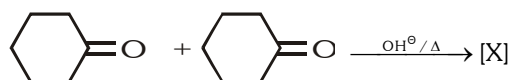


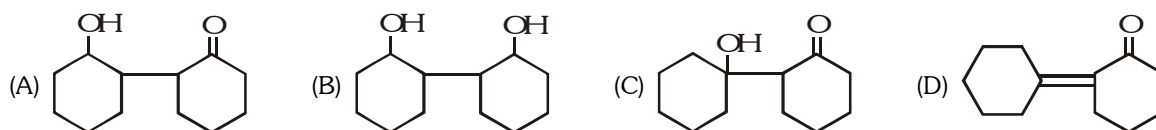
EXERCISE-01**CHECK YOUR GRASP****SELECT THE CORRECT ALTERNATIVE (ONLY ONE CORRECT ANSWER)**

1. Which of the following reacts with water to form very stable product ?
(A) CH_3Cl (B) CCl_4 (C) CCl_3CHO (D) $\text{CH}_2\text{ClCH}_2\text{Cl}$
2. The compound that gives a positive iodoform test is :-
(A) 1-pentanol (B) 2-pentanone (C) 3-pentanone (D) pentanal
3. Which of the following does not undergo aldol condensation ?
(A) HCHO (B) CH_3CHO (C) CH_3COCH_3 (D) $\text{CH}_3\text{CH}_2\text{CHO}$
4. Cannizzaro reaction is not given by :
(A) Trimethylacetaldehyde (B) Acetaldehyde (C) Benzaldehyde (D) Formaldehyde

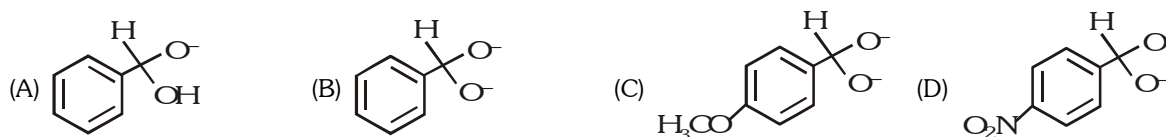
5. In the reaction :



[X] will be :-



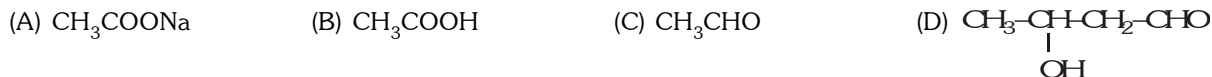
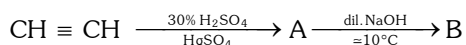
6. In a Cannizzaro reaction, the intermediate that will be the best hydride donor is :



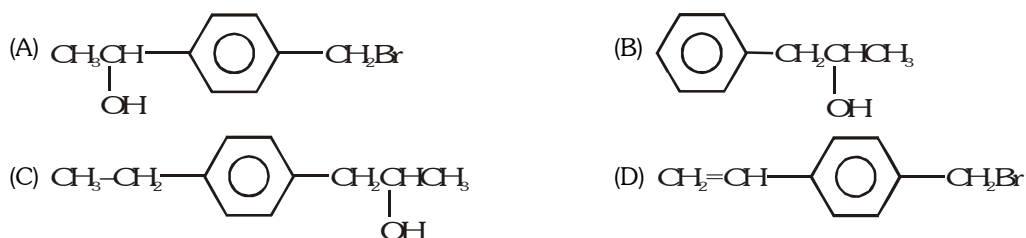
7. If 3-hexanone is reacted with NaBH_4 followed by hydrolysis with D_2O , the product will be :



8. Predict the product 'B' in the sequence of reaction



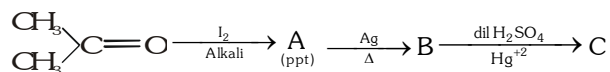
9. In the reaction $\text{CH}_2\text{Br} + \text{Mg} \xrightarrow{\text{dry ether}} \text{A} + \text{CH}_3\text{CHO} \longrightarrow \text{adduct} \xrightarrow{\text{H}_3\text{O}^+} \text{B}$.
The product (B) is :



10. Which one of the following reagents is suitable for the conversion of 2-cyclohexenone into 3-methylcyclohexanone ?
 (A) CH_3MgI (B) $(\text{CH}_3)_2\text{CuLi}$ (C) CH_3I_2 and Zn (D) CH_3AlCl_2
11. Acetaldehyde reacts with NaOH to form :-



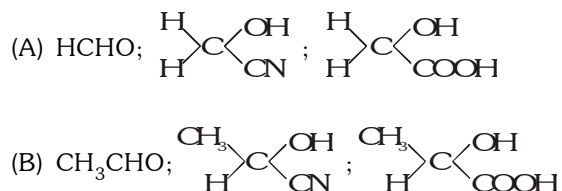
12. Benzaldehyde reacts with formaldehyde in the presence of alkali to form :-
 (A) Methyl alcohol and sodium benzoate (B) Benzyl alcohol and sodium formate
 (C) Benzoic acid and ethanol (D) Formic acid and benzyl alcohol
13. The compounds A, B and C in the reaction sequence



are given by the set :-

- (A) Iodoform, ethylene, ethyl alcohol (B) Iodoform, acetylene, acetaldehyde
 (C) Iodoform, propyne, acetone (D) Iodoform, 2-propanol, propanone
14. In the reaction sequence
- $$\text{RCOCl} + \text{H}_2 \xrightarrow{\text{Pd}+\text{BaSO}_4} \text{A} \xrightarrow{\text{HCN}} \text{B} \xrightarrow{\text{H}_3\text{O}^+} \text{C}$$
- A, B and C are given by the set :-
- (A) RCHO , RCH(OH)CN , $\text{RCH(OH)CH}_2\text{NH}_2$ (B) RCHO , RCH(OH)CN , RCH(OH)COOH
 (C) RCHO , $\text{R}-\overset{\text{O}}{\underset{||}{\text{C}}}-\overset{\text{CN}}{\underset{|}{\text{CH}_2}}$, $\text{R}-\overset{\text{O}}{\underset{||}{\text{C}}}-\overset{\text{CN}}{\underset{|}{\text{CH}_2}}-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{OH}$ (D) RCHO , $\text{R}-\text{CH}_2-\text{CN}$, $\text{R}-\text{CH}_2-\text{COOH}$

15. Oxidation of 2-methyl propane-1,2-diol with periodic acid gives :-
 (A) Propionic acid and formaldehyde (B) Acetone and formaldehyde
 (C) Acetone and acetic acid (D) Acetone and propionic acid
16. A carbonyl compound gives a positive iodoform test but does not reduce Tollen's reagent or Fehling's solution. It forms a cyanohydrin with HCN, which on hydrolysis gives a hydroxy acid with a methyl side chain. The compound is :-
 (A) Acetaldehyde (B) Propionaldehyde (C) Acetone (D) Crotonaldehyde
17. A carbonyl compound 'A' reacts with hydrogen cyanide to form a cyanohydrin 'B' which on hydrolysis gives an optically active alpha hydroxy acid 'C'. 'A' gives a positive iodoform test 'A', 'B' and 'C' are given by the set :-

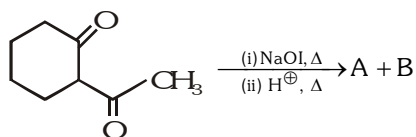


EXERCISE-02

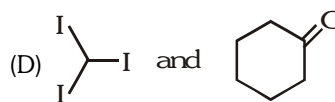
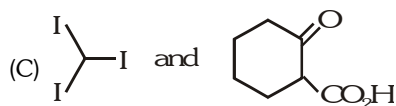
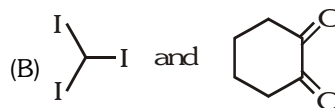
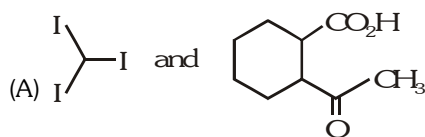
BRAIN TEASERS

