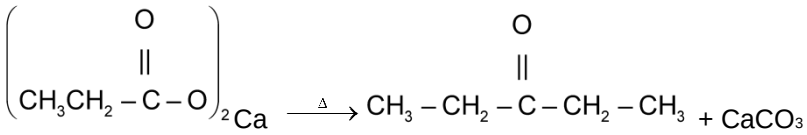
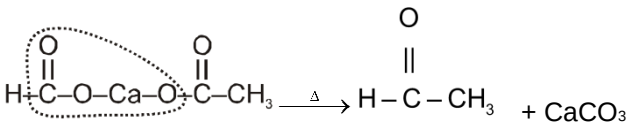
Exercise-1

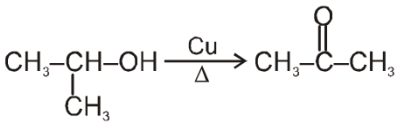
Marked Questions may have for Revision Questions.

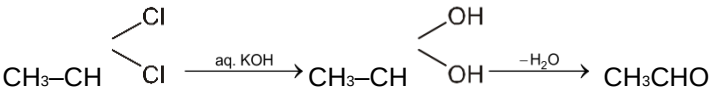
OBJECTIVE QUESTIONS

Section (A) : Preparation of Carbonyl Compounds

A-1. Sol. 

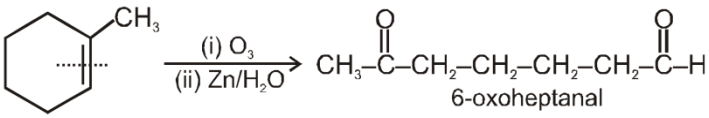
A-2. Sol. 

A-4. Sol. 

A-5. Sol. 

A-6. Sol. Electrophilic substitution (Friedel Craft acylation reaction).

A-7. Sol. Name reaction

A-8. Sol. 

Section (B) : Aldol condensation

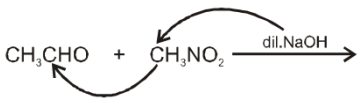
B-1. Sol. Aldehydes and ketones having atleast one α-H, give aldol condensation.

B-3. Sol. Basic Information.

B-4. Sol. It is a self aldol reaction.

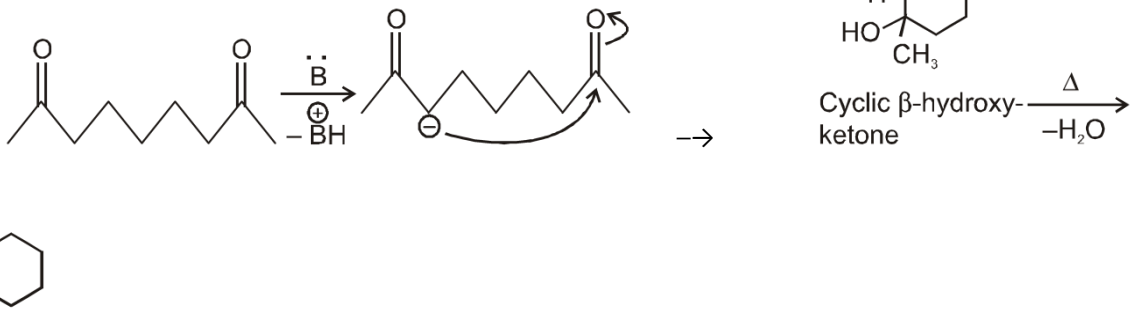
B-5. Sol. It is aldol condensation reaction and base will break C–H bond not C–D bond, as we know that C–D bond is stronger than C–H bond.

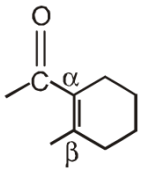
B-6. Sol. It is aldol condensation reaction

B-7. Sol. 

B-8. Sol. It is a cross Aldol condensation reaction.

B-9. Sol.





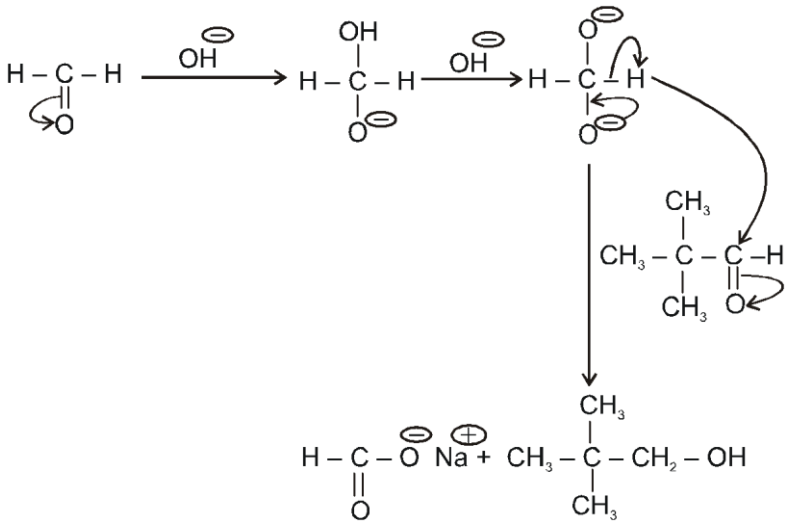
Section (C) : Cannizzaro's reaction

C-1. Sol. Disproportionation and redox reaction.

C-2. Sol. $Ph–CH=O \xrightarrow[\text{Cannizzaro reaction}]{\text{Conc. KOH}} Ph–CH_2OH + Ph–COOK$

C-3. Sol. CH_3CHO had α-hydrogen. So will not give Cannizaro reaction.

C-6. Sol.



Section (D) : Perkin, Haloform and other name reaction

D-1. Sol. Name reaction.

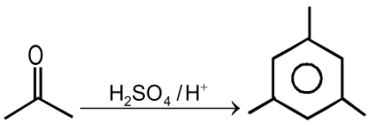
D-2. Sol. Haloform reaction can give by $-\overset{\overset{O}{\|}}{C}-CH_3$ group.
CH_3CHO has this group.

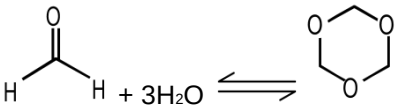
D-3. Sol. Compound containing chiral carbon with carbonyl group.

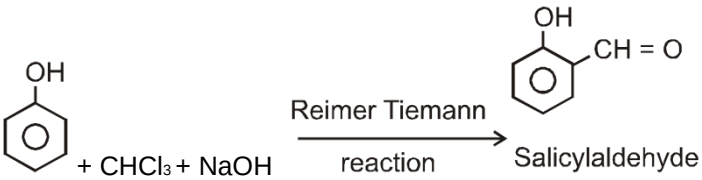
D-4. Sol. Compound containing $-\overset{\overset{O}{\|}}{C}-CH_3$ group give iodoform test.

D-5. Sol. $CH_3–CH=O \xrightarrow{PCl_5} CH_3–CH(Cl)_2 + POCl_3$

D-6. Sol. Basic Information.

D-7. Sol. 

D-8. Sol. 

D-9. Sol. 

D-10. Sol. It is an Haloform reaction.

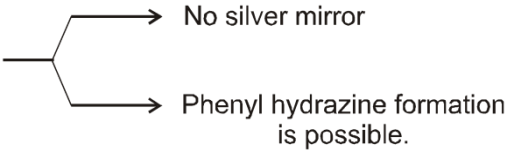
D-11. Sol. $AgNO_3 + NH_4OH$ or $[Ag(NH_3)_2]^{\oplus}$

D-12. Sol. Lab test.

D-13. Sol. Basic Information.

D-14. Sol. Basic Information.

D-15. Sol. Aldehydes give silver mirror test but ketones do not.



$(CH_3)_2CHOH \xrightarrow{[O]} (CH_3)_2C=O$

D-16. Sol. Rochelle salt is sodium salt of tartric acid.

D-18. Sol. Molecular weight = 2 × vapour density

Section (E) : Preparaction and chemical reaction of carboxylic acid

E-1. **Sol.** $CH_3–C\equiv N \xrightarrow{\text{dil. } H^{\oplus}} CH_3COOH$
Acetonitrile

E-2. **Sol.** $C_2H_5Br \xrightarrow{KCN} C_2H_5CN \xrightarrow[\text{Boil}]{\text{Dil.}H_2SO_4} C_2H_5COOH$

E-4. **Sol.** $C_2H_5Br \xrightarrow{\text{Alc.KOH}} CH_2=CH_2 \xrightarrow[CCl_4]{Br_2} CH_2(Br)–CH_2(Br) \xrightarrow[(\text{excess})]{KCN} CH_2(CN)–CH_2(CN) \xrightarrow{H_3O^{\oplus}}$

$CH_2(CH_2–COOH)–COOH$

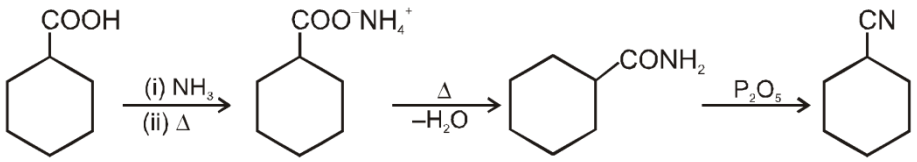
E-7. **Sol.** Aromatic aldehyde do not give Fehling solution test.

E-8. **Sol.** HVZ reaction.

E-9. **Sol.** α-halogenation reaction [α-H must present].

E-10. **Sol.** $CH_3I \xrightarrow[\text{Ether}]{Mg} CH_3MgI \xrightarrow[(ii)\ H_3O^{+}]{(i)\ \text{Dry ice}} CH_3COOH \xrightarrow[\text{Red P}]{Cl_2} Cl–CH_2–COOH$
(α-halogenation)

E-12. **Sol.** Steric hindrance

E-13. **Sol.** 

E-14. **Sol.** $Ph–COCl \xrightarrow{NH_3} Ph–CONH_2 + HCl$

E-15. **Sol.** $CH_3COONa + CH_3COCl \longrightarrow CH_3–COO–COCH_3$

E-16. **Sol.** $R–CH_2OH + RCOCl \longrightarrow R–CH_2–O–CO–R$

E-17. **Sol.** $R–C(=O)–OH \xrightarrow[\text{(Insertion reaction)}]{CH_2N_2} R–C(=O)–O–CH_3$

E-19. **Sol.** $CH_3–C(=O)–NH_2 + Br_2 + NaOH \longrightarrow CH_3NH_2 + Na_2CO_3$

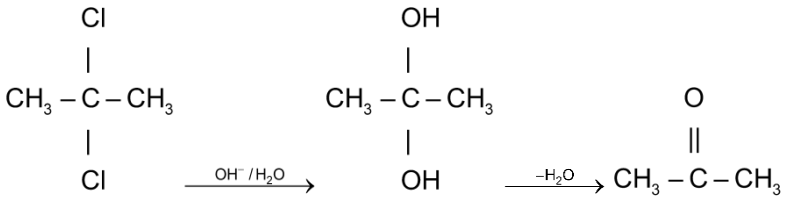
E-20. Sol. It is a Hoffmann Bromide reaction.

