

Aldehydes, Ketones and Carboxylic Acids Amines

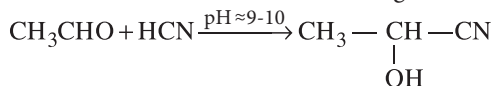
 Time Allowed : 3 hours
 Maximum Marks : 70

GENERAL INSTRUCTIONS

- (i) All questions are compulsory.
- (ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- (iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- (iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
- (v) Q. no. 23 is a value based question and carries 4 marks.
- (vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
- (vii) Use log tables if necessary, use of calculators is not allowed.

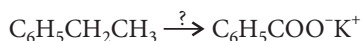
Previous Years Analysis						
	2016		2015		2014	
	Delhi	AI	Delhi	AI	Delhi	AI
VSA	1	–	1	–	2	2
SA-I	–	1	1	1	–	–
SA-II	1	1	1	1	1	1
VBQ	–	–	–	–	–	–
LA	1	1	1	1	1	1

1. Write the mechanism of the following reaction :



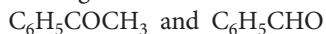
2. What is the IUPAC name of $\text{CH}_2=\text{CHCH}_2\text{NHCH}_3$?

3. Name the reagent used in the following reaction :



4. What is the best reagent to convert nitrile to primary amine?

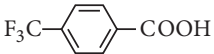
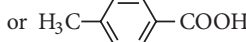
5. Distinguish between the following compounds :



6. Why aniline does not give Friedel-Crafts reaction?

7. Which acid of each pair given below would you expect to be stronger and why?

- (i) $\text{CH}_3\text{CO}_2\text{H}$ or $\text{CH}_2\text{FCO}_2\text{H}$

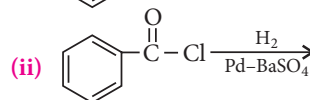
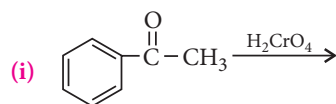
- (ii)  or 

8. Write the chemical equation to illustrate each of the following name reactions :

- (i) Rosenmund reduction (ii) Cannizzaro reaction

OR

Predict the products of the following reactions :



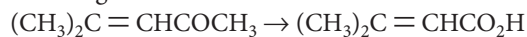
9. Why is methylamine stronger base than ammonia?

10. Give the chemical tests to distinguish between the following pairs of compounds :

- (i) Methylamine and dimethylamine

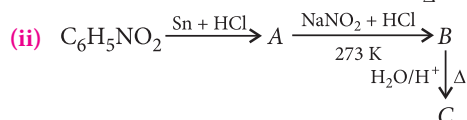
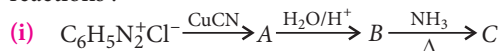
- (ii) Aniline and *N*-methylaniline

11. (i) Suggest a suitable oxidising agent for the following conversion :



(ii) Fluorine is more electronegative than chlorine even then *p*-fluorobenzoic acid is a weaker acid than *p*-chlorobenzoic acid. Explain

12. Give the structures of A, B and C in the following reactions :



13. (i) Out of toluene and benzene which is more easily nitrated ? Explain

(ii) State reasons for the following :

(a) Ethylamine is soluble in water whereas aniline is not soluble in water.

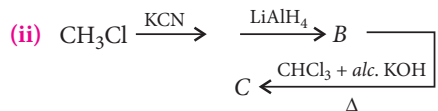
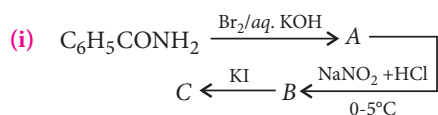
(b) Primary amines have higher boiling points than tertiary amines.