SELECT THE CORRECT ALTERNATIVES (ONE OR MORE THEN ONE CORRECT ANSWERS)

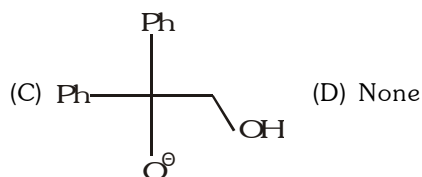
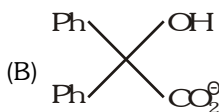
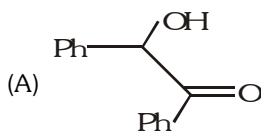
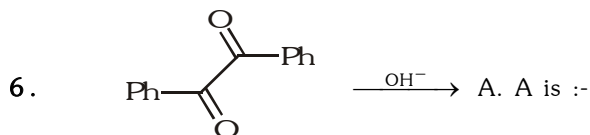
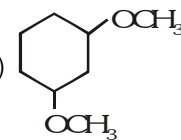
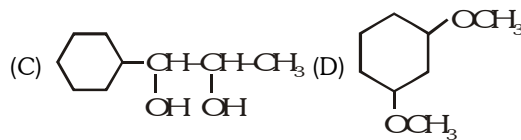
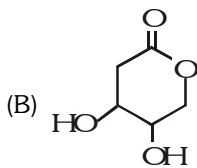
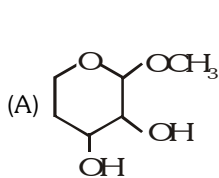
1. End products of the following sequence of reaction is



A & B are :



2. Which of the following compound on treatment with LiAlH_4 will give a product that will give positive iodoform test?
- (A) $\text{CH}_3\text{CH}_2\text{CHO}$ (B) $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3$ (C) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ (D) CH_3COCH_3
3. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is
- (A) CH_3COCl (B) CH_3CHO (C) $\text{CH}_3\text{COOCH}_3$ (D) $\text{CH}_3\text{COOCOCH}_3$
4. Which of the following does not give iodoform reaction ?
- (A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (B) CH_3OH (C) CH_3CHO (D) PhCOCH_3
5. Which of the following compounds undergo periodic oxidation

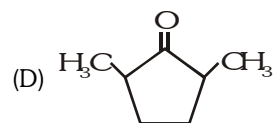
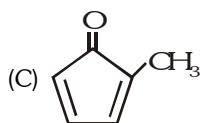
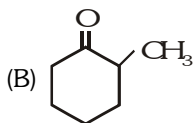
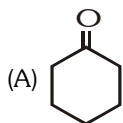


(D) None

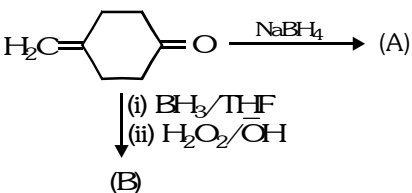
7. In the reaction sequence, [X] is ketone :



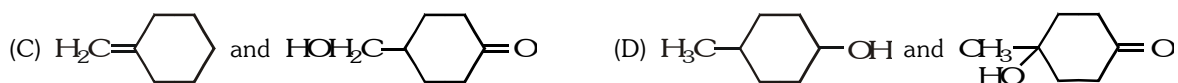
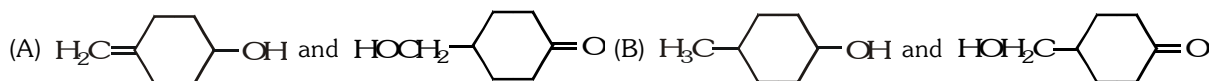
[X] will be :-



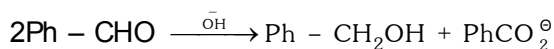
8. In the given reaction :



(A) and (B) are :

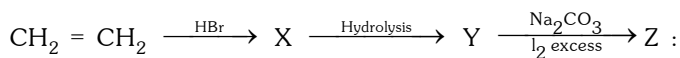


9. In the Cannizzaro reaction given below,



the slowest step is :

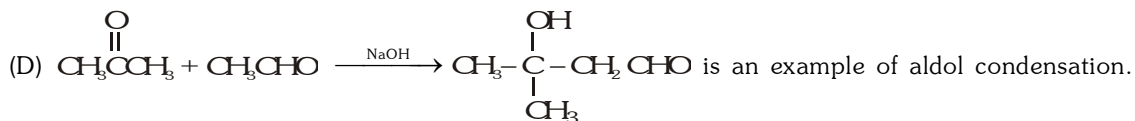
- (A) the attack of OH^- at the carbonyl group
 (B) the transfer of hydride to the carbonyl group
 (C) the abstraction of proton from the carboxylic acid
 (D) the deprotonation of $\text{Ph} - \text{CH}_2\text{OH}$
10. Which of the possible compound will be formed in the following sequence of reaction.

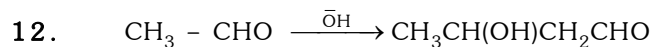


- (A) $\text{C}_2\text{H}_5\text{Br}$ (B) $\text{C}_2\text{H}_5\text{OH}$ (C) CHI_3 (D) CH_3CHO

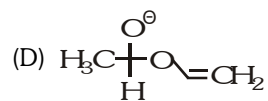
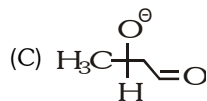
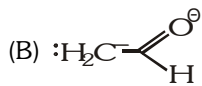
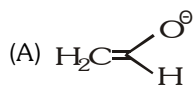
11. Which of the following statements are correct ?

- (A) Benzaldehyde reduces Fehling's solution
 (B) $\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CHO} \xrightarrow{\text{NaOH}} \text{C}_6\text{H}_5\text{CH} = \text{CHC}_6\text{H}_5 + \text{O}_2$ is a Claisen-Schmidt reaction.
 (C) pK_a (formic acid) is less than pK_a (acetic acid)

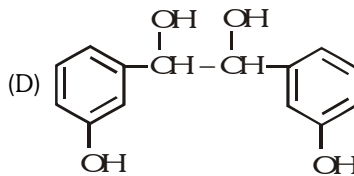
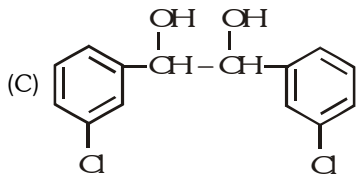
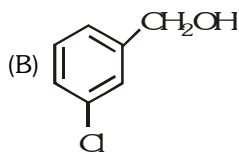
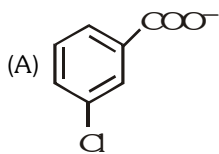




In the aldol condensation of acetaldehyde represented above, which of the following intermediate species are obtained ?

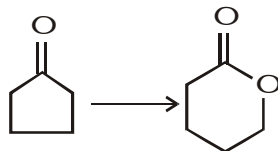


13. When m-Chlorobenzaldehyde is treated with 50% KOH solution, the products obtained is (are)

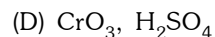
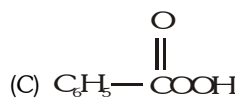
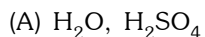


14.