Exercise-2

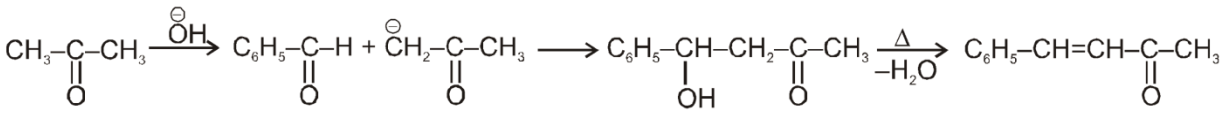
Tough Problems (can be taken from previous years' IIT-JEE Sheets single choice question + AIPMT Previous years questions + AIIMS previous years' questions.

PART - I : OBJECTIVE QUESTIONS

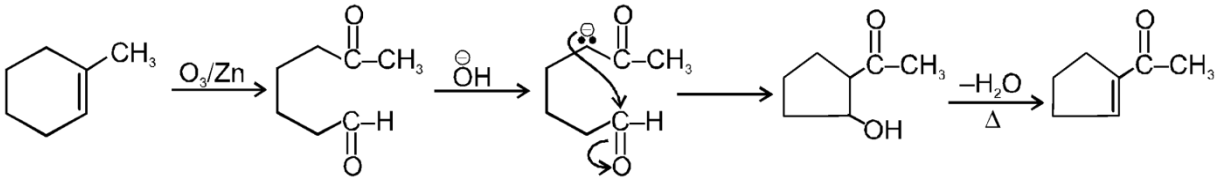
1. Sol.



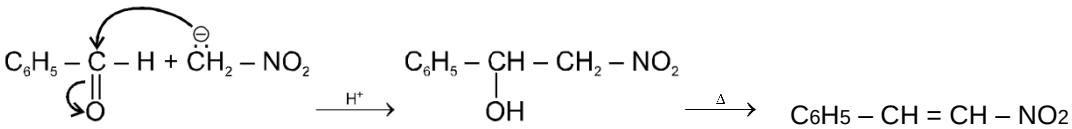
2. Sol.



3. Sol.

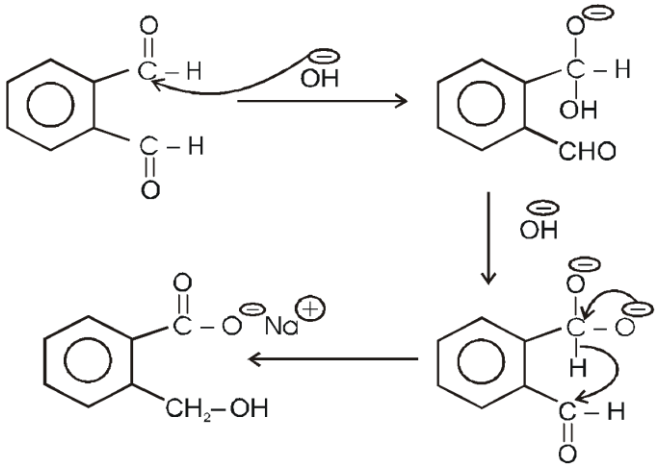


4. Sol.



5. Sol. Perkin reaction

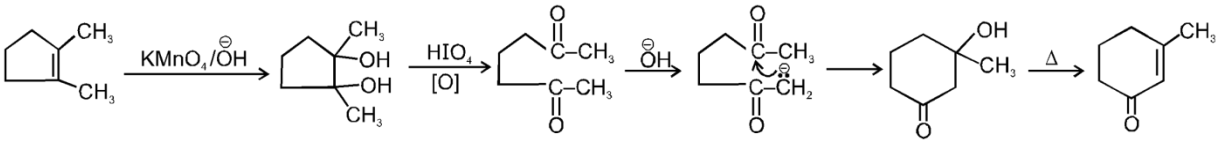
6. Sol. $CH_3 - CHO$ (α – Hydrogen is present).



7. Sol.

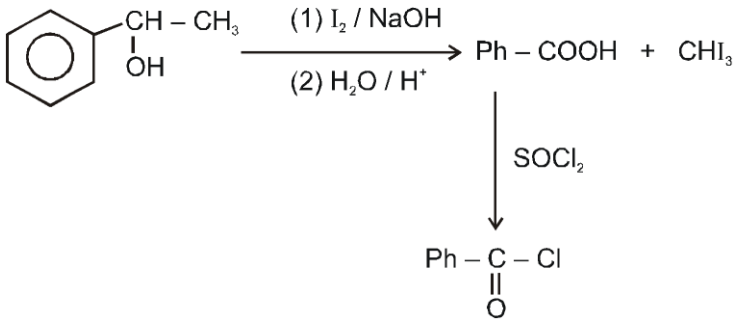
8. Sol. $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_3$ gives positive Iodoform test

9. Sol

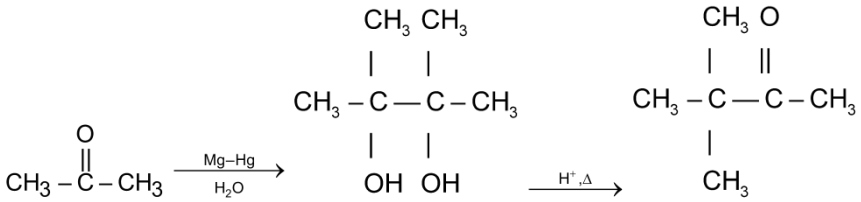


10. Sol. The compound which contains $CH_3-\overset{\overset{O}{\|}}{C}-$ or $CH_3-\overset{\overset{OH}{|}}{CH}-$ group gives iodoform test.

11. Sol.



12. Sol.

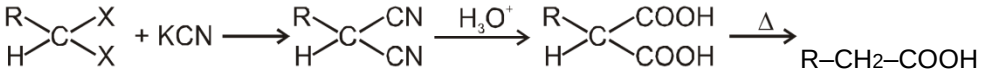


(Pinacol) (Pinacolone)

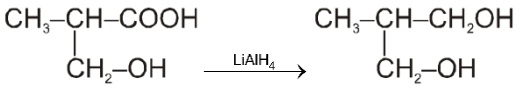
13. Sol. Tollen's reagent.

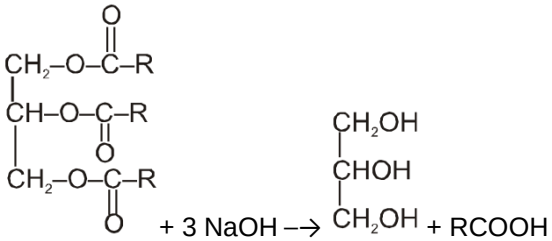
Carboxylic Acid and Derivatives

15. Sol. $HCN \xrightarrow{H_3O^+} H-\underset{\underset{O}{\|}}{C}-OH$

16. Sol. 

17. Sol. $RCOOAg + Br_2 \xrightarrow{CCl_4, \text{Reflux}} R-Br + AgBr + CO_2$

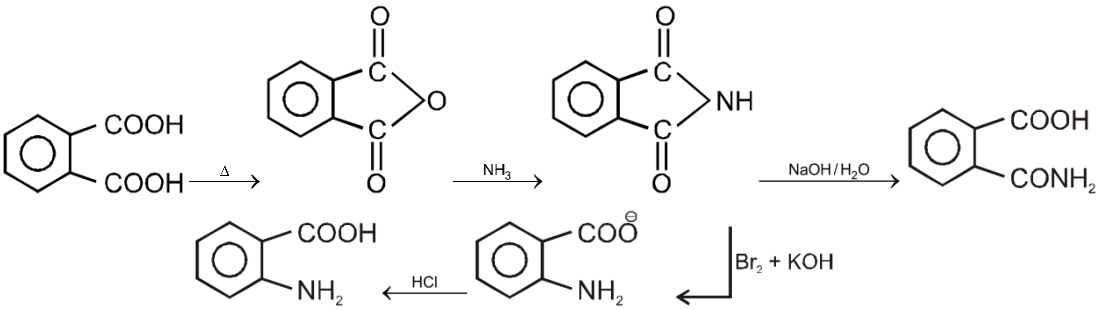
18. Sol. 

19. Sol. 

20. Sol. Rate of esterfication $\propto$ electrophilicity of $>C=O$ groups in acid.

21. Sol. As increases nucleophilicity of phenol rate of esterification increases

22. Sol. $CH_3CH_2COOH \xrightarrow{SOCl_2} CH_3CH_2COCl \xrightarrow{NH_3} CH_3CH_2CONH_2 \xrightarrow{Br_2+KOH} CH_3CH_2NH_2$

23. Sol. 

Comprehension # 1

24.

(b) Sol. Less hindered $>C=O$ group oxidised in cross Cannizzaro reaction.

Comprehension # 2

25.

(a) Sol. α – H hydrogen is present.

(b) Sol. It is cross aldol condensation reaction.

(c) **Sol.** Polycarbonyl compound with α hydrogen gives intramolecular aldol condensation reaction in presence of alkaline medium.

Comprehension - 3

26.

(a) **Sol.** Hoffmann rearrangement is shown by 1º amide only.

(b) **Sol.** Hoffmann rearrangement is 100% intramolecular. one amide will give only one amine with $Br_2/OH^{\ominus}$.

PART - II : MISCELLANEOUS QUESTIONS

Section (A) : ASSERTION/REASONING

DIRECTIONS :

Each question has 4 choices (1), (2), (3) and (4) out of which ONLY ONE is correct.