14. How will you convert ethanal into the following compounds?

(i) Butan-1,3-diol (ii) But-2-enal

(iii) But-2-enoic acid

15. Write the structures of A, B and C in the following :



16. How are the following conversions carried out :

(i) Ethyl cyanide to ethanoic acid

(ii) Butan-1-ol to butanoic acid

(iii) Methylbenzene to benzoic acid

17. Amines are more basic than comparable alcohols. Explain giving two reasons.

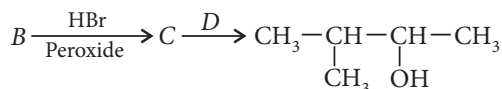
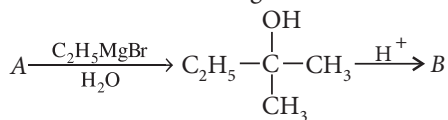
OR

Suggest chemical reactions for the following conversions :

(i) Cyclohexanol \rightarrow Cyclohexylamine

(ii) 1-Hexanenitrile \rightarrow 1-Aminopentane

18. Write the structural formulae of compounds A, B and C and name the reagent D in the following reaction :



19. Write the products formed when ethanal reacts with the following reagents :

(i) CH_3MgBr / H_3O^+ (ii) Zn-Hg/conc. HCl

(iii) $C_6H_5CHO / \text{dilute NaOH}$

20. Why is carboxyl group in benzoic acid *meta*-directing? Support your answer with two examples.

21. Account for the following observations :

(i) pK_b for aniline is more than that for methylamine.

(ii) Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.

(iii) Nitro compounds have higher boiling points than the hydrocarbons having almost the same molecular mass.

22. Write the steps and conditions involved in the following conversions :

(i) Acetophenone to 2-phenylbutan-2-ol

(ii) Propene to acetone

23. Surbhi, a class XII student was discussing about the wide use of colours in fabrics as well as in the food items with her mother. She told her about the harmful effects of azo dyes and colouring components particularly used in food items and stressed on the use of only natural dyes for colouring of food items.

(i) What are azo dyes? Give example.

(ii) Name an azo dye which has been used in food items and considered to be a cancer suspect.

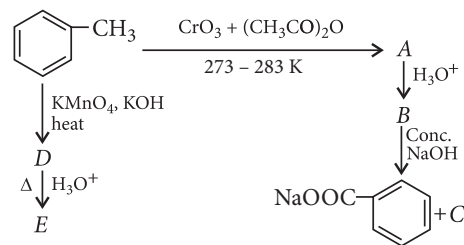
(iii) Name two natural food dyes.

(iv) What are the values expressed by surbhi?

24. A ketone A (C_4H_8O), which undergoes haloform reaction gives compound B on reduction. B on heating with sulphuric acid gives a compound C which forms monozonide D. D on hydrolysis in presence of zinc dust gives E. Identify A, B, C, D and E. Write the reactions involved.

OR

Identify A to E in the following series of reactions :



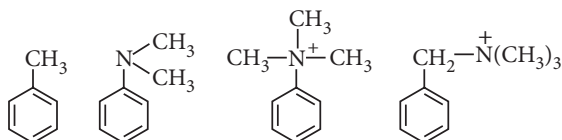
25. (i) How will you convert acetic acid to
 (a) malonic acid
 (b) *tert*-butyl alcohol
 (ii) Give chemical tests to distinguish between the following pairs of compounds :
 (a) Methyl acetate and ethyl acetate.
 (b) Benzaldehyde and benzoic acid.
 (c) Phenol and benzoic acid.

OR

- (i) State reasons for the following :
 (a) Monochloroethanoic acid has a higher pK_a value than dichloroethanoic acid.
 (b) Ethanoic acid is a weaker acid than benzoic acid.
 (ii) How will you convert acetic acid to
 (a) glycine (b) acetylene
 (c) ethylamine?

