CARBONYL COMPOUND, ALDOL & SIMILAR NAME REACTIONS

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EXERCISE # I

Q.1 Arrange these compounds in decreasing order of reactivity for the nucleophilic attack :

(I) Acid chloride (II) Aldehyde (III) Ketone (IV) Ester

Select the correct answer from the codes given below :

(A) I > II > III > IV (B) IV > III > II > I (C) III > II > I > IV (D) I > IV > II > III

Q.2 In the given reaction

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2COOC_2H_5 \xrightarrow{[X]} (A) \xrightarrow[(ii)\ H_2O/H^{\oplus}]{(i)\ LiAlH_4} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_2OH+C_2H_5OH$$

[X] will be :

(A) HCHO (B) $\begin{matrix}CH_2-OH\\|\\CH_2-OH\end{matrix} + H^{\oplus}$ (C) $\begin{matrix}CH_2-OH\\|\\CH_2-OH\end{matrix} + \overset{\ominus}{O}H$ (D) HCN

Q.3 In the given reaction : $C_6H_5-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NH_2OH/H^{\oplus}} [X]$

[X] will be:

(A) Only syn oxime (B) Only anti oxime

(C) Mixture of syn and anti oxime (D) Secondary amide

Q.4 Acetophenone can be obtained by the distillation of :

(A) $(C_6H_5COO)_2Ca$ (B) $(CH_3COO)_2Ca$

(C) $(C_6H_5COO)_2Ca$ and $(CH_3COO)_2Ca$ (D) $(C_6H_5COO)_2Ca$ and $(HCOO)_2Ca$

Q.5 Gem dihalide on hydrolysis gives :

(A) Vic diol (B) Gem diol (C) Carbonyl compound (D) Carboxylic acid

Q.6 Acetal or ketal is:

(A) Vic dialkoxy compound (B) α, ω-dialkoxy compound

(C) α-alkoxy alcohol (D) Gem dialkoxy compound

Q.7 Cross cannizzaro reaction is example of :

(A) Redox reaction (B) Disproportionation (C) Both (A) and (B) (D) Only oxidation

Q.8 Acetaldehyde can be converted into $HOCH_2-\overset{CH_2OH}{\overset{|}{C}}-CH_2OH$ by which reagent ?

(A) KOH (B) KOH followed by LAH

(C) excess of HCHO and KOH (D) KCN followed by SBH

Q.9 Which one of the combinations will give propanaldehyde on dry distillation ?

(A) $(C_6H_5COO)_2Ca$ and $(HCOO)_2Ca$ (B) $(CH_3COO)_2Ca$ and $(CH_3CH_2-COO)_2Ca$

(C) $(CH_3-CH_2-COO)_2Ca$ and $(HCOO)_2Ca$ (D) $(CH_3COO)_2Ca$ and $(CH_3COO)_2Ca$

Q.10 In the given reaction : $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{Distillation}]{\text{Conc.}H_2SO_4} [X]$

[X] will be :

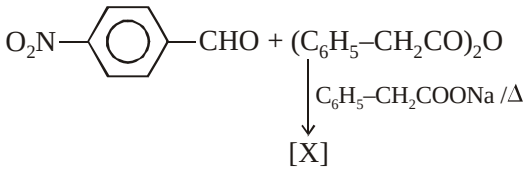
(A) Methyl oxide (B) Phorone

(C) 1, 3, 5-Trimethylbenzene (D) 2-Butyne

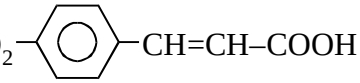
Q.11 Grignard reagents can not give carbonyl compounds with :

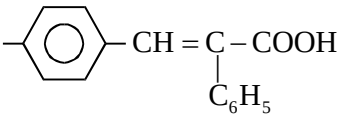
(A) CO_2 (B) RCOCl (C) RCN (D) RCOOR

Q.12 The product of the reaction :



will be :

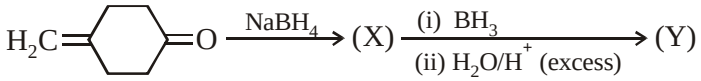
(A) $C_6H_5-CH=CH-COOH$ (B) 

(C) $C_6H_5-CH=\underset{\underset{CH_3}{|}}{C}-COOH$ (D) 

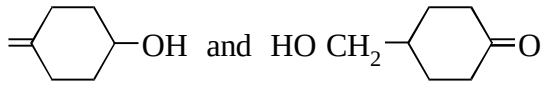
Q.13 Cyanohydrin of which compound on hydrolysis will give lactic acid ?

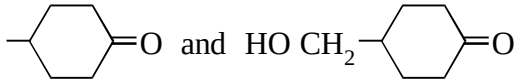
(A) C_6H_5CHO (B) HCHO (C) CH_3CHO (D) CH_3-CH_2-CHO

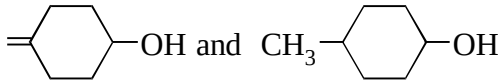
Q.14 In the given reaction :

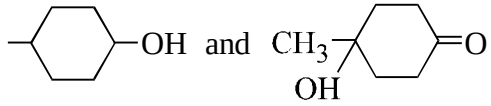


(X) and (Y) are :

(A) 

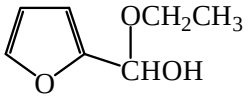
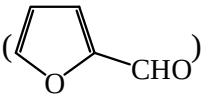
(B) 

(C) 

(D) 

Q.15 Acetaldehyde cannot give :

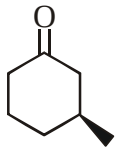
(A) Iodoform test (B) Lucas test (C) Benedict test (D) Tollens test

Q.16 Compound  formed by the reaction of furfural () with ethanol is :

(A) an aldol (B) an acetal (C) a ketal (D) a hemiacetal

Q.17 A compound with molecular formula $C_8H_{18}O_4$ does not give litmus test and does not give colour with 2,4–DNP. It reacts with excess MeCOCl to give a compound whose vapour density is 152. Compound A contains how many hydroxy groups ?

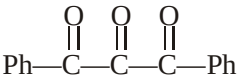
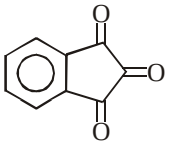
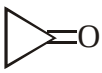
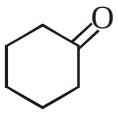
(A) 1 (B) 2 (C) 3 (D) 4

Q.18  $\xrightarrow[(2)\ H_2O]{(1)\ NaBH_4}$ A + B

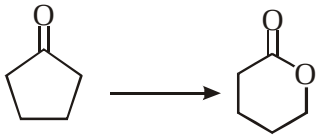
Identify relationship between A & B products ?

(A) Diastereoisomers (B) Enantiomers (C) Positional isomer (D) Identical

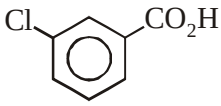
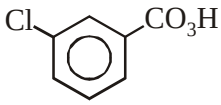
Q.19 Which of the following does not form a stable hydrate by the addition of H_2O?

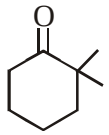
(A)  (B)  (C)  (D) 

Q.20 The conversion

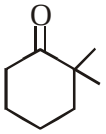


can be effected by using the reagent

(A) Tollen's reagent (B) O_3 (C)  (D) 

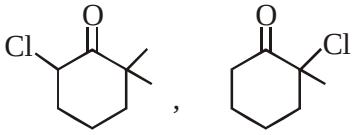
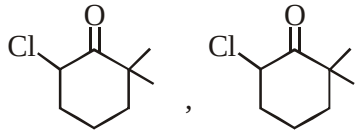
Q.21 (I)  + Cl_2 $\xrightarrow{NaOH}$ P

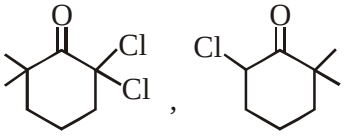
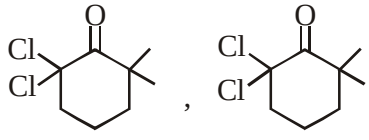
1 (mole) : 1 (mole)

(II)  + Cl_2 $\xrightarrow{CH_3COOH}$ Q

1 (mole) : 1 (mole)

Organic product P & Q are respectively -

(A)  (B) 

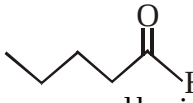
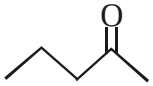
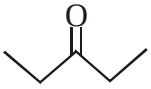
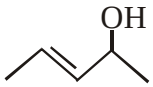
(C)  (D) 

Q.22 Total number of stereoisomers of major product (Q) are :

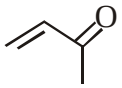
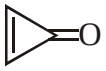
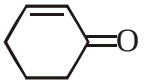
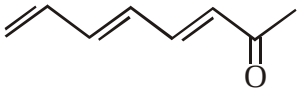
$$CH_3–CHO + 4HCHO \xrightarrow[-HCOONa]{NaOH} (P) \xrightarrow[H^{\oplus}]{2CH_3–CHO} (Q)$$

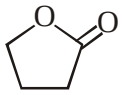
(A) 0 (B) 4 (C) 8 (D) 2

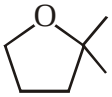
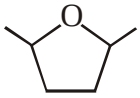
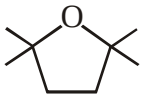
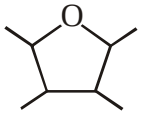
Q.23 An organic compound (A), $C_5H_{10}O$, reacts with hydrazine to form a hydrazone derivative (B). The hydrazone (B) on being heated with KOH at about 180ºC, gives n-pentane. The compound (A) does not respond positively to Tollen's reagent and to the iodoform test. The compound (A) is

(A)  (B)  (C)  (D) 

Q.24 The compound having the highest dipole moment is :

(A)  (B)  (C)  (D) 

Q.25  $\xrightarrow[(2)\ H_2O]{(1)\text{ Excess MeMgCl}}$ (A) $\xrightarrow[H_2SO_4]{\text{conc.}}$ 'B' Identify 'B' product ?

(A)  (B)  (C)  (D) 

Question No. 26 to 28 (3 questions)

An alkene (A) $C_{16}H_{16}$ on ozonolysis gives only product (B) C_8H_8O. (B) also can be obtained by hydrolysis of the product obtained by reaction between cyano benzene and CH_3MgBr. (A) can show geometrical isomerism and it can decolourise Br_2 water. (B) on treatment with SeO_2 produces (C)

Q.26 Which is not correct about (A) ?

(A) A is optically inactive

(B) On catalytic hydrogenation 'trans' form of A produces racemic mixture

(C) A can be prepared by Witting reaction on acetophenone with $Ph_3P = C(CH_3)Ph$.

(D) On treatment with per acid followed by hydrolysis 'trans' form of A produces racemic mixture

Q.27 Which is not correct about B ?

(A) It gives iodoform test

(B) On treatment with $LiAlH_4$, H_2O it produces a compound which also responds to iodoform test.

(C) It gives Tollen's test

(D) On treatment with NH_2NH_2 followed by alc. KOH at high temperature, it produces ethyl benzene

Q.28 Which is not correct about C?

(A) On treatment with $NaBH_4$ it will produce a diol.

(B) On treatment with OH^- (conc.) followed by acidification racemic mixture of a carboxylic acid is obtained

(C) It gives Tollen's test

(D) It can take part in aldol condensation

(Question No. 29 & 30)

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

(A) If both (A) and (R) are true and (R) is the correct explanation of (A)

(B) If both (A) and (R) are true but (R) is not correct explanation of (A)

(C) If (A) is true but (R) is false

(D) If (A) is false and (R) is true

Q.29 **Assertion** : Benzaldehyde with HCN gives two isomeric compounds

Reason : Both nitrile and isonitrile compounds are possible when HCN reacts with carbonyl group.

Q.30 **Assertion :** $Cl_3C-\overset{\overset{O}{\|}}{C}-H \xrightarrow{NaOH} Cl_3C—CH_2OH + Cl_3C—COONa$

Reason : There are no α–H in this compound, so it can't give aldol.

EXERCISE # II

Q.1 Two isomeric ketones, 3-pentanone and 2-pentanone can be distinguished by :

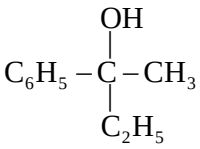
(A) I_2 / NaOH (B)$NaSO_3H$ (C) NaCN / HCl (D) 2,4-DNP

Q.2 An optically inactive alcohol (A) $C_6H_{12}O$ is oxidized by MnO_2 to produce optically inactive carbonyl compound while reduction of (A) by H_2/Ni produces optically active compound. Possible structure(s) of alcohol is/are

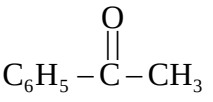
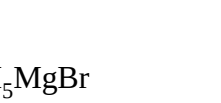
(A) Hex-2-ene-1- ol (B) Hex-3-ene-2- ol

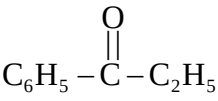
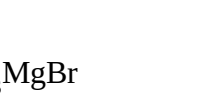
(C) 2-Methyl pent-2 - ene-1-ol (D) 3-Methyl pent-2 - ene-1-ol

Q.3 Consider the structure of given alcohol:



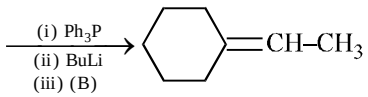
This alcohol can be prepared from:

(A)  and C_2H_5MgBr (B)  and C_6H_5MgBr

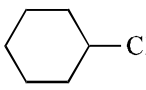
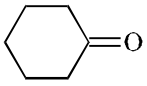
(C)  and CH_3MgBr (D)  and C_2H_5MgCl

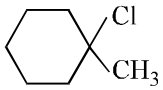
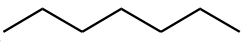
Q.4 Which of the following compounds will not give aldol condensation :

(A) Acetaldehyde (B) Formaldehyde (C) Pivaldehyde (D) Crotonaldehyde

Q.5 (A) 

In above reaction (A) and (B) will respectively be

(A)  & CH_3CHO (B) CH_3CH_2Cl & 

(C)  & HCHO (D)  & CH_3CHO

Q.6 Stability of hydrates of carbonyl compounds depends on:

(A) Steric hindrance (B) Presence of –I group on gemdiol carbon

(C) Intramolecular hydrogen bonding (D) angle strain in carbonyl compound

Q.7 Which of the following can be used for protection of carbonyl group

(A) $CH_2OH–CH_2OH$ / $H^{\oplus}$ (B) $CH_2OH–CH_2–CH_2OH$ / $H^{\oplus}$

(C) $HS–(CH_2)_3–SH$ (D) $CH_2OH–CH_2–CHO$

Q.8 Which of the following(s) will form stable hemiketal :

(A) $Ph-\overset{\overset{O}{\|}}{C}-Ph$ (B) $HO-(CH_2)_3-\overset{\overset{O}{\|}}{C}-CH_3$

(C) $CH_2OH-\overset{\overset{O}{\|}}{C}-(CHOH)_3-CH_2-OH$ (D) $H_3C-O-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

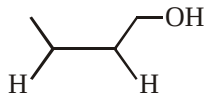
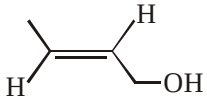
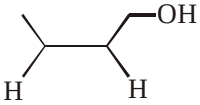
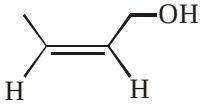
Q.9 Mixture of Ph–CHO & HCHO is treated with NaOH then Cannizzaro reaction involves:

(A) Oxidation of HCHO (B) Reduction of HCHO

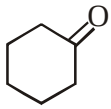
(C) Oxidation of Ph–CHO (D) Reduction of Ph–CHO

Q.10 Final product in the given reaction sequence is :

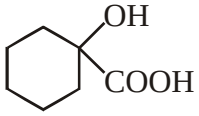
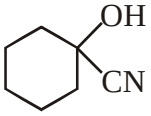
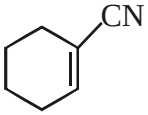
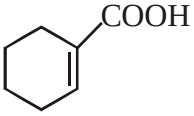
$CH_3-C\equiv CH \xrightarrow{PhMgBr}$  $+ [A] \xrightarrow[ii)\ H^{\oplus}]{i)\ H-\overset{\overset{O}{\|}}{C}-H} [B] \xrightarrow[Pd/BaSO_4]{H_2} [C]$

(A)  (B)  (C)  (D) 

Q.11 Consider the following sequence of reactions.

 $\xrightarrow[H_2SO_4]{NaCN}$ A $\xrightarrow[H_2O,\ heat]{H_2SO_4}$ B

The major product (B) is :

(A)  (B)  (C)  (D) 

Q.12 In the reaction

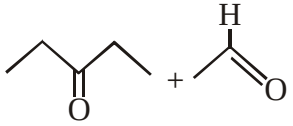
$(CH_3)_2CHNO_2 + HCHO \xrightarrow{NaOH}$

the major product is

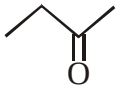
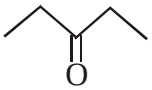
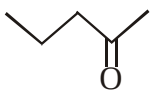
(A) $(CH_3)_2CHCH_2ONO_2$ (B) $(CH_3)_2C(NO_2)(CH_2OH)$

(C) $(CH_3)_2CH-\underset{\diagdown O \diagup}{CH}-CHNO_2$ (D) $(CH_3)_2CH-\underset{\diagdown O \diagup}{CH}-CH_2NO_2$

Q.13 Consider the following sequence of reactions.

Ketone A $\xrightarrow[2.\ H_2O]{1.\ C_2H_5MgBr}$ B $\xrightarrow[-H_2O]{H_2SO_4,\ heat}$ C $\xrightarrow[2.\ Zn,\ H_2O]{1.\ O_3}$ 

The ketone (A) is :

(A)  (B)  (C)  (D) 

Q.14 Which of the following reactions will give(s) 2° alcohol as a major product :

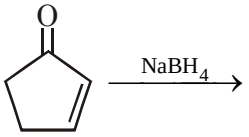
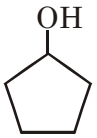
(A) $CH_3—CH_2—\overset{\overset{O}{\|}}{C}—NH_2 \xrightarrow[(ii)\ NaNO_2/HCl]{(i)\ LAH}$

(B) $H—\overset{\overset{O}{\|}}{C}—OR \xrightarrow[(ii)\ H^+]{(i)\ CH_3MgX(excess)}$

(C) $H_3C—\underset{\diagdown\ \diagup\ O}{HC}—CH_2 \xrightarrow[(ii)\ H^+]{(i)\ RMgX}$

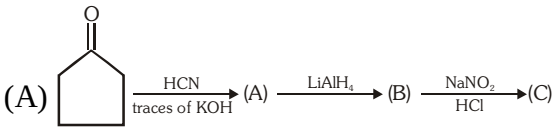
(D) $CH_3—\overset{\overset{O}{\|}}{C}—Cl \xrightarrow[H^+]{CH_3MgX\ (excess)}$

Q.15 Match list-I with list-II :

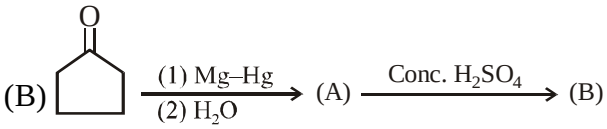
List - I	**List - II**
(A) 	(P) Acetal
(B) $C_6H_5CHO + Ph–NH_2 \xrightarrow{H^\oplus}$	(Q) Schiff's base
(C) $C_6H_5COCH_3 + CH_3–CH_2–NH_2 \xrightarrow{H^\oplus}$	(R) 
(D) $RCHO + 2RCH_2OH \xrightarrow{H^\oplus}$	(S) Imine

EXERCISE # III

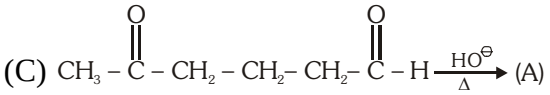
Q.1 **Column - I** **Column - II**

(A) 

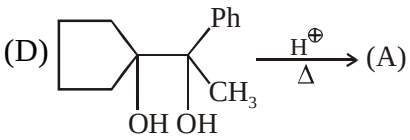
(P) Formation of six member ring takes place

(B) 

(Q) Final product is Ketone

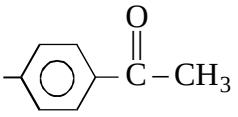
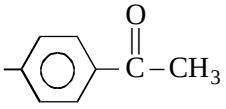
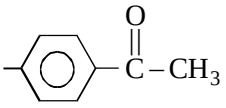
(C) 

(R) Final product formed will give positive Idoform test

(D) 

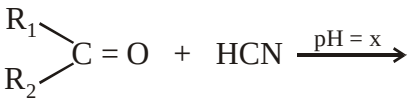
(S) Final product formed will react with 2,4-DNP. (2,4-Di-nitrophenyl hydrazine)

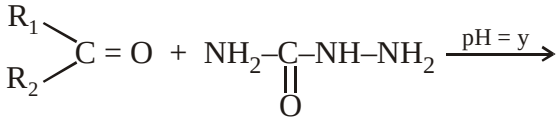
Q.2 Arrange the following compounds in decreasing order of $K_{eq.}$ for hydrate formation.

