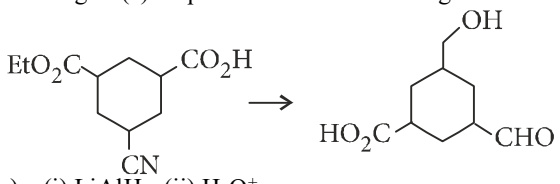
CHAPTER

25

Aldehydes, Ketones and Carboxylic Acids

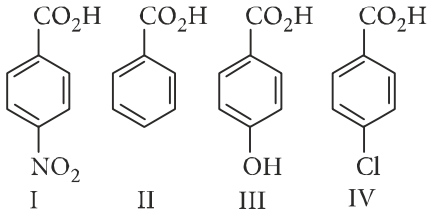
1. The reagent(s) required for the following conversion are



(a) (i) $LiAlH_4$, (ii) H_3O^+
(b) (i) B_2H_6, (ii) DIBAL-H, (iii) H_3O^+
(c) (i) B_2H_6, (ii) $SnCl_2/HCl$, (iii) H_3O^+
(d) (i) $NaBH_4$, (ii) Raney Ni/H_2, (iii) H_3O^+

(Online 2018)

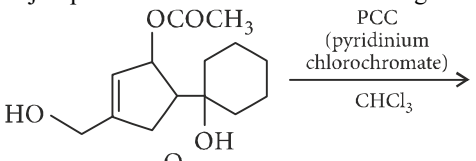
2. The increasing order of the acidity of the following carboxylic acid is



(a) I < III < II < IV (b) II < IV < III < I
(c) IV < II < III < I (d) III < II < IV < I

(Online 2018)

3. The major product formed in the following reaction is



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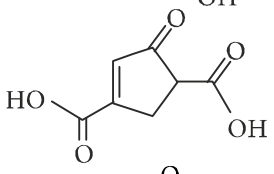

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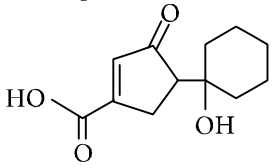

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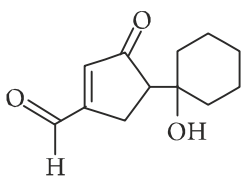

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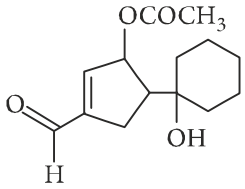
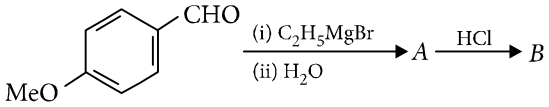
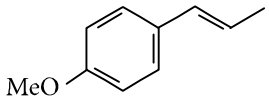


(Online 2018)

4. The major product *B* formed in the following reaction sequence is



(a)



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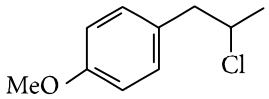

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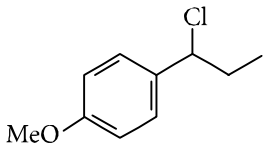

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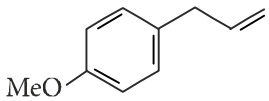
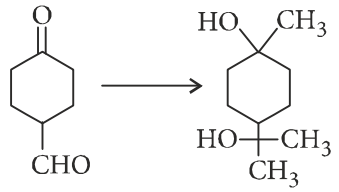


(Online 2018)

5. Which of the following compounds will most readily be dehydrated to give alkene under acidic condition?
(a) 4-Hydroxypentan-2-one
(b) 2-Hydroxycyclopentanone
(c) 3-Hydroxypentan-2-one
(d) 1-Pentanol *(Online 2018)*

6. Sodium salt of an organic acid '*X*' produces effervescence with conc. H_2SO_4. '*X*' reacts with the acidified aqueous $CaCl_2$ solution to give a white precipitate which decolourises acidic solution of $KMnO_4$. '*X*' is
(a) CH_3COONa (b) $Na_2C_2O_4$
(c) C_6H_5COONa (d) $HCOONa$ *(2017)*

7. The correct sequence of reagents for the following conversion will be



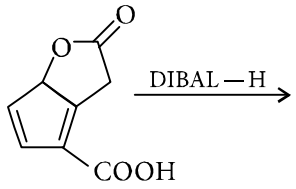
(a) CH_3MgBr, $[Ag(NH_3)_2]^+OH^-$, H^+/CH_3OH

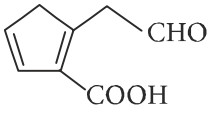
(b) $[Ag(NH_3)_2]^+OH^-$, CH_3MgBr, H^+/CH_3OH

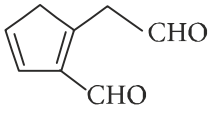
(c) $[Ag(NH_3)_2]^+OH^-$, H^+/CH_3OH, CH_3MgBr