26. (i) Rearrange the following in an increasing order of their basic strengths :
 $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_6H_5)_2NH$ and CH_3NH_2

- (ii) Give increasing order towards electrophilic substitution of the following compounds :

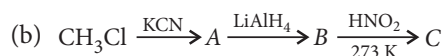
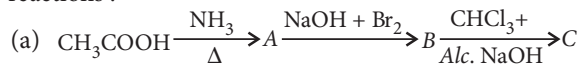


OR

- (i) Write the structures of main products when benzenediazonium chloride ($C_6H_5N_2^+Cl^-$) reacts with the following reagents :

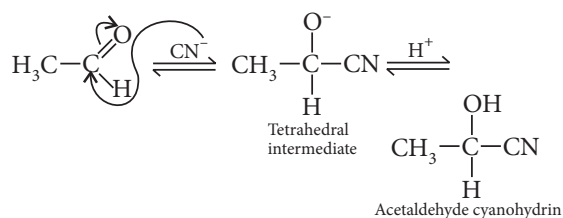
- (a) HBF_4/Δ (b) Cu/HBr

- (ii) Write the structures of A, B and C in the following reactions :

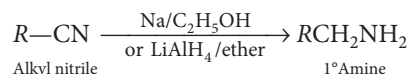


SOLUTIONS

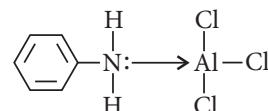
1. $HCN + OH^- \rightleftharpoons CN^- + H_2O$



2. $CH_2 = CHCH_2NHCH_3$
N-Methylprop-2-en-1-amine
 3. Alkaline potassium permanganate ($KMnO_4$, KOH)
 4. Reduction of nitriles with Na/C_2H_5OH or $LiAlH_4$ gives primary amines.



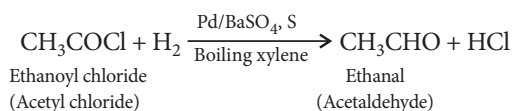
5. Benzaldehyde and acetophenone can be distinguished by Tollens' test. Benzaldehyde reduces Tollens' reagent whereas acetophenone does not.
 6. Lone pair of electrons on nitrogen atom of $-NH_2$ group in aniline conjugates with $AlCl_3$ catalyst to form a salt, which acts as a strong electron withdrawing group. As a result, it reduces the electron density in the benzene ring. Hence, aniline does not undergo Friedel-Crafts reaction.



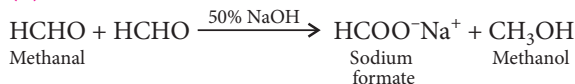
7. (i) H_2CF_3COOH is a stronger acid. Fluorine is an electronegative atom. Electron withdrawing group or atom stabilises the carboxylate ion and increases the acidity due to dispersal of negative charge.

- (ii) $F_3C-C_6H_4-COOH$ is a stronger acid. $-CF_3$ is an electron withdrawing group thus, increases the acid strength.

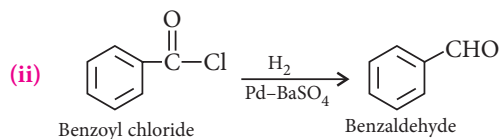
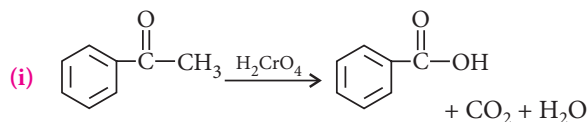
8. (i) Rosenmund reduction :



- (ii) Cannizzaro reaction :



OR



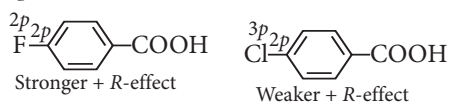
9. Both ammonia and methylamine have a lone pair of electrons and therefore, behave as Lewis bases. The alkyl group in CH_3NH_2 is electron releasing in nature thus, exhibit +I inductive effect. As a result, its electron releasing tendency becomes more. Thus, methylamine is more basic than ammonia.

10. (i) Methylamine (1° amine) gives carbylamine test, *i.e.*, on treatment with alc. KOH and chloroform, followed by heating it gives offensive odour of methyl isocyanide. Dimethylamine (2° amine) does not give this test.