(1) Both assertion and reason are correct, and the reason is the correct explanation for the assertion

(2) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion

(3) The assertion is incorrect, but the reason is correct

(4) Both are assertion and reason are incorrect

A-1. Ans. (2)

A-2. Ans. (2)

A-3. Ans. (1)

Sol. $PhCHO \xrightarrow[(2)\ H^+]{(1)\ NaOH} Ph\ CH_2OH + PhCOOH$

A-4. **Ans.** (1)

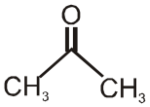
A-5. **Ans.** (1)

Section (B) : MATCH THE COLUMN

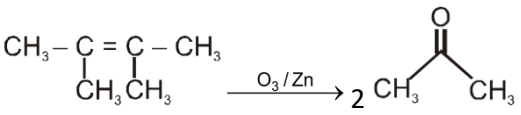
Note : Only one answer type (1 × 1)

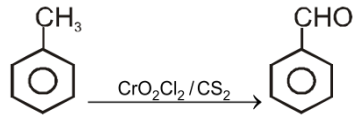
B-1._ **Ans.** (A : Q) ; (B : P) ; (C : S) ; (D : R)

B-2._ **Ans.** (A : P) ; (B : S) ; (C : P) ; (D : Q)

Sol. (a) $2CH_3COOH \xrightarrow{Ca(OH)_2,\ \Delta}$ 

(b) $PhCN + CH_3MgBr \xrightarrow{Ether} Ph-C(CH_3)=NMgBr \xrightarrow{H_2O} Ph-C(CH_3)=O + NH_3 + Mg(OH)I$

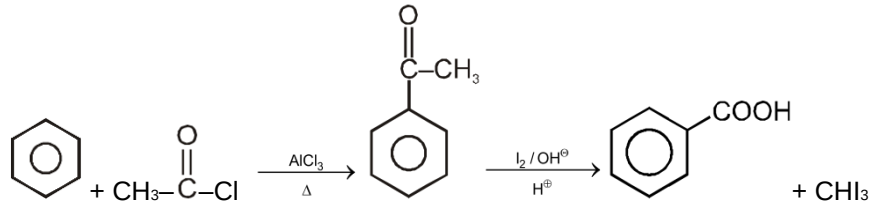
(c) 

(d) 

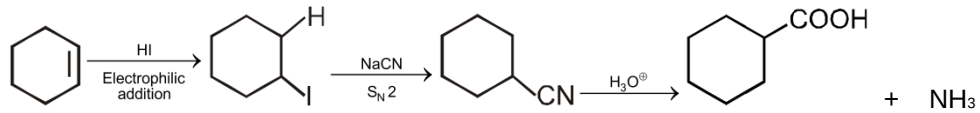
Section (C) : ONE OR MORE THAN ONE OPTIONS CORRECT

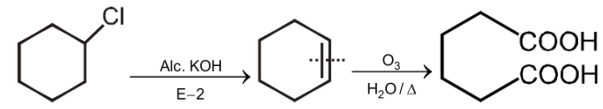
CORRECT½

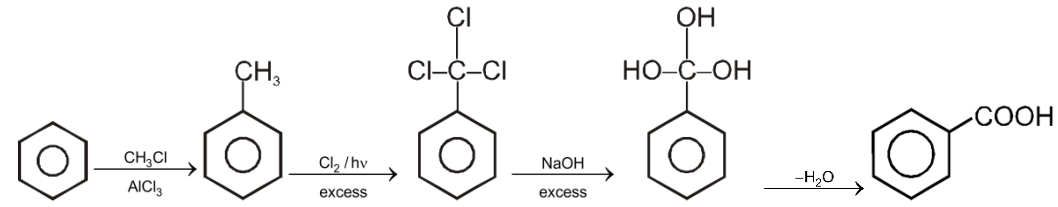
C-1. **Ans.** (1, 2, 3, 4)

Sol. (1) 

Friedel craft acylation Iodoform reaction

(2) 

(3) 

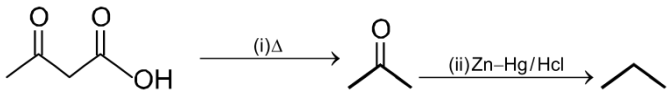
(4) 

C-2. **Sol.** (1) $(CH_3CH_2COO)_2Ca \xrightarrow{\Delta} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$

(2) $CH_3-CH_2-C\equiv N \xrightarrow{CH_3-CH_2-MgBr} CH_3-CH_2-\underset{\underset{CH_2CH_3}{|}}{C}=N\,MgBr \xrightarrow{H_3O^+} CH_3-CH_2-\underset{\underset{CH_2CH_3}{|}}{C}=NH \xrightarrow{H_3O^+} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$

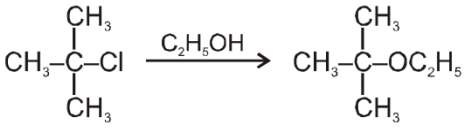
(3) $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OC_2H_5 \xrightarrow{H_2O/H^+} CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{NaOH/CaO} CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$

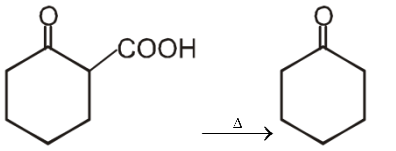
(4) $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[-CO_2]{\Delta} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$

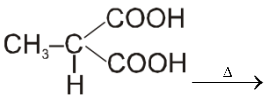
C-3. **Sol.** (1) 

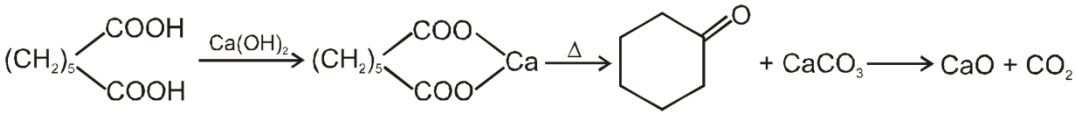
(2) $CH_3COOAg \xrightarrow{Br_2/CCl_4} CH_3Br$

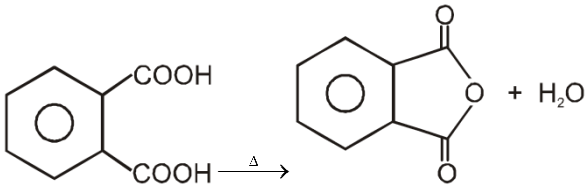
(3) $Ph–COOH \xrightarrow[CaO,\Delta]{NaOH} Ph–H$

(4)  (d + ℓ)

C-4. **Sol.** (1)  + CO_2

(2)  $CH_3–CH_2COOH + CO_2$

(3) 

(4) 

Exercise-3

PART - I : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

OFFLINE JEE-MAIN

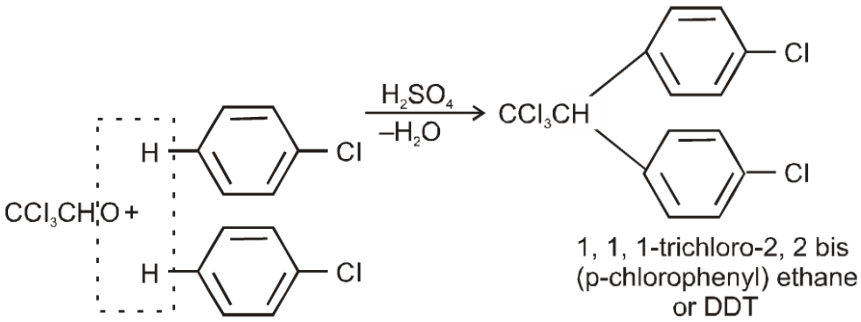
ALDEHYDES & KETONES

1. **Sol.** Benzaldehyde undergoes disproportionation with 50% NaOH to given benzyl alcohol and sodium benzoate

$C_6H_6CHO \xrightarrow{50\%\ NaOH} C_6H_5CH_2OH + C_6H_5COONa$

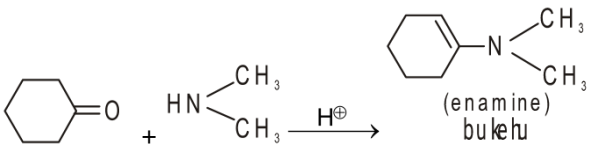
This is Cannizzaro's reaction.

2. **Sol.** DDT is prepared by heating chlorobenzene and chloral with concentrated sulphuric acid.



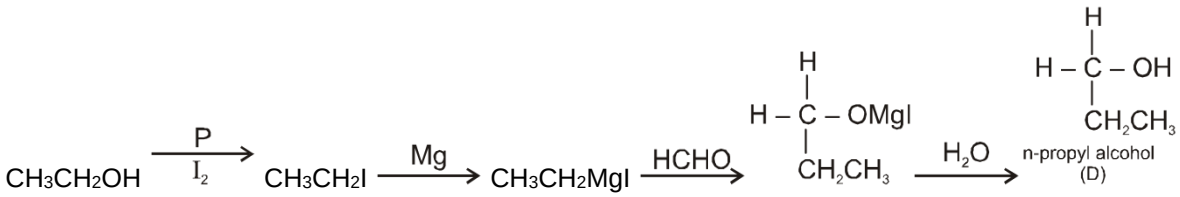
1, 1, 1-trichloro-2, 2 bis (p-chlorophenyl) ethane or DDT

3. **Sol.**

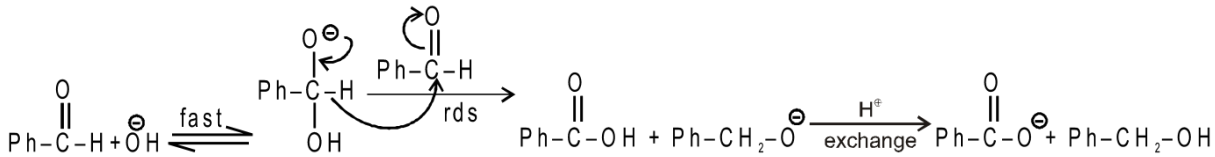


4.

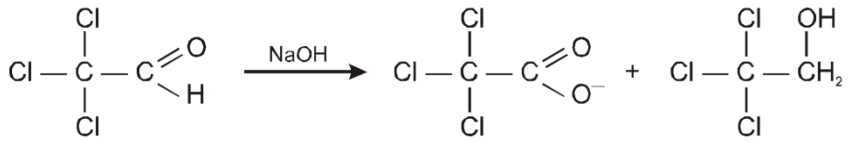
Sol.