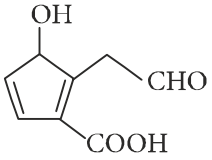
(d) CH_3MgBr, H^+/CH_3OH, $[Ag(NH_3)_2]^+OH^-$ *(2017)*

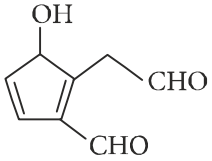
8. The major product obtained in the following reaction is



(a) 

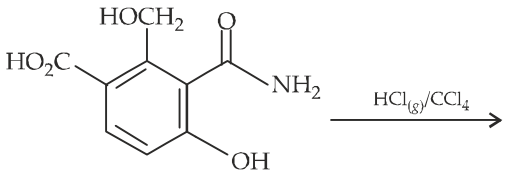
(b) 

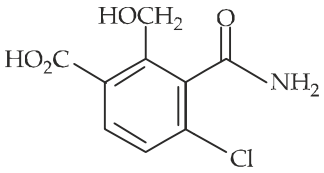
(c) 

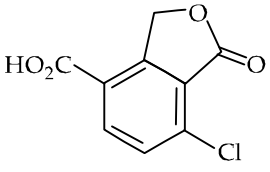
(d) 

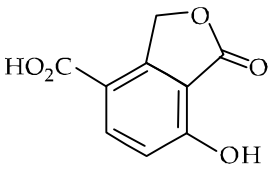
(2017)

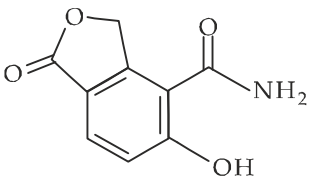
9. The major product expected from the following reaction is



(a) 

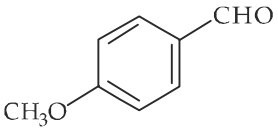
(b) 

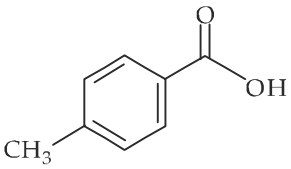
(c) 

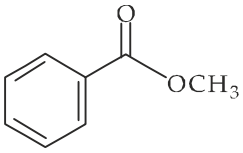
(d) 

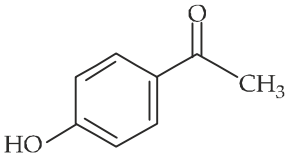
(Online 2017)

10. A compound of molecular formula $C_8H_8O_2$ reacts with acetophenone to form a single cross-aldol product in the presence of base. The same compound on reaction with conc. NaOH forms benzyl alcohol as one of the products. The structure of the compound is

(a) 

(b) 

(c) 

(d) 

(Online 2017)

11. Bouveault-Blanc reduction reaction involves

(a) reduction of an acyl halide with H_2/Pd

(b) reduction of an anhydride with $LiAlH_4$

(c) reduction of an ester with Na/C_2H_5OH

(d) reduction of a carbonyl compound with Na/Hg and HCl. *(2016)*

12. The correct statement about the synthesis of erythritol ($C(CH_2OH)_4$) used in the preparation of PETN is

(a) the synthesis requires three aldol condensations and one Cannizzaro reaction

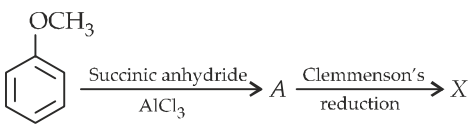
(b) alpha hydrogens of ethanol and methanol are involved in this reaction.

(c) the synthesis requires two aldol condensations and two Cannizzaro reactions.

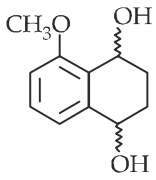
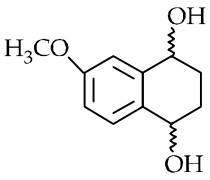
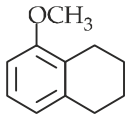
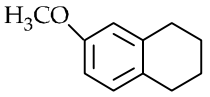
(d) the synthesis requires four aldol condensations between methanol and ethanol.

(Online 2016)

13. Consider the reaction sequence below :



X is

(a) 
(b) 
(c) 
(d) 

(Online 2016)

14. In the following sequence of reactions :

$$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C$$

the product (C) is

(a) $C_6H_5CH_2OH$ (b) C_6H_5CHO

(c) C_6H_5COOH (d) $C_6H_5CH_3$ *(2015)*

15. In the reaction sequence, $2CH_3CHO \xrightarrow{OH^-} A \xrightarrow{\Delta} B$; the product B is

(a) $CH_3CH_2CH_2CH_2OH$

(b) $CH_3CH = CHCHO$

(c) $CH_3 - \overset{\overset{O}{\|}}{C} - CH_3$

(d) $CH_3 - CH_2 - CH_2 - CH_3$ *(Online 2015)*

16. In the presence of a small amount of phosphorus, aliphatic carboxylic acids react with chlorine or bromine to yield a compound in which α-hydrogen has been replaced by halogen. This reaction is known as