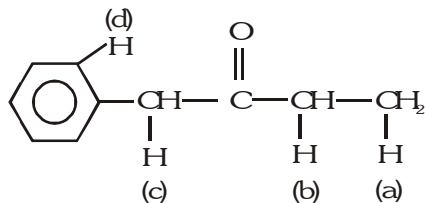
The conversion :



can be effected by using the reagent



15. Which of the following hydrogens will be the most acidic?



(A) a

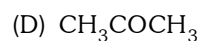
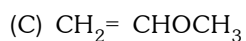
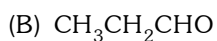
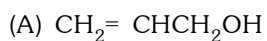
(B) b

(C) c

(D) d

16.

An organic compound with the molecular formula $\text{C}_3\text{H}_6\text{O}$ does not respond positively to the silver mirror test with Tollens reagent but produces an oxime. The compound is



EXERCISE-03

MISCELLANEOUS TYPE QUESTIONS

TRUE OR FALSE :

1. The reaction of methyl magnesium bromide with acetone followed by hydrolysis gives secondary alcohol.
2. Aldehydes are more reactive than ketones.
3. The yield of ketone, when a secondary alcohol is oxidised, is more than the yield of aldehyde when primary alcohol is oxidised by $K_2Cr_2O_7/H^+$
4. Both aldehydes and ketones reduce Tollen's reagent.
5. Aldol condensation is given by all carbonyl compounds.
6. Acetaldehyde and acetone can be distinguished by iodoform test.
7. $LiAlH_4$ converts ketones into secondary alcohols.
8. Methanol can be distinguished from ethanol by haloform reaction.
9. Propanone does not show tautomerism.
10. Ketones restore pink colour of Schiff's reagent.

FILL IN THE BLANKS :

1. To prepare ethanol, CH_3MgI is treated with the other reagent
2. Urotropine is formed by the action of with
3. The conversion of acid chlorides into aldehydes by reduction is termed
4. Aldehyde show reducing properties due to their ready conversion into
5. Hydrazone of an aldehyde when heated with sodium ethoxide forms This is known as reaction.
6. Cannizzaro's reaction is followed by those aldehydes which α -hydrogen atom.
7. Two separate solutions, Fehling's solution A(.....) and Fehling's solution B($NaOH + \dots$) are at first mixed up together and is then heated with the aldehyde. A precipitate is formed.
8. Tollen's reagent gives with acetaldehyde.
9. Aldehydes have boiling points lower than those of and higher than those of of comparable molecular masses.
10. When calcium acetate is distilled alone is formed.

MATCH THE COLUMN

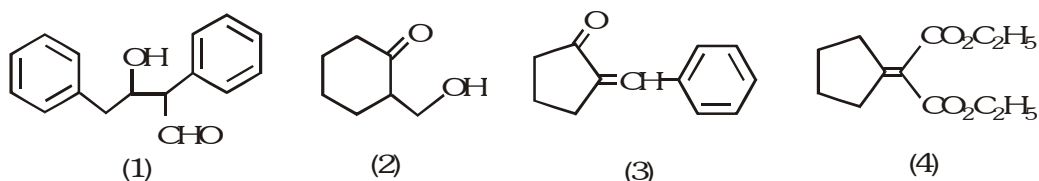
1. Match the compounds/ions in Column I with their properties/reactions in Column. II

Column -I		Column -II	
(A)	C_6H_5CHO	(p)	gives precipitate with 2,4-dinitrophenylhydrazine
(B)	$CH_3C \equiv CH$	(q)	give precipitate with $AgNO_3$
(C)	CN^-	(r)	is a nucleophile
(D)	I^-	(s)	is involved in cyanohydrin formation

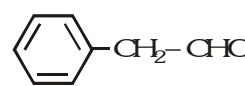
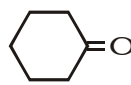
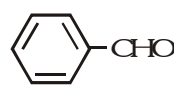
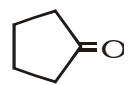
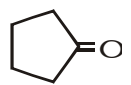
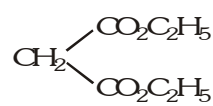
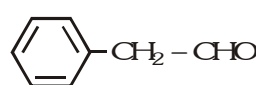
2. Match the column I with column II.

Column-I		Column-II	
(A)	$\text{RMgX}_{n\text{-carbon}} + \text{HCHO} \longrightarrow$ Adduct $\xrightarrow{\text{H}_3\text{O}^+}$	(p)	Ketone
(B)	$\text{RMgX}_{n\text{-carbon}} + (\text{CH}_2)_2\text{O} \longrightarrow$ Adduct $\xrightarrow{\text{H}_3\text{O}^+}$	(q)	1°Alcohol (n + 1) carbon
(C)	$\text{RMgX}_{n\text{-carbon}} + \text{CO}_2 \longrightarrow$ Adduct $\xrightarrow{\text{H}_3\text{O}^+}$	(r)	Acid (n + 1) carbon
(D)	$\text{RMgX}_{n\text{-carbon}} + \text{Ph-C}\equiv\text{N} \longrightarrow$ Adduct $\xrightarrow{\text{H}_3\text{O}^+}$	(s)	1°Alcohol (n + 2) carbon

3. Aldol condensation proceeds by carbon-carbon bond formation between an enolate donor and a carbonyl acceptor. For each of the following aldol products (1 through 4)



match the donor and acceptor compound.

Column -I [Donor]		Column -II [Acceptor]	
(A)		(p)	$\text{CH}_2 = \text{O}$
(B)		(q)	
(C)		(r)	
(D)		(s)	

ASSERTION & REASON QUESTION :

These questions contains, Statement-I (assertion) and Statement-II (reason).

- (A) Statement-I is True, Statement-II is True ; Statement-II is a correct explanation for Statement-I
 (B) Statement-I is True, Statement-II is True ; Statement-II is NOT a correct explanation for Statement-I
 (C) Statement-I is True, Statement-II is False.
 (D) Statement-I is False, Statement-II is True.

1. **Statement-I** : 2, 2,-dimethyl propanol undergoes Cannizaro reaction with concentrated NaOH.
Because
Statement-II : Cannizarro reaction is a disproportionation reaction.

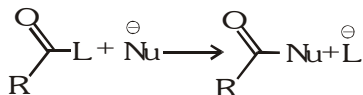
2. **Statement-I** : Benzaldehyde does not undergoes aldol condensation.
Because
Statement-II : Benzaldehyde does not contains acidic α -Hydrogen.
3. **Statement-I** : Acetaldehyde is less reactive than trichloro acetaldehyde.
Because
Statement-II : Chlorine atom exhibit -I effect in trichloro acetaldehyde.
4. **Statement-I** : Benzaldehyde gives a positive test with Benedict's and Fehling's solution.
Because
Statement-II : Benzaldehyde gives silver mirror with Tollen's reagent.
5. **Statement-I** : $R-C\equiv O^+$ is more stable than $R-C^+=O$.
Because
Statement-II : Resonance in carbonyl compound provides $\text{>}\overset{\oplus}{C}-$ and O^- .
6. **Statement-I** : Rate of addition of HCN on carbonyl compounds increases in presence of NaCN.
Because
Statement-II : Reaction involves the addition of CN^- in rate determining step.
7. **Statement-I** : Fehling's solution can be used to distinguish benzaldehyde from acetaldehyde.
Because
Statement-II : Both benzaldehyde and acetaldehyde reduces tollens's reagent.
8. **Statement-I** : Ketones are less reactive than aldehydes.
Because
Statement-II : Ketones do not give Schiff's test.
9. **Statement-I** : Benzaldehyde is more reactive than ethanol towards nucleophilic attack.
Because
Statement-II : The overall effect of -I and +R effect of phenyl group decreases the electron density on the carbon atom of $>C=O$ group in benzaldehydes.
10. **Statement-I** : In formaldehyde all the four atoms are in same plane.
Because
Statement-II : The carbon atom in formaldehyde is sp^2 hybridised.