(1) $C_6H_5COCH_3$ (2)  (3)  (4) 

Paragraph for Q. 03 to 04

Two reactions which are example of nucleophilic attack are given as below .

Reaction - I : 

Reaction - II : 

Q.3 Value of x is :

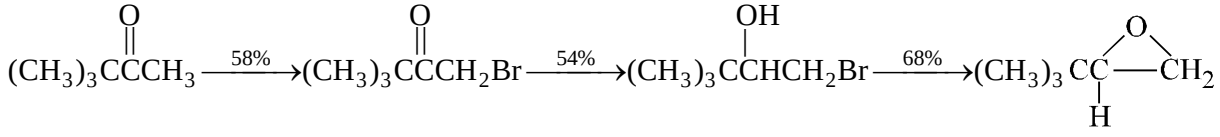
(A) $x \leq 4.5$ (B) x = 6 (C) x > 7 (D) Can't decide

Q.4 Value of y is :

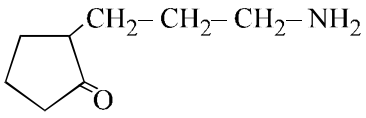
(A) x = 4.5 (B) x = 1.5 (C) x = 7 (D) x = 9

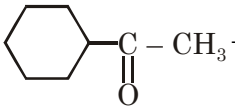
Q.5 Some Grignard reagents react with ethyl orthoformate, followed by acidic hydrolysis, to give aldehydes. Propose mechanisms for the two steps in this synthesis.

Q.6 A synthesis that begins with 3,3-dimethyl-2-butanone gives the epoxide shown. Suggest reagents appropriate for each step in the synthesis.



Q.7 Predict the organic products :

(a) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3-CH_2-NH_2 \xrightarrow[(ii)\ H_2/Pt]{(i)\ H^+/\Delta}$ (b)  $\xrightarrow[(ii)\ H_2/Pt]{(i)\ H^+/\Delta}$

(c)  $\xrightarrow[(ii)\ \overset{\oplus}{H}]{(i)\ Cl_2/NaOH/HOH}$ z

Paragraph for Q.No.8 to 9

A(Hydrocarbon) (C ⇒ 88.24%) [Molecular weight of A = 68]

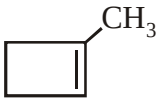
$A \xrightarrow[(ii)\ \text{n-propyl bromide}]{(i)\ Na} B\ (C_8H_{14})$

$A \xrightarrow[\text{dil. } H_2SO_4]{Hg^{2+}} C_5H_{10}O\ (C)$

$A \xrightarrow[H^+]{KMnO_4}$ Carboxylic acid + Gas

Q.8 'A' can be :

(A) $H_3C-H_2C-C\equiv C-CH_3$ (B) $CH_3-CH_2-CH_2-C\equiv C-H$

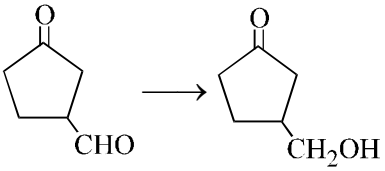
(C) $CH_3-\underset{\underset{CH_3}{|}}{CH}-C\equiv CH$ (D) 

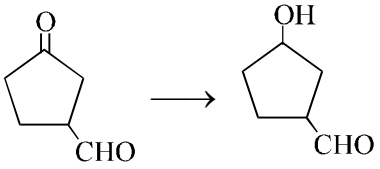
Q.9 Correct statement reagarding C is.

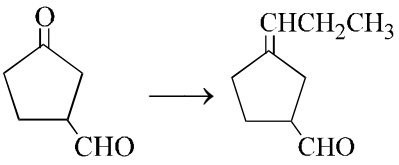
(A) C reacts with fehling solution to give red ppt. (B) C gives +ve iodoform test

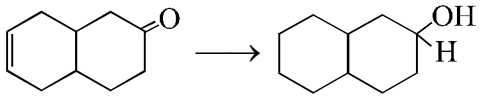
(C) C give –ve 2, 4, D.N.P test (D) C is aldehyde

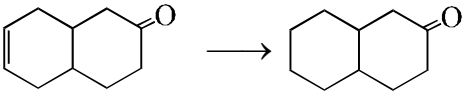
Q.10 Show how you would accomplish the following syntheses efficiently and in good yield. You may use any necessary reagents.

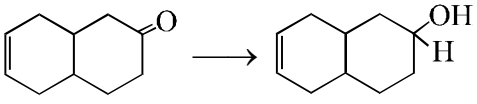
(a) 

(b) 

(c) 

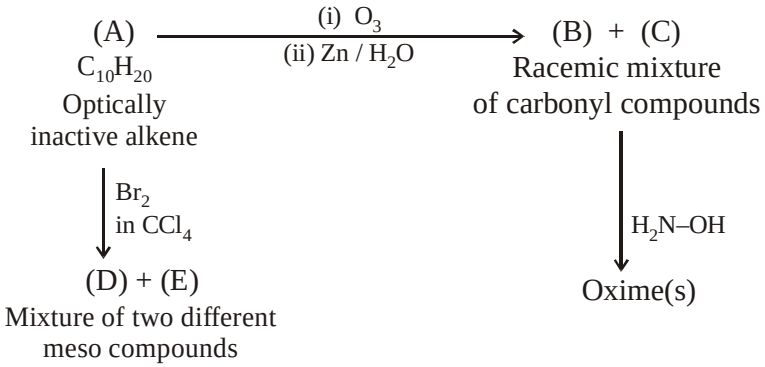
(d) 

(e) 

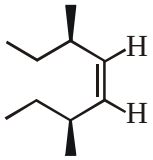
(f) 

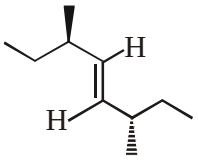
Paragraph for Q.No. 11 to 12

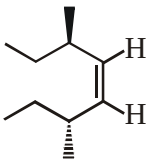
In given reaction sequence

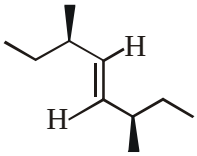


11. Alkene A is :

(A) 

(B) 

(C) 

(D) 

12. How many total oxime(s) is/are obtained

(A) 1 (B) 2 (C) 3 (D) 4

EXERCISE # IV (MAINS)

Q.1 When $CH_2 = CH–COOH$ is reduced with $LiAlH_4$, the compound obtained will be - **[AIEEE-2003]**

(1) $CH_3–CH_2–CH_2OH$ (2) $CH_3–CH_2–CHO$

(3) $CH_3–CH_2–COOH$ (4) $CH_2=CH–CH_2OH$

Q.2 Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid ? **[AIEEE-2004]**

(1) Phenol (2) Benzaldehyde (3) Butanal (4) Benzoic acid

Q.3 Which one of the following is reduced with Zn-Hg/HCl to give the corresponding hydrocarbon **[AIEEE-2004]**

(1) Butan-2-one (2) Acetic acid (3) Acetamide (4) Ethyl acetate

Q.4 On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is **[AIEEE-2004]**

(1) $CH_3COOC_2H_5 + NaCl$ (2) $CH_3COONa + C_2H_5OH$

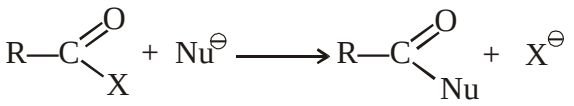
(3) $CH_3COCl + C_2H_5OH + NaOH$ (4) $CH_3Cl + C_2H_5COONa$

Q.5 The best reagent to convert pent–3–en–2–ol into pent –3–en –2–one is - **[AIEEE-2005]**

(1) Acidic dichromate (2) Acidic permanganate

(3) Pyridinium chloro-chromate (4) Chromic anhydride in glacial acetic acid

Q.6 Rate of the reaction- **[AIEEE-2005]**

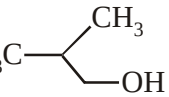


is fastest when X is -

(1) NH_2 (2) Cl (3) OCOR (4) OC_2H_5

Q.7 Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is- **[AIEEE-2006]**

(1) $CH_3CH_2CH(OH)CH_2CH_3$ (2) $C_6H_5CH_2CH_2OH$

(3)  (4) $PhCHOHCH_3$

Q.8 In the following sequence of reactions

$CH_3CH_2OH \xrightarrow{P + I_2} A \xrightarrow[Ether]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$, then compound 'D' is - **[AIEEE-2007]**

(1) Butanal (2) n–Butyl alcohol

(3) n–Propyl alcohol (4) Propanal

Q.9 In the following sequence of reactions, the alkene affords the compound 'B' :- **[AIEEE-2008]**

$$CH_3CH = CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B.$$

The compound B is

(1) CH_3CH_2CHO (2) CH_3COCH_3 (3) $CH_3CH_2COCH_3$ (4) CH_3CHO

Q.10 Bakelite is obtained from phenol by reacting with **[AIEEE-2008]**

(1) $(CH_2OH)_2$ (2) CH_3CHO (3) CH_3COCH_3 (4) HCHO

Q.11 Which of the following on heating with aqueous KOH, produces acetaldehyde ? **[AIEEE-2009]**

(1) CH_2ClCH_2Cl (2) CH_3CHCl_2 (3) CH_3COCl (4) CH_3CH_2Cl

Q.12 In Cannizzaro reaction given below :- **[AIEEE-2009]**

$2PhCHO \xrightarrow{:\overset{\ominus}{O}H} PhCH_2OH + PhCO_2^{\ominus}$

the slowest step is :-

(1) The abstraction of proton from the carboxylic group

(2) The deprotonation of $PhCH_2OH$

(3) The attack of $:\overset{\ominus}{O}H$ at the carboxyl group

(4) The transfer of hydride to the carbonyl group

Q.13 One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is :- **[AIEEE-2010]**

(1) Ethene (2) Propene (3) 1-Butene (4) 2-Butene

Q.14 Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of :- **[AIEEE-2011]**

(1) An isopropyl group (2) An acetylenic triple bond

(3) Two ethylenic double bonds (4) A vinyl group

Q.15 Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds : - **[AIEEE-2011]**

(1) 2-Methyl - 1- pentene (2) 1-Pentene

(3) 2-Pentene (4) 2-Methyl-2-pentene

Q.16 Trichloroacetaldehyde was subjected to assumed Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate and another compound. The other compound is :- **[AIEEE-2011]**

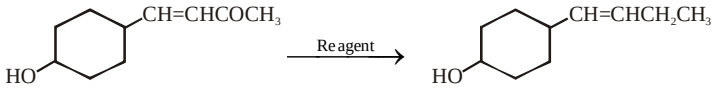
(1) 2,2,2–Trichloropropanol (2) Chloroform

(3) 2,2,2–Trichloroethanol (4) Trichloromethanol

Q.17 Silver Mirror test is given by which one of the following compounds? **[AIEEE-2011]**

(1) Formaldehyde (2) Benzophenone (3) Acetaldehyde (4) Acetone

Q.18 In the given transformation, which of the following is the most appropriate reagent ? **[AIEEE-2012]**



(1) $NaBH_4$ (2) $NH_2NH_2, \overset{\ominus}{O}H$ (3) Zn – Hg / HCl (4) Na, Liq.NH_3

Q.19 Iodoform can be prepared from all except :- **[AIEEE-2012]**

(1) Isobutyl alcohol (2) Ethyl methyl ketone

(3) Isopropyl alcohol (4) 3-Methyl–2–butanone

Q.20 A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is :-

(1) 2 (2) 5 (3) 4 (4) 6 **[JEE(Main)-2013]**

Q.21 The major organic compound formed by the reaction of 1, 1, 1–trichloroethane with silver powder is :-

[JEE(Main)-2014]

(1) 2-Butyne (2) 2-Butene (3) Acetylen (4) Ethene

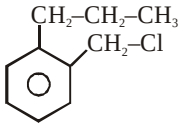
Q.22 The most suitable reagent for the conversion of $R - CH_2 - OH \rightarrow R - CHO$ is :-

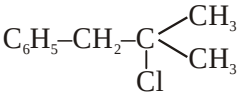
[JEE(Main)-2014]

(1) CrO_3 (2) PCC (Pyridinium chlorochromate)

(3) $KMNO_4$ (4) $K_2Cr_2O_7$

Q.23 A compound A with molecular formula $C_{10}H_{13}Cl$ gives a white precipitate on adding silver nitrate solution. A on reacting with alcoholic KOH gives compound B as the main product. B on ozonolysis gives C and D. C gives Cannizaro reaction but not aldol condensation. D gives aldol condensation but not Cannizaro reaction. A is : **[JEE(Main)-2015]**

(1) 

(2) 

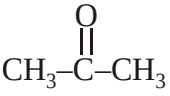
(3) $C_6H_5–CH_2–CH_2–CH_2–CH_2–Cl$

(4) 

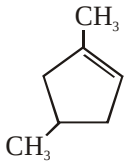
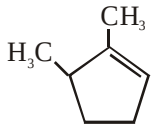
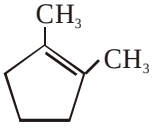
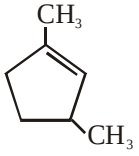
Q.24 In the reaction sequence **[JEE(Main)-2015]**

$2CH_3CHO \xrightarrow{OH^-} A \xrightarrow{\Delta} B$; the product B is:-

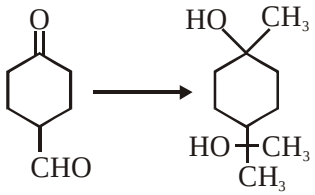
(1) $CH_3–CH=CH–CHO$ (2) $CH_3–CH_2–CH_2–CH_3$

(3) $CH_3–CH_2–CH_2–CH_2–OH$ (4) 

Q.25 Which compound would give 5-keto-2-methyl hexanal upon ozonlysis? **[JEE(Main) 2015]**

(1)  (2)  (3)  (4) 

Q.26 The correct sequence of reagents for the following conversion will be :- **[JEE(Main)-2017]**



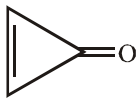
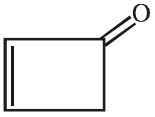
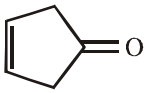
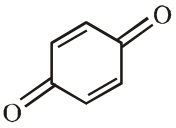
(1) $[Ag(NH_3)_2]^+ OH^-$, H^+/CH_3OH, CH_3MgBr

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

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

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

Q.27 Which of the following compounds will show highest dipole moment ? **[JEE(Main-on-line)-2017]**

(I)  (II)  (III)  (IV) 

(1) (II) (2) (III) (3) (I) (4) (IV)

Q.28 Glucose on prolonged heating with HI gives : **[JEE(Main)-2018]**

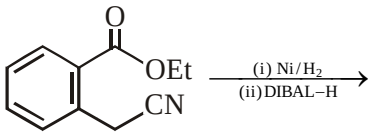
(1) 1–Hexene (2) Hexanoic acid (3) 6-iodohexanal (4) n-Hexane

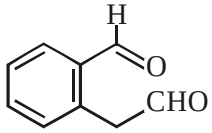
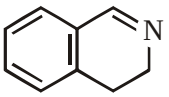
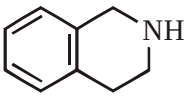
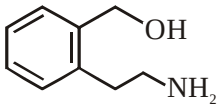
Q.29 Which of the following compounds will most readily be dehydrated to give alkene under acidic condition? **[JEE(Main-on-line)-2018]**

(1) 4-Hydroxypentan-2-one (2) 2-Hydroxycyclopentanone

(3) 3-Hydroxypentan-2-one (4) 1-Pentanol

Q.30. The major product of the following reaction is: **[JEE-Main(January)-2019]**



(1)  (2)  (3)  (4) 

Q.31 In the following reaction **[JEE-Main(January)-2019]**

Aldehyde + Alcohol $\xrightarrow{HCl}$ Acetal

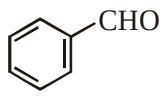
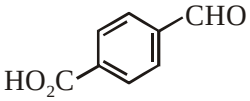
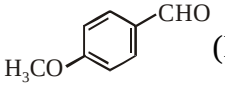
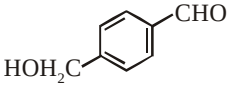
Aldehyde	Alcohol
HCHO	^{t}BuOH
CH_3CHO	MeOH

The best combinations is :

(1) HCHO and MeOH (2) HCHO and ^{t}BuOH

(3) CH_3CHO and MeOH (4) CH_3CHO and ^{t}BuOH

Q.32 The aldehydes which will not form Grignard product with one equivalent Grignard reagents are : **[JEE-Main(January)-2019]**

(A)  (B)  (C)  (D) 

(1) (B), (C), (D) (2) (B), (D) (3) (B), (C) (4) (C), (D)

EXERCISE-IV # (A) (OBJECTIVE QUESTIONS)

Q.1 Which of the following has the most acidic hydrogen: **[IIT 2000]**

(A) 3-hexanone (B) 2,4-hexanedione

(C) 2,5-hexanedione (D) 2,3-hexandione

Q.2 A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives:

(A) benzyl alcohol and sodium formate (B) sodium benzoate and methyl alcohol

(C) sodium benzoate and sodium formate (D) benzyl alcohol and methyl alcohol **[IIT 2001]**

Q.3 1-propanol & 2-propanol can be best distinguished by : **[IIT 2001]**

(A) Oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution

(B) Oxidation with acidic dichromate followed by reaction with Fehling solution

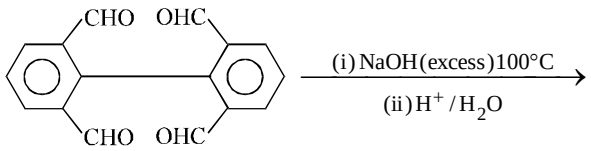
(C) Oxidation by heating with copper followed by reaction with Fehling solution

(D) Oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution

Q.4 Compound A (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product B (molecular formula C_3H_6O). B forms a shining silver mirror on warming with ammonical silver nitrate. B when treated with an aqueous solution of $H_2NCONHNH_2$. HCl and sodium acetate gives a product C. Identify the structure of C. **[IIT 2002]**

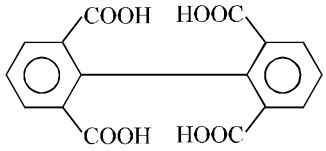
(A) $CH_3CH_2CH = NNHCONH_2$ (B) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=NNHCONH_2$

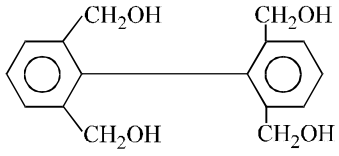
(C) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=NCONHNH_2$ (D) $CH_3CH_2CH=NCONHNH_2$

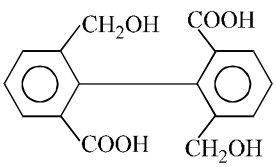
Q.5 

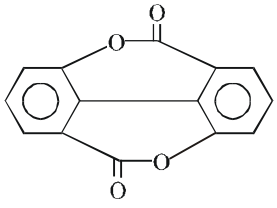
[IIT 2003]

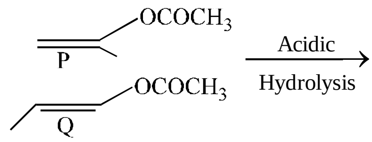
any one of the products formed is :

(A) 

(B) 

(C) 

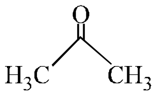
(D) 

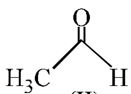
Q.6  Products formed by P & Q can be differentiated by: **[IIT 2003]**

(A) 2, 4 DNP (B) Lucas reagent ($ZnCl_2$) conc. HCl

(C) $NaHSO_3$ (D) Fehlings solution

Q.7 The order of reactivity of phenyl Magnesium Bromide with the following compounds is **[IIT 2004]**


(I)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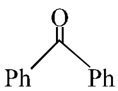
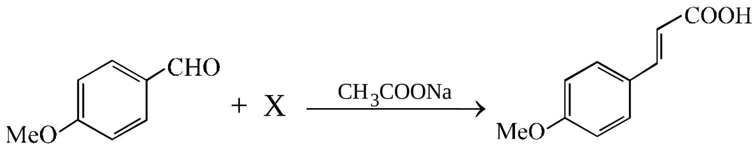

(III)

(A) II > III > I (B) I > III > II (C) II > I > III (D) All react with the same rate

Q.8  **[IIT 2005]**

What is X?

(A) CH_3COOH (B) $BrCH_2$, COOH (C) $(CH_3CO)_2O$ (D) CHO–COOH

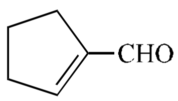
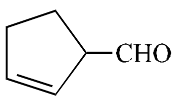
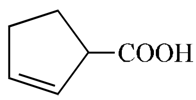
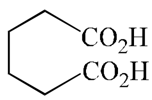
Q.9 The smallest ketone and its next homologue are reacted with NH_2OH to form oxime.