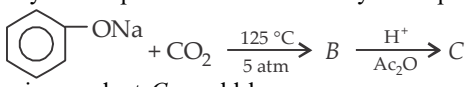
(a) Wolff-Kishner reaction

(b) Etard reaction

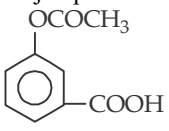
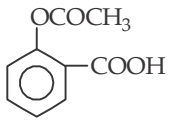
(c) Hell-Volhard-Zelinsky reaction

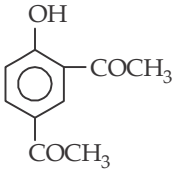
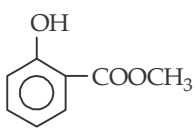
(d) Rosenmund reaction. *(Online 2015)*

17. Sodium phenoxide when heated with CO_2 under pressure at 125 °C yields a product which on acetylation produces C.



The major product C would be

(a)  (b) 

(c)  (d) 

(2014)

18. In the reaction,

$$CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{\text{Alc. KOH}} C,$$

the product C is

(a) acetyl chloride (b) acetaldehyde

(c) acetylene (d) ethylene. *(2014)*

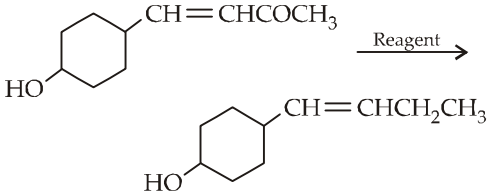
19. An organic compound A upon reacting with NH_3 gives B. On heating, B gives C. C in presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. A is

(a) CH_3CH_2COOH (b) CH_3COOH

(c) $CH_3CH_2CH_2COOH$ (d) $CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH$

(2013)

20. In the given transformation, which of the following is the most appropriate reagent?



(a) Zn-Hg/HCl (b) Na, liq. NH_3

(c) $NaBH_4$ (d) NH_2-NH_2, OH^- *(2012)*

21. Silver mirror test is given by which one of the following compounds?

(a) Acetaldehyde (b) Acetone

(c) Formaldehyde (d) Benzophenone *(2011)*

22. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of

(a) two ethylenic double bonds

(b) a vinyl group (c) an isopropyl group

(d) an acetylenic triple bond. *(2011)*

23. The strongest acid amongst the following compounds is

(a) CH_3COOH (b) HCOOH

(c) $CH_3CH_2CH(Cl)CO_2H$

(d) $ClCH_2CH_2CH_2COOH$ *(2011)*

24. Trichloroacetaldehyde was subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compound is

(a) 2,2,2-trichloroethanol

(b) trichloromethanol (c) 2,2,2-trichloropropanol

(d) chloroform *(2011)*

25. In Cannizzaro reaction given below

$$2PhCHO \xrightarrow{:OH^-} PhCH_2OH + PhCOO^-$$

the slowest step is

(a) the attack of $:OH^-$ at the carboxyl group

(b) the transfer of hydride to the carbonyl group

(c) the abstraction of proton from the carboxylic group

(d) the deprotonation of $PhCH_2OH$. *(2009)*

26. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was

(a) CH_3OH (b) HCHO

(c) CH_3COCH_3 (d) CH_3COOH *(2009)*

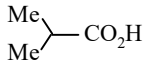
27. The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is

(a) benzyl alcohol (b) benzophenone

(c) acetophenone (d) benzoic acid. *(2007)*

28. The correct order of increasing acid strength of the compounds

(*A*) CH_3CO_2H (*B*) $MeOCH_2CO_2H$

(*C*) CF_3CO_2H (*D*)  is

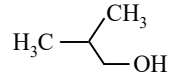
(a) $B < D < A < C$ (b) $D < A < C < B$

(c) $D < A < B < C$ (d) $A < D < C < B$. *(2006)*

29. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is

(a) $CH_3CH_2CH(OH)CH_2CH_3$

(b) $C_6H_5CH_2CH_2OH$

(c)  (d) $PhCHOHCH_3$ *(2006)*

30. The increasing order of the rate of HCN addition to compounds *A* - *D* is

A. HCHO *B*. CH_3COCH_3

C. $PhCOCH_3$ *D*. PhCOPh.

(a) $A < B < C < D$ (b) $D < B < C < A$

(c) $D < C < B < A$ (d) $C < D < B < A$ *(2006)*

31. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid?

(a) Phenol (b) Benzaldehyde

(c) Butanol (d) Benzoic acid *(2004)*

32. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is

(a) $CH_3COOC_2H_5 + NaCl$

(b) $CH_3COONa + C_2H_5OH$

(c) $CH_3COCl + C_2H_5OH + NaOH$

(d) $CH_3Cl + C_2H_5COONa$. *(2004)*

33. Consider the acidity of the carboxylic acids:

(i) PhCOOH (ii) *o*-$NO_2C_6H_4COOH$

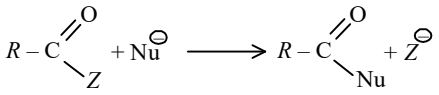
(iii) *p*-$NO_2C_6H_4COOH$ (iv) *m*-$NO_2C_6H_4COOH$

Which of the following order is correct?