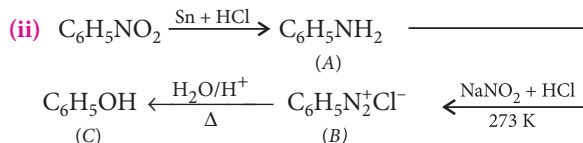
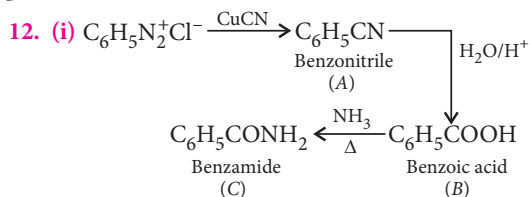
(ii) Aniline gives carbylamine test, *i.e.*, on treatment with alc. KOH and chloroform followed by heating it gives offensive odour of phenyl isocyanide but *N*-methylaniline being secondary amine, does not show this test.

11. (i) The most suitable reagent for this oxidation is NaOI (I_2/NaOH) since methyl ketones on treatment with NaOI undergo iodoform reaction to give iodoform along with the sodium salt of a carboxylic acid having one carbon atom less than the starting methyl ketone.

(ii) Since halogens are more electronegative than carbon and also possess lone pairs of electrons, therefore, they exert both $-I$ and $+R$ -effects. Now in F, the lone pairs of electrons are present in $2p$ -orbitals but in Cl, they are present in $3p$ -orbitals. Since $2p$ -orbitals of F and C atoms are of almost equal size, therefore, the $+R$ -effect is more pronounced in *p*-fluorobenzoic acid than in *p*-chlorobenzoic acid.



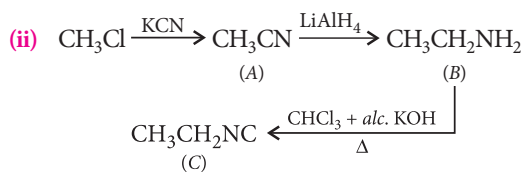
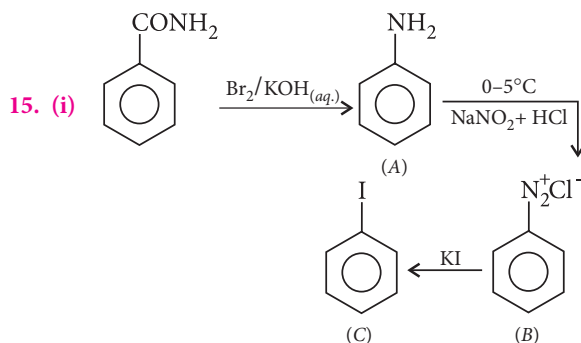
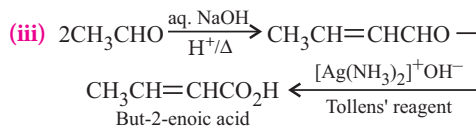
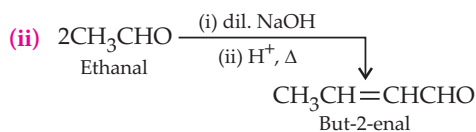
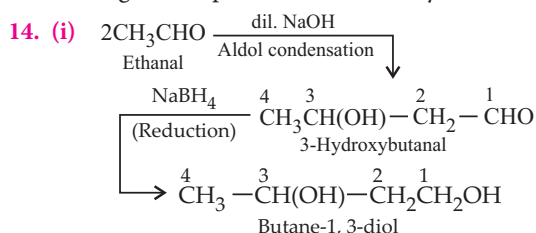
Thus, in *p*-fluorobenzoic acid, $+R$ -effect outweighs the $-I$ -effect but in *p*-chlorobenzoic acid, it is the $-I$ -effect which outweighs the $+R$ -effect. Consequently, *p*-fluorobenzoic acid is a weaker acid than *p*-chlorobenzoic acid.