COMPREHENSION BASED QUESTIONS :

Comprehension # 1

Aldehyde, ketone, acid and acid derivatives contain $>C=O$ group. Aldehyde and ketones gives nucleophilic addition reactions where as acid and acid derivatives gives nucleophilic addition followed by elimination reactions. Nucleophilic addition reactions followed by elimination of acid derivatives is known as acyl substitution reaction. This substitution reaction takes places by formation of tetrahedral intermediate.

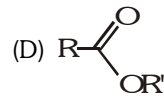
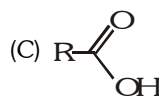
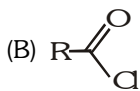
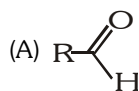
1. For the given reaction



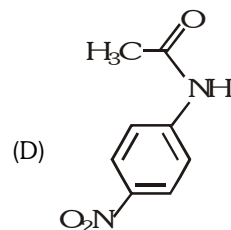
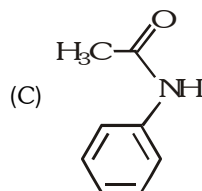
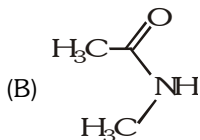
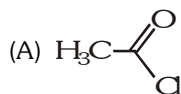
which of these is correct ?

- (A) L must be better leaving group than Nu
- (B) Nu^- must be strong enough nucleophile to attack carbonyl carbon
- (C) Carbonyl carbon must be enough electrophilic to react with Nu^-
- (D) All of these

2. Which of the following compounds has very poor leaving group ?



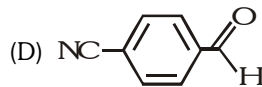
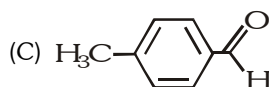
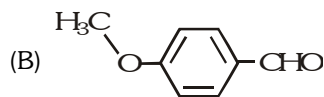
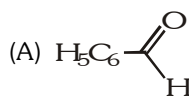
3. Which one of the following is least reactive compound for nucleophilic acyl substitution.



Comprehension # 2

Aldehydes and ketones are amphoteric. Thus they can act both as acids and bases. Under acidic conditions, the carbon of the protonated carbonyl group is much more electrophilic, reacting even with weak nucleophile. Carbonyl compound gives nucleophilic addition reaction. In this reaction the nucleophilic attack precedes the electrophilic attack.

- Which of these statements are correct ?
 (A) Carbonyl compound is amphoteric in character
 (B) Acid catalyst makes the carbonyl carbon more electrophilic
 (C) basic catalyst makes the nucleophilic attack more faster.
 (D) All of these
- Which of the statements are/is correct ?
 (A) The rate determining step of addition reaction is the addition of nucleophile
 (B) The rate-determining step is addition of electrophile
 (C) The reaction intermediate of the reaction is alkoxide ion
 (D) both (A) and (C)
- Which one of the carbonyl compounds is more reactive towards NaCN/H^+ ?



4. Carbonyl compounds gives nucleophilic addition with
- carbon nucleophile
 - oxygen nucleophile
 - Nitrogen nucleophile
 - All of these

Comprehension # 3

Aldehyde and ketones are specially susceptible to nucleophile addition because carbonyl group >C=O is polar (due to electronegativity different between carbon and oxygen).



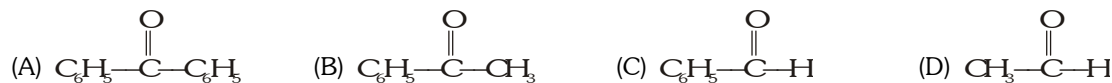
Positive charge on carbon makes it reactive towards the nucleophile. This addition is catalysed by acid.

Reactivity of carbonyl compound towards nucleophilic addition increases with increase in the electron deficiency at carbonyl carbon. Thus, (-I.E.) group increase while (+I.E.) groups decrease the reactivity of carbonyl compound.

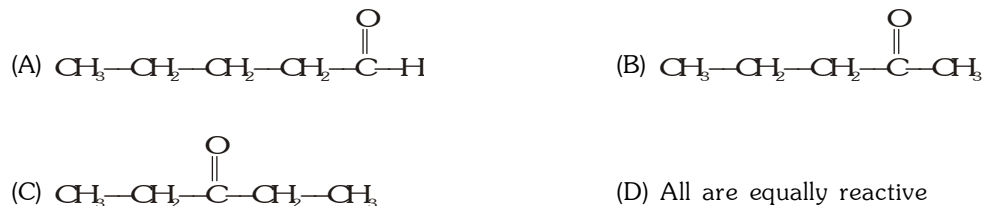
- Which of the following is most reactive to give nucleophilic addition?
(A) FCH_2CHO (B) ClCH_2CHO (C) BrCH_2CHO (D) ICH_2CHO
- Carbonyl compounds show nucleophilic addition with :
(A) HCN (B) NaHSO_3 (C) $(\text{CH}_3\text{OH} + \text{HCl})$ (D) all of these
- Which among the following carbonyl compounds is most polar?



- Select the least reactive carbonyl compound for nucleophilic addition:



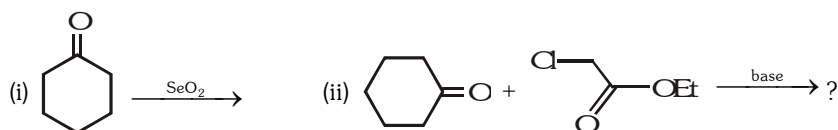
- Which among the following isomeric compound is most reactive?



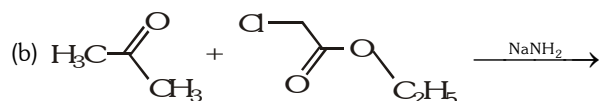
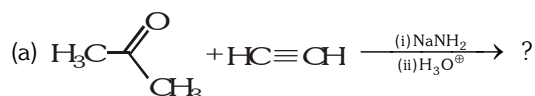
MISCELLANEOUS TYPE QUESTION	ANSWER KEY	EXERCISE -3
<ul style="list-style-type: none"> True / False <ol style="list-style-type: none"> F T T F F F T T F F Fill in the Blanks <ol style="list-style-type: none"> HCHO HCHO, NH_3 Rosenmund reduction acids alkane, wolf-kishner do not have CuSO_4, roscheil salt, Cu_2O silver mirror alcohol, alkane acetone Match the Column <ol style="list-style-type: none"> (A) \rightarrow p,s ; (B) \rightarrow q,r ; (C) \rightarrow q,r,s ; (D) \rightarrow q,r (A) \rightarrow q ; B \rightarrow s ; (C) \rightarrow r ; (D) \rightarrow p (A) \rightarrow s ; (B) \rightarrow p ; (C) \rightarrow q ; (D) \rightarrow r Assertion - Reason Questions <ol style="list-style-type: none"> D A A D B A B B A A Comprehension Based Questions <p>Comprehension #1 : 1. (D) 2. (A) 3. (B)</p> <p>Comprehension #2 : 1. (D) 2. (D) 3. (D) 4. (D)</p> <p>Comprehension #3 : 1. (A) 2. (D) 3. (A) 4. (A) 5. (A)</p> 		