(a) i > ii > iii > iv (b) ii > iv > iii > i

(c) ii > iv > i > iii (d) ii > iii > iv > i *(2004)*

34. Rate of the reaction,



is fastest when *Z* is

(a) Cl (b) NH_2

(c) OC_2H_5 (d) $OCOCH_3$. *(2004)*

35. In the anion $HCOO^-$ the two carbon-oxygen bonds are found to be of equal length. What is the reason for it?

(a) Electronic orbitals of carbon atom are hybridised.

(b) The C = O bond is weaker than the C – O bond.

(c) The anion $HCOO^-$ has two resonating structures.

(d) The anion is obtained by removal of a proton from the acid molecule. *(2003)*

36. The general formula $C_nH_{2n}O_2$ could be for open chain

(a) diketones (b) carboxylic acids

(c) diols (d) dialdehydes. *(2003)*

37. When $CH_2 = CH - COOH$ is reduced with $LiAlH_4$, the compound obtained will be

(a) $CH_3 - CH_2 - COOH$

(b) $CH_2 = CH - CH_2OH$

(c) $CH_3 - CH_2 - CH_2OH$

(d) $CH_3 - CH_2 - CHO$. *(2003)*

38. The IUPAC name of $CH_3COCH(CH_3)_2$ is

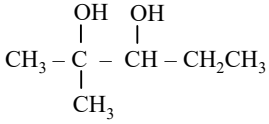
(a) isopropylmethyl ketone

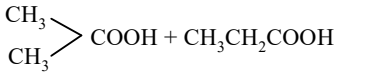
(b) 2-methyl-3-butanone

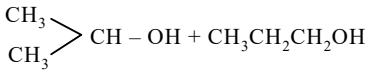
(c) 4-methylisopropyl ketone

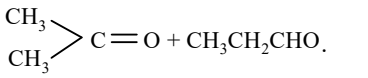
(d) 3-methyl-2-butanone. *(2003)*

39. On vigorous oxidation by permanganate solution, $(CH_3)_2C = CH - CH_2 - CHO$ gives

(a) 

(b) 

(c) 

(d)  *(2002)*

40. 

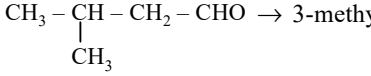
What is *B* ?

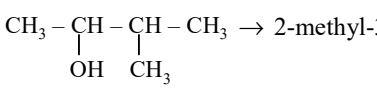
(a) CH_3CH_2COCl (b) CH_3CH_2CHO

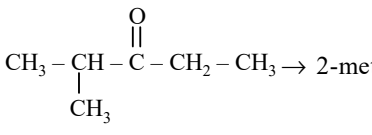
(c) $CH_2 = CHCOOH$ (d) $ClCH_2CH_2COOH$ *(2002)*

41. Which of the following compounds has wrong IUPAC name?

(a) $CH_3 - CH_2 - CH_2 - COO - CH_2CH_3$ → ethyl butanoate

(b)  → 3-methylbutanal

(c)  → 2-methyl-3-butanol

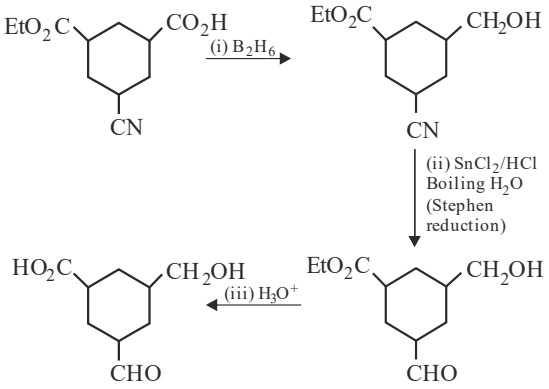
(d)  → 2-methyl-3-pentanone

ANSWER KEY

1. (c)	**2.** (d)	**3.** (d)	**4.** (c)	**5.** (a)	**6.** (b)	**7.** (c)	**8.** (d)	**9.** (d)	**10.** (a)	**11.** (c)	**12.** (a)
13. (d)	**14.** (b)	**15.** (b)	**16.** (c)	**17.** (b)	**18.** (d)	**19.** (a)	**20.** (d)	**21.** (a, c)	**22.** (b)	**23.** (c)	**24.** (a)
25. (b)	**26.** (d)	**27.** (d)	**28.** (c)	**29.** (d)	**30.** (c)	**31.** (b)	**32.** (a)	**33.** (d)	**34.** (a)	**35.** (c)	**36.** (b)
37. (b)	**38.** (d)	**39.** (b)	**40.** (c)	**41.** (c)							

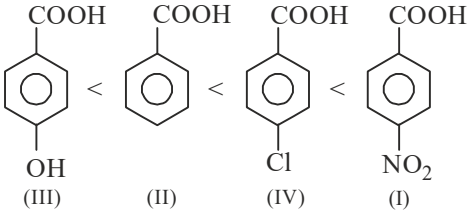
Explanations

1. (c) :

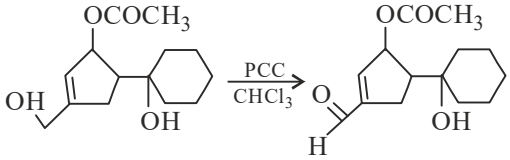


2. (d) : Electron withdrawing groups increase the acidity of substituted benzoic acids whereas electron donating groups decrease the acidity.