(A) Two different oximes are formed (B) Three different oximes are formed

(C) Two oximes are optically active (D) All oximes are optically active **[IIT 2006]**

Q.10 Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous KOH yields compound F. Compound F is

[IIT-JEE(ADV.)- 2007]

(A)  (B)  (C)  (D) 

Q.11 **Statement-1 :** Glucose gives a reddish-brown precipitate with Fehling's solution.

because

Statement-2 : Reaction of glucose with Fehling's solution gives CuO and gluconic acid.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(C) Statement-1 is True, Statement-2 is False.

(D) Statement-1 is False, Statement-2 is True. **[IIT-JEE(ADV.)- 2007]**

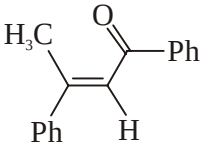
Q.12 Match the compounds/ion in column I with their properties/ reaction in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.

[IIT-JEE(ADV.)- 2007]

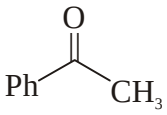
Column I	**Column II**
(A) C_6H_5CHO	(P) gives precipitate with 2,4-dinitrophenylhydrazine
(B) $CH_3C{\equiv}CH$	(Q) gives precipitate with $AgNO_3$
(C) CN^-	(R) is a nucleophile
(D) I^-	(S) is involved in cyanohydrin formation

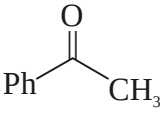
Paragraph for Question No. 13 to 15

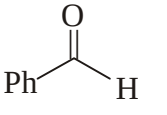
A tertiary alcohol **H** upon acid catalysed dehydration gives a product **I**. Ozonolysis of **I** leads to compounds **J** and **K**. Compound **J** upon reaction with KOH gives benzyl alcohol and a compound **L**, whereas **K** on reaction with KOH gives only **M**.

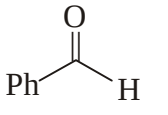
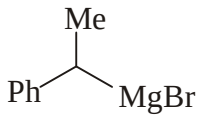
M = 

Q.13 Compound **H** is formed by the reaction of **[IIT-JEE(ADV.)- 2008]**

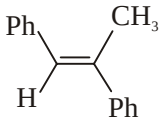
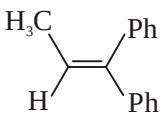
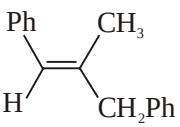
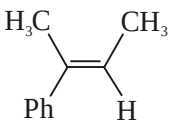
(A)  + PhMgBr

(B)  + $PhCH_2MgBr$

(C)  + $PhCH_2MgBr$

(D)  + 

Q.14 The structure of compound **I** is **[IIT-JEE(ADV.)- 2008]**

(A)  (B)  (C)  (D) 

Q.15 The structures of compounds **J**, **K** and **L**, respectively, are **[IIT-JEE(ADV.)- 2008]**

(A) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^-K^+$

(B) PhCHO, $PhCH_2CHO$ and $PhCOO^-K^+$

(C) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$

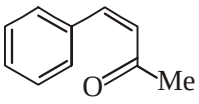
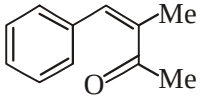
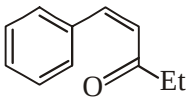
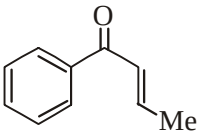
(D) PhCHO, $PhCOCH_3$ and $PhCOO^-K^+$

Paragraph for Question Nos. 16 to 38

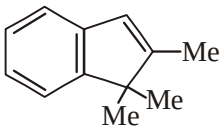
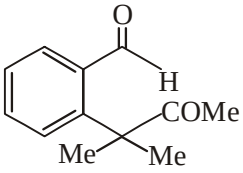
A carbonyl compound **P**, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin **Q**. Ozonolysis of **Q** leads to a dicarbonyl compound **R**, which undergoes intramolecular aldol reaction to give predominantly **S**.

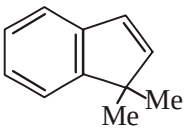
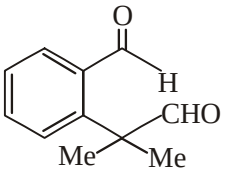
$$\mathbf{P} \xrightarrow[\substack{2.H^+,H_2O \\ 3.H_2SO_4,\Delta}]{1.MeMgBr} \mathbf{Q} \xrightarrow[2.\ Zn,H_2O]{1.\ O_3} \mathbf{R} \xrightarrow[2.\ \Delta]{1.\ OH^-} \mathbf{S}$$

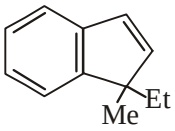
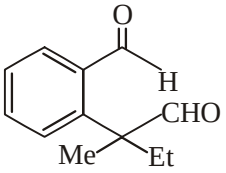
Q.16 The structure of the carbonyl compound **P** is **[IIT-JEE(ADV.)- 2009]**

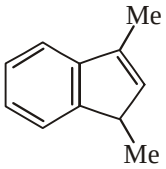
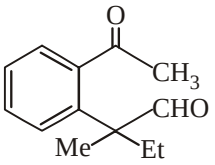
(A)  (B)  (C)  (D) 

Q.17 The structure of the products **Q** and **R**, respectively, are **[IIT-JEE(ADV.)- 2009]**

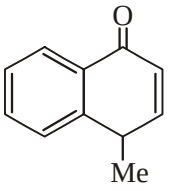
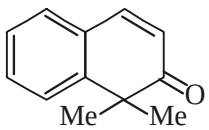
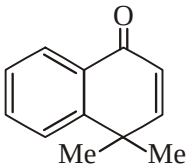
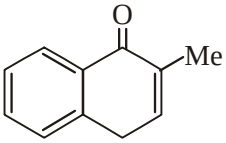
(A)  , 

(B)  , 

(C)  , 

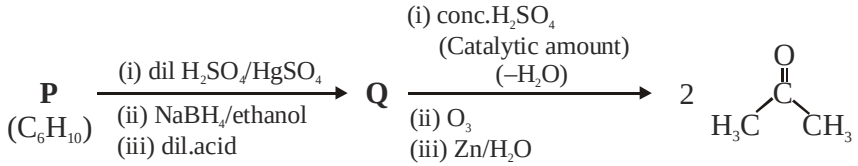
(D)  , 

Q.18 The structure of the product **S** is **[IIT-JEE(ADV.)- 2009]**

(A)  (B)  (C)  (D) 

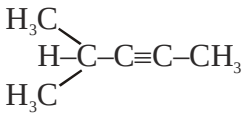
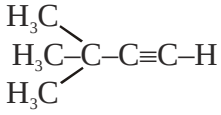
Paragraph for Questions Nos. 19 to 20

An acyclic hydrocarbon P, having molecular formula C_6H_{10}, gave acetone as the only organic product through the following sequence of reactions, in the which Q is an intermediate organic compound.

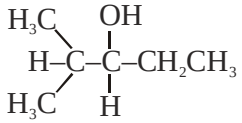
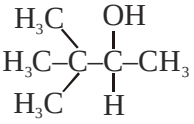
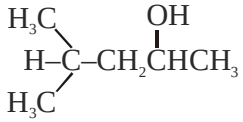


Q.19 The structure of compound P is - **[IIT-JEE(ADV.)- 2011]**

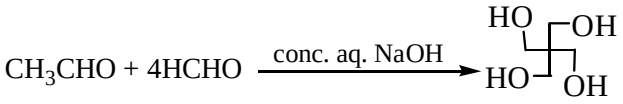
(A) $CH_3CH_2CH_2CH_2–C\equiv C–H$ (B) $H_3CH_2C\equiv C–CH_2CH_3$

(C)  (D) 

Q.20 The structure of the compound Q is - **[IIT-JEE(ADV.)- 2011]**

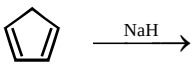
(A)  (B)  (C)  (D) 

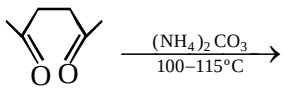
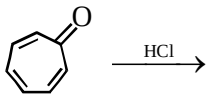
Q.21 The number of aldol reaction(s) that occurs in the given transformation is **[IIT-JEE(ADV.)- 2012]**



(A) 1 (B) 2 (C) 3 (D) 4

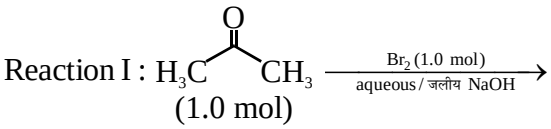
Q.22 Among P, Q, R and S, the aromatic compound(s) is / are : **[IIT-JEE(ADV.)- 2013]**

 P  Q

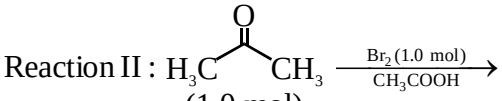
 R  S

(A) P (B) Q (C) R (D) S

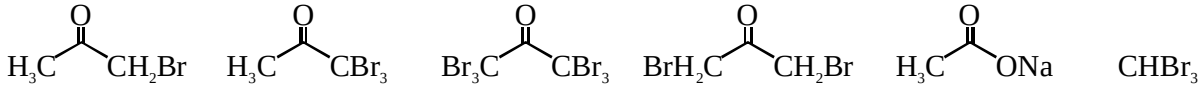
Q.23 After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are)

Reaction I :  **[IIT-JEE(ADV.)- 2013]**

(1.0 mol)

Reaction II : 

(1.0 mol)



P Q R S T U

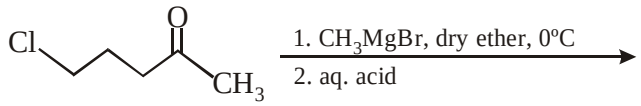
(A) Reaction I : P and Reaction II : P

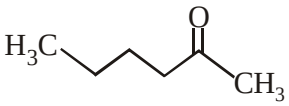
(B) Reaction I : U, acetone and Reaction II : Q acetone

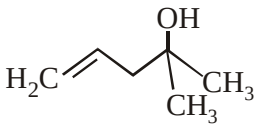
(C) Reaction I : T, U, acetone and Reaction II : P

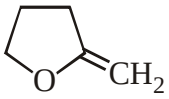
(D) Reaction I : R, acetone and Reaction II : S acetone

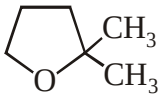
Q.24 The major product in the following reaction is **[IIT-JEE(ADV.)- 2014]**



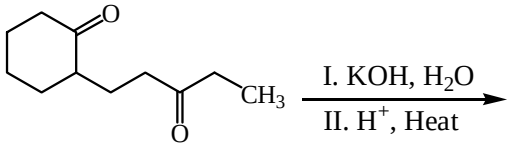
(A) 

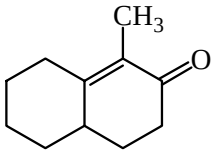
(B) 

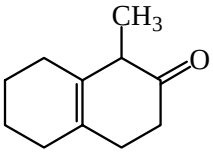
(C) 

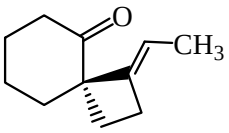
(D) 

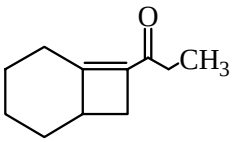
Q.25 The major product of the following reaction is - **[IIT-JEE(ADV.)- 2015]**



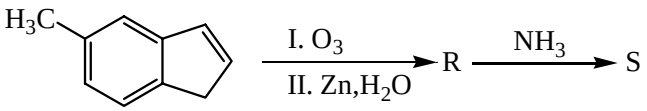
(A) 

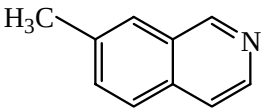
(B) 

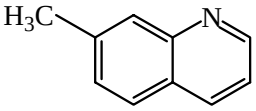
(C) 

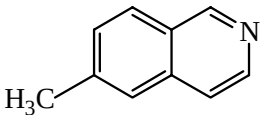
(D) 

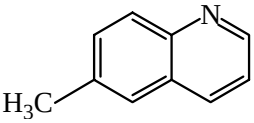
Q.26 In the following reactions, the product S is - **[IIT-JEE(ADV.)- 2015]**



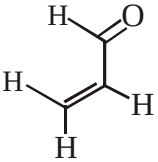
(A) 

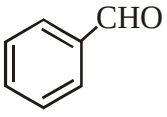
(B) 

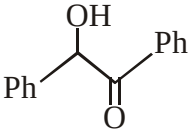
(C) 

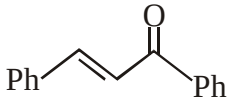
(D) 

Q.27 Positive Tollen's test is observed for : **[IIT-JEE(ADV.)- 2016]**

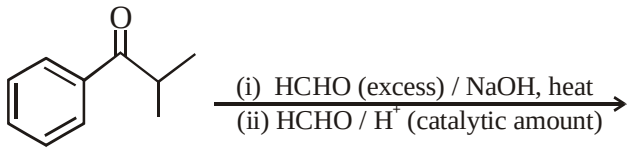
(A) 

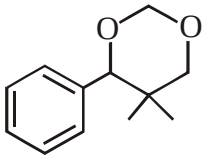
(B) 

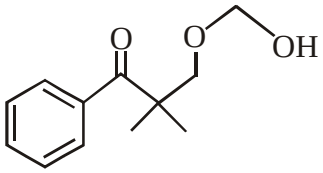
(C) 

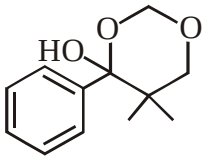
(D) 

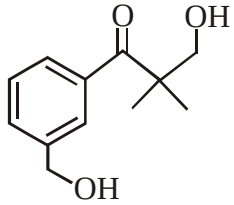
Q.28 The major product of the following reaction sequence is : **[IITJEE(ADV.)-2016]**



(A) 

(B) 

(C) 

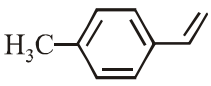
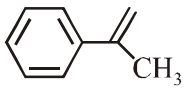
(D) 

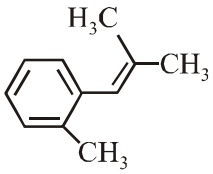
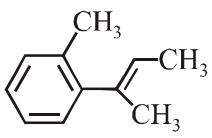
Q.29 Compound **P** and **R** upon ozonolysis produce **Q** and **S**, respectively. The molecular formula of **Q** and **S** is C_8H_8O. **Q** undergoes Cannizzaro reaction but not haloform reaction, whereas **S** undergoes haloform reaction but not Cannizzaro reaction : **[IIT-JEE(ADV.)- 2017]**

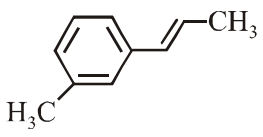
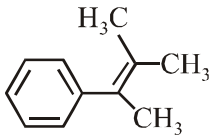
(i) $P \xrightarrow[(ii)\ Zn / H_2O]{(i)\ O_3 / CH_2Cl_2} \underset{(C_8H_8O)}{Q}$

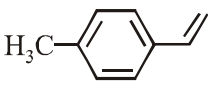
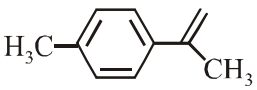
(ii) $R \xrightarrow[(ii)\ Zn / H_2O]{(i)\ O_3 / CH_2Cl_2} \underset{(C_8H_8O)}{S}$

The option(s) with suitable combination of P and R, respectively, is(are)

(A)  and 

(B)  and 

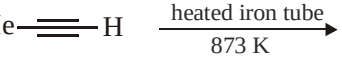
(C)  and 

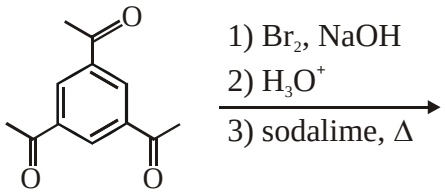
(D)  and 

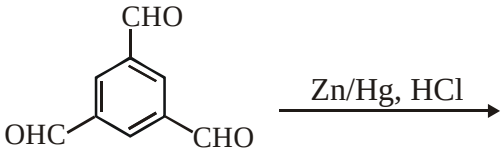
30. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are)

[IIT-JEE(ADV.)- 2018]

(A) 

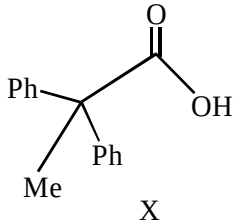
(B) 

(C) 

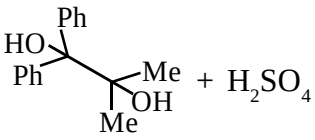
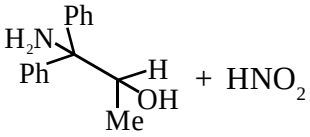
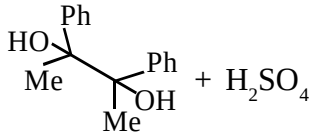
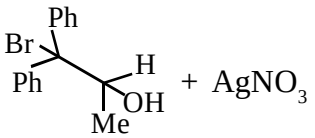
(D) 

31. The desired product X can be prepared by reacting the major product of the reactions in LIST-I with one or more appropriate reagents in LIST-II. **[IIT-JEE(Adv.)-2018]**

(given, order of migratory aptitude: aryl > alkyl > hydrogen)



X

LIST-I	**LIST-II**
P.  + H_2SO_4	1. I_2, NaOH
Q.  + HNO_2	2. $[Ag(NH_3)_2]OH$
R.  + H_2SO_4	3. Fehling solution
S.  + $AgNO_3$	4. HCHO, NaOH
	5. NaOBr

The correct option is

(A) P → 1; Q → 2,3; R → 1,4; S → 2,4 (B) P → 1,5; Q → 3,4; R → 4,5; S → 3

(C) P → 1,5; Q → 3,4; R → 5; S → 2,4 (D) P → 1,5; Q → 2,3; R → 1,5; S → 2,3

ANSWER-KEY

EXERCISE # I

1	**Ans. (A)**	**2**	**Ans. (B)**	**3**	**Ans. (C)**	**4**	**Ans. (C)**
5	**Ans. (C)**	**6**	**Ans. (D)**	**7**	**Ans. (A)**	**8**	**Ans. (C)**
9	**Ans. (C)**	**10**	**Ans. (C)**	**11**	**Ans. (A)**	**12**	**Ans. (D)**
13	**Ans. (C)**	**14**	**Ans. (C)**	**15**	**Ans. (B)**	**16**	**Ans. (D)**
17	**Ans. (C)**	**18**	**Ans. (A)**	**19**	**Ans. (D)**	**20**	**Ans. (D)**
21	**Ans. (C)**	**22**	**Ans. (D)**	**23**	**Ans. (C)**	**24**	**Ans. (B)**
25	**Ans. (A)**	**26**	**Ans. (D)**	**27**	**Ans. (C)**	**28**	**Ans. (D)**
29	**Ans. (C)**	**30**	**Ans. (D)**				

EXERCISE # II

1	**Ans. (A,B)**	**2**	**Ans. (C,D)**	**3**	**Ans. (A,B,C)**	**4**	**Ans. (B,C)**
5	**Ans. (A,B)**	**6**	**Ans. (A,B,C,D)**	**7**	**Ans. (A,B,C)**	**8**	**Ans. (B,C)**
9	**Ans. (A,D)**	**10**	**Ans. (D)**	**11**	**Ans. (D)**	**12**	**Ans. (B)**
13	**Ans. (B)**	**14**	**Ans. (A,B,C)**	**15**	**Ans. (A)→R ; (B)→Q,S ; (C)→S ; (D)→P**		

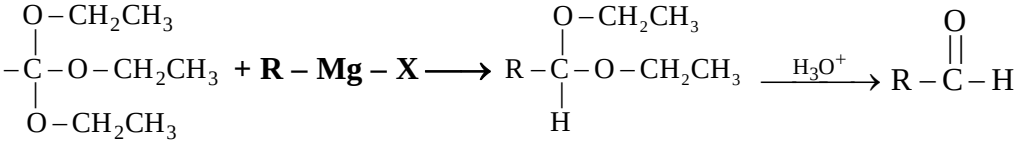
EXERCISE # III

1. **Ans. (A) P,Q,S ; (B) P,Q,S ; (C) P,Q,S ; (D) P,Q,S**

2. **Ans. 3 > 2 > 1 > 4**

3. **Ans. (C)** **4.** **Ans. (A)**

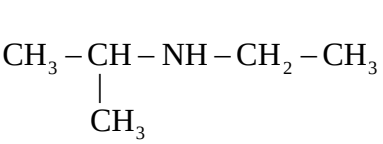
5. **Ans.**



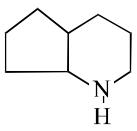
Ethyl orthoformate **Acetal** **aldehyde**