EXERCISE-04 [A]**CONCEPTUAL SUBJECTIVE EXERCISE**

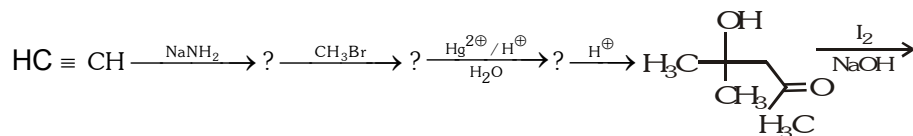
- Which of the carbonyl groups in $p\text{-MeOC}_6\text{H}_4\text{COMe}$ and $p\text{-NO}_2\text{C}_6\text{H}_4\text{COMe}$ protonates more readily in acid solution and why ?
- Identify (A) and (B) in the given sequence of reaction $\text{PhCH}_2\text{CHO} \xrightarrow{\text{SeO}_2} \text{(A)} \xrightarrow[\text{(ii)H}^+]{\text{(i)con.OH}^-} \text{(B)}$
- Distinguish between PhCOEt and $p\text{-MeC}_6\text{H}_4\text{COMe}$ by a chemical method.
 - Arrange the following in the order of increasing reactivity towards nucleophilic addition reactions.
 - CH_3CHO , $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$, $\text{CH}_3\text{COC}_6\text{H}_5$, CH_3COCH_3
 - CH_3CHO , CF_3CHO , $\text{CH}_2 = \text{CHCHO}$
- Compound X with molecular formula $\text{C}_9\text{H}_{10}\text{O}$ form a semicarbazone and give negative Tollen's and Iodoform tests. Upon reduction it gives n-propyl benzene. Deduce the structure of X.
- The double bond in aldehydes and ketones is reactive towards nucleophilic reagents like CN^- whereas that in an alkene is not.
 - Alkenes undergo electrophilic addition whereas aldehydes and ketones undergo nucleophilic addition.
- Complete the following equations giving the structures of the major organic product.



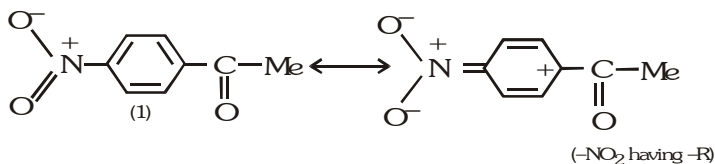
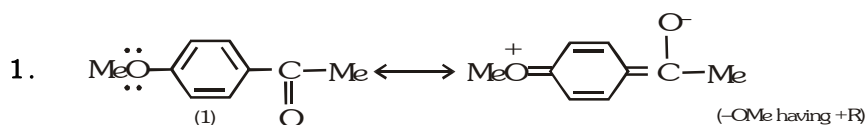
7. Complete the following equation :



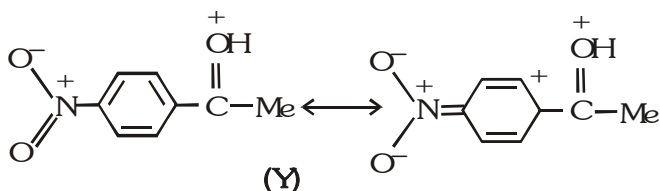
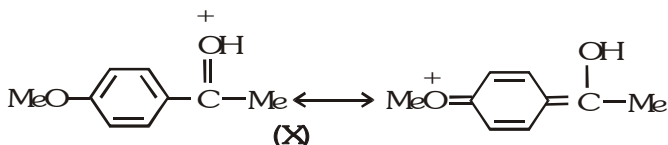
- Two organic compounds (A) and (B) have same empirical formula CH_2O . Vapour density of (B) is twice the vapour density of (A). (A) reduces Fehling solution but does not react with NaHCO_3 . Compound (B) neither reacts with NaHCO_3 nor reduces Fehling solution. What are (A) and (B) ? Also report an isomer of (B) if it reacts with NaHCO_3 .
- Complete the following equation :



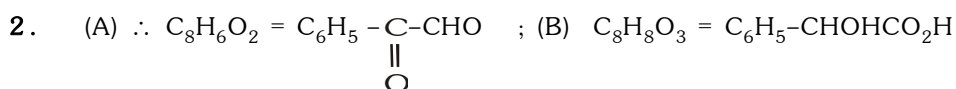
- A compound has two isomers (A) and (B) of formula $\text{C}_5\text{H}_{10}\text{O}$. Isomer (A) on treating with NaOH (aq.) give 2, 2-dimethylpropan-1-ol and 2, 2-dimethylpropanoic acid salt. The isomer (B) on treating with NaOH (aq.) gives 3-hydroxy-2-propylheptanal. What are A and B ?



I will be more readily protonated than (II). Alternative protonated (I) is more stabilised by resonance than protonated (II).



In (X) there is extended conjugation and only one charge is involved. In (Y) there is not this extended conjugation and the relative close proximity of two positive charges is a destabilising factor. Hence (X) is more stable than (Y).



3. (a) I does not undergo haloform reaction whereas II does.
 (b) A = $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5 < \text{CH}_3\text{COC}_6\text{H}_5 < \text{CH}_3\text{COCH}_3 < \text{CH}_3\text{CHO}$
 B = $\text{CH}_2=\text{CHCHO} < \text{CH}_3\text{CHO} < \text{CF}_3\text{CHO}$

4. (i) X forms semicarbazone and thus possesses carbonyl group.

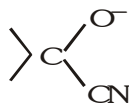
$$>\text{C}=\text{O} + \text{H}_2\text{N.NHCONH}_2 \longrightarrow >\text{C}=\text{N.NHCONH}_2$$

 (ii) It does not give Tollen's reagent test and thus it is ketone.
 (iii) It does not give iodoform test and thus it is not methyl ketone.
 (iv) Keeping in view of the above facts and molecular formula ; X is

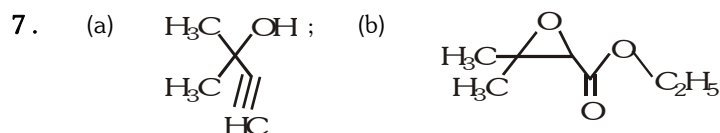
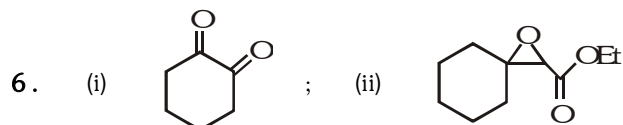


- (v) This on reduction will give n-propyl benzene.

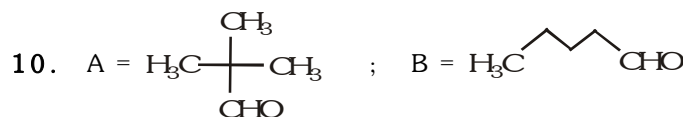
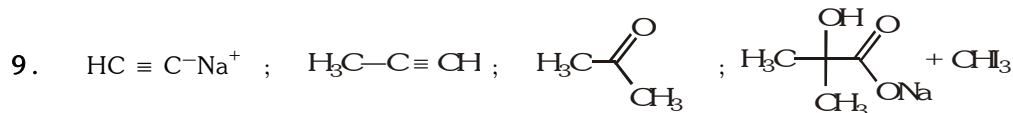
5. (a) The carbonyl group in aldehydes and ketones add on CN^- resulting in the formation of an anion where the negative charge resides on oxygen. However if a nucleophile adds on to an alkene the negative charge resides on carbon. Since carbon is much less strongly electron attracting than oxygen, this species is less stable and hence not readily formed.



- (b) In alkenes the double bond joins two carbon atoms and there is no resultant polarity. In carbonyl compounds, the carbonyl group is highly polar and the high partial positive charge on the C atom makes it susceptible to nucleophilic attack.