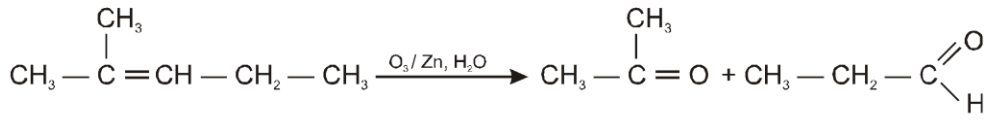
5. **Sol.**



6. **Sol.** The cannizzaro product of given reaction yields 2, 2, 2-trichloroethanol.

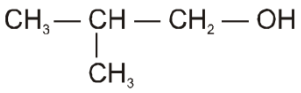


7.



(2-Methyl-2-pentene) (A) Acetone Propionaldehyde

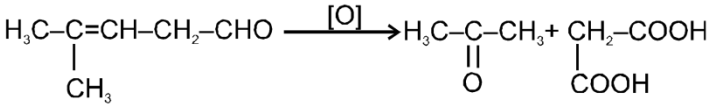
Sol.



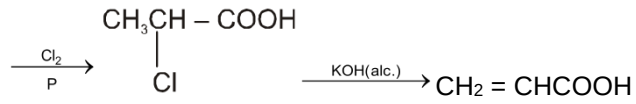
8. **Sol.** isobutyl alcohol doesn't give positive iodoform test.

CARBOXYLIC ACID & DERIVATIVES

9. Sol.

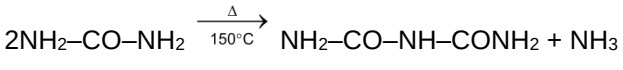


10. Sol.



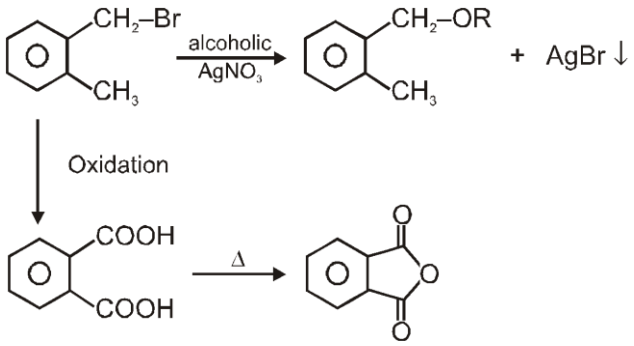
11. Sol. When two electron releasing groups are present the incoming group will occupy para or ortho position to the group which has more + R effect.

12. Sol. The empirical formula from given percentage data is N_2H_4CO. Urea on heating gives biurate & ammonia. Biurate gives violet colour with $CuSO_4$ solution.



Biurate

13. Sol.



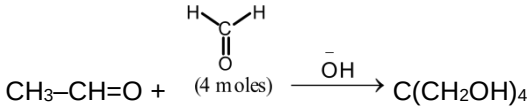
(Phthalic anhydride)

ONLINE JEE-MAIN

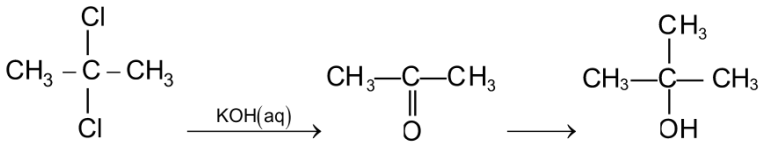
ALDEHYDES & KETONES

6. Sol. It is aldol condensation reaction.

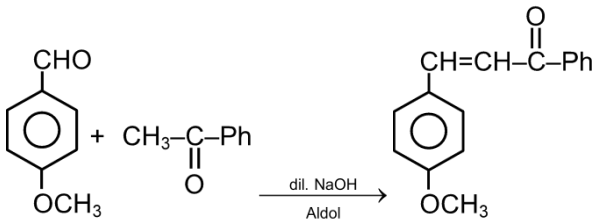
7. Sol. The synthesis requires three aldol & one cannizzaro reaction.

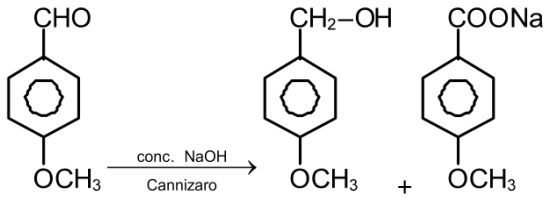


8. Sol.



9. Sol.

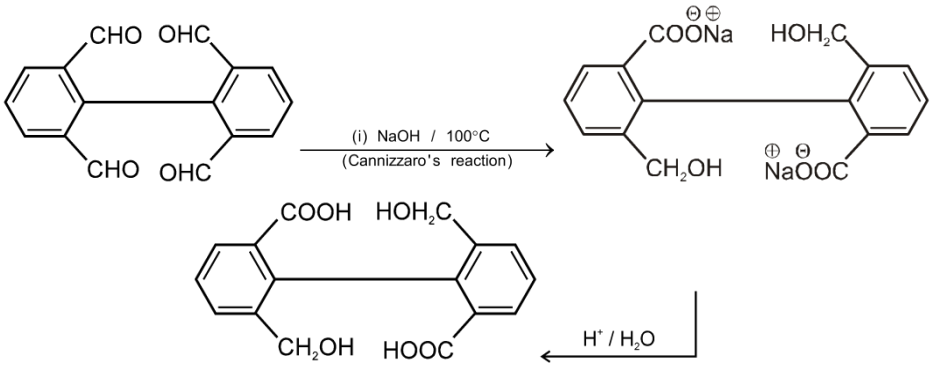

CHO
OCH3
CH3–C–Ph
O
dil. NaOH
Aldol
CH=CH–C–Ph
O
OCH3


CHO
OCH3
conc. NaOH
Cannizaro
CH2–OH
OCH3
+
COONa
OCH3

PART - II : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

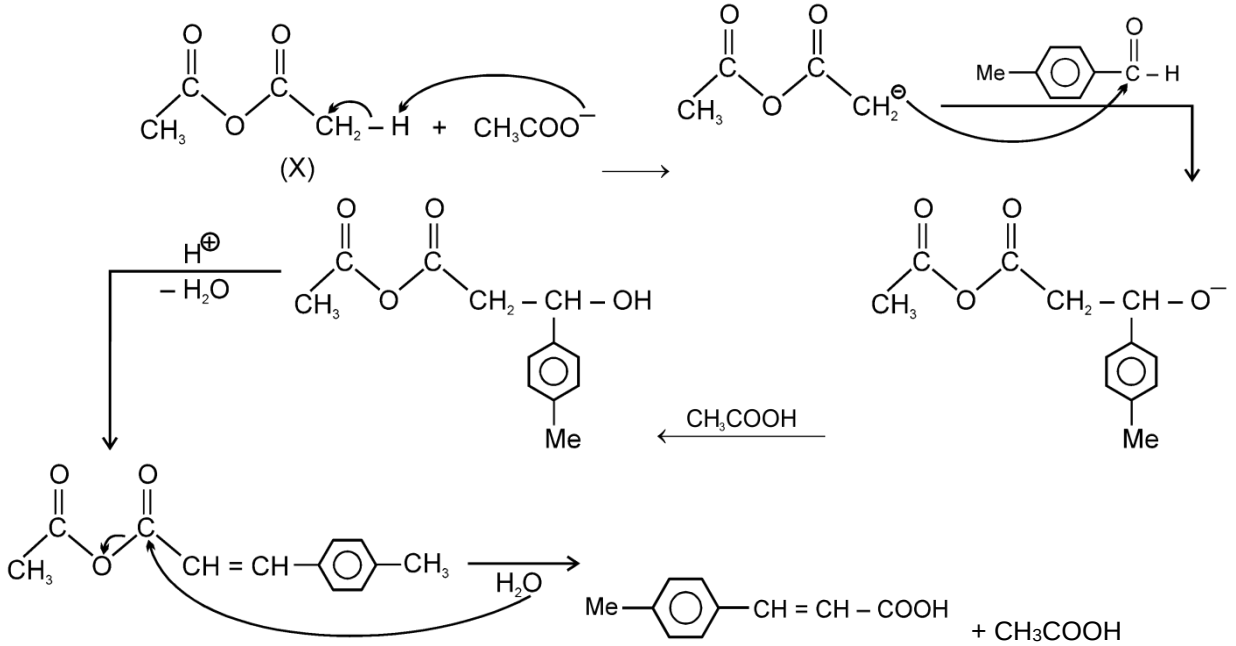
ALDEHYDES & KETONES

1. Sol.

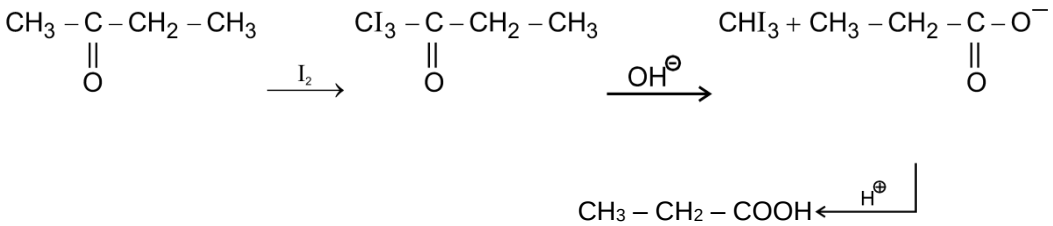


Note : Cannizzaro's reaction is due to the absence of α-hydrogen atom.

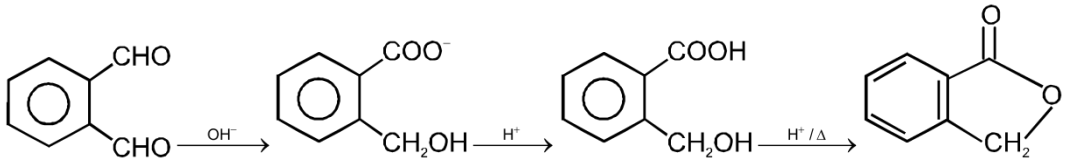
2. Sol. This is Perkin reaction



3. Sol.

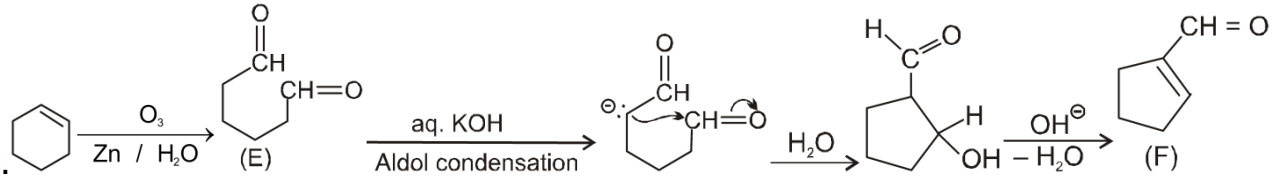


4. **Sol.**



5.

