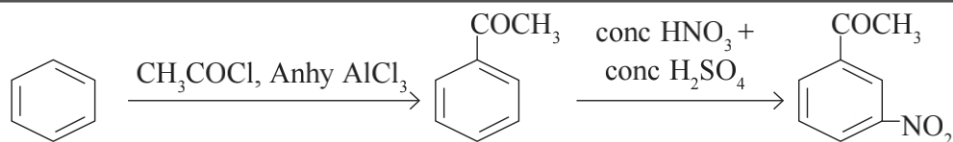
(ii) Benzoic acid to benzaldehyde :



(iii) Ethanol to 3-hydroxy butanal :



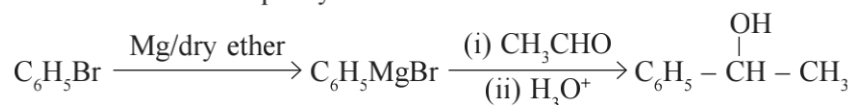
(iv) Benzene to *m*-nitroacetophenone :



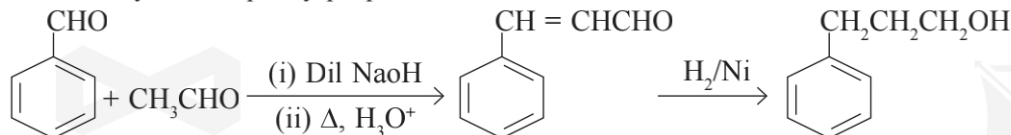
⇒ (v) Benzaldehyde to benzophenone :



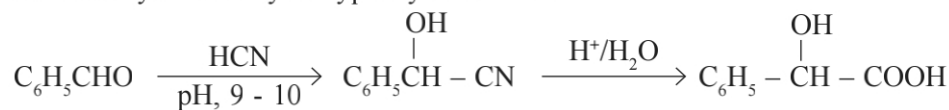
⇒ (vi) Bromobenzene to 1-phenylethanol :



⇒ (vii) Benzaldehyde to 3-phenylpropan-1-ol



⇒ (viii) Benzaldehyde to α -hydroxyphenylacetic acid :



⇒ (ix) Benzoic acid to *m*-nitrobenzyl alcohol :