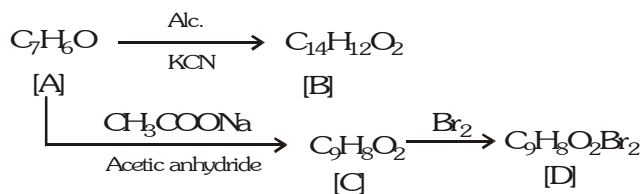


8. A = HCHO (Formaldehyde) B = HCOOCH_3 (Methyl methanoate)

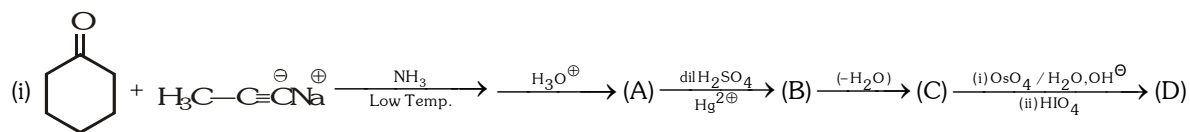


EXERCISE-04 [B]**BRAIN STORMING SUBJECTIVE EXERCISE**

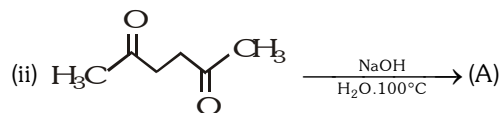
1. Identify (A) to (D) as reactant, reagent, product as name of the reaction in following :
- (i) $3(\text{CH}_3)_2\text{C}=\text{O} \xrightarrow{\text{HCl}}$ (A) Aldol condensation
- (ii) $\text{CH}_3\text{COCl} + \text{H}_2 \xrightarrow{\text{(B)}}$ (C) Rosenmund's reaction
- (iii) (D) $\xrightarrow[\text{(ii) } \text{C}_2\text{H}_5\text{ONa}]{\text{(i) } \text{NH}_2\text{NH}_2} \text{CH}_3\text{CH}_2\text{CH}_3$
- (iv) (D) $\xrightarrow{\ominus\text{OBr}} \text{CHBr}_3 + \text{CH}_3\text{COO}^\ominus$
2. Two different Grignard reagents, (X) and (Y) produce $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ on reaction with (P) and (Q) respectively. Give structures of (X), (Y) and (Q).
3. (a) 2-methyl-1,3-cyclohexanedione is more acidic than cyclohexanone - explain with reason
(b) Explain why HCN will add to the double bond in $\text{CH}_2=\text{CHCOOH}$ but not in $\text{RCH}=\text{CHR}$
4. A compound $\text{C}_5\text{H}_{10}\text{O}$ does not reduce Fehling's solution, form a phenyl hydrazone, shows the haloform reaction, and can be converted into n-pentane by Zn-Hg and conc. HCl. What is this compound ?
5. (a) Convert PhCHO into $\text{PhCH}=\text{CHCOPh}$
(b) Identify A, B, C and D in the following reaction.



6. A ketone (A) which undergoes haloform reaction gives compound B on reduction. B on heating with sulphuric acid gives compound C, which form mono ozonide D. D on hydrolysis in presence of Zn dust gives only acetaldehyde. Identify A, B and C. Write down the reactions involved.
7. Complete the following reactions :

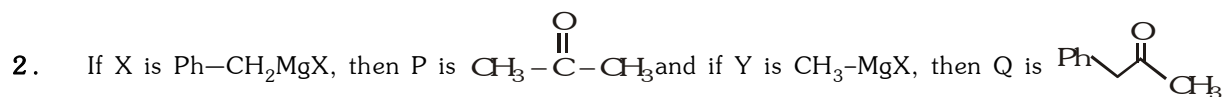
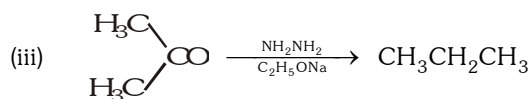
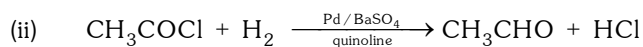
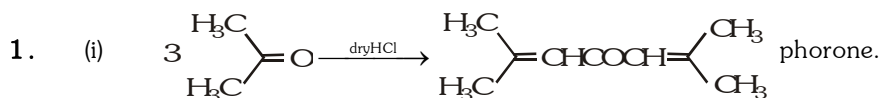
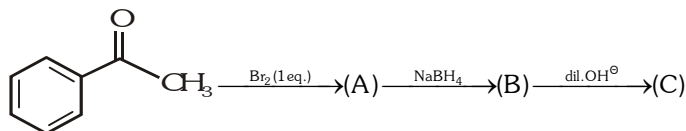


Write the structures of A to D and give the IUPAC name of (D).

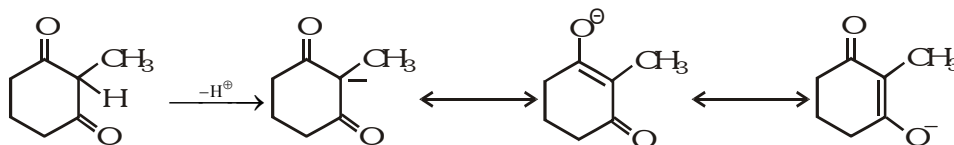


8. The sodium salt of a carboxylic acid, A, was produced by passing a gas, B, into an aqueous solution of caustic alkali at an elevated temperature and pressure. A on heating in presence of sodium hydroxide followed by treatment with sulphuric acid gave a dibasic acid C. A sample of 0.4 g of C on combustion gave 0.08 g of water and 0.39 g of carbon dioxide. The silver salt of acid weighin 1g on ignition yielded 0.71 g of silver as residue. Identify A, B and C.

9. Give reasons for the following :
- Ketones are less electrophilic than aldehydes.
 - Aldehydes are reducing agents and ketones are not.
 - HBr fails to give addition products with carbonyl compounds.
10. Identify A, B and C ?

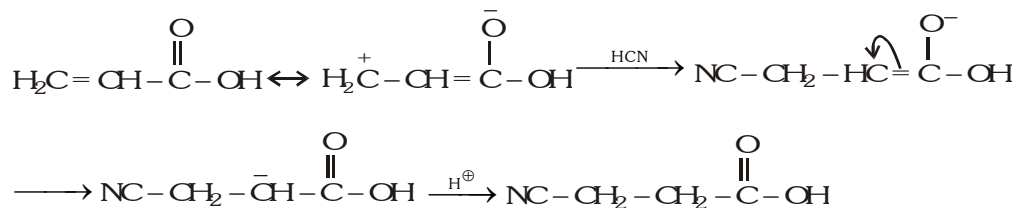


3. (a) 2-methyl-1, 3-cyclohexanedione is more acidic because its enolate ion is stabilized by an additional resonance structure.



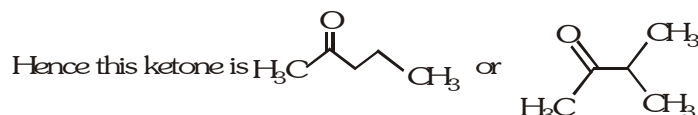
Resonance stabilized conjugate base.