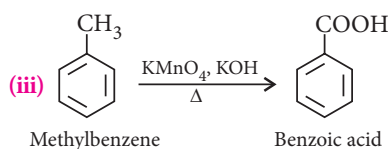
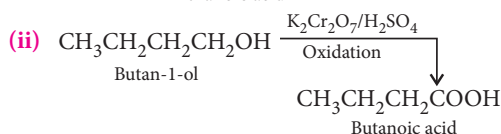
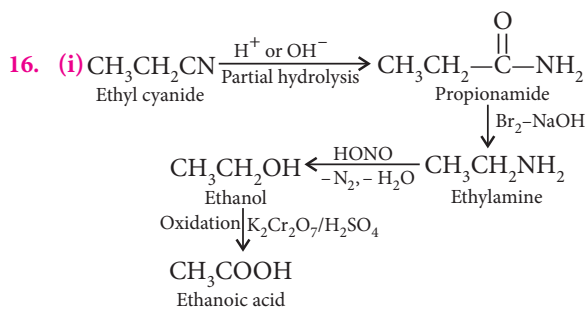


13. (i) Nitration is an electrophilic substitution reaction and thus, occurs more readily at a site where the electron-density is more. In toluene, there is electron-donating $-\text{CH}_3$ group. In other words, the electron density in the toluene ring is much more than in the benzene ring. As a result, toluene is nitrated more easily than benzene.

(ii) (a) Ethylamine is soluble in water due to formation of intermolecular hydrogen bonds with water molecules. However, in aniline due to large hydrophobic aryl group the extent of hydrogen bonding decreases considerably and hence, aniline is insoluble in water.

(b) Primary amines ($R-\text{NH}_2$) have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen bonding whereas no such hydrogen bonding is present in tertiary amines ($R_3\text{N}$). So, primary amines boil at a higher temperature than tertiary amines.

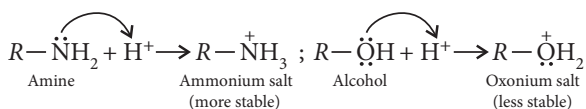




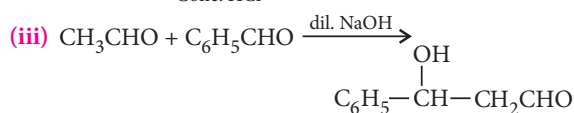
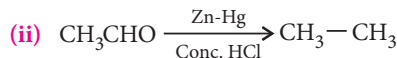
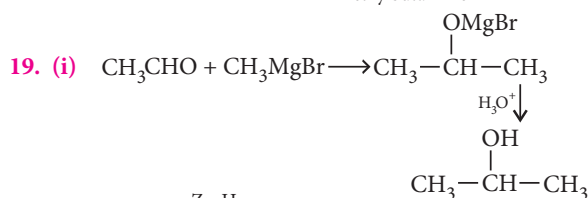
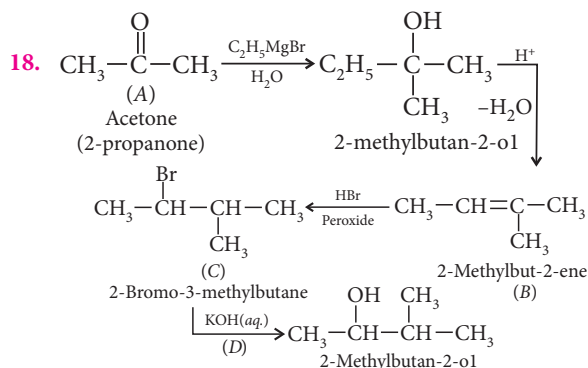
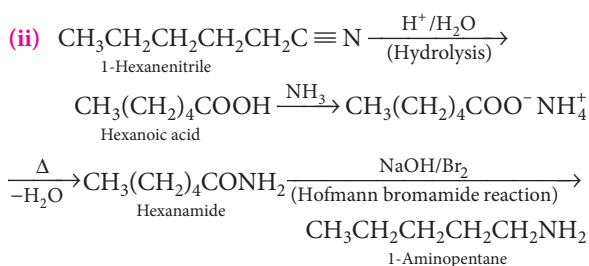
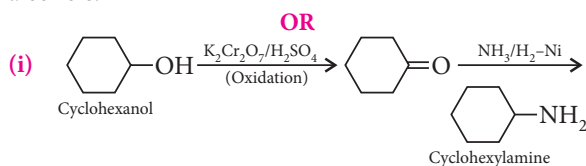
17. Amines are more basic than comparable alcohols because of the following two reasons :

(i) N being less electronegative is more willing to donate its lone pair of electrons to a proton than the more electronegative O atom. Therefore, amines are more basic than alcohols.