6. Ans. H^+/Br_2 ; H_2 / Ni ; NaOH

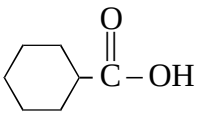
7. **Ans. (a)**



(b)



(c) $CHCl_3$ +

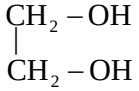


8. **Ans. (B,C)**

9. **Ans. (B)**

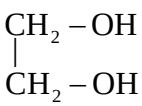
10. **Ans.**

(a) (i) $KMnO_4$, **(ii)**

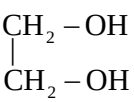


, **(iii)** $LiAlH_4$, **(iv)** $H_3O^{\oplus}$

(b) (i)



, **(ii)** $NaBH_4$, **(iii)** H_3O^+, **(c) (i)**



, **(ii)** $Ph_3P{=}CH{-}Et$

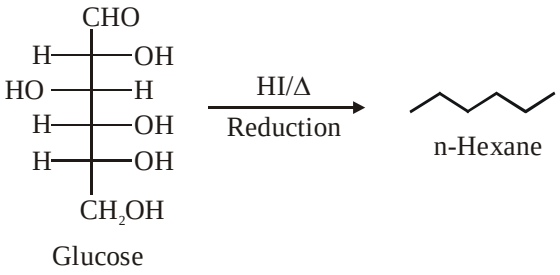
(d) (i) H_2, Ni **(e)** NH_2NH_2/H_2O_2 **(f)** $NaBH_4$

11. **Ans. (B)** **12.** **Ans. (D)**

EXERCISE # IV (MAINS)

1.	**Ans. (4)**	**2.**	**Ans. (2)**	**3.**	**Ans. (1)**	**4.**	**Ans. (2)**
5.	**Ans. (4)**	**6.**	**Ans. (2)**	**7.**	**Ans. (4)**	**8.**	**Ans. (3)**
9.	**Ans. (4)**	**10.**	**Ans. (4)**	**11.**	**Ans. (2)**	**12.**	**Ans. (4)**
13.	**Ans. (4)**	**14.**	**Ans. (4)**	**15.**	**Ans. (4)**	**16.**	**Ans. (3)**
17.	**Ans. (1 , 3)**	**18.**	**Ans. (2)**	**19.**	**Ans. (1)**	**20.**	**Ans. (2)**
21.	**Ans. (1)**	**22.**	**Ans. (2)**	**23.**	**Ans. (2)**	**24.**	**Ans. (1)**
25.	**Ans. (4)**	**26.**	**Ans. (1)**	**27.**	**Ans. (3)**		
28.	**Ans. (4)**						

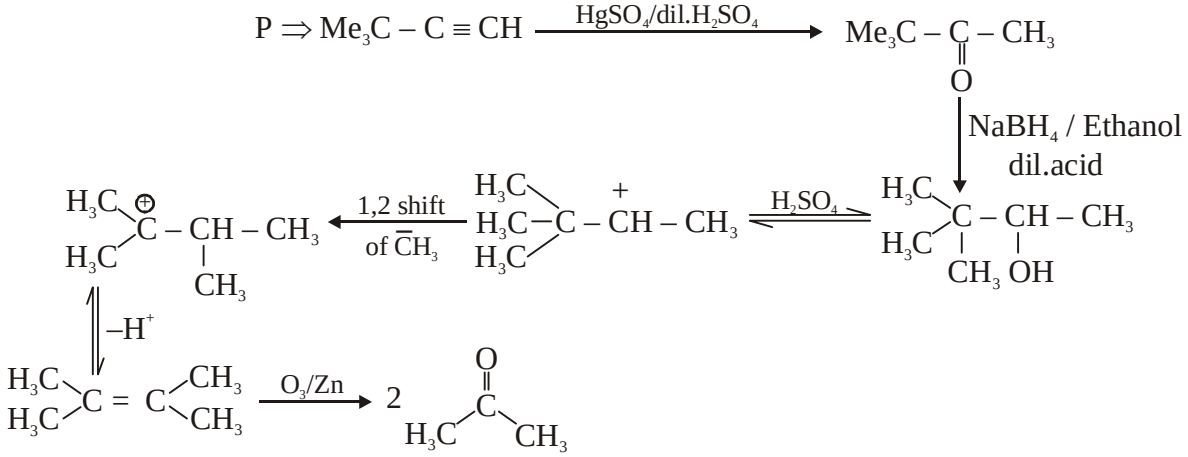
Sol.



29.	**Ans. (1)**	**30.**	**Ans. (2)**	**31.**	**Ans. (1)**	**32.**	**Ans. (2)**

EXERCISE-IV # (A) (OBJECTIVE QUESTIONS)

1.	**Ans. (B)**	**2.**	**Ans. (A)**	**3.**	**Ans. (C)**	**4.**	**Ans. (A)**
5.	**Ans. (C)**	**6.**	**Ans. (D)**	**7.**	**Ans. (C)**	**8.**	**Ans. (C)**
9.	**Ans. (B)**	**10.**	**Ans. (A)**	**11.**	**Ans. (C)**		
12.	**Ans. (A) P,S; (B) Q; (C) Q,R,S; (D) Q,R**			**13.**	**Ans. (B)**	**14.**	**Ans. (A)**
15.	**Ans. (D)**	**16.**	**Ans. (B)**	**17.**	**Ans. (A)**	**18.**	**Ans. (B)**
19.	**Ans. (D)**						
20.	**Ans.(B)**						



21. Ans. (C)

Sol. $CH_3CH=O + \bar{O}H \rightleftharpoons \bar{C}H_2-CH=O \xrightleftharpoons{H-\overset{O}{\overset{\|}{C}}-H} H_2C(CH_2OH)-CH=O$

(1 time aldol)

$\xrightleftharpoons{\bar{O}H} \ominus CH_2(CH_2OH)-CH=O \xrightleftharpoons{H-\overset{O}{\overset{\|}{C}}-H} HOH_2C-CH(CH_2OH)-CH=O$

(2 time aldol)

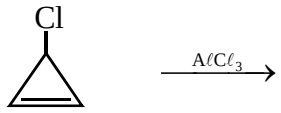
$\xrightleftharpoons{\bar{O}H} HOH_2C-\overset{\ominus}{C}(CH_2OH)-CH=O \xrightleftharpoons{H-\overset{O}{\overset{\|}{C}}-H} HOCH_2-C(CH_2OH)_2-CH=O$

(3 times aldol)

$H-\overset{O}{\overset{\|}{C}}-H + \overset{\ominus}{O}H \rightleftharpoons HOH_2C-C(CH_2OH)_2-CH_2OH + H-\overset{O}{\overset{\|}{C}}-O^{\ominus}$

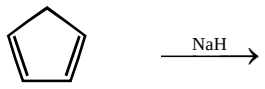
(crossed cannizaro product)

22. Ans. (A,B,C,D)

Sol. 

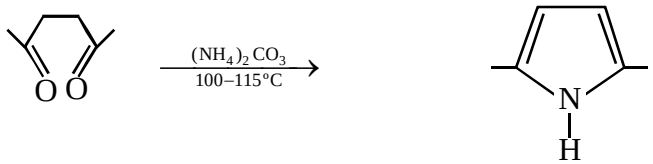
(P)

2π electron (delocalised)
(Aromatic Nature)



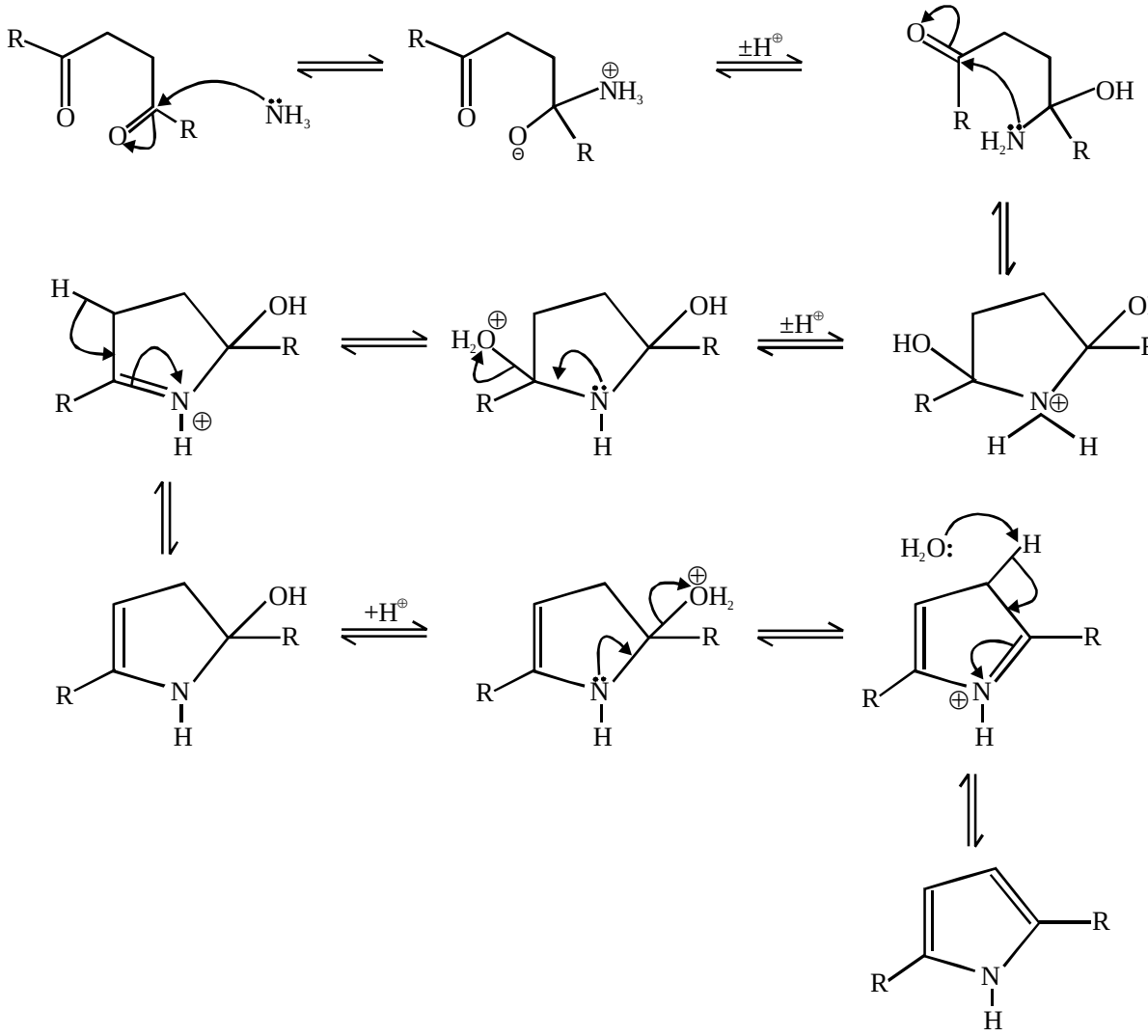
(Q)

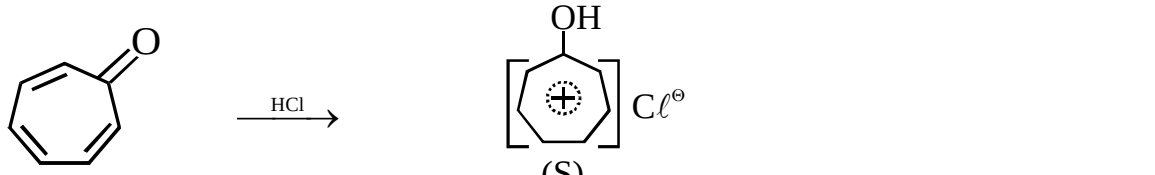
6π electron (delocalised)
(Aromatic Nature)



(R) 6π-electron (delocalised)
(Aromatic nature)

Mechanism :

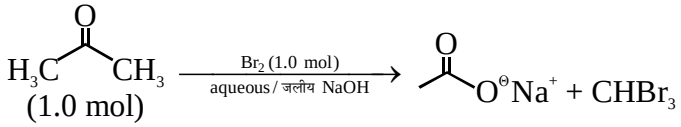




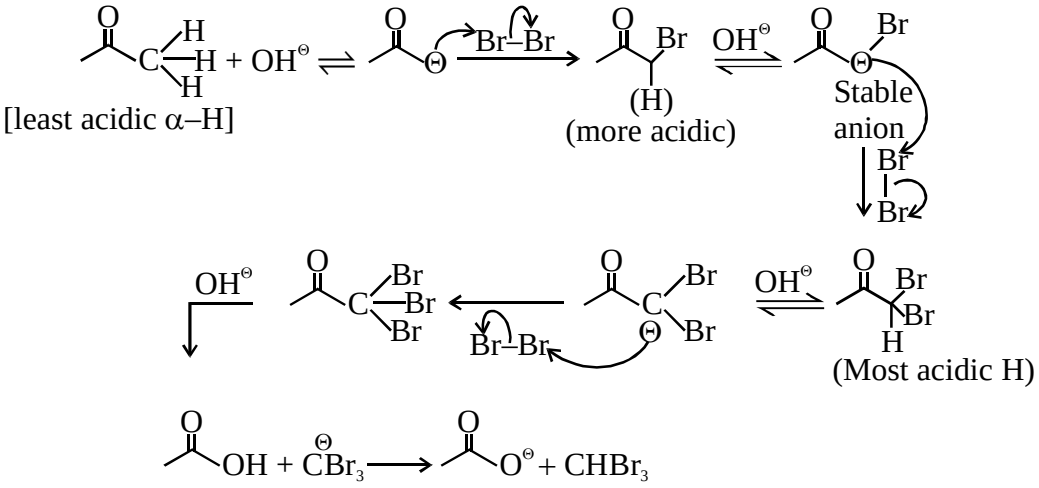
(S)

6π electron (delocalised)
(Aromatic Nature)

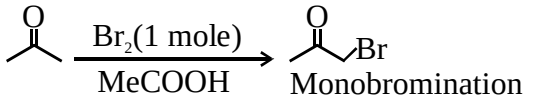
23. Ans. (C)

Sol. Reaction I : 

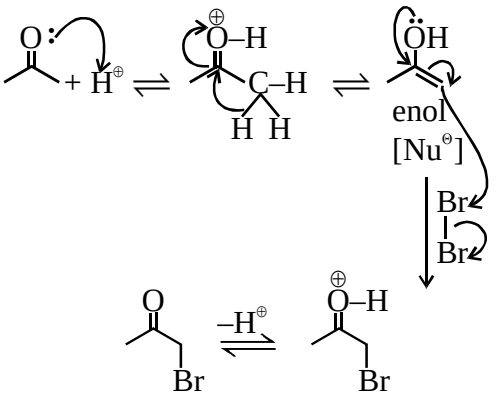
Mechanism



In basic medium halogenation dose not stop with replacement of just one hydrogen and poly halogenation takes place because α-haloketones are more reactive towards base and haloform reaction takes place In above reaction Br_2 is limiting agents.

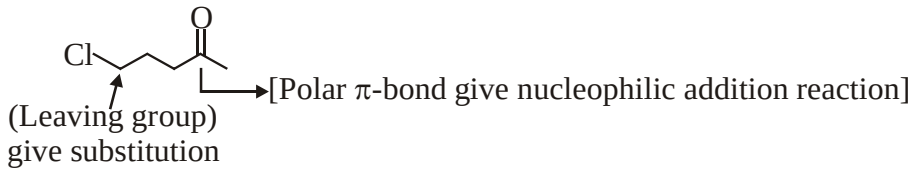
Reaction II : 

Mechanism :



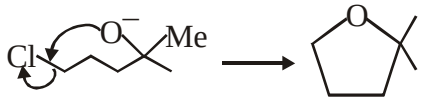
Further bromination is less favourable because of less amount of Br_2

24. Ans. (D)

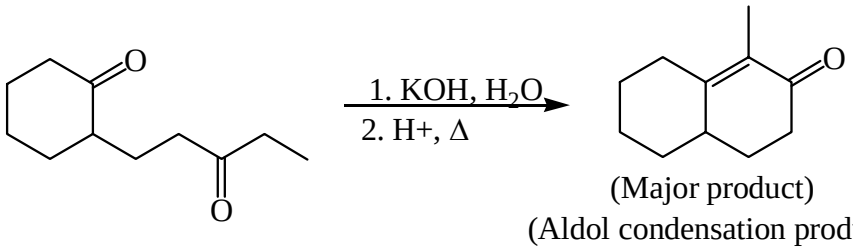


(i) Grignard prefer to give nucleophilic addition on polar π-bond and form anion intermediate.

(ii) In next step anion give intramolecular nucleophilic substitution reaction & form 5 membered ring.

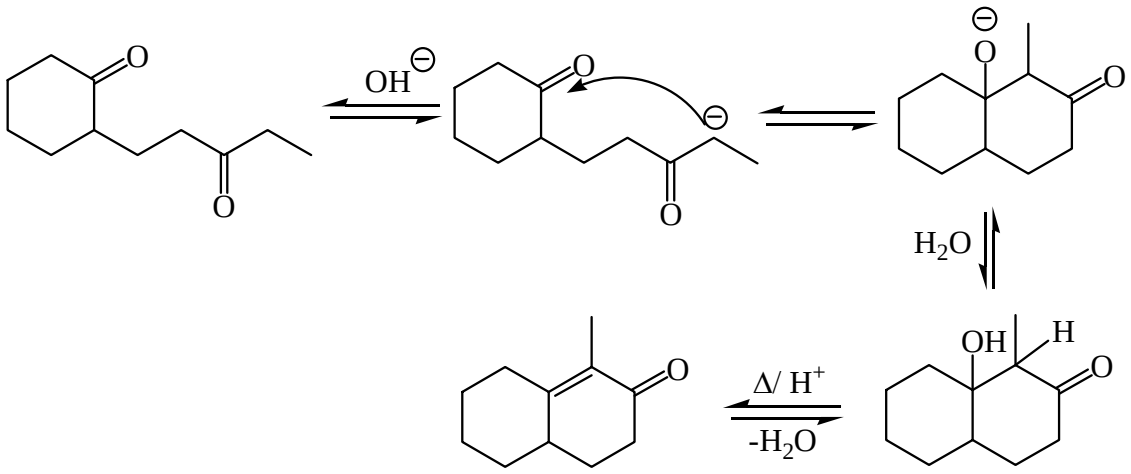


25. Ans. (A)



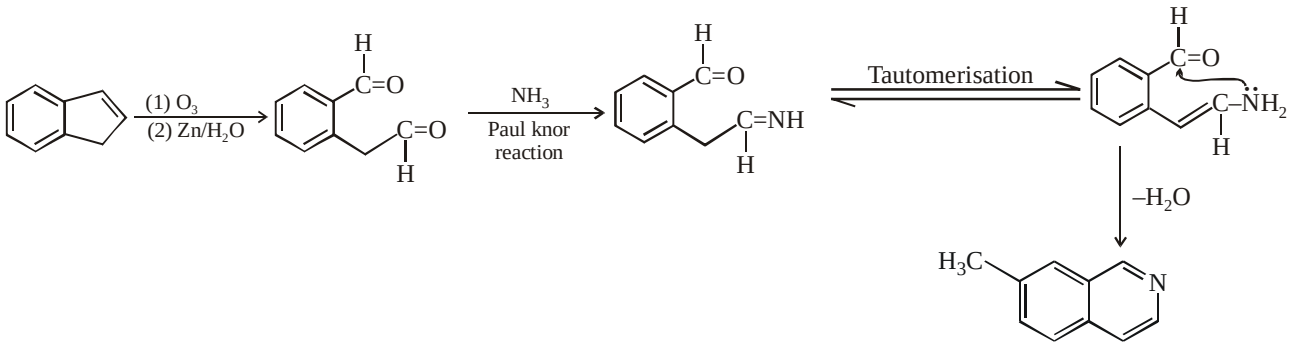
(Major product)
(Aldol condensation product)

Mechanism :



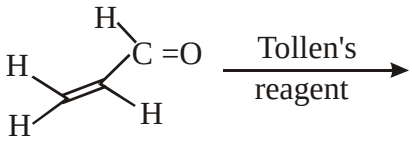
26. Ans.(A)

Sol.



27. Ans. (A,B,C)

Sol. Tollens's test is given by compounds having aldehyde group. Also α-hydroxy carbonyl gives positive tollen's test.