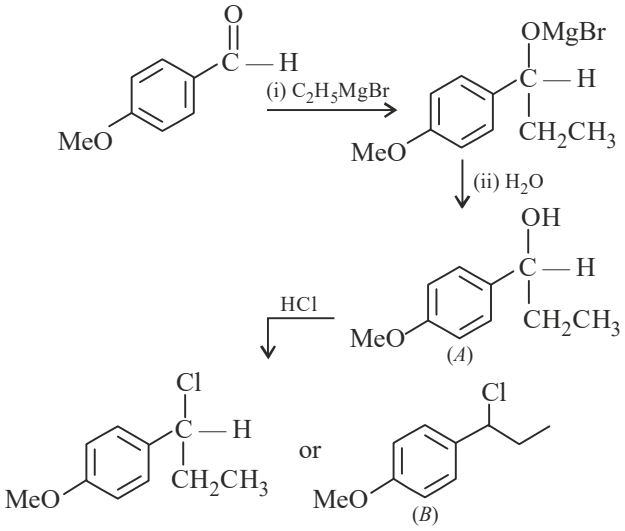
$—NO_2$ and —Cl are electron withdrawing, $—NO_2$ has stronger $-I$ effect than that of —Cl. Whereas, —OH has electron releasing effect. Thus, the order of acidity is,



3. (d) : Pyridinium chlorochromate selectively oxidises 1° alcohol to aldehyde.



4. (c) :



5. (a) : The compound containing most acidic hydrogen will undergo dehydration most readily. Thus, 4-hydroxypentan-2-one undergoes most rapid dehydration under acidic condition.

6. (b) :

$$\underset{(X)}{Na_2C_2O_4} + \underset{(conc.)}{H_2SO_4} \longrightarrow Na_2SO_4 + \underset{(Oxalic\ acid)}{H_2C_2O_4}$$

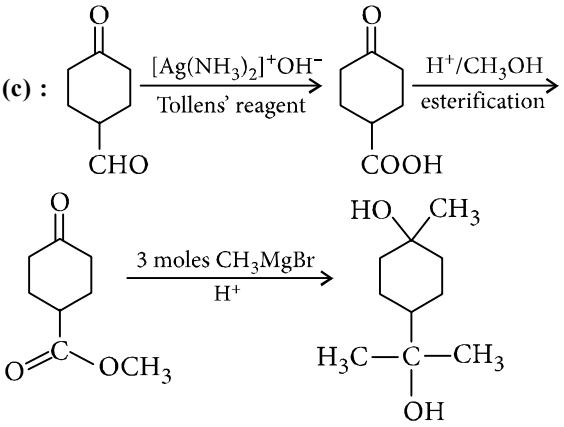
$$H_2C_2O_4 \xrightarrow[-H_2O]{conc.\ H_2SO_4/\Delta} \underbrace{CO\uparrow + CO_2\uparrow}_{Effervescence}$$

$$\underset{(X)}{Na_2C_2O_4} + CaCl_{2(aq)} \longrightarrow \underset{(White\ ppt.)}{CaC_2O_4\downarrow} + 2NaCl$$

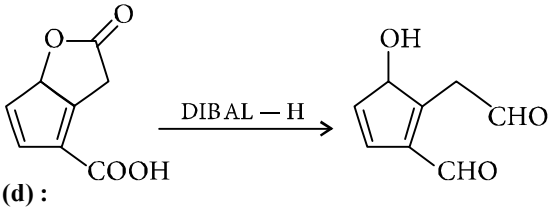
$$\underset{(Purple)}{5CaC_2O_4\downarrow} + 2KMnO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 5CaSO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

(Colourless)

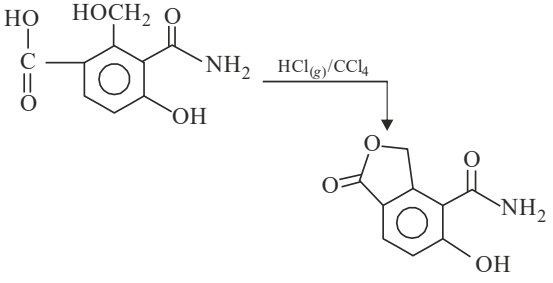
7. (c) :