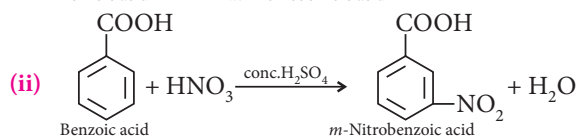
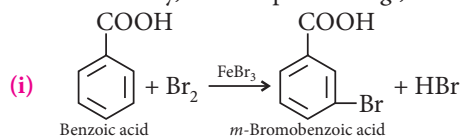
(ii) When an amine accepts a proton, ammonium salt is formed and when an alcohol accepts a proton oxonium salt is formed.



Since N being less electronegative can accommodate the positive charge better than the more electronegative O atom, therefore, ammonium salt is more stable than oxonium salt. As a result, amines are more basic than alcohols.



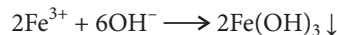
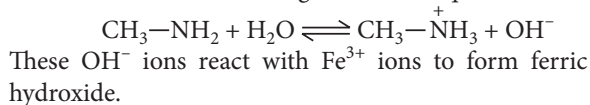
20. In benzoic acid, carboxyl group is *meta*-directing because it is electron withdrawing, therefore, there is +ve charge on *o*- and *p*-positions, therefore, electrophilic substitution takes place at *m*-position due to greater electron density, at *meta*-position *e.g.*,



21. (i) In aniline, the lone pair of electrons on N-atom are delocalised over the benzene ring. As a result, electron density on the nitrogen decreases. In contrast, in CH_3NH_2 , +I-effect of $-\text{CH}_3$ group increases the electron density on N-atom.

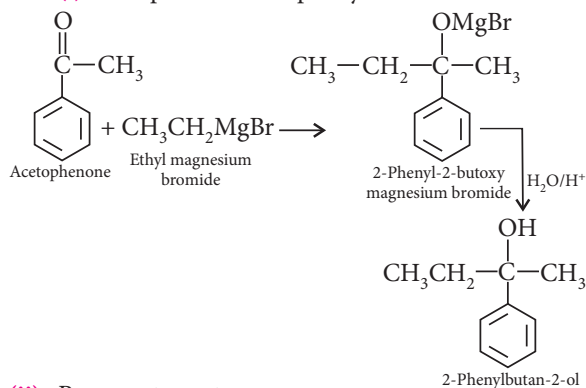
Therefore, aniline is a weaker base than methylamine and hence, its pK_b value is higher than that of methylamine.

(ii) Methylamine forms hydroxide ions when dissolved in water due to the following acid - base equilibrium.

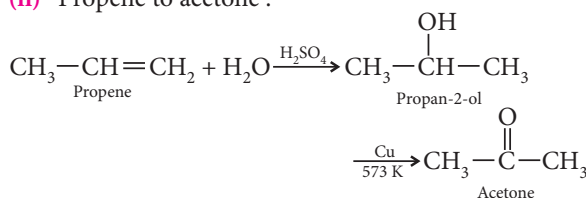


(iii) Nitro compounds are highly polar molecules. Due to this polarity they have strong intermolecular dipole-dipole interactions so, nitro compounds have higher boiling points in comparison to the hydrocarbons having almost same molecular mass.

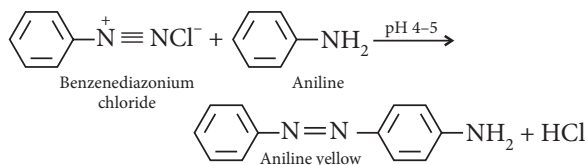
22. (i) Acetophenone to 2-phenylbutan-2-ol :



(ii) Propene to acetone :



23. (i) Dyes containing -N=N- as functional group are called azo dyes. For example, the simplest azo dye is aniline yellow obtained by coupling benzenediazonium chloride with aniline.