(A) 

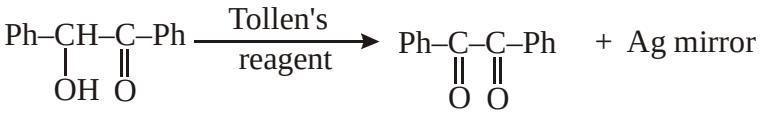
(+ve test)

Acraldehyde

(B) 

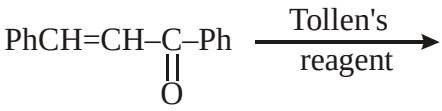
(+ve test)

Benzaldehyde

(C) 

(+ve test)

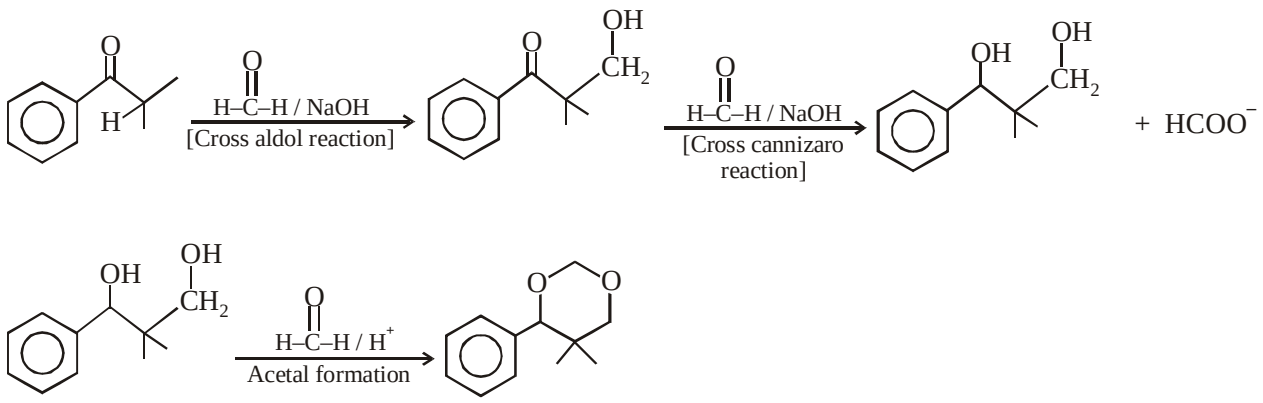
Benzoin

(D) 

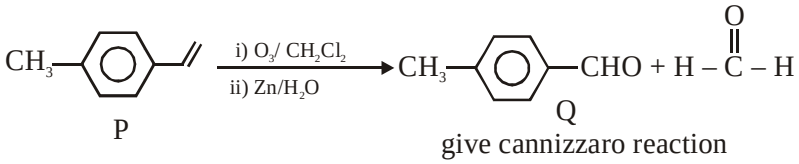
(–ve test)

28. Ans. (A)

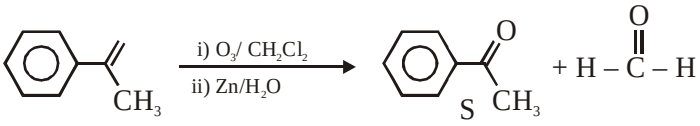
Sol.



29. Ans. (A,C)

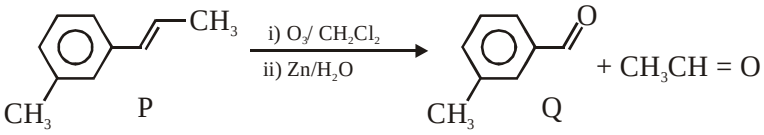
Sol. (A) 

give cannizzaro reaction
but no haloform

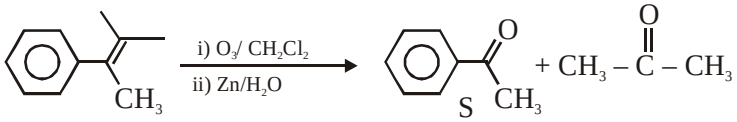


no cannizzaro
but give haloform

(B) Product of ozonolysis of R is having 9 carbon.

(C) 

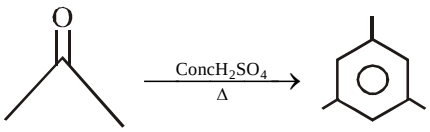
give cannizzaro reaction
but no haloform

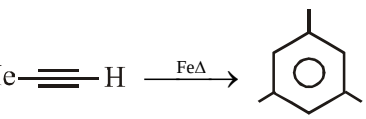


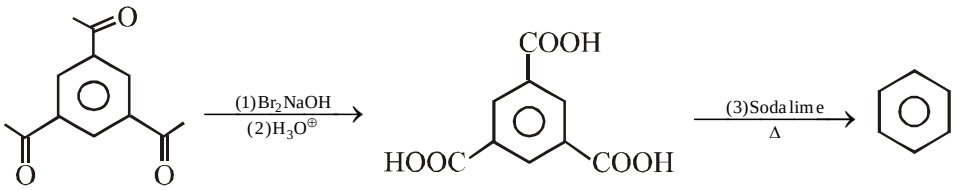
no cannizzaro
but give haloform

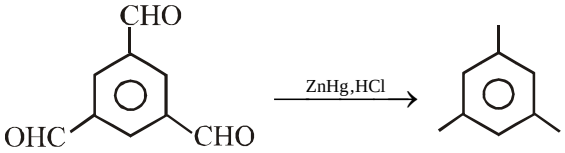
(D) Product of ozonolysis of R is having 9 carbon.

30. Ans. (A,B,D)

Sol. (A) 

(B) 

(C) 

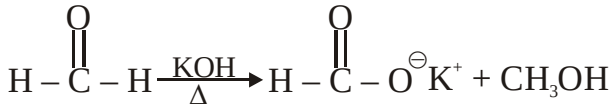
(D) 

31. Ans. (D)

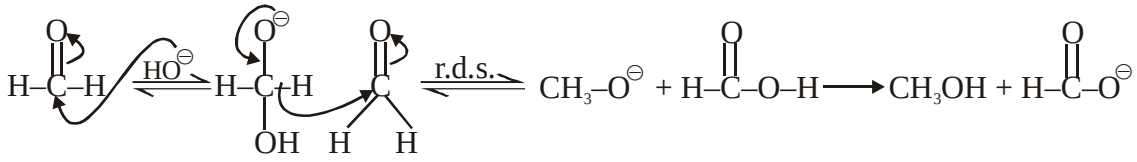
ALDOL & SIMILAR NAME REACTIONS

(1) CANNIZARO REACTION

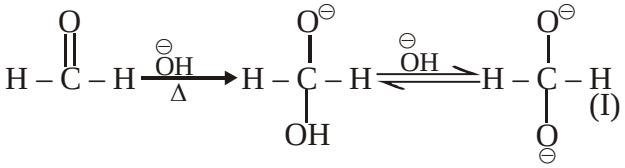
This reaction is given by aldehyde having no α- hydrogen in the presence of conc. NaOH/Δ or KOH/Δ.

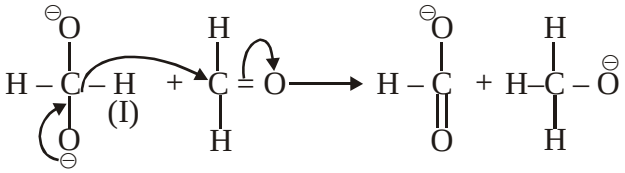


Mechanism :

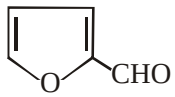
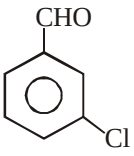
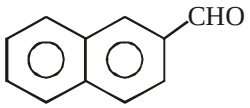


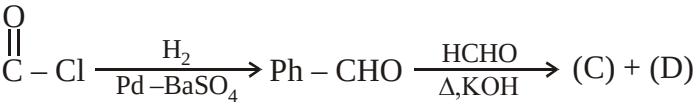
In the presence of a very strong concentration of alkali, aldehyde first forms a doubly charged anion (I) from which a hydride anion is transferred to the second molecule of the aldehyde to form acid and an alkoxide ion. Subsequently, the alkoxide ion acquires a proton from the solvent.





Q.1 Which of following will not undergo Cannizaro reaction

(A)  (B)  (C)  (D) $Cl_3C–CHO$

Q.2 

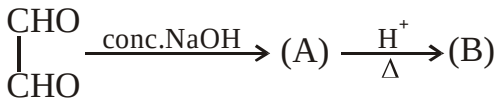
Product (C) & (D) are :

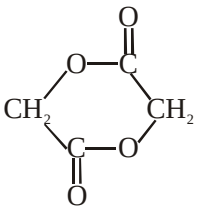
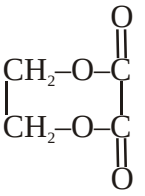
(A) $Ph–CO_2H$, Ph–OH

(B) $Ph–CO_2^-$,HCO_2^-

(C) $Ph–CH_2OH$, $H–CO_2^-$

(D) $Ph–CO_2^-$,CH_3OH

Q.3  ; Product (B) is :

(A) $H_2C=CH-CO_2H$ (B)  (C)  (D) $H_2C=C=O$

Q.4 (i) $HCHO \xrightarrow[\Delta]{NaOD}$ (ii) $DCHO \xrightarrow[\Delta]{NaOD}$

Q.5 (i) $Ph-CHO \xrightarrow[\Delta]{\overset{\ominus}{O}D / DOD}$ (ii) $Ph-CHO \xrightarrow[\Delta]{{}^{18}\overset{\ominus}{O}H}$

Q.6 (i) $Ph - CHO + HCHO \xrightarrow[\Delta]{KOH}$ (ii) $Ph - \underset{\underset{O}{\|}}{C} - \underset{\underset{O}{\|}}{C} - H \xrightarrow[\Delta]{KOH}$

Q.7 (i) $MeCH_2 - CHO \xrightarrow[\Delta]{KOH}$ (ii) $Me_2CH - CHO \xrightarrow[\Delta]{conc.KOH}$

Q.8 (i) $Me-NO_2 + HCHO \xrightarrow[(excess)]{KOH}$ (ii) $MeCHO - HCHO \xrightarrow[(excess)]{KOH}$

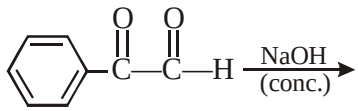
Q.9 $PhCOCHBr_2 \xrightarrow{Aq.\bar{O}H} A \xrightarrow{Conc.\ \bar{O}H} B \xrightarrow{H^+}$; the compound 'C' is :

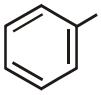
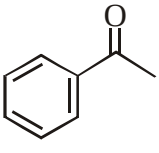
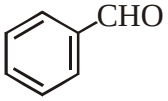
(A) PhCH(OH)CHO (B) PhCH(OH)COOH

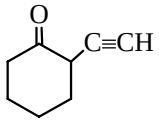
(C) PhCOOH (D) None of these

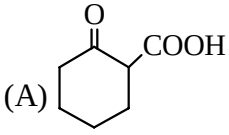
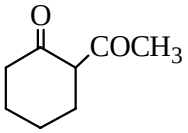
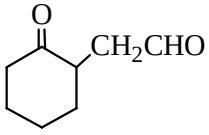
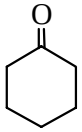
Q.10 Match the column :

Column - I	**Column - II**
(A) HCHO + NaOD (conc.)	(P) $DCOO^- + CDH_2OH$
(B) DCHO + NaOH (conc.)	(Q) $DCOO^- + CD_3OH$
(C) DCDO + NaOH (conc.)	(R) $DCOO^- + CDH_2OD$
(D) DCHO + NaOD (conc.)	(S) $HCOO^- + CH_3OD$

Q.11  ; Product 'C' is :

(A)  (B)  (C)  (D) 

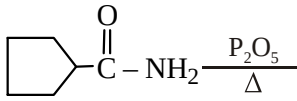
Q.12  $\xrightarrow{1\%\ HgSO_4\ /\ Dil.H_2SO_4}$ $\xrightarrow[H^+]{I_2\ /\ NaOH}$ $\xrightarrow{\Delta}$ X ; X is :

(A)  (B)  (C)  (D) 

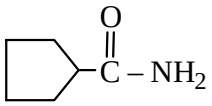
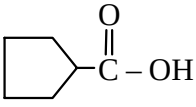
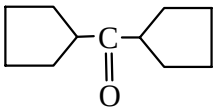
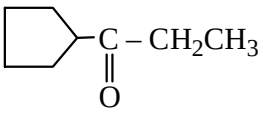
Q.13 The cannizaro reaction of Ph COCHO forms the product(s)

(A) $PhCOCH_2OH + PhCOCO_2^-$ (B) $PhCH(OH) - CO_2^-$

(C) $PhCO_2^- + PhCOCH_2OH$ (D) Both (A) and (C)

Q.14  $\xrightarrow[\Delta]{P_2O_5}$ A $\xrightarrow[(ii)H_3O^+]{(i)CH_3MgBr}$ B $\xrightarrow[(iii)\ -CHI_3]{(i)I_2+Ca(OH)_2\ (ii)\Delta}$ C ;

Product is:

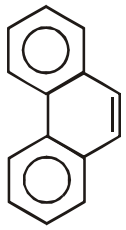
(A)  (B)  (C)  (D) 

Q.15  $\xrightarrow{conc.\ KOH}$

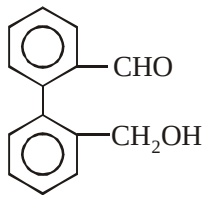
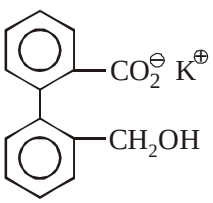
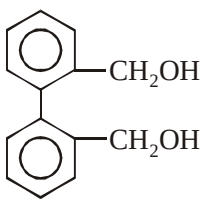
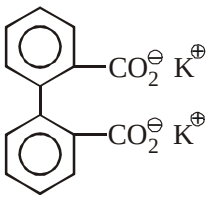
True about this reaction is / are

(A) Cannizaro name is associated with this reaction (B) It is a disproportion reaction

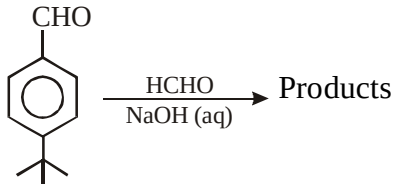
(C) It is a bimolecular reaction in r.d.s. (D) All of these

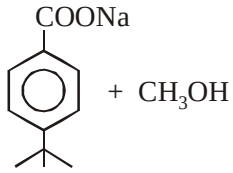
Q.16  $\xrightarrow[Zn]{O_3}$ (1 mole) (A) $\xrightarrow{conc.KOH}$ (B)

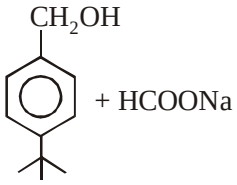
End product (B) of above reaction is :

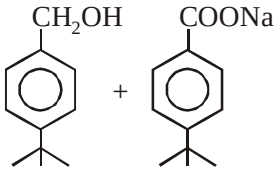
(A)  (B)  (C)  (D) 

Q.17 The major product pair of the following reaction will be :



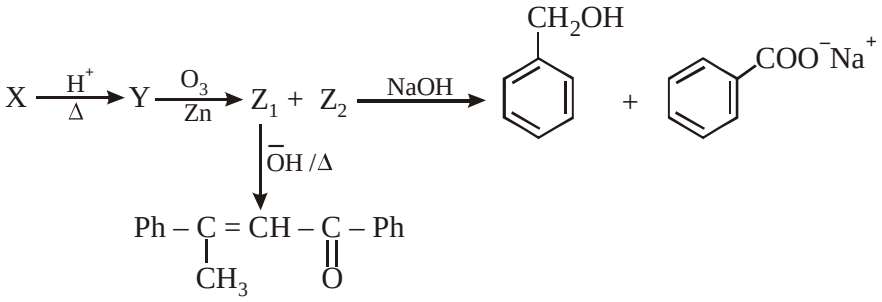
(A) 

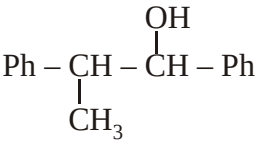
(B) 

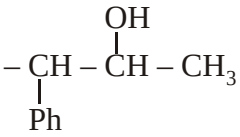
(C) 

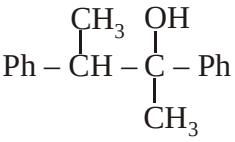
(D) CH_3OH + HCOONa

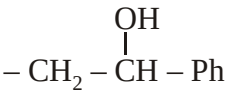
Q.18 Reactant 'X' will be :



(A) 

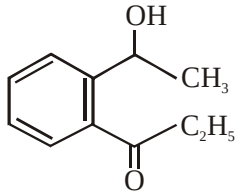
(B) 

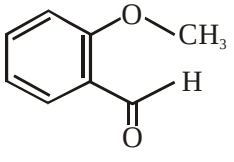
(C) 

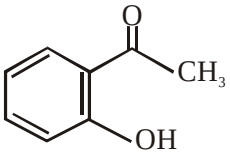
(D) 

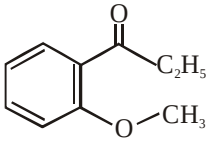
Q.19 An organic compound neither reacts with neutral ferric chloride solution nor with Fehling solution, It however, reacts with Grignard reagent and gives positive iodoform test. The compound is -

[JEE-MAIN (APRIL)-2019]

(1) 

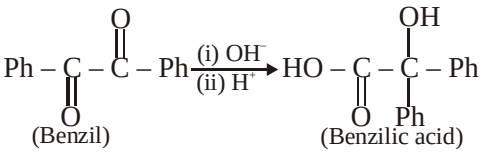
(2) 

(3) 

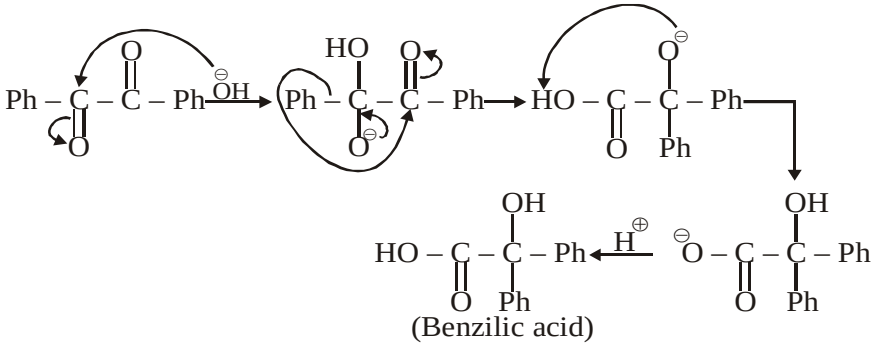
(4) 

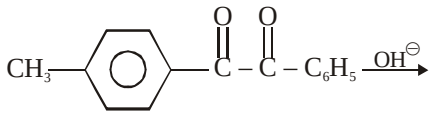
(2) BENZIL-BENZILIC REARRANGEMENT OR BENZILIC ACID REARRANGEMENT

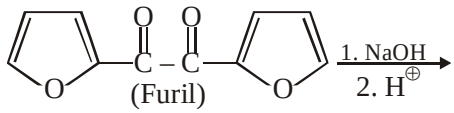
The base catalysed reaction of 1,2-diketones to a salt of –2– hydroxy carboxylic acid is known as Benzilic acid rearrangement, this reaction is mainly applicable when aryl group is present on both carbonyl carbons.

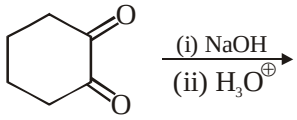


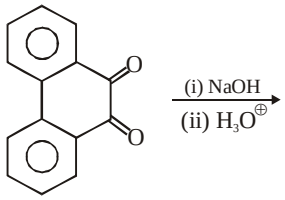
Mechanism :



Q.1 

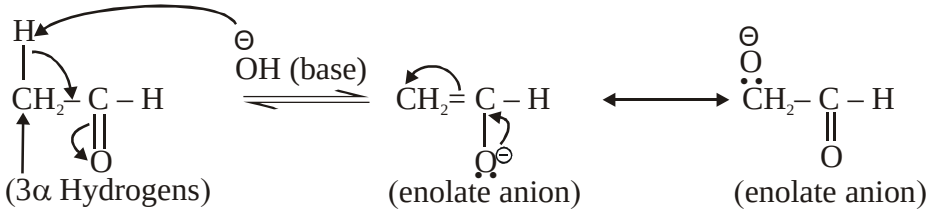
Q.2 

Q.3 

Q.4 

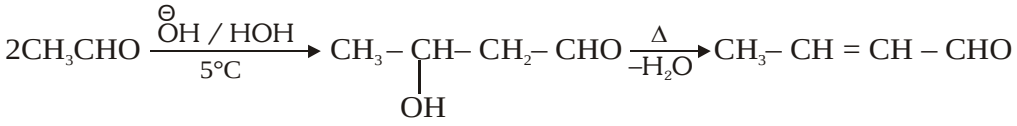
(3) ALDOL CONDENSATION

The α- hydrogen of carbonyl compounds are acidic due to the fact that the anion (enolate ion) is stabilized by resonance.