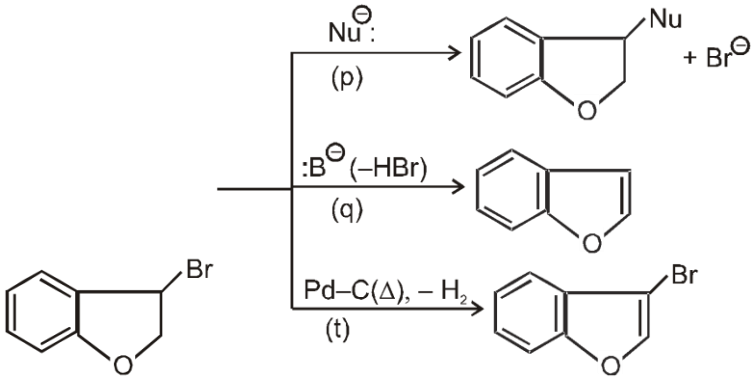
Sol.



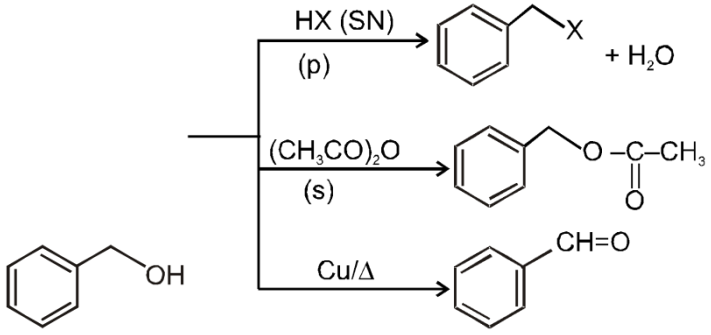
Ozonolysis product of cyclohexene will give hexandial and this undergoes intramolecular aldol condensation in presence of alkali to give cyclic α,β-unsaturated aldehyde.

6. **Ans.** (A) - p, q, t ; (B) - p, s, t ; (C) - r, s ; (D) - p

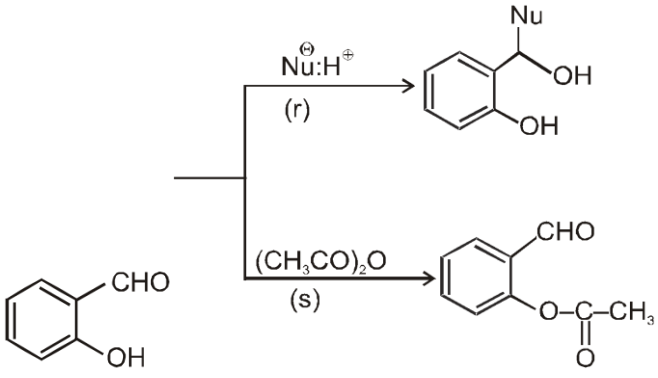
Sol. (A)

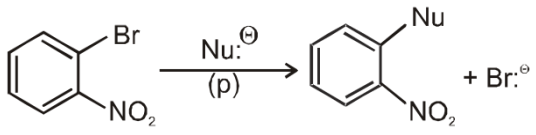


(B)

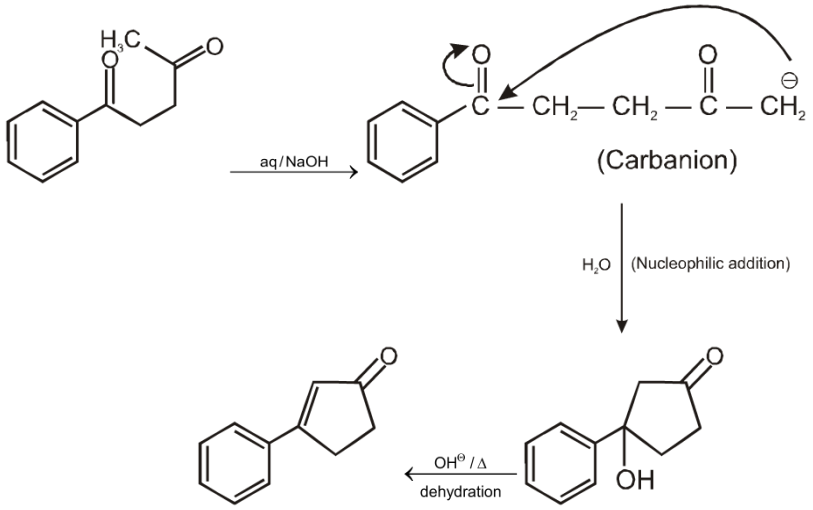


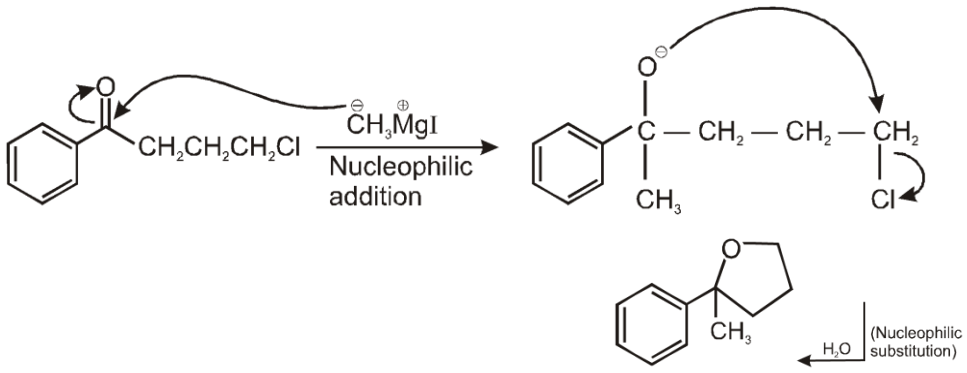
(C)

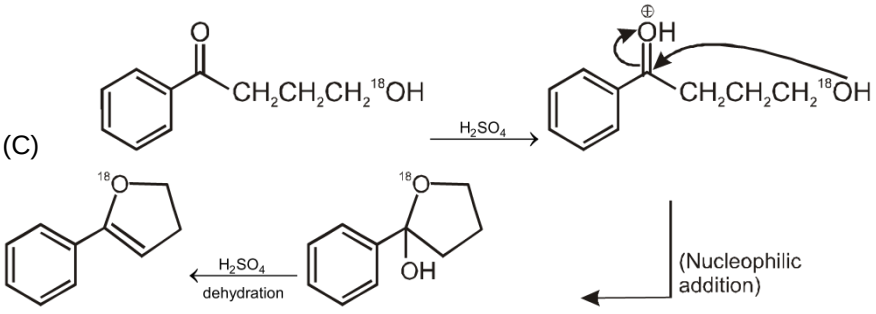


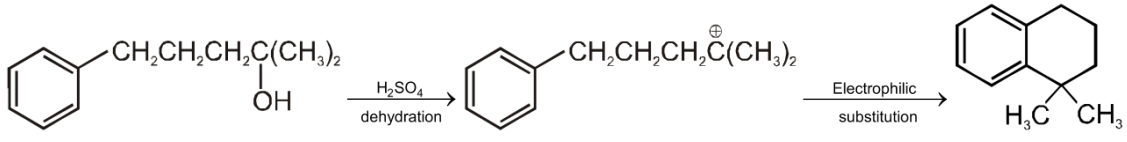
(D) 

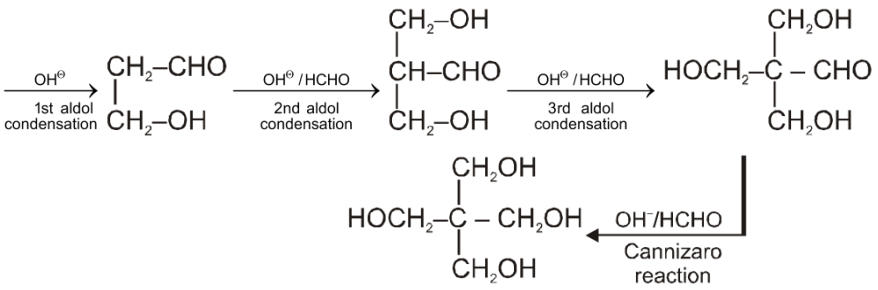
7. **Ans.** (A-r, s, t) ; (B-p, s) ; (C-r, s) ; (D-q, r)

Sol. (A) 

(B) 

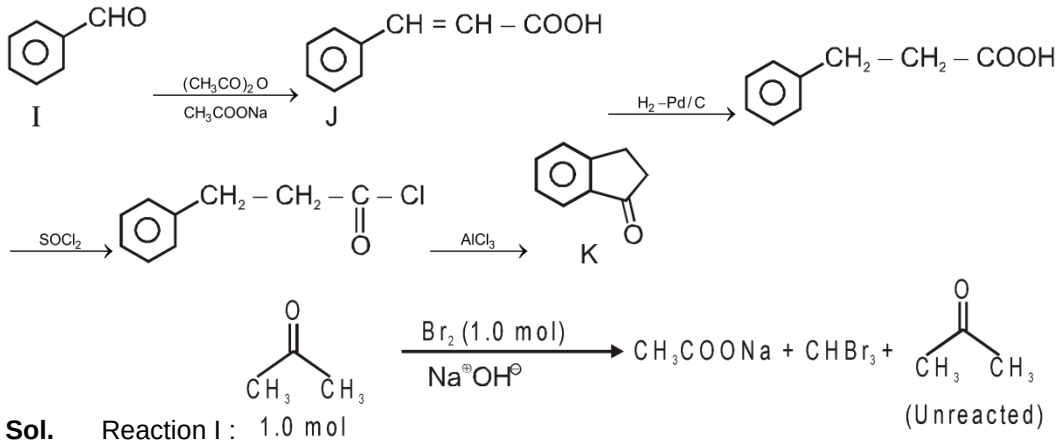
(C) 