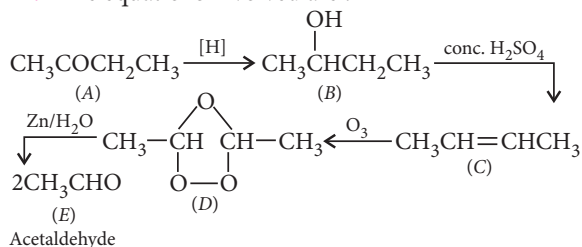


(ii) Tartrazine is a synthetic azo dye which has been used in food items but considered to be a cancer suspect.

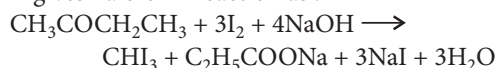
(iii) Natural food dyes are saffron and turmeric.

(iv) Surbhi has shown her concern about healthcare and applied her knowledge on the use of only natural dyes for colouring of food items.

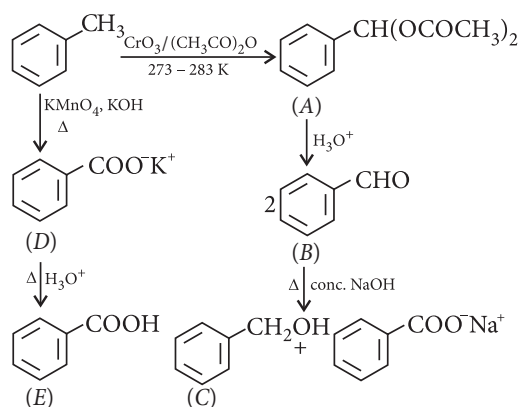
24. The equations involved are :



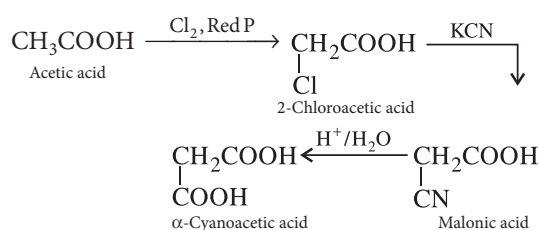
A gives haloform reaction as :



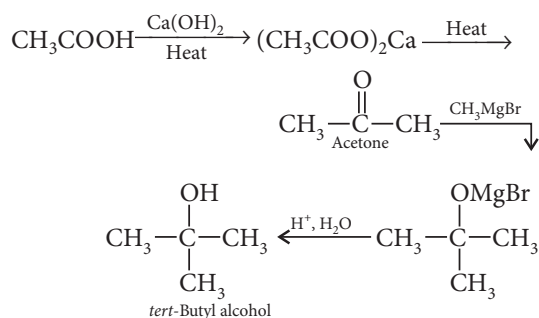
OR



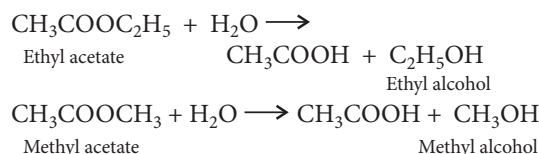
25. (i) (a) Acetic acid to malonic acid :



(b) Acetic acid to *tert*-butyl alcohol :

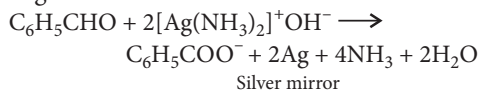


(ii) (a) Ethyl acetate is hydrolysed slowly by water to form ethyl alcohol while methyl acetate gives methyl alcohol.

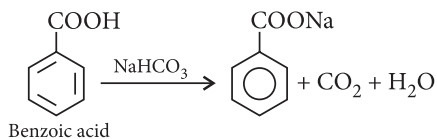


The hydrolysis product of ethyl acetate *i.e.*, ethanol undergoes iodoform test with iodine and alkali.

(b) Benzaldehyde when treated with ammoniacal silver nitrate gives silver mirror.



Benzoic acid reacts with sodium bicarbonate to liberate CO_2 .