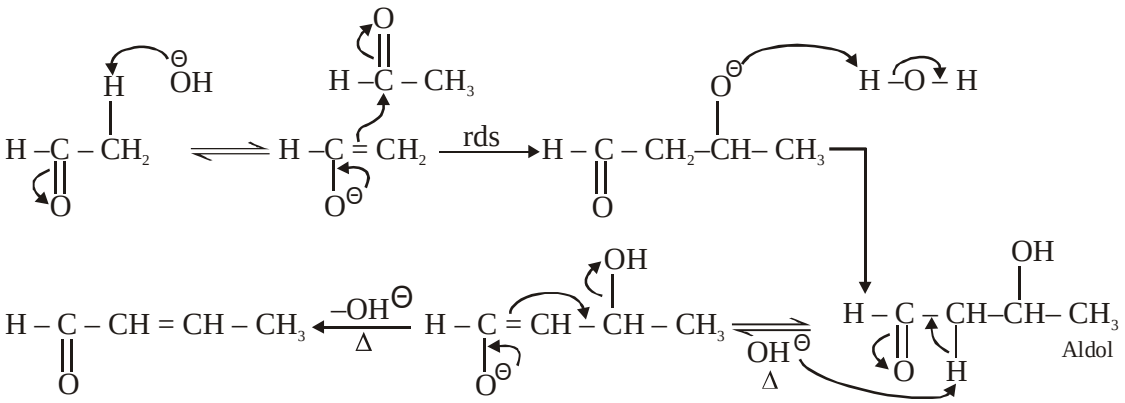
Base catalysed Aldol

In aqueous base, two acetaldehyde molecules react to form β-hydroxy aldehyde called aldol. The reaction is called Aldol condensation. The enolate ion is the intermediate in the aldol condensation of aldehyde and ketone. Acetaldehyde for instance, forms a dimeric product aldol in presence of a dilute base (≈ 10% NaOH)



β–hydroxy butyraldehyde (Aldol)

Mechanism :

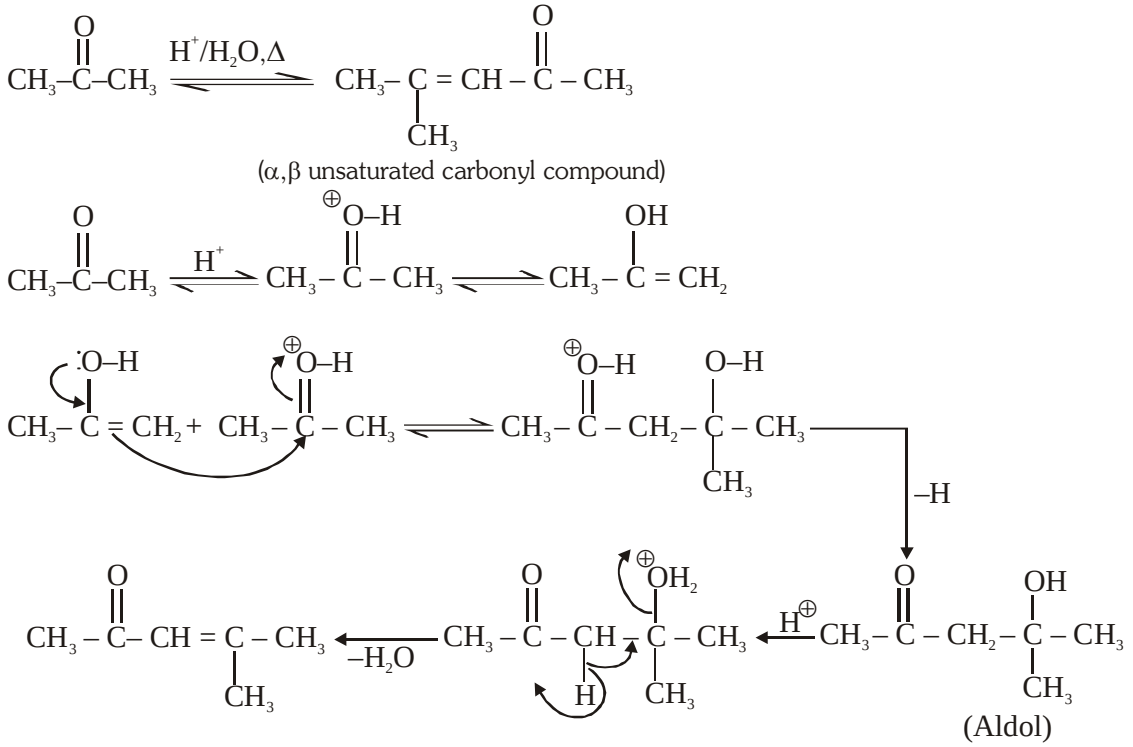


Aldols are stable and may be isolated. They, however can be dehydrated easily by heating the basic reaction mixture or by a separate acid catalyzed reaction. Thus if the above reaction is heated the product is dehydrated to 2-butenal (crotonaldehyde).

Acid cataysed Aldol

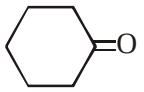
In acid catalysed aldol condensation enol form of carbonyl is the nucelophile in place of enolate.

Mechanism :

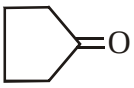


Q.1 Write the product and mechanism for given reactions.

(I) $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-H \xrightarrow[\text{Dil NaOH}]{} (A) \xrightarrow{\Delta} (B)$

(II)  $\xrightarrow{\text{Dil NaOH}} (C)$

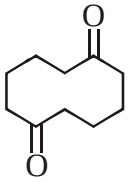
(III) $C_6H_5-CH_2-CHO \xrightarrow{\text{Dil NaOH}} (D)$

(IV)  $\xrightarrow{\text{Dil NaOH}} (E) \xrightarrow{\Delta} (F)$

(V) $C_6H_5-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{\text{Dil NaOH}} (G) \xrightarrow{\Delta} (H)$

Q.2 Identify the intramolecular aldol product ?

(I) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{\text{Dil NaOH}} (A) \xrightarrow{\Delta} (B)$

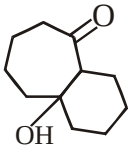
(II)  $\xrightarrow[\Delta]{\text{Dil NaOH}} (E) \longrightarrow (F)$

Q.3 Find out the total number of possible aldol products (including and excluding stereo products).

(I) $C_6H_5-CHO + CH_3-CHO \xrightarrow[5°C]{\text{NaOH/ HOH}}$

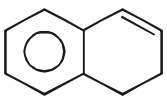
(II) $CH_3-CH=O + CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[5°C]{\text{NaOH/ HOH}}$

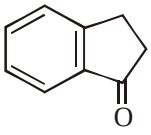
Q.4 Identify the structure of substrate ?

(I) $A \xrightarrow{\text{Dil. NaOH}}$  A = ?

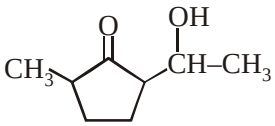
(II) $\underset{(2\text{ mole})}{A} \xrightarrow[5°C]{\text{Dil.NaOH}} CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$ A = ?

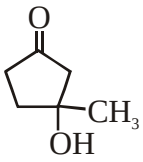
Q.5 Complete reaction sequence :

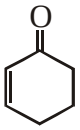
(I)  $\xrightarrow[(ii)\ Zn / H_2O]{(i)\ O_3(1eq)} (a) \xrightarrow[(ii)\ \Delta]{(i)\ \overset{\ominus}{O}H} (b)$

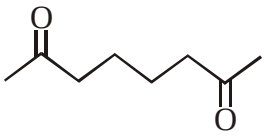
(II)  $\xrightarrow[(ii) C_6H_5CHO \\ (iii)\ \Delta]{(i)\ \overset{\ominus}{O}H}$ Product

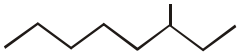
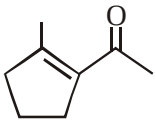
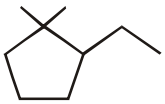
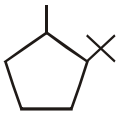
Q.6 Complete the following reactions :

(I) (X) + (Y) $\xrightarrow{\ominus OH}$ 

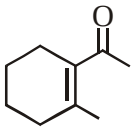
(II) (X) $\xrightarrow{OH^{\ominus}}$ 

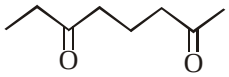
(III) [X] $\xrightarrow[(ii)\Delta]{(i)\ OH^{\ominus}}$ 

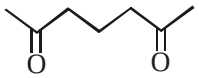
Q.7  $\xrightarrow[heat]{\bar{O}H}$ A $\xrightarrow[CuBr]{CH_3MgBr}$ B $\xrightarrow[conc.HCl]{Zn-Hg}$ C ; the product 'C' is

(A)  (B)  (C)  (D) 

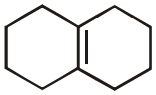
Q.8 Consider following intramolecular aldol condensation reaction :

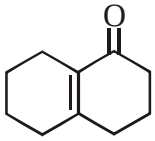
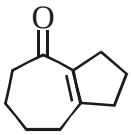
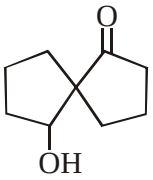
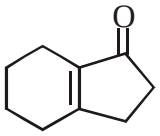
X $\xrightarrow[\Delta]{^{-}OH}$  ; X can be :

(A)  (B) 

(C)  (D) 

Q.9 Product 'Y' formed in the given reaction is :

 $\xrightarrow{O_3/Zn}$ X $\xrightarrow{\bar{O}H/\Delta}$ Y

(A)  (B)  (C)  (D) 

Q.10 Product 'D' is :

 $\xrightarrow{\ominus OH}$ A $\xrightarrow{\Delta}$ B $\xrightarrow[(excess)]{H_2/Pt}$ C $\xrightarrow[H_2SO_4]{CrO_3}$ D

(A) $CH_3-CH_2-CH=CH_2$ (B) $CH_3-CH_2-CH_2-CHO$

(C) $CH_3-CH_2-CH_2-COOH$ (D) $CH_2=CH-CH=CH_2$

Q.11 $CH_3CH=CHCHO \xrightarrow[aldol]{OH^-} \xrightarrow{\Delta}$ A, A is :

(A) $CH_3(CH=CH)_3CHO$ (B) $CH_3CH_2CH_2(CH=CH)_2CHO$

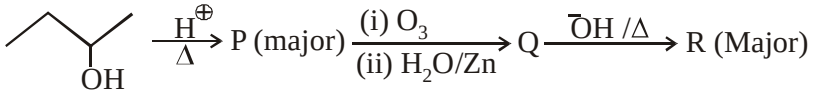
(C) $CH_3(CH_2CH_2)_3CH=CH-CHO$ (D) None is correct

Q.12 $MeCHO \xrightarrow{NaOH,\Delta} A \xrightarrow{NaOH,\Delta} B$; B is :

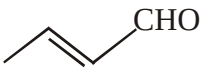
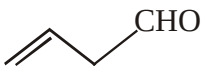
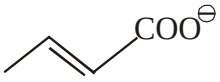
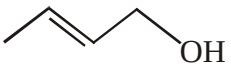
(A) $Me(CH=CH)_3CHO$ (B) $MeCH=CHCHO$

(C) $Me(CH=CH)_2-CHO$ (D) $Me-(CH=CH)_4CHO$

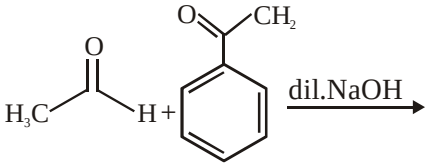
Q.13 For the given reaction :

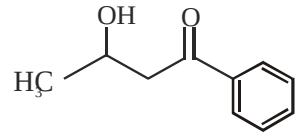
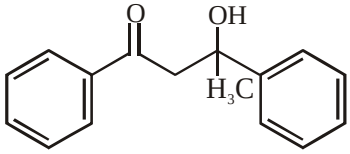


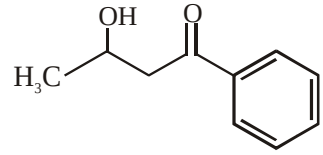
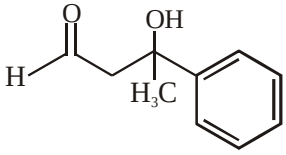
The (R) is :

(A)  (B)  (C)  (D) 

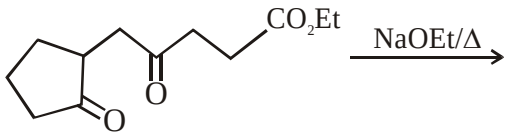
Q.14 The major product formed in the following reaction is: **[JEE-MAIN (JANUARY)-2019]**

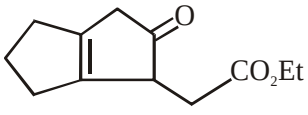
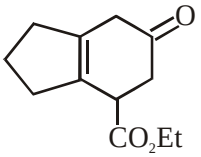


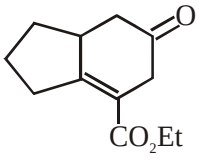
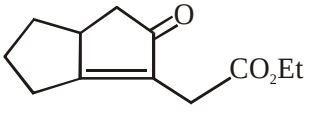
(1)  (2) 

(3)  (4) 

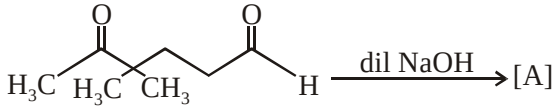
Q.15 The major product obtained in the following reaction is : **[JEE-MAIN (JANUARY)-2019]**

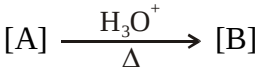


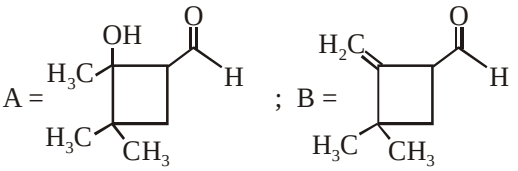
(1)  (2) 

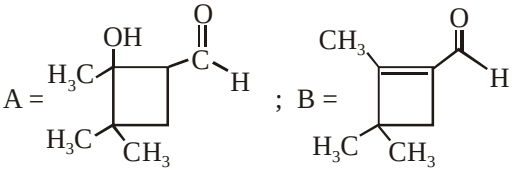
(3)  (4) 

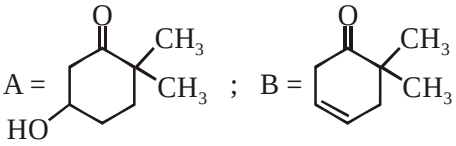
Q.16 In the following reactions, products A and B are : **[JEE-MAIN (JANUARY)-2019]**

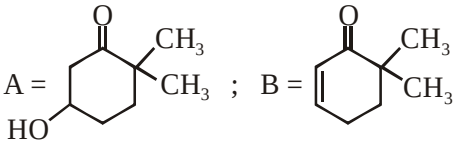




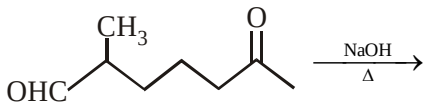
(1) 

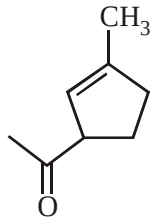
(2) 

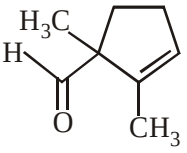
(3) 

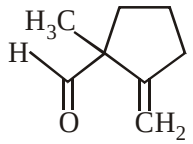
(4) 

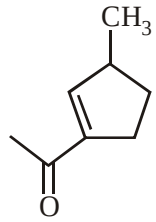
Q.17 The major product obtained in the following reaction is **[JEE-MAIN (APRIL)-2019]**



(1) 

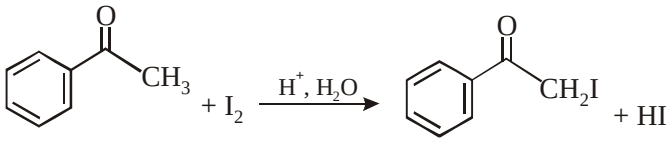
(2) 

(3) 

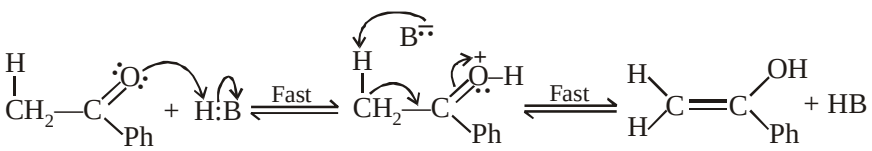
(4) 

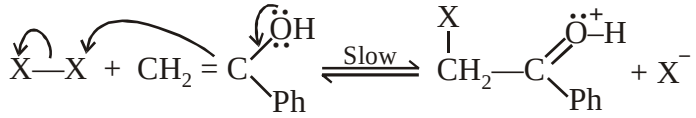
(4) HALOGENATION OF THE α-CARBON OF ALDEHYDES AND KETONES

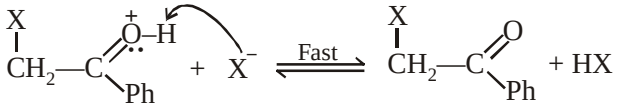
I[st] Acid-Catalyzed halogenation : - When Br_2, Cl_2 and I_2 is added to an acidic solution of an aldehyde or a ketone, a halogen replaces one of the α-hydrogens of the carbonyl compound. Halogenation takes place through the slow formation of an enol followed by rapid reaction of the enol with the halogen.



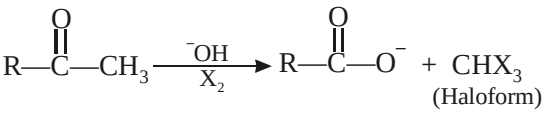
Mechonism :

Step - I : 

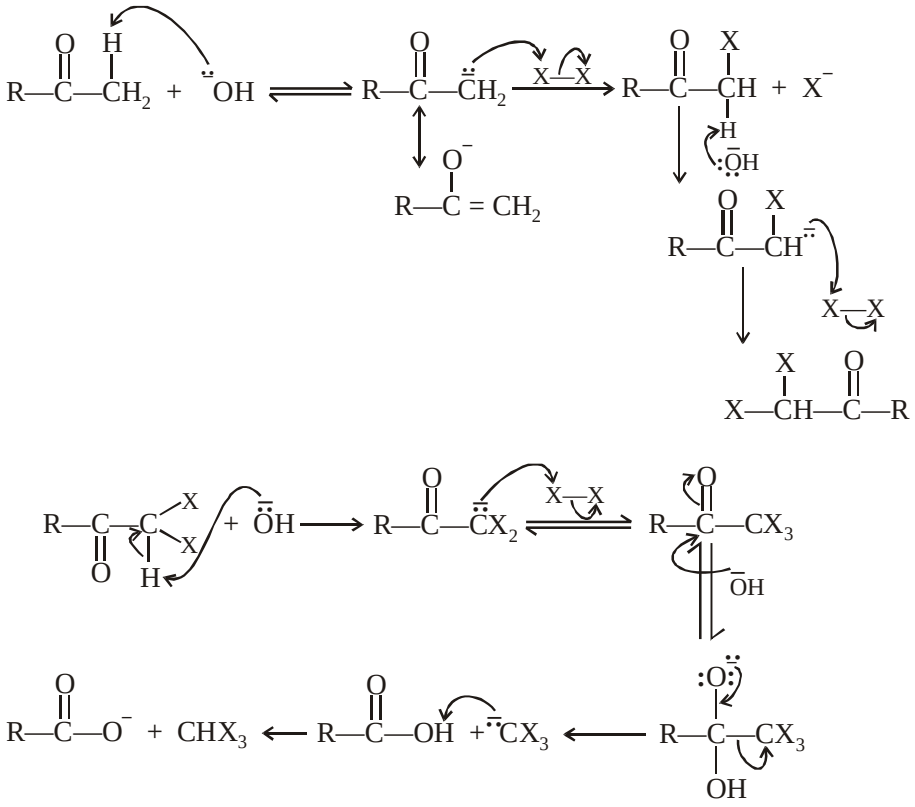
Step - II : 

Step - III : 

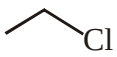
II[nd] Base-Catalyzed halogenation : - In the presence of excess base and excess halogen, a methyl ketone is converted first into a trihalo-substituted ketone and then into a carboxylic acid.

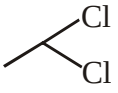


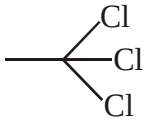
Mechanism :

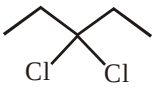


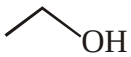
Q.1 Identify the compounds which can show iodoform test and complete the reaction ?