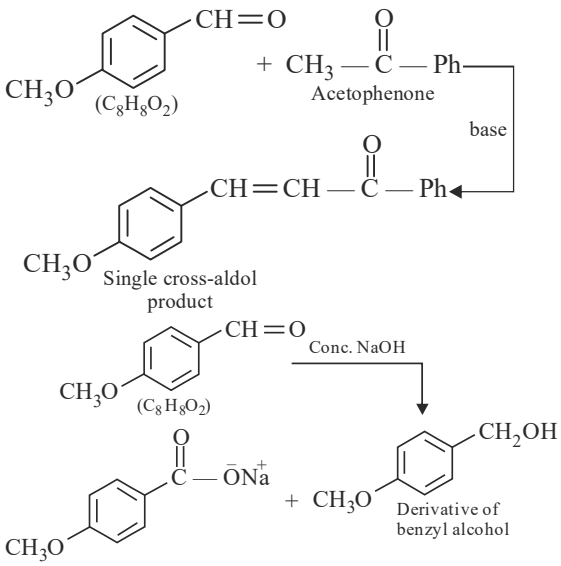
8. (d) : DIBAL – H is a bulkier compound and a strong reducing agent which reduces cyanide, esters, lactone, amide, carboxylic acids into their corresponding aldehydes (partial reduction).



9. (d) :



10. (a) :



11. (c) : $CH_3COOC_2H_5 + 2H_2 \xrightarrow{Na/C_2H_5OH} 2CH_3CH_2OH$

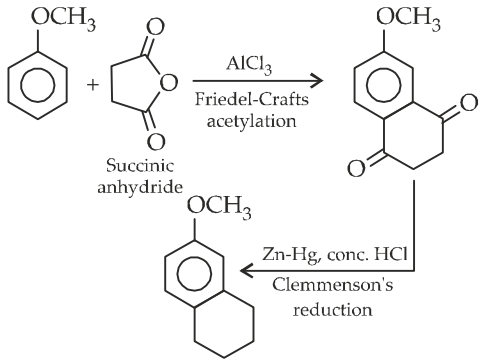
Ester → Alcohol

This reduction is known as Bouveault-Blanc reduction.

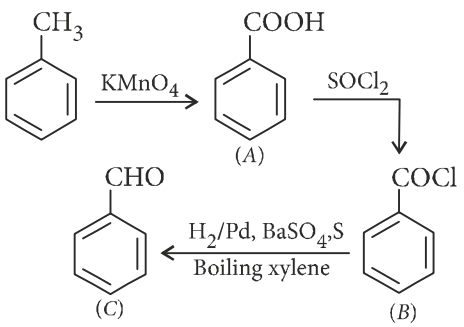
12. (a) : $CH_3CHO \xrightarrow[\bar{O}H]{3HCHO} OHC-C(OH)(CH_2OH)_2$ (3 Aldol reactions)

$\xrightarrow[\bar{O}H]{HCHO}$ (1 Cannizzaro reaction)

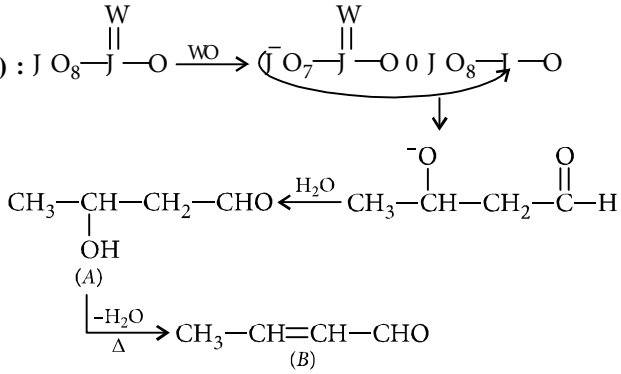
13. (d) :



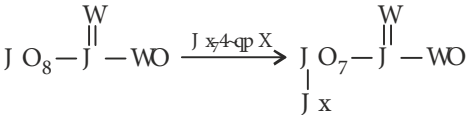
14. (b) :



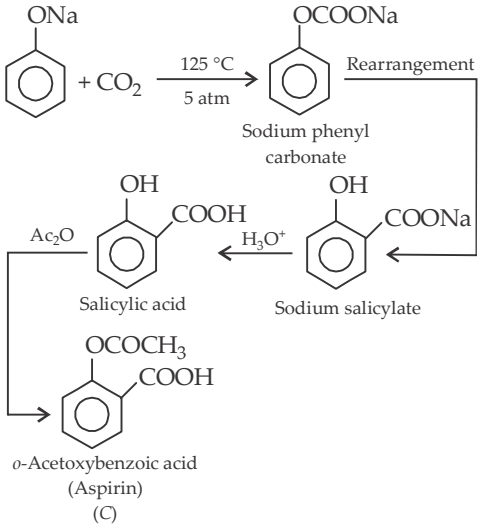
15. (b) :