- (b) In the case of the acid the double bond is activated due to the presence of a -COOH group



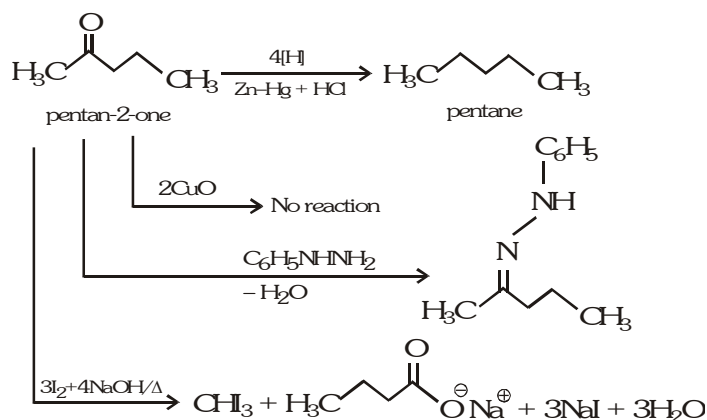
4. (i) Since $\text{C}_5\text{H}_{10}\text{O}$ forms a phenyl hydrazone, hence it is an aldehyde or ketone.
 (ii) As it does not reduce Fehling's solution, hence it is not aldehyde but a ketone.


- (iii) Since it undergoes haloform reaction, therefore it is $\text{CH}_3\text{-C(=O)-R}$ type of ketone. The value of R - can be derived as follows : $\text{R} = \text{-C}_3\text{H}_7$

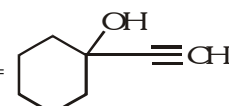
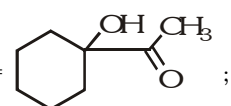
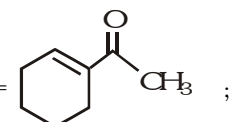
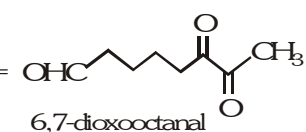


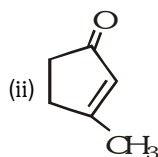
(iv) Ketone on Clemmensen reduction yields n-pentane; hence R is n-propyl and not isopropyl.


5. (a) CH_3MgI , H_3O^+ , $\text{H}^+/\text{K}_2\text{Cr}_2\text{O}_7$, $\text{PhCHO}/\text{OH}^-/\Delta$
 (b) $\text{A} = \text{C}_6\text{H}_5\text{CHO}$; $\text{B} = \text{PhCH}(\text{OH})\text{COPh}$;
 $\text{C} = \text{C}_6\text{H}_5\text{CH}=\text{CH}-\text{COOH}$; $\text{D} = \text{C}_6\text{H}_5\text{CHBr}-\text{CHBr}-\text{COOH}$



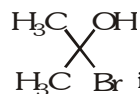
6. $\text{A} = \text{H}_3\text{C}-\overset{\text{O}}{\parallel}\text{CH}-\text{CH}_2-\text{CH}_3$; $\text{B} = \text{H}_3\text{C}-\text{CH}(\text{OH})-\text{CH}_2-\text{CH}_3$; $\text{C} = \text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}_3$; $\text{D} =$ 

7. (i) $\text{A} =$  ; $\text{B} =$  ; $\text{C} =$  ; $\text{D} =$ 
 6,7-dioxooctanal

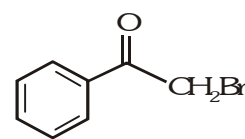
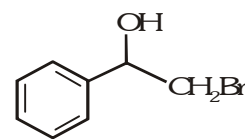
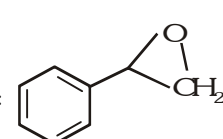


8. $\text{A} = \text{HCOOH}$; $\text{B} = \text{CO}$; $\text{C} =$ 

9. (a) The positive inductive effect of the second alkyl radical reinforces that of the first one decreasing still further the partial positive charge on the carbonyl carbon atom. This reduces the attraction of the atom for nucleophilic reagents. Hence ketones are less electrophilic.
 (b) The $>\text{C}=\text{O}$ group in aldehydes activates the H atom attached to the carbonyl group. This is due to the relaying of the $-I$ effect of the oxygen atom to the $\text{C}-\text{H}$ bond so that partial positive charge is created on the H atom. The result of this activation is that the H atom of the $-\text{CHO}$ group can be oxidised readily to a (OH) group. Thus aldehydes are reducers.
 (c) HBr is strongly polar and is hence readily added to the polarized $>\text{C}=\text{O}$ group. The addition product



is however unstable and decomposes to give the original carbonyl compound and HBr .

10. (A) :  ; (B) :  ; (C) : 

EXERCISE-05**PREVIOUS YEARS QUESTIONS**

1. The formation of cyanohydrin from a ketone is an example of [IIT-90]
(A) Electrophilic addition (B) Nucleophilic addition
(C) Nucleophilic substitution (D) Electrophilic substitution
2. The enolic form of acetone contains - [IIT-90]
(A) 9 sigma bonds, 1 pi bond and 2 lone pairs (B) 8 sigma bonds, 2 pi bond and 2 lone pairs
(C) 10 sigma bonds, 1 pi bond and 1 lone pairs (D) 9 sigma bonds, 2 pi bond and 1 lone pairs
3. m-chlorobenzaldehyde on reaction with conc. KOH at room temperature gives [IIT-91]
(A) Potassium m-chlorobenzoate and m-hydroxybenzaldehyde
(B) m-hydroxy benzaldehyde and m-chlorobenzyl alcohol
(C) m-chlorobenzyl alcohol and m-hydroxybenzyl alcohol
(D) Potassium m-chlorobenzoate and m-chlorobenzyl alcohol
4. Hydrogenation of benzoyl chloride in the presence of Pd on BaSO₄ gives [IIT-92]
(A) Benzyl alcohol (B) Benzaldehyde
(C) Benzoic acid (D) Phenol
5. An organic compound C₃H₆O does not give a precipitate with 2,4-Dinitrophenyl hydrazine reagent- [IIT-93]
(A) CH₃CH₂CHO (B) CH₃COCH₃
(C) CH₂=CH-CH₂OH (D) 
6. Under Wolff Kishner reduction conditions, the conversion which may be through about is - [IIT-95]
(A) Benzaldehyde into Benzyl alcohol (B) Cyclohexanol into Cyclohexane
(C) Cyclohexanol into Cyclohexanol (D) Benzophenone into Diphenylmethane
7. In the reaction, P is, [IIT-95]

(A) CH₃COCHO (B) CH₃COOCH₃ (C) CH₃COCH₂OH (D) None
8. In the Cannizzaro reaction given below $2 \text{ Ph-CHO} \xrightarrow{\text{OH}^-} \text{Ph-CH}_2\text{OH} + \text{PhCO}_2^-$ the slowest step is- [IIT-96]
(A) the attack of OH⁻ at the carbonyl group
(B) the transfer of hydride to the carbonyl group
(C) the abstraction of proton from the carboxylic acid
(D) the deprotonation of Ph-CH₂OH
9. Which of the following will give yellow precipitate with I₂/NaOH- [IIT-97]
(A) ICH₂COCH₂CH₂ (B) CH₃COOCOCH₃
(C) CH₃CONH₂ (D) CH₃CH(OH)CH₂CH₃
10. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is - [IIT-97]
(A) MeCOCl (B) MeCHO
(C) MeCOOMe (D) MeCOOCOMe

11. In a Cannizzaro reaction the intermediate which is the best hydride donor is - [IIT-97]



12. $\text{CH}_3\text{CHO} + \text{H}_2\text{NOH} \rightarrow \text{CH}_3-\text{CH}=\text{N}-\text{OH}$. The above reaction occurs at - [IIT-97]

(A) pH = 1 (B) pH \approx 4.5 (C) Any value of pH (D) pH = 12

13. Among the following compounds, which will react with acetone to give a product containing $>\text{C}=\text{N}-$ [IIT-98]