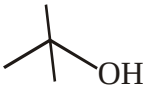
(1) 

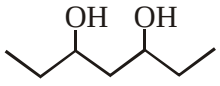
(2) 

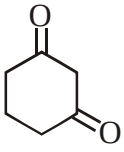
(3) 

(4) 

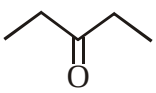
(5) 

(6) 

(7) 

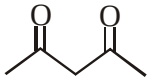
(8) 

(9) 

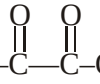
(10) 

(11) CI_3CHO

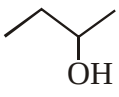
Q.2 Complete the following given reaction :

(i) 

$\xrightarrow{I_2/\ddot{O}H}$ Product

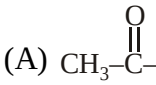
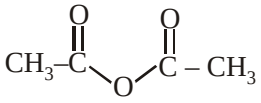
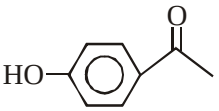
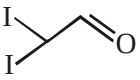
(ii) CH_3– 

–OH $\xrightarrow{I_2/\ddot{O}H}$ Product

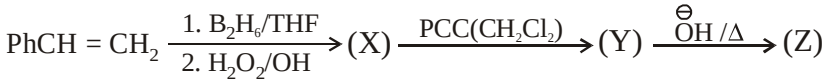
(iii) 

$\xrightarrow{I_2/\ddot{O}H}$ Product

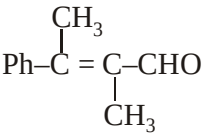
Q.3 Select the compound which does not show haloform reaction is/are :

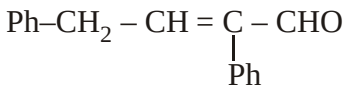
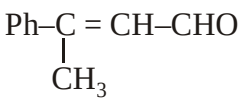
(A)  (B)  (C)  (D) 

Q.4 For the reaction



(Z) is :

(A) Ph–CH=CH–CHO (B) 

(C)  (D) 

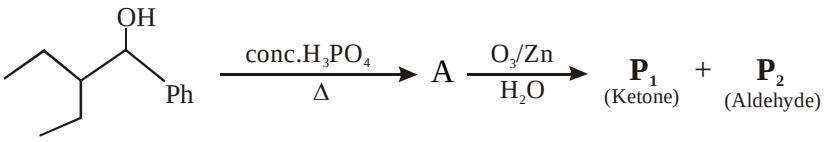
Q.5 Two isomeric ketones, 3-pentanone and 2-pentanone can be distinguished by :

(A) I_2 / NaOH (B) NaOH (C) NaCN / HCl (D) 2,4-DNP

Q.6 Which of the reagent is used to convert 2–Butanone into propanoic acid -

(A) NaOH, I_2/H^+ (B) Tollen's reagent (C) Fehling solution (D) NaOH, NaI/H^+

Paragraph for Q.07 to Q.09



Q.7 Which one of the following reagent is best suitable for distinction between P_1 and P_2 -

(A) Braddy's reagent (2,4 DNP) (B) $NaHSO_3$

(C) $NaHCO_3$ (D) NaOH / I_2

Q.8 Select the correct statement among the following -

(A) P_1 will show aldol reaction & P_2 will show cannizaro reaction

(B) P_1 will show cannizaro reaction & P_2 will show aldol reaction

(C) Both P_1 & P_2 will show cannizaro reaction

(D) Both P_1 & P_2 will show aldol reaction

Q.9 $P_2 \xrightarrow[(ii)\ H^+]{\text{conc. NaOH}}$ products

Select incorrect statement for the above reaction -

(A) It is a redox reaction

(B) It is a disproportion reaction

(C) Two products formed are alcohol & carboxylic acid

(D) It is an intramolecular reaction

Q.10 Which of the following will give yellow precipitate with NaOH / I_2

(A) $Ph-\underset{\underset{OH}{|}}{CH}-Me$ (B) CI_3CHO (C) $Me-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH$ (D) EtOH

Q.11 Ethylmethanoate $\xrightarrow[(ii)H_3O^+]{(i)MeMgBr(2eq)}$ $\underbrace{W+X}_{\text{organic product}}$

$W \xrightarrow{CaOCl_2} CHCl_3 + Y$

$X \xrightarrow{CaOCl_2} CHCl_3 + Z$

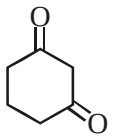
$Y + Z \xrightarrow[\text{Distillation}]{\text{Dry}}$ Organic product(s) + $CaCO_3$

Which of the following organic product can be formed on dry distillation reaction

(I) CH_3-CHO (II) $CH_3-CO-CH_3$ (III) $CH_3-CH=CH-CH_3$ (IV) HCHO

(A) I and II only (B) II and III only (C) I, II and IV only (D) II and IV only

Q.12 Which of the following compounds(s) give a sweet smelling product having anesthetic use in presence of Cl_2, NaOH, Δ.

(A)  (B) $CH_3-\underset{\underset{I}{|}}{CH}-CH_3$ (C) $CH_3-\overset{\overset{O}{\|}}{C}-OH$ (D) $Ph-\overset{\overset{O}{\|}}{C}-CH_3$

Q.13 Reaction in which product can show positive haloform test :-

(A) $CH_3MgBr + PhCN \xrightarrow[H_3O^{\oplus}]{}$ (B) $\underset{(1:1)}{CH_3-CH_2MgBr} + Ph-COOEt \xrightarrow[H_3O^{\oplus}]{}$

(C) $\underset{(1:1)}{CH_3MgBr} + H-\overset{\overset{O}{\|}}{C}-OMe \xrightarrow{NH_4Cl}$ (D) $CH_3MgBr + H-\overset{\overset{O}{\|}}{C}-H \xrightarrow{NH_4Cl}$

Q.14 In which reaction haloform is obtained as one product :-

(A) Electrolysis of ethanolic aqueous solution of NaCl

(B) Isopropanol with bleaching powder

(C) Chlorination of methane in sun light

(D) Chloral is treated with NaOH

Q.15. Fructose and glucose can be distinguished by : **[JEE-MAIN (APRIL)-2019]**

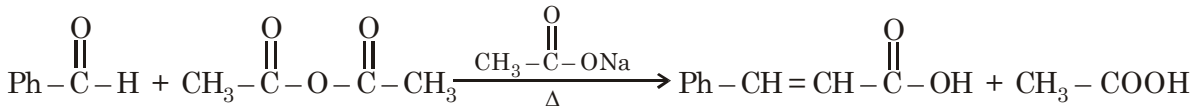
(1) Fehling's test (2) Barfoed's test (3) Benedict's test (4) Seliwanoff's test

(5) PERKIN CONDENSATION

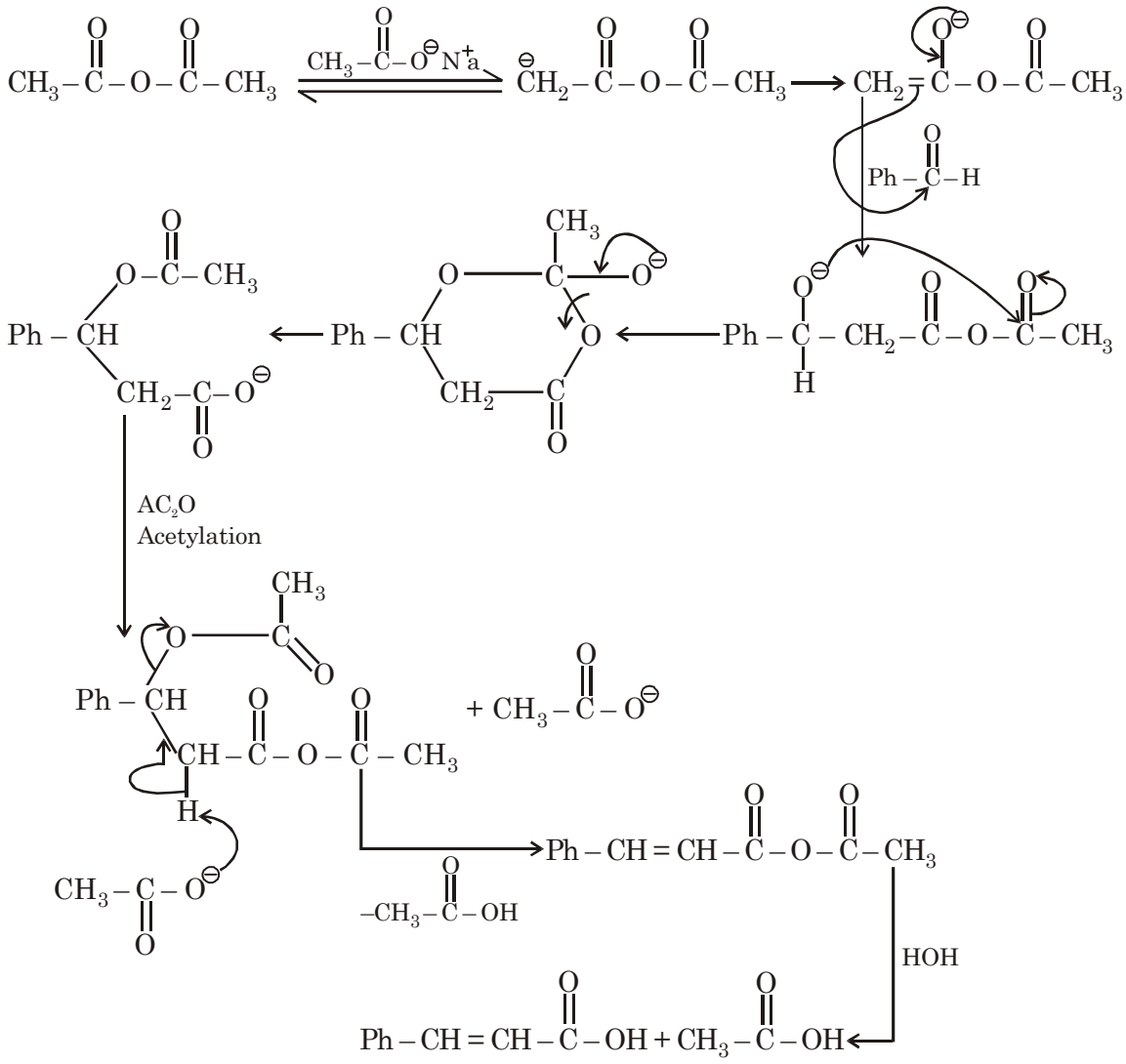
Perkin Reaction :

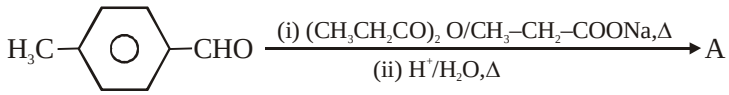
Condensation reaction between aromatic aldehyde and aliphatic acid anhydride having at least two alpha hydrogen in the presence of a base is known as **Perkin reaction**.

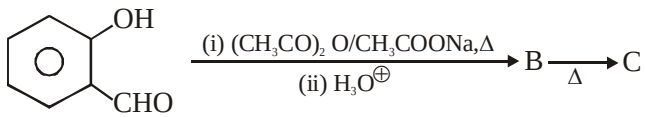
In this reaction, the anion of an acid anhydride adds to an aromatic aldehyde to produce an β aryl α,β, unsaturated acid. In order to prevent side reactions, the base that is used to make the anion of the anhydride is usually the sodium salt of the acid corresponding to the anhydride.

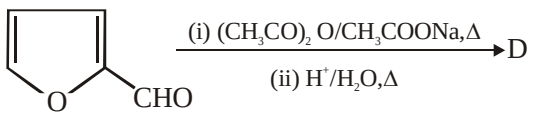


Mechanism :

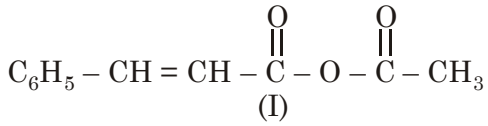


Q.1 

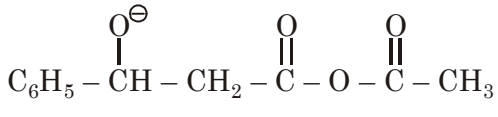
Q.2 

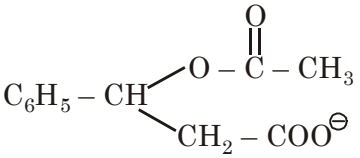
Q.3 

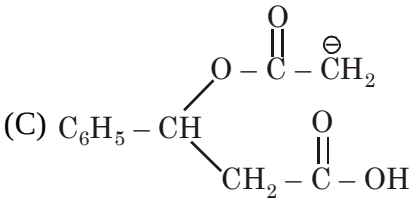
4. In the perkin reaction which one of the following intermediates gives compound (I)

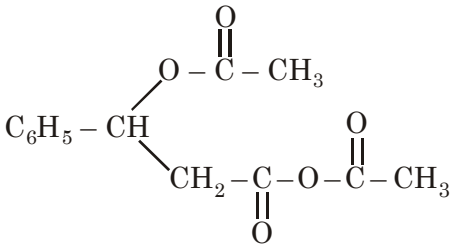


(I)

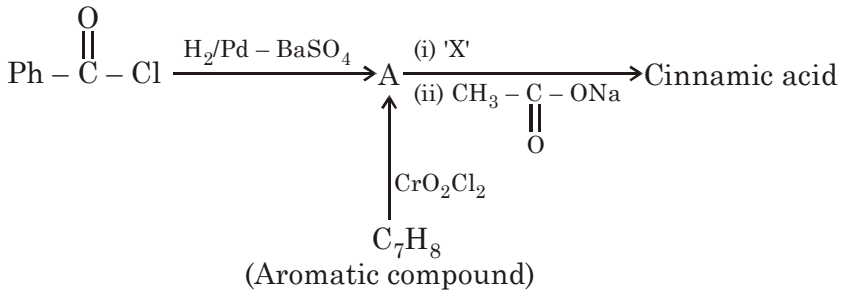
(A) 

(B) 

(C) 

(D) 

Paragraph for Q.no. 5-6

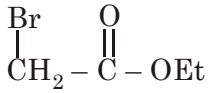


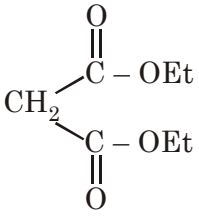
5. Compound 'A' on treatment with conc. NaOH followed by acidification can give :

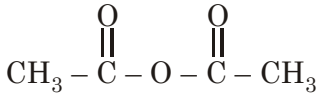
(A) Ph – CH_2 – COOH (B) Ph – OH

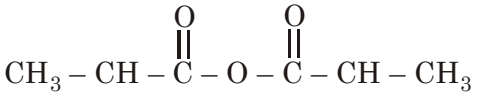
(C) Ph – COOH (D) Ph – CH_2 – OH

6. In the above reaction the reagent "X" can be :

(A) 

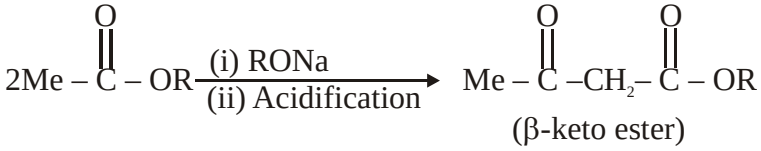
(B) 

(C) 

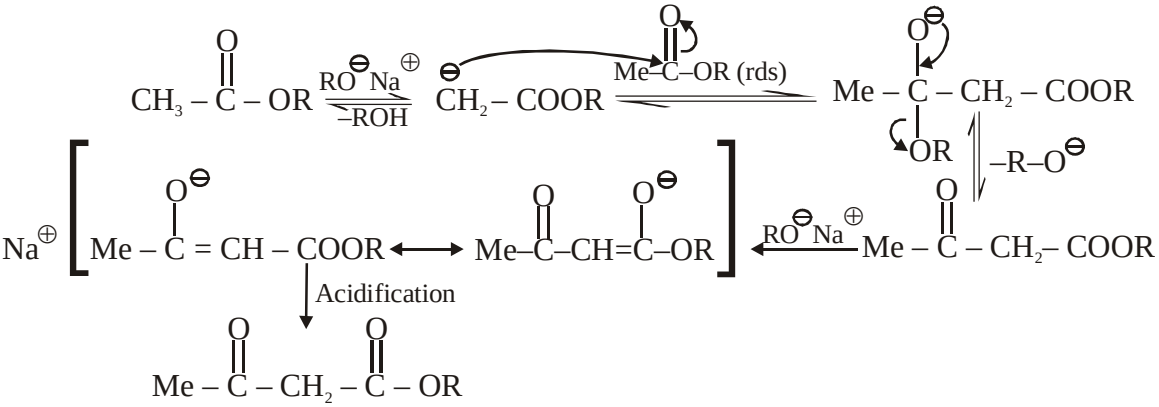
(D) 

(6) CLAISEN CONDENSATION

Esters undergo S_NAE Reaction. when attacked by a Nu^- generated by the interaction of a base (usually base related to the Alkoxy anion of ester) with one of the molecule of ester and this Nu^- attacks on another molecule. The reaction over all is considered as condensation of ester known as claisen ester condensation.



Mechanism :



Some times, when two ester group are p;resent within the molecule then the condensation occurs intramolecular then cyclization caused thus is known as Dieckmann cyclization or Dieckmann's condensation.

Q.1 $MeCOOEt \xrightarrow[(ii)\ Acidification]{(i)\ EtOK} A$

Q.2 $EtCOOMe \xrightarrow[(ii)\ Acidification]{(i)\ MeOK} B$

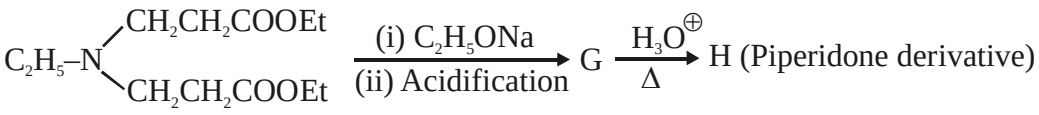
Q.3 $MeCOOMe + EtCOOMe \xrightarrow[(ii)\ Acidification]{(i)\ MeOK} C$

Q.4 $C_6H_5COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow[(ii)\ Acidification]{(i)\ C_2H_5ONa} D + D'$

Ethyl benzoate

Q.5 $\begin{matrix}COOC_2H_5\\ |\\ COOC_2H_5\end{matrix} + C_6H_5CH_2COOC_2H_5 \xrightarrow[(ii)\ Acidification]{(i)\ C_2H_5ONa} E$ [Cross Product]

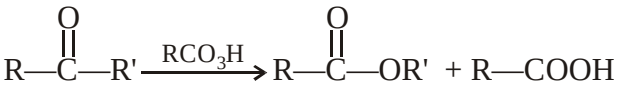
Q.6 

Q.7 

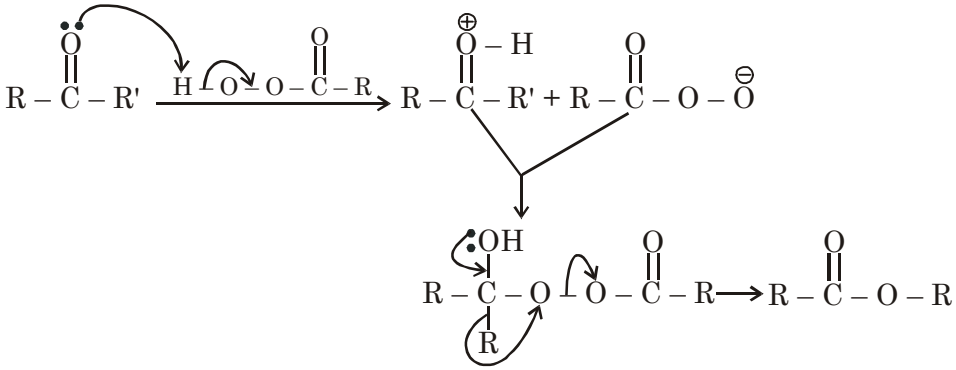
(7) Beayer villiger oxidation

Reaction involve the oxidation of ketone to aster by treatment with per acid such as per acetic acid, MCPBA, per trifloroacetic acid etc.

- It is a redox reaction
- Cyclic ketones are converted to lectone with ring expention.



Mechanism

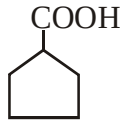


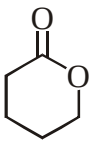
Note : In above reaction for shifting of groups migratory apptitude is applicable

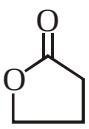
Migratory order for above reaction

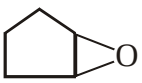
$-H > 3^{o} > 2^{o} > -Ph > 1^{o} > -Me$

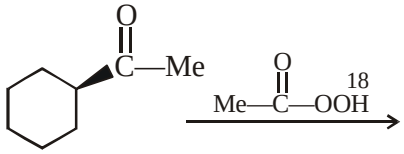
Q.1  Major product is :

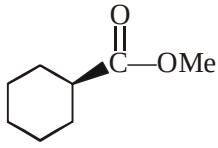
(A) 

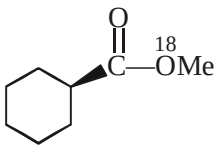
(B) 

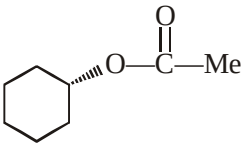
(C) 

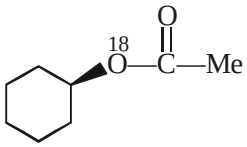
(D) 

Q.2  Major product is :

(A) 

(B) 

(C) 

(D) 

ANSWER KEY

(1) CANNIZARO REACTION

Q.1 Ans. (D)

As $Cl_3C–CHO$ given chloroform

Q.2 Ans. (C)

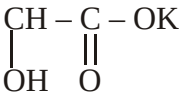
In crom cannizzaro reaction move reactive carbonyl compound is oxidised & less in reduced.