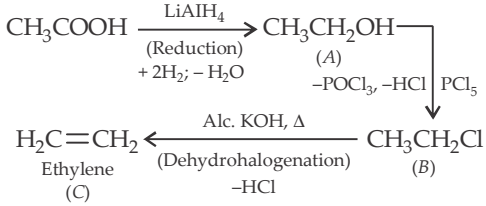
16. (c) : Hell-Volhard-Zelinsky reaction



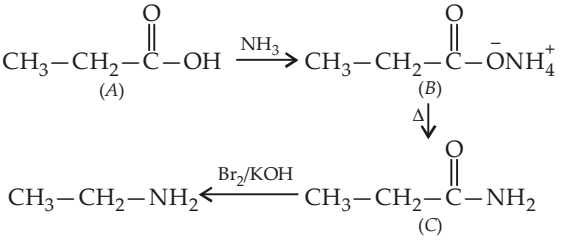
17. (b) :



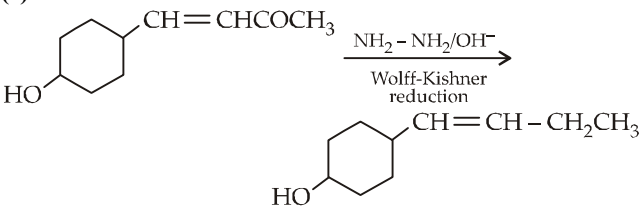
18. (d) :



19. (a) :

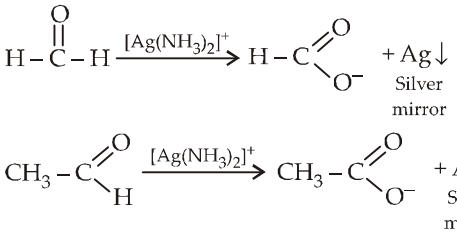


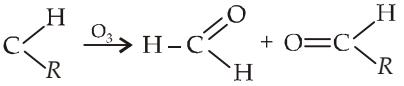
20. (d) :



– OH group and alkene are acid-sensitive groups so Clemmensen reduction cannot be used and $NaBH_4$ reduces to – CHOH only.

21. (a, c) : Formaldehyde and acetaldehyde can be oxidised by Tollen's reagent to give silver mirror.

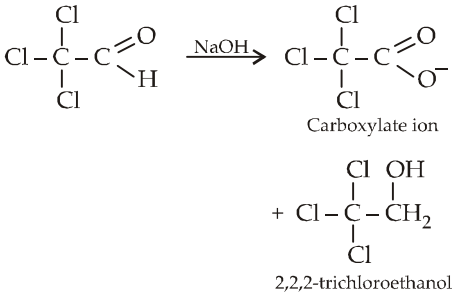


22. (b) : 

Vinyl group ($CH_2 = CH -$) on ozonolysis gives formaldehyde.

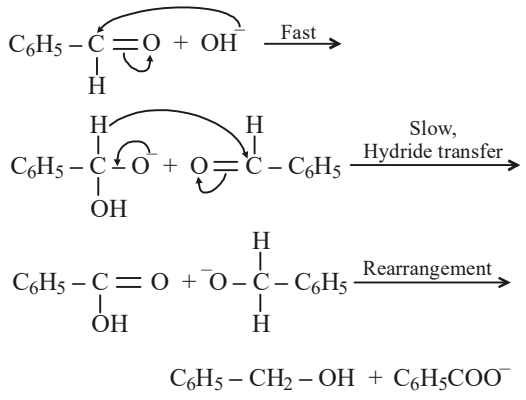
23. (c) : $CH_3CH_2CH(Cl)COOH$ is the strongest acid due to $-I$ effect of Cl.

24. (a) : In Cannizzaro's reaction one molecule is oxidised to carboxylate ion and the other is reduced to alcohol.



25. (b) : Rate determining step is always the slowest step. In case of Cannizzaro reaction, H-transfer to the carbonyl group is the rate determining step and hence the slowest.

Mechanism :

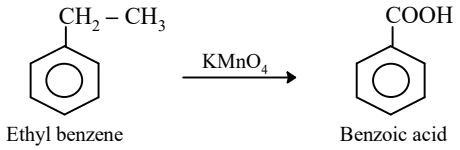


$$C_6H_5 - CH_2 - OH + C_6H_5COO^-$$

26. (d) : Since the compound formed has a fruity smell, it is an ester, thus the liquid to which ethanol and conc. H_2SO_4 are added must be an acid.

$$\therefore CH_3COOH + C_2H_5OH \xrightarrow{conc.H_2SO_4} CH_3COOC_2H_5 + H_2O$$

27. (d) :



When oxidises with alkaline $KMnO_4$ or acidic $Na_2Cr_2O_7$, the entire side chain (in benzene homologues) with atleast one H at α-carbon, regardless of length is oxidised to – COOH.

28. (c) : Effect of substituent on the acid strength of aliphatic acids:

(i) Acidity decreases as the $+I$-effect of the alkyl group increases.

$HCOOH > CH_3COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$

(ii) Acidity decreases as the $-I$-effect as well as number of halogen atoms decreases.