(D) 

8. Sol. $CH_3–CHO + HCHO$ 

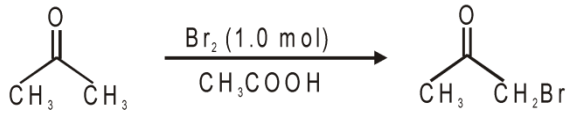
Comprehension :

10. Sol. (9 to 10)



11. Sol. Reaction I : 1.0 mol

(In basic medium complete haloform reaction takes place since the rate of reaction increases with each α-halogenation)

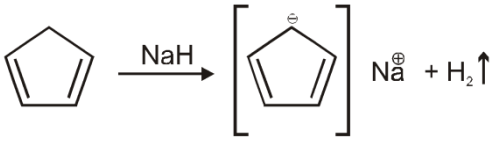


Reaction II : 1.0 mol

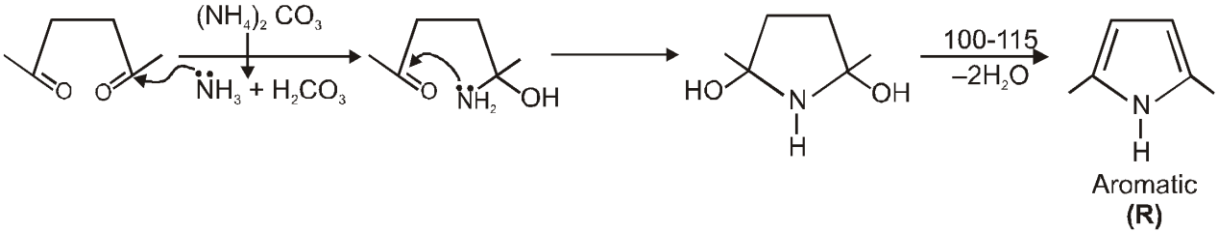
(In acidic medium monohalogenation takes place with 1-mol of halogen)

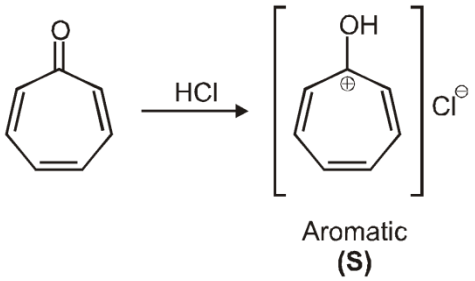
Aromatic
(P)

12. Sol. ;

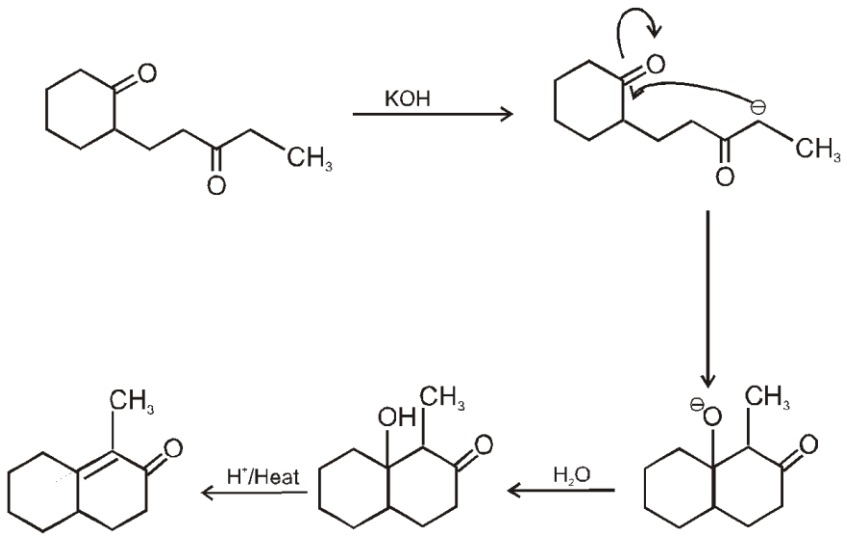


Aromatic
(Q)

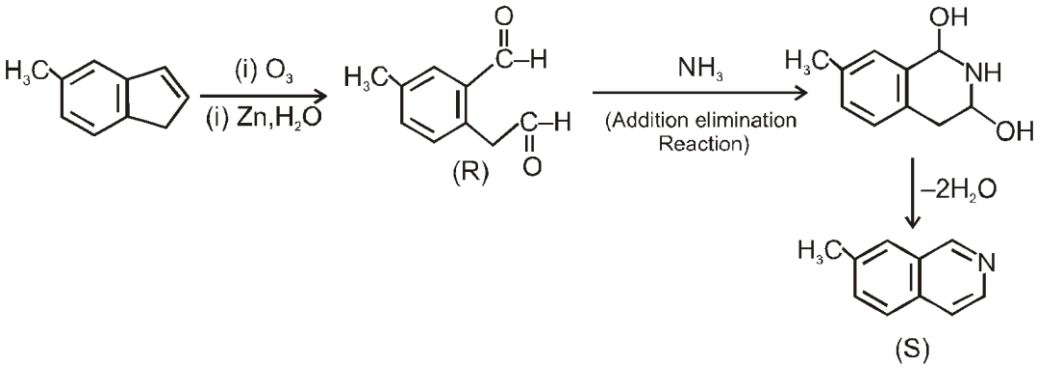




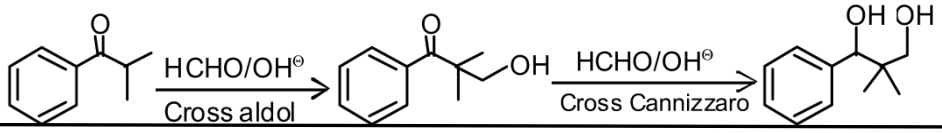
13. Sol.

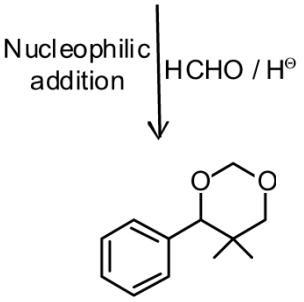


14. Sol.

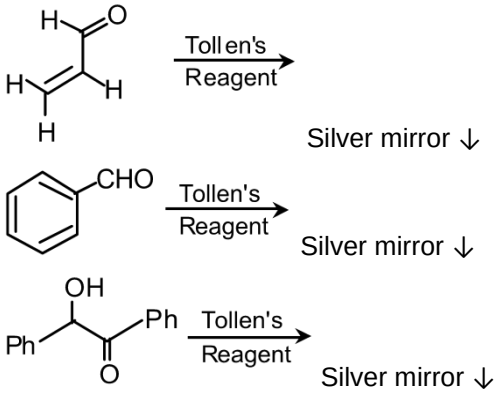


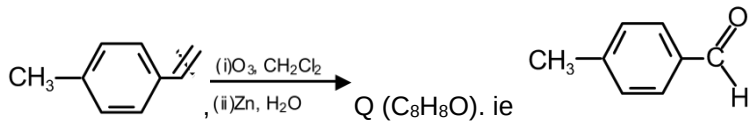
15. Sol.

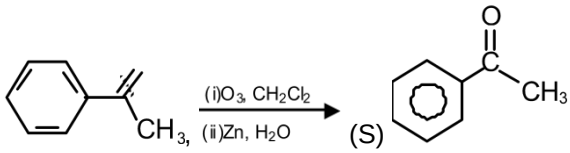


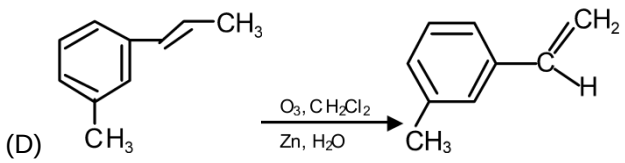


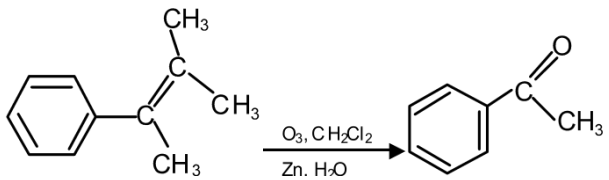
16.* **Sol.** Aldehydes and α-Hydroxyketone show positive tollen's test.



17. **Sol.** (C)  Q (C_8H_8O). ie



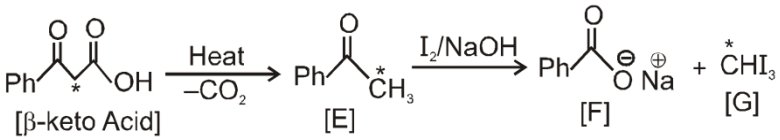




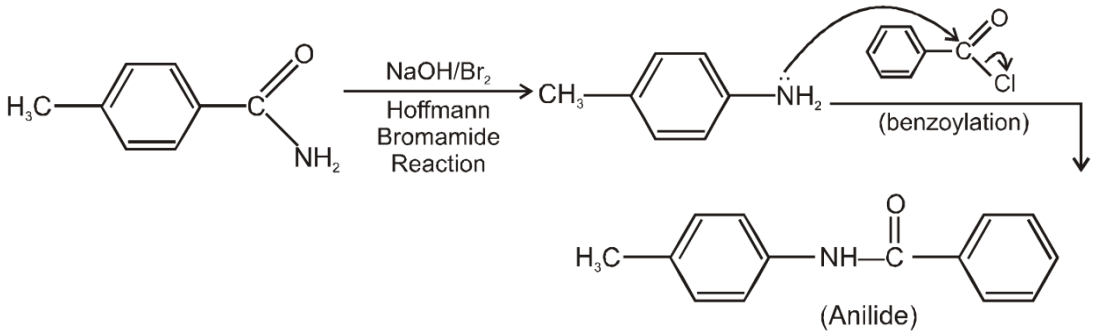
CARBOXYLIC ACID & DERIVATIVES

18. **Sol.** Benzamide on treatment with $POCl_3$ gives benzonitrile (phenyl cyanide) because in this reaction $POCl_3$ acts as dehydrating agent.