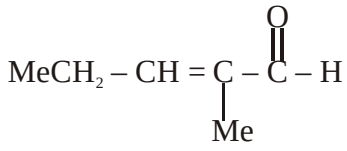
Q.3 Ans. (B)

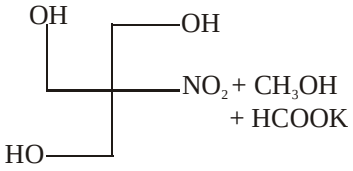
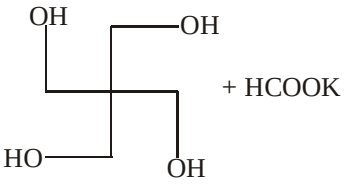
Intramoecular cannizzaro followed by heating effect

Q.4 Ans. (i) $CH_3OD + HCOONa$ **(ii) $DCH_2OD + DCOONa$**

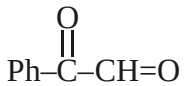
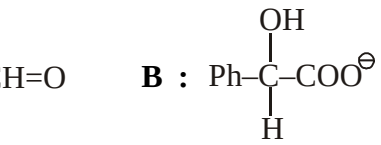
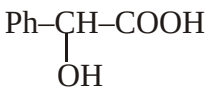
Q.5 Ans. (i) $PhCH_2OD + PhCOONa$ **(ii)** $Ph-CH_2OH + PhCO\overset{18}{O}Na$

Q.6 Ans. (i) $Ph–CH_2OH + HCOOK$ **(ii)** 

Q.7 Ans. (i)  **(ii) $Me_2CH–CH_2OH + Me_2CHCOOK$**

Q.8 Ans. (i)  **(ii)** 

Q.9 Ans. (B)

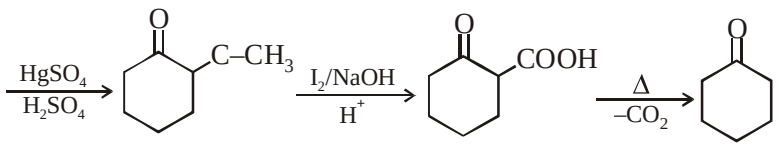
A :  **B :**  **C :** 

Q.10 Ans. (A)→S ; (B)→P ; (C)→Q ; (D)→R

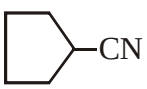
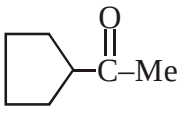
Q.11 Ans. (A)

A :  **B : PhCOOH** **C :** 

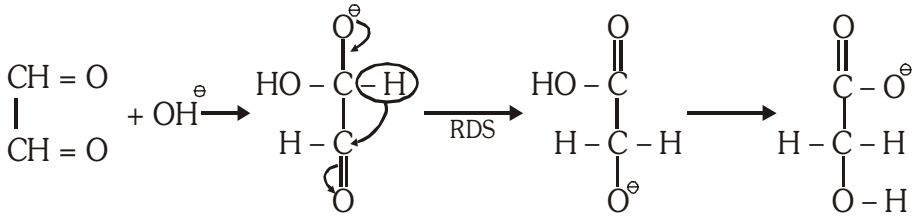
Q.12 Ans. (D)



Q.13 Ans. (B)

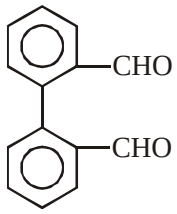
Q.14 Ans. (C) A :  **B :** 

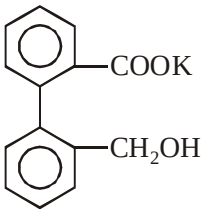
Q.15 Ans. (A)



option A is correct.

Q.16 Ans. (B)

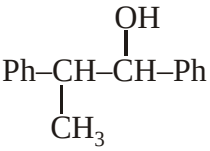
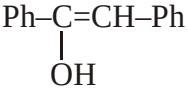
A : 

B : 

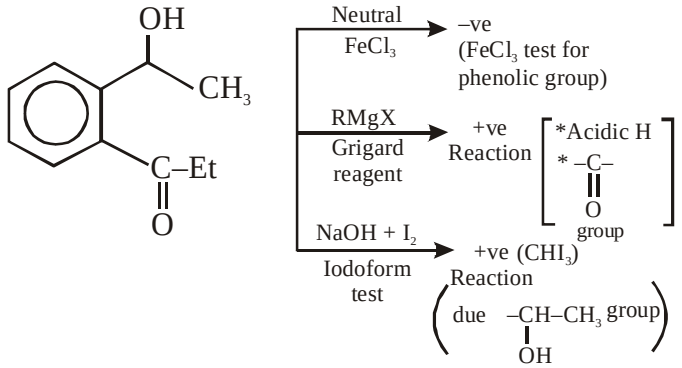
Q.17 Ans. (B)

Cron cannizaro reaction

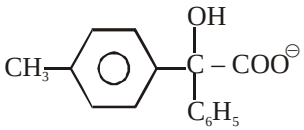
Q.18 Ans. (A)

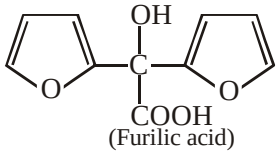
X :  **Y :**  **Z_1 :**  **Z_2 : Ph–CH=O**

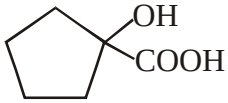
Q.19 Ans. (1)

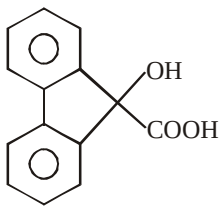
Sol. 

(2) BENZIL-BENZILIC REARRANGEMENT OR BENZILIC ACID REARRANGEMENT

1. Ans. 

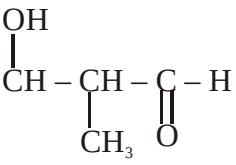
2. Ans. 
(Furilic acid)

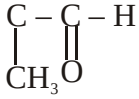
3. Ans. 

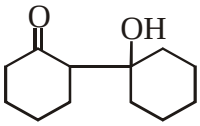
4. Ans. 

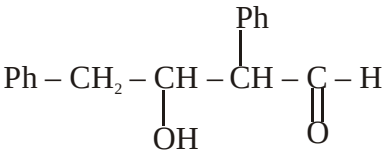
(3) ALDOL CONDENSATION

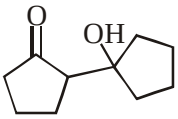
Q.1 Ans.

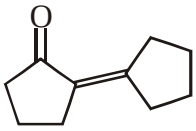
Q.1 (I) (A) 

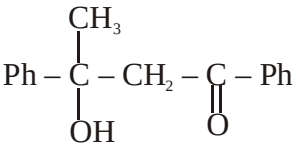
(B) 

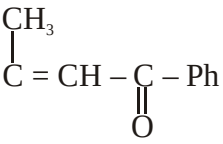
(II) (C) 

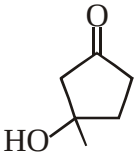
(III) (D) 

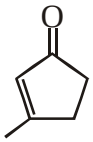
(IV) (E) 

(F) 

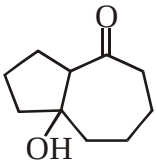
(V) (G) 

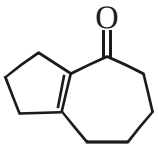
(H) 

Q.2 Ans. (I) (A) 

(B) 

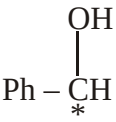
;

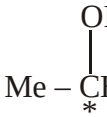
(II) (E) 

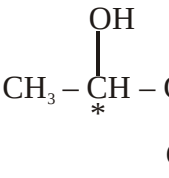
(F) 

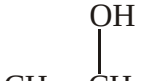
Q.3

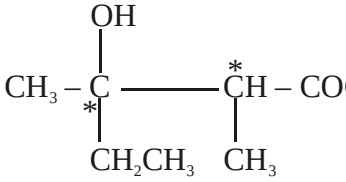
Ans. **Excluding Stereo** **Including Stereo**

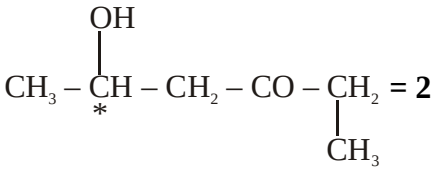
(I)  **= 2 ,**

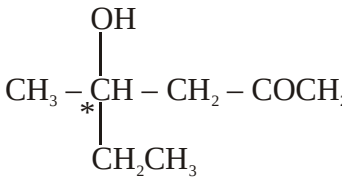
 **= 2**

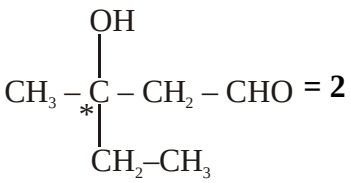
(II)  **= 4**

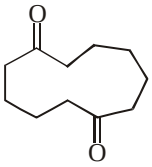
 **= 2**

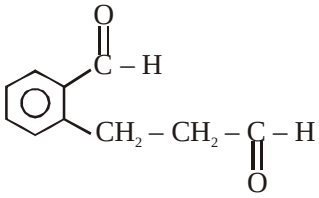
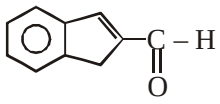
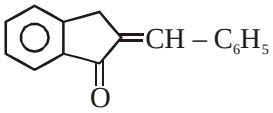
 **= 4 ,**

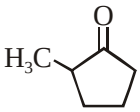
 **= 2**

 **= 2 ,**

 **= 2**

Q.4 Ans. (I)  **(II)** $CH_3 - \underset{\underset{O}{\|}}{C} - CH_3$

Q.5 Ans. (i) **(a)**  **(b)**  **(ii)** 

Q.6 Ans. (i) X =  $Y = CH_3 - \underset{\underset{O}{\|}}{C} - H$

(ii) $X = CH_3 - \overset{\overset{O}{\|}}{C} - CH_2 - CH_2 - \overset{\overset{O}{\|}}{C} - CH_3$ **(iii)** $X = CH_3 - \overset{\overset{O}{\|}}{C} - CH_2 - CH_2 - CH_2 - CHO$

Q.7 Ans. (C)

Intramolecular aldol condensation the 1,4-additon and finally clemmesion reduction.

Q.8 Ans. (D)

Q.9 Ans. (B)

Ozonolysis followed by intramolecular aldol.

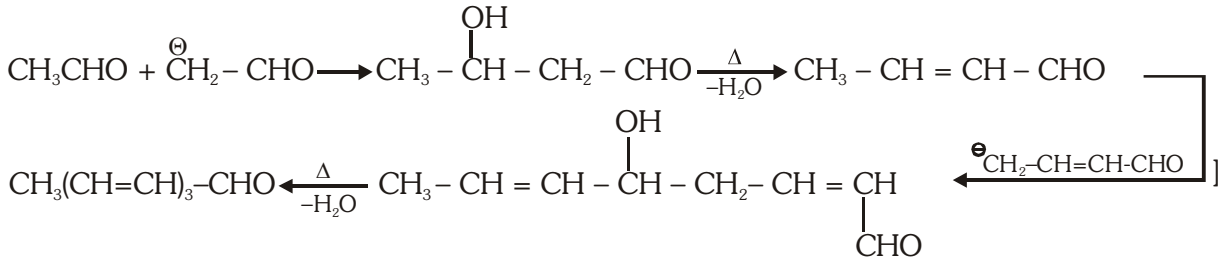
Q.10 Ans. (C)

(A) $CH_3–\underset{\underset{OH}{|}}{CH}–Cl_2CHO$ (B) $CH_3CH=CH–CH=O$

(C) $CH_3CH_2CH_2CH_2OH$ (D) $CH_3CH_2CH_2COOH$

Q.11 Ans. (A)

Q.12 Ans. (A)



Q.13 Ans. (A)

P :  Q : Me–CH=O R : Me–CH=Ch–CH=O

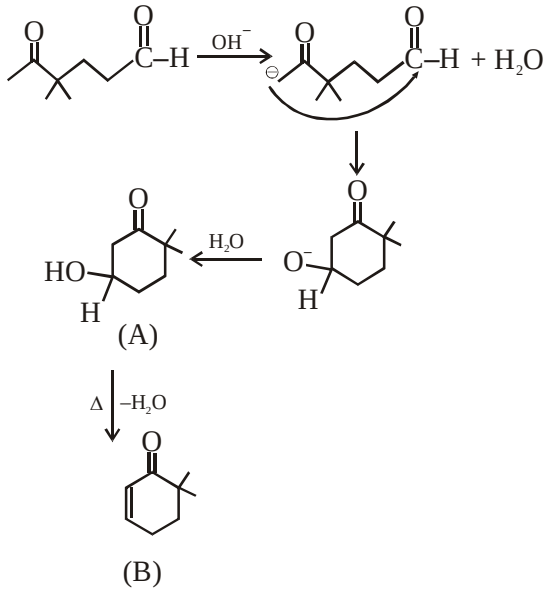
Q.14 Ans. (1)

Sol. Aldehyde reacts at a faster rate than keton during aldol and stericall less hindered anion will be a better nucleophile so sefl aldol at $CH_3 - \overset{\overset{O}{\|}}{C} - H$ will be the major product.

Q.15 Ans. (4)

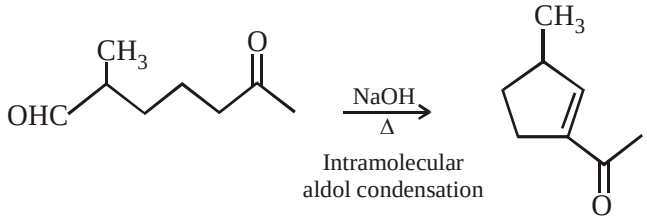
Q.16 Ans. (4)

Sol.



Q.17 Ans. (4)

Sol.



(4) HALOGENATION OF THE α-CARBON OF ALDEHYDES AND KETONES

Q.1 Ans. (1 , 2 , 5 , 7 ,8, 9 , 11)

Q.2 Ans. (i) $CH_3–COO^-$ + CHI_3 ; (ii) $^-O–\overset{O}{\overset{\|}{C}}–\overset{O}{\overset{\|}{C}}–O^-$ + CHI_3 **; (iii)**  + CHI_3

Q.3 Ans. (A,B,C)

Q.4 Ans. (C)

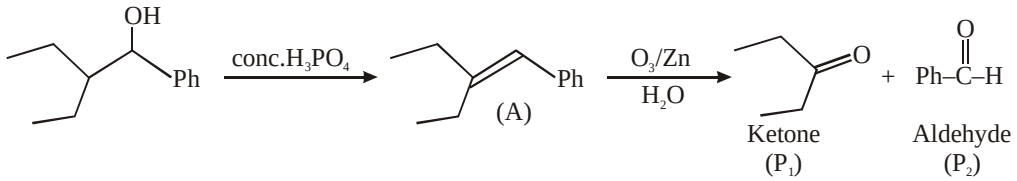
X : $PhCH_2CH_2OH$ Y : $PhCH_2CHO$ Z : $Ph–CH_2–CH=\overset{Ph}{\overset{|}{C}}–CHO$

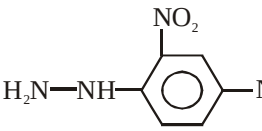
Q.5 Ans. (A)

Q.6 Ans. (A)

$$C–C–\overset{O}{\overset{\|}{C}}–C \xrightarrow[I_2]{NaOH} CHI_3 + CH_3CH_2COONa \xrightarrow{H^\oplus} CH_3CH_2COOH$$

Q.7 Ans. (B)



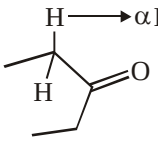
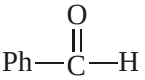
(A) Both ketone & aldehyde react with braddy's reagent  2, 4 dinitrophenyl hydrazine.

(B) With $NaHSO_3$ only aldehyde give crystalline bisulphite adduct whereas hindered ketone is unable react.

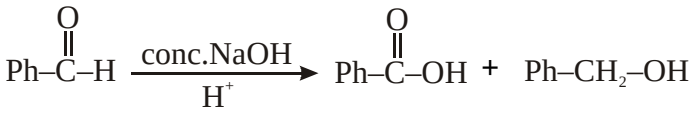
(C) $NaHCO_3$ will not react any of them.

(D) Both P_1 & P_2 are unable to form idoform with $NaOH/I_2$

Q.8 Ans. (A)

For aldol αH should be present i.e.  P_1 where as P_2  will give cannizaro's as there is no. αH in P_2.

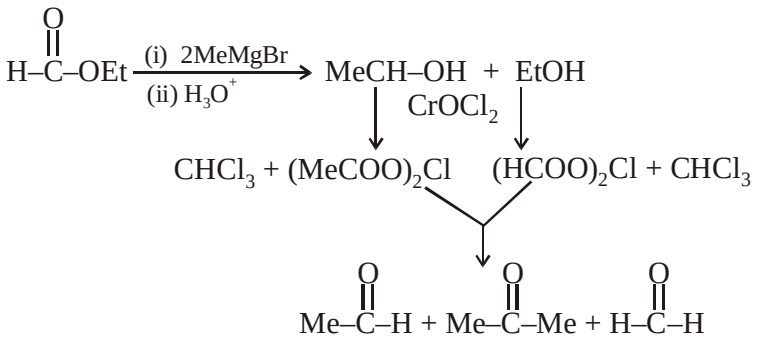
Q.9 Ans. (D)



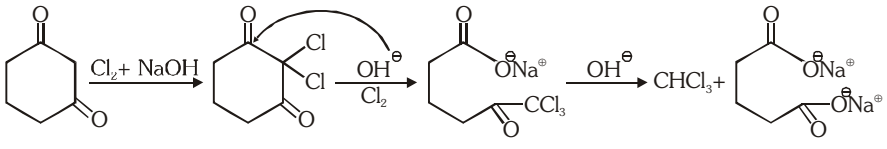
The above reaction is intermolecular redox reaction. In which desprotionation is taking place as a result of which 2 different products are formed from singlet reactant.

Q.10 Ans. (A,B,C,D)

Q.11 Ans. (C)



Q.12 Ans. (A,B,D)



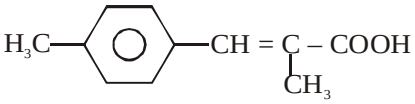
Q.13 Ans. (A,B,C,D)

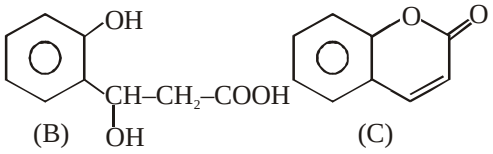
Q.14 Ans. (A,B,C,D)

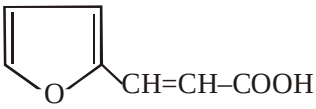
Q.15. Ans. (4)

Sol. Seliwanoff's test is used to distinguished aldose and ketose group.

(5) PERKIN CONDENSATION

Q.1 Ans. 

Q.2 Ans. 
(B) (C)

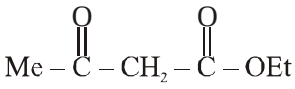
Q.3 Ans. 

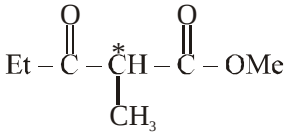
Q.4 Ans. (A)

Q.5 Ans. (C, D)

Q.6 Ans. (C)

(6) CLAISEN CONDENSATION

Q.1 Ans. 

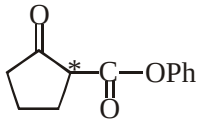
Q.2 Ans. 
(R / S)

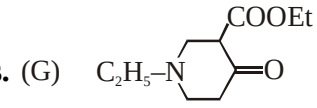
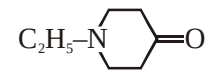
Q.3 Ans. 4 products

Q.4 Ans. $C_6H_5COCH_2COOC_2H_5$, $CH_3COCH_2COOC_2H_5$

Ethtl benzolyacetate

Q.5 Ans. 
Diethyl-α-oxalyphenyl acetate

Q.6 Ans. 
(R / S)

Q.7 Ans. (G)  , (H) 

1-Ethyl-4-piperiodone

(7) Beayer villiger oxidation

Q.1 Ans.(B)

Q.2. Ans.(D)