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH > CH_3COOH$

$F_3CCOOH > F_2CHCOOH > FCH_2COOH > CH_3COOH$

(iii) Electron donating substituents like $-R$, $-OH$, $-NH_2$ etc. tend to decrease while electron withdrawing substituents like $-NO_2$, –CHO, etc. tend to increase the acid strength of substituted acid.

On the basis of given information the relative order of increasing acid strength of the given compounds is

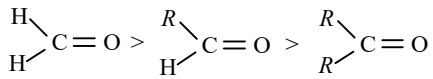
$(CH_3)_2COOH < CH_3COOH < CH_3OCH_2COOH < CF_3COOH$

29. (d) : Iodoform test is given by only the compounds containing $CH_3CO -$ or $CH_3CHOH -$ group.

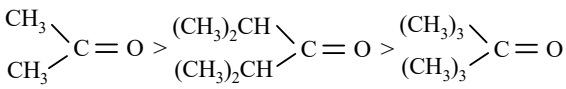
$$PhCHOHCH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + PhCOONa + 5NaI + 5H_2O$$

30. (c) : Addition of HCN to carbonyl compounds is a characteristic nucleophilic addition reaction of carbonyl compounds.

Order of reactivity:



The lower reactivity of ketones over aldehydes is due to $+I$-effect of the alkyl (R) group and steric hindrance. As the size of the alkyl group increases, the reactivity of the ketones further decreases.



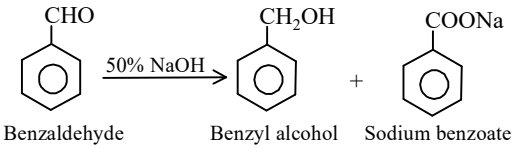
The aromatic aldehydes and ketones are less reactive than their aliphatic analogous. This is due to the $+R$ effect of the benzene ring.

$$PhCHO > PhCOCH_3 > PhCOPh$$

From the above information, it is clear that increasing order of the rate of HCN addition to compounds HCHO, CH_3COCH_3, $PhCOCH_3$ and PhCOPh is

$PhCOPh < PhCOCH_3 < CH_3COCH_3 < HCHO$.

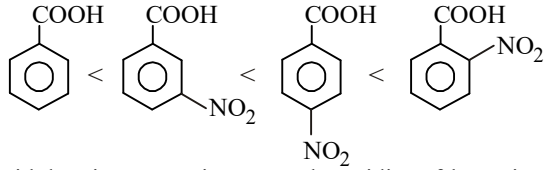
31. (b) : Benzaldehyde will undergo Cannizzaro reaction on treatment with 50% NaOH to produce benzyl alcohol and benzoic acid as it does not contain α-hydrogen.



Benzaldehyde Benzyl alcohol Sodium benzoate

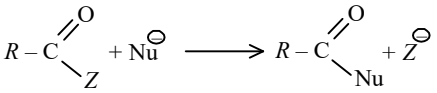
32. (a) : $CH_3COOC_2H_5 + NaCl_{(aq)} \rightarrow$ no reaction
i.e., the resultant solution contains ethyl acetate and sodium chloride.

33. (d) :



Electron withdrawing group increases the acidity of benzoic acid, *o*-isomer will have higher acidity then corresponding *m* and *p* isomer due to *ortho*-effect.
As *M* group (*i.e.* NO_2) at *p*-position have more pronounced electron withdrawing effect than as $-NO_2$ group at *m*-position (*–I* effect)
∴ Correct order of acidity is ii > iii > iv > i.

34. (a) :

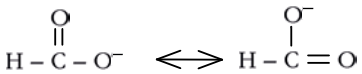


Reactivity of the acid derivatives decreases as the basicity of the leaving group increases. The basicity of the leaving group increases as

$$Cl^- < RCOO^- < RO^- < NH_2^-$$

Secondly least stabilization by resonance due to ineffective overlapping between the 3*p* orbital of Cl and 2*p* orbital of carbon.

35. (c) : $HCOO^-$ exists as



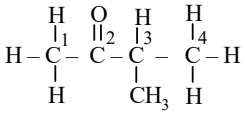
So, the two carbon-oxygen bonds are found to be of equal length.

36. (b) : Diketones - $C_nH_{2n-2}O_2$, Carboxylic acid - $C_nH_{2n}O_2$
Diols - $C_nH_{3n}O_2$, Dialdehydes - $C_nH_nO_2$.

37. (b) : $LiAlH_4$ is a strong reducing agent, it reduces carboxylic group into primary alcoholic group without affecting the basic skeleton of compound.

$$CH_2{=}CH - COOH \xrightarrow[[H^+]]{LiAlH_4} CH_2{=}CH - CH_2OH$$

38. (d) :

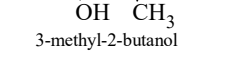


3-methyl-2-butanone

39. (b) : Aldehydic group gets oxidised to carboxylic group. Double bond breaks and carbon gets oxidised to carboxylic group.

40. (c) :

41. (c) :



3-methyl-2-butanol