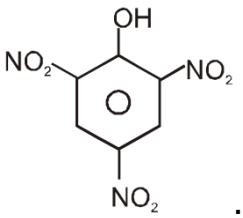
19. **Sol.**

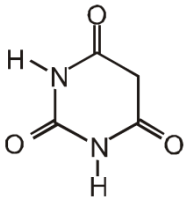


20. **Sol.**

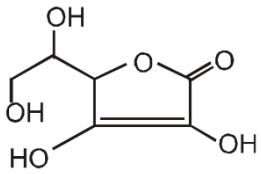


21. **Sol** **.** picric acid ;

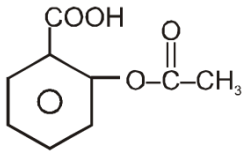




barbituric acid

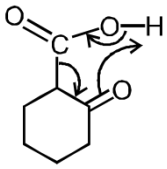


ascorbic acid ;

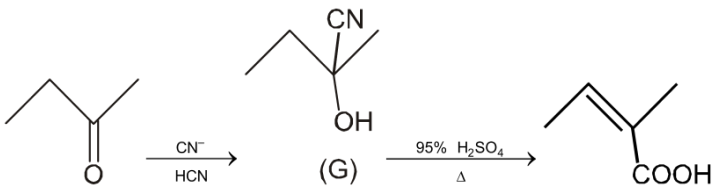


aspirin

22. **Sol.** In decarboxylation, β-carbon acquires δ– charge. Whenever δ– charge is stabilized, decarboxylation becomes simple. In (B), it is stabilized by –m & –I of C = O, which is best amongst the options offered,

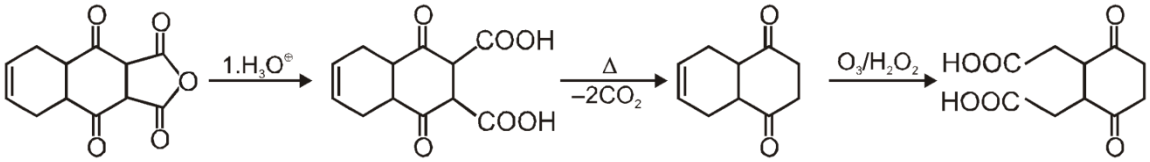


23. **Sol.**



24. **Ans.** **2**

Sol.



No. of –COOH group is '2'.

25. **Sol.** Substitution reaction of toluene takes place through radical mechanism.

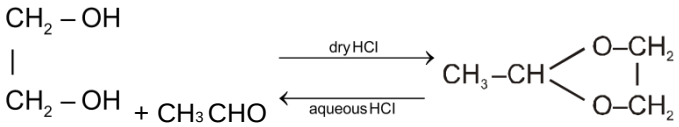
26. **Sol.** Haloform reaction of acetophenone yields benzoic acid.

27.

Sol. Perkin condensation of benzaldehyde with $(CH_3CO)_2O/CH_3COOK$ yields cis and trans form of cinnamic acid.

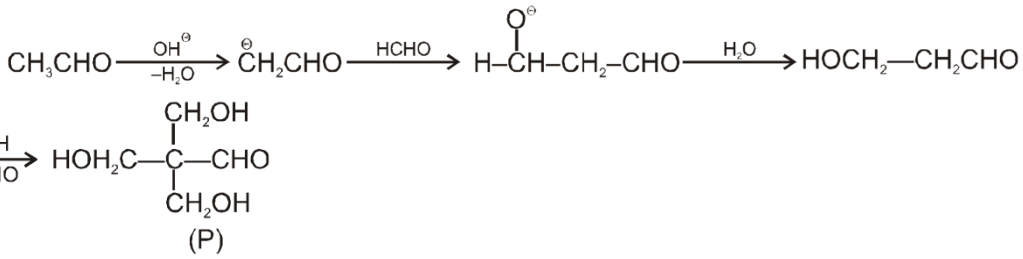
Additional Problems For Self Practice (APSP)

1. **Sol.**



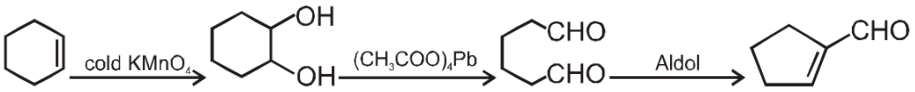
2. **Sol.** Basic Information. (No active H)

3. **Sol.**



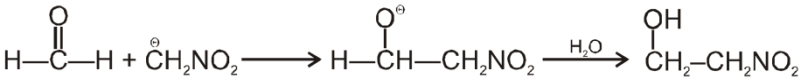
This is cross aldol condensation. Now (P) does not contain α - H atom so further addition of HCHO will lead to cross Cannizaro reaction.

4. **Sol.**



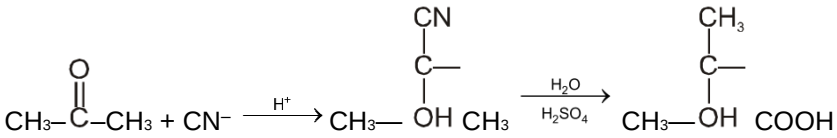
5. **Sol.** Since all compounds do not contain 'α' H atom thus, all can show Cannizaro reaction

6. **Sol.** Because after the removal of α-H atom carbanion is formed which is stabilized by resonance.

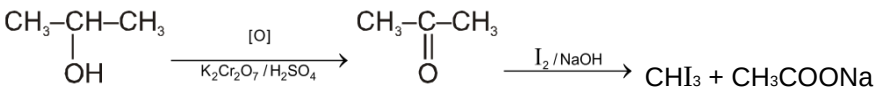


7. **Sol.** +M effect of NH_2 group helps in the dissociation of C — H bond

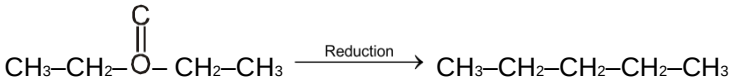
8. **Sol.**



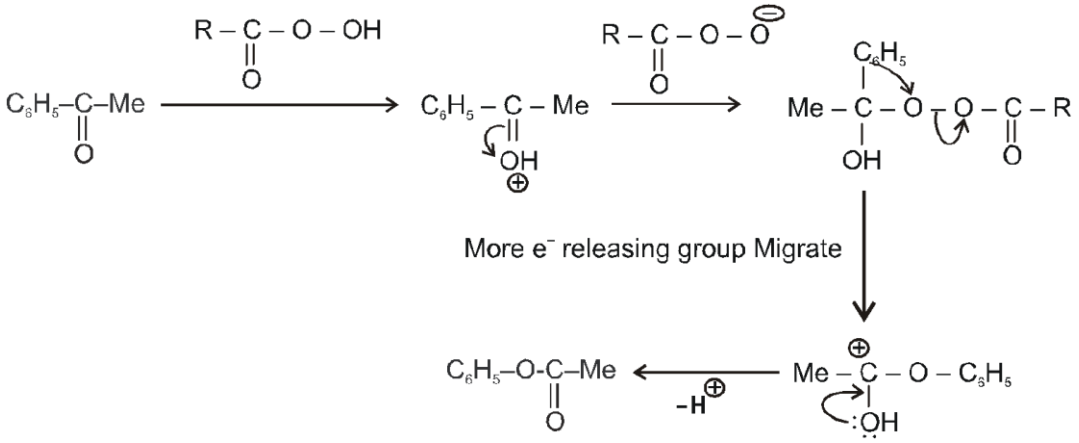
9. **Sol.**



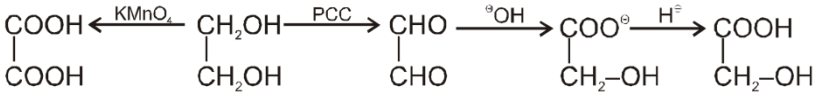
10. **Sol.**



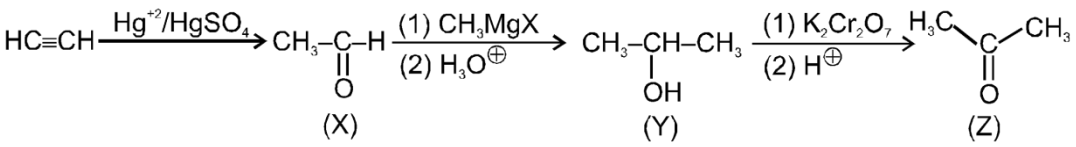
11. Sol.



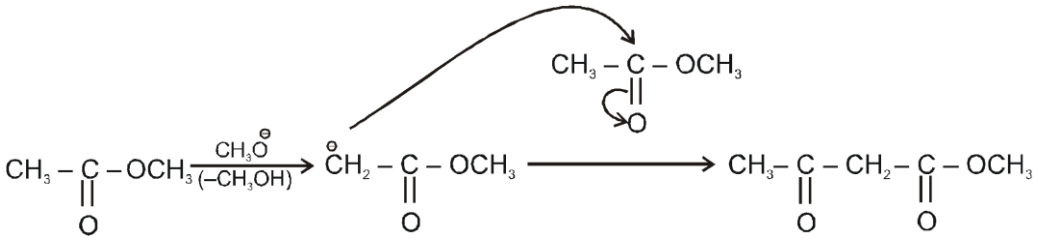
12. Sol.



13. Sol.



14. Sol. It is the claisen condensation reaction.



15. Sol. $C_6H_5CHO + HCHO + \xrightarrow[(conc.)]{NaOH} C_6H_5CH_2OH + HCOONa$

It is crossed Cannizzaro's reaction.

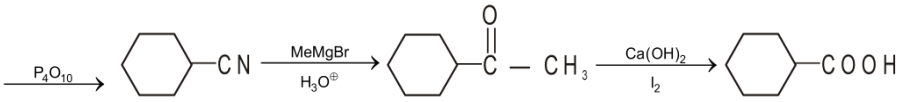
Carboxylic Acid and Derivatives

16. Sol. It is Hell Volhard Zelinsky reaction.

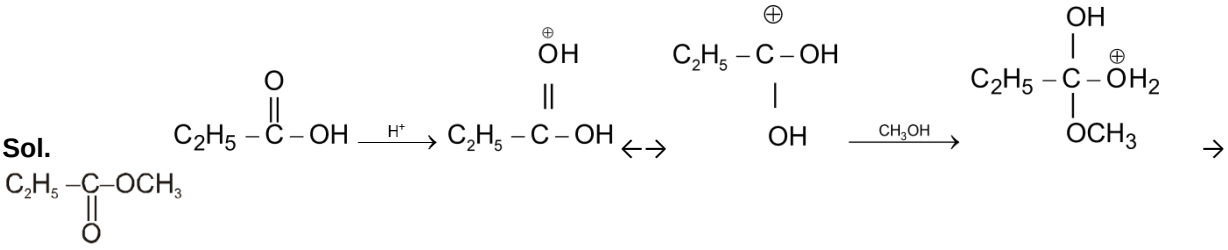
17. Sol. Rate of hydrolysis ∝ partial positive charge on >C= O groups.