(c) Phenol and benzoic acid can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with NaHCO_3 but phenol will not react.

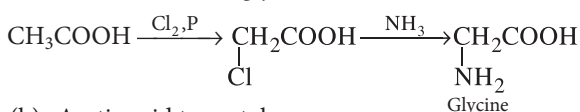
OR

(i) (a) The strength of an acid is indicated by $\text{p}K_a$ value, where, $\text{p}K_a = -\log K_a$

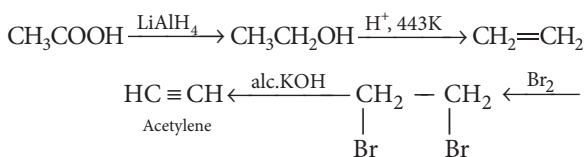
Since monochloroethanoic acid is weaker acid than dichloroethanoic acid so, it has lower value of dissociation constant K_a . Therefore, it has higher value of $\text{p}K_a$.

(b) $-\text{COOH}$ group in benzoic acid is attached to sp^2 -carbon of the phenyl ring and is more acidic than acetic acid in which $-\text{COOH}$ group is attached to sp^3 -carbon atom of $-\text{CH}_3$ group.

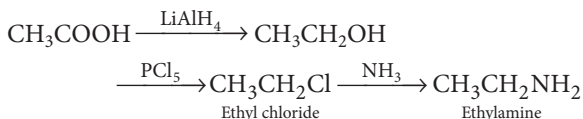
(ii) (a) Acetic acid to glycine :



(b) Acetic acid to acetylene :



(c) Acetic acid to ethylamine :



26. (i) (a) Due to delocalisation of lone pair of electrons of the N-atom over the benzene ring, all aromatic amines are less basic than alkylamines, *i.e.*, CH_3NH_2 .

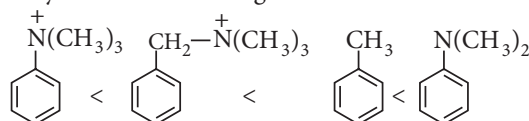
(b) Presence of electron donating groups (*i.e.*, CH_3) on the N-atom increases the basicity of substituted aniline w.r.t. $\text{C}_6\text{H}_5\text{NH}_2$.

(c) In $(\text{C}_6\text{H}_5)_2\text{NH}$, the lone pair of electrons on the N-atom is delocalised over two benzene rings instead of one in $\text{C}_6\text{H}_5\text{NH}_2$, therefore, $(\text{C}_6\text{H}_5)_2\text{NH}$ is much less basic than $\text{C}_6\text{H}_5\text{NH}_2$.

Combining all the three trends together the basicity of the four amines increases in the order :

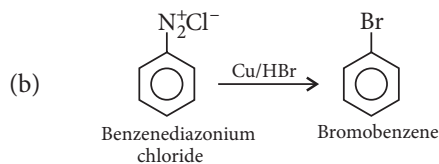
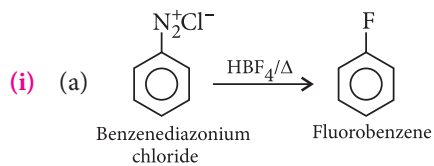


(ii) Higher the electron density in the benzene ring, more reactive is the aromatic compound towards electrophilic substitution reaction. Now due to the presence of a lone pair of electrons on the N-atom which it can directly donate to the benzene ring, $-\text{N}(\text{CH}_3)_2$ is a much stronger electron donating group than $-\text{CH}_3$ group. The remaining two groups contain a positive charge on the N-atom and hence, act as electron withdrawing groups. But in $(\text{CH}_3)_3\text{N}^+$ -group, the +vely charged N is directly attached to the benzene ring, therefore, its electron withdrawing ability is much stronger than $-\text{CH}_2\text{N}^+(\text{CH}_3)_3$. Thus, the electron density in the benzene ring increases in the order :



Therefore, their reactivity towards electrophilic substitution reactions also increases in the same order.

OR



(ii) (a)