18. Sol. $\textbf{Rate} \propto \frac{1}{\text{basicity of leaving group}}$

19. Sol.

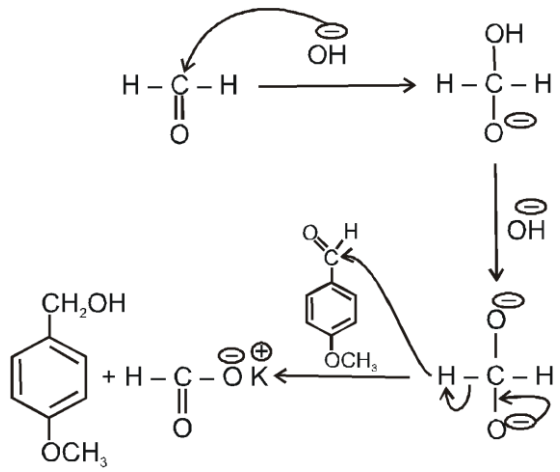
20. **Sol.** X 

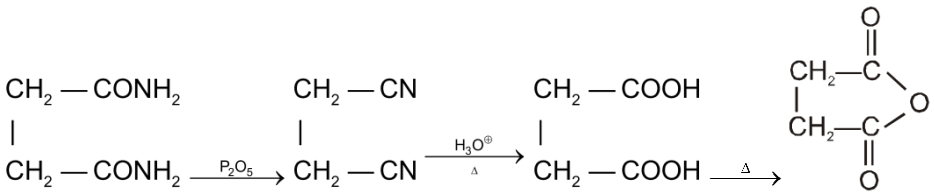
21. **Sol.** β-Keto acid decarboxylates faster through 6 member cyclic transition state.

22. **Sol.** 

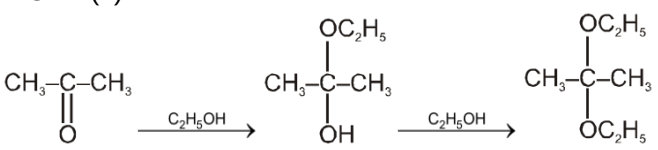
23. **Sol.** (1) R–N=C=O
(2) R–N=C=O
(3) R–N=C=O
(4) + N3H R–N=C=O

24. **Sol.** Rate of esterification $\propto \frac{1}{\text{Steric crowding}}$.

25. **Sol.** 

26. **Sol.** 

28. **Ans.** (4)

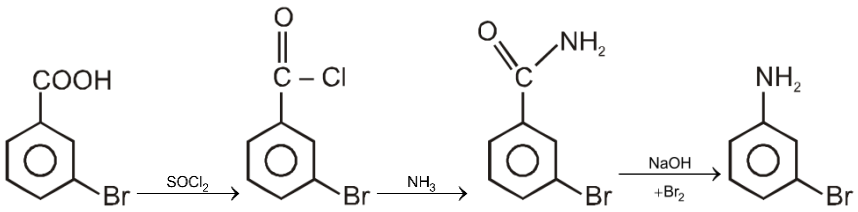
Sol. 

Hemiacetal Acetal

29. Sol.

$$\underset{(A)}{CH_3-CH_2-COOH} \xrightarrow{NH_3} \underset{(B)}{CH_3-CH_2-COO^{-}NH_4^{+}} \xrightarrow{\Delta} \underset{(C)}{CH_3-CH_2-CONH_2} \xrightarrow[\text{Hoffmann bromamide reaction}]{KOH+Br_2} \underset{\text{(Ethylamine)}}{CH_3-CH_2-NH_2}$$

30. Sol.



PART - II : PRACTICE QUESTIONS

1. Sol. $CH_3COOC_2H_5 \xrightarrow{NaOH} CH_3-COO^{\ominus} + C_2H_5OH$ [Ethanol can give iodoform test]

3. Sol. Iodoform test is carried out in hot alkaline medium. Under these conditions the esters will hydrolyse to give corresponding alcohols. Now ethyl alcohol will repond to iodoform test to give yellow ppt. of iodoform while methanol will not give iodoform.

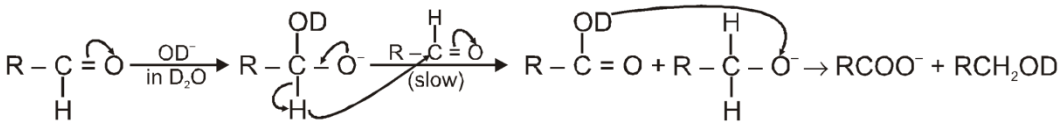
4. Sol. Aldehydes having α-H atoms undergo aldol condensation in the presence of dil. NaOH and yield β- hydroxy aldehydes.

$$CH_3CHO + CH_3CHO \xrightarrow{NaOH} \underset{\text{3-hydroxy butanal}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_2CHO}$$

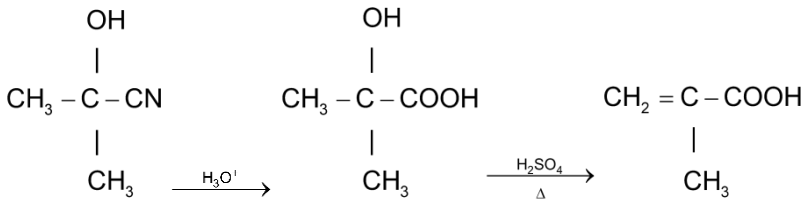
5. Sol. $\underset{(X)}{C_2H_5OH} + [O] \xrightarrow[\text{in } CH_2Cl_2]{PCC} \underset{(Y)}{CH_3CHO}$

$$CH_3CHO + 4NaOH + 3I_2 \longrightarrow \underset{\substack{\text{yollow ppt.}\\ \text{(triiodomethane)}}}{\overset{CHI_3}{}} + HCOONa + 3H_2O + 3NaI$$

6. Sol. If D_2O (heavy water) is taken instead of H_2O, as solvent, the reaction takes place in the following manner :



7. Sol.

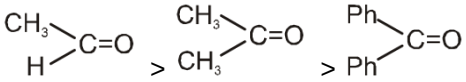


10. Sol. Clemmensen reduction

$$>C=O \xrightarrow{Zn-Hg/HCl} >CH_2$$

11. **Sol.** (1) Electrophilic addition (2) Nucleophilic addition
(3) Nucleophilic Substitution (4) Nucleophilic addition

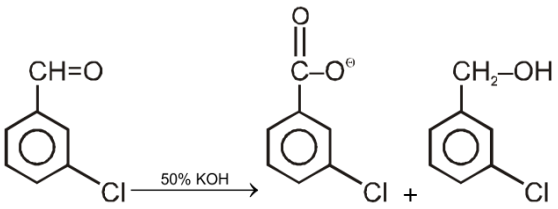
12. **Sol.** Correct reactivity order for nucleophilic addition reaction with PhMgBr



(due to steric crowding).

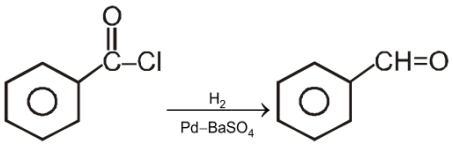
13. **Ans.** (3)

Sol. Cannizzaro reaction



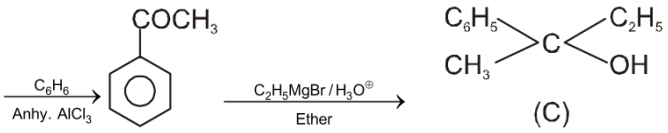
14. **Ans.** **(1)**

Sol.

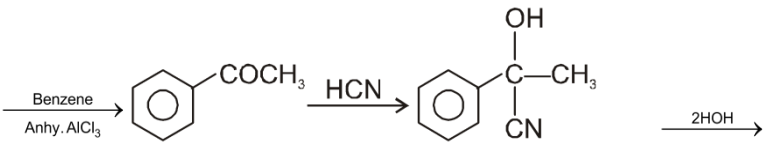


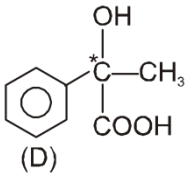
It is Rosenmund reaction.

15. **Sol.** $CH_3COOH + PCl_5 \longrightarrow CH_3COCl$



16. **Sol.** $CH_3COOH \xrightarrow{SOCl_2} CH_3COCl$

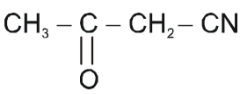




17. **Ans.** (4)

Sol. $CH_3–Br \xrightarrow{KCN} \underset{(A)}{CH_3–CN} \xrightarrow{H_3O^+} \underset{(B)}{CH_3–COOH} \xrightarrow{LiAlH_4} \underset{\text{Ethylalcohol}}{\underset{(C)}{CH_3–CH_2–OH}}$

18. **Sol.**

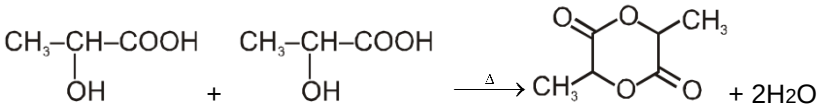


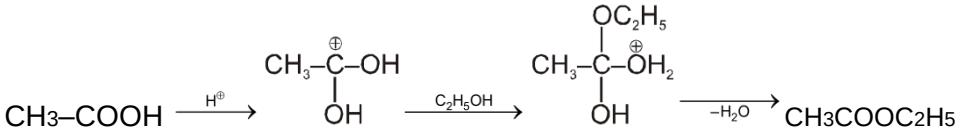
19. **Sol.** Iodoform test.

20. **Sol.** $Ph–CH_3 \xrightarrow{\text{Hot Alkaline } KMnO_4} Ph–COO^-$

$Ph–CH=CH–CH_3 \xrightarrow{\text{Hot Alkaline } KMnO_4} Ph–COO^-$

$Ph–C\equiv C–CH_3 \xrightarrow{\text{Hot Alkaline } KMnO_4} Ph–COO^-$

21. **Sol.** 

22. **Sol.** 

23. **Sol.**