(A) $\text{C}_6\text{H}_5\text{NH}_2$ (B) $(\text{CH}_3)_3\text{N}$ (C) $\text{C}_6\text{H}_5\text{NHC}_6\text{H}_5$ (D) $\text{C}_6\text{H}_5\text{NHNH}_2$

14. The product obtained via oxymercuration ($\text{HgSO}_4 + \text{H}_2\text{SO}_4$) of 1-butyne would be - [IIT-98]



15. Which of the following will not undergo aldol condensation - [IIT-98]

(A) Acetaldehyde (B) Propanaldehyde

(C) Benzaldehyde (D) Trideutero acetaldehyde

16. Which of the following will react with water to form a stable hydrate - [IIT-98]

(A) CHCl_3 (B) Cl_3CCHO (C) CCl_4 (D) $\text{ClCH}_2\text{CH}_2\text{Cl}$

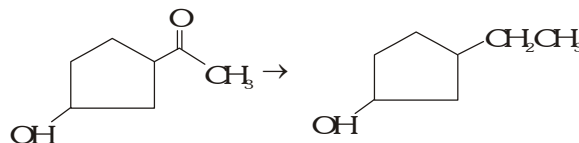
17. The enol form of acetone, after treatment with D_2O gives - [IIT-99]



18. 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 hexanedione

19. The appropriate reagent for the following transformation - [IIT-2000]



(A) $\text{Zn}(\text{Hg}), \text{HCl}$ (B) $\text{NH}_2\text{NH}_2, \text{OH}^-$ (C) H_2/Ni (D) NaBH_4

20. Read the following statement and explanation and answer as per the option given below : [IIT-01]

Statment-I : Dimethylsulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compounds.

Statment-II : It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates.

(A) If both assertion and reason are correct, and reason is the correct explanation of the assertion

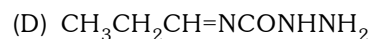
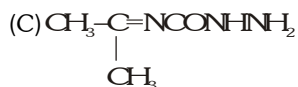
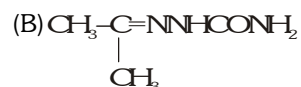
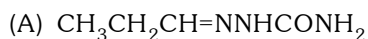
(B) If both assertion and reason are correct, but reason is not correct explanation of the assertion

(C) If assertion is correct but reason is incorrect

(D) If assertion is incorrect but reason is correct

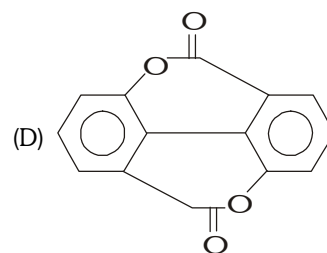
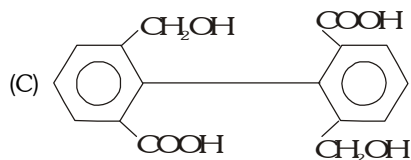
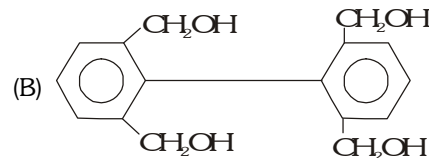
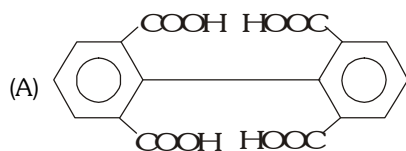
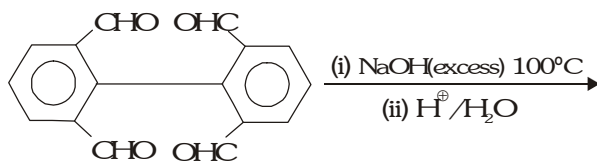
21. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives - [IIT-01]
 (A) benzyl alcohol and sodium formate (B) sodium benzoate and methyl alcohol
 (C) sodium benzoate and sodium formate (D) benzyl alcohol and methyl alcohol

22. 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 ammoniacal 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-02]

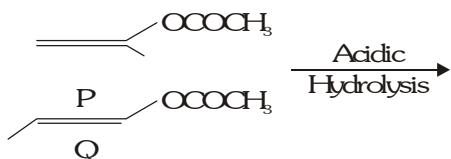


23. Any one of the product formed is :

[IIT-02]



- 24.



[IIT-03]

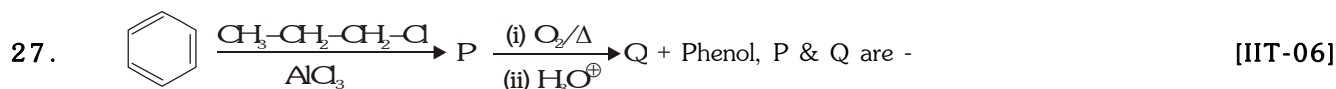
Product formed by P & Q can be differentiated by :

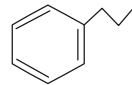
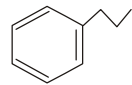
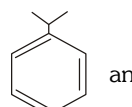
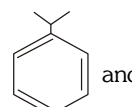
- (A) 2, 4-DNP (B) Lucas reagent ($ZnCl_2 + \text{conc. HCl}$)
 (C) $NaHSO_3$ (D) Fehling's solution
25. Which of the reagent is used to convert 2-Butanone into propanoic acid - [IIT-05]
 (A) $NaOH, I_2/H^+$ (B) Tollen's reagent (C) Fehling solution (D) $NaOH, NaI/H^+$

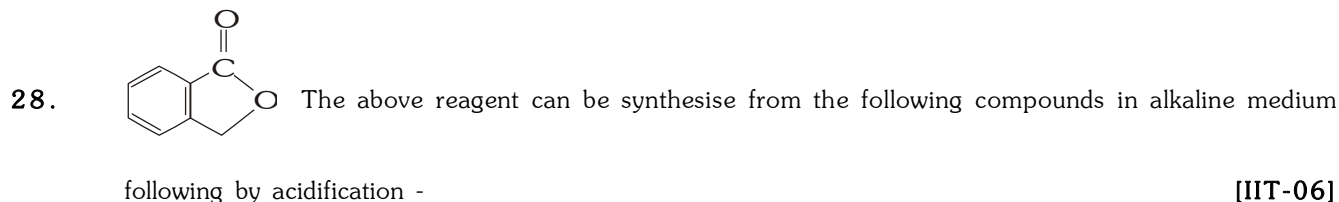


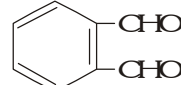
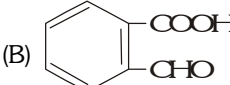
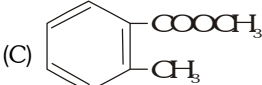
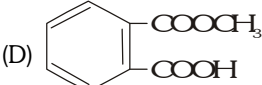
Following statements is/are correct about mixture :

- (A) mixture is 3-types of oximes (B) mixture is 2-types of oximes
 (C) all are optically active (D) one is optically active



- (A)  and $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ (B)  and $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$
 (C)  and $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ (D)  and $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$



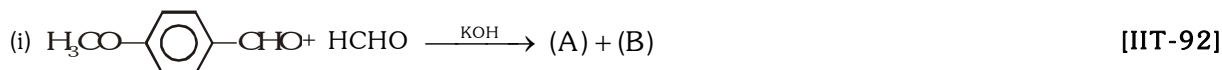
- (A)  (B)  (C)  (D) 

29. An unknown compound of carbon, hydrogen and oxygen contains 69.77% C and 11.63% H, and has a molecular weight of 86. It does not reduce Fehling solution but forms a bisulphate addition compound and gives a positive iodoform test. What are the possible structures ? [IIT-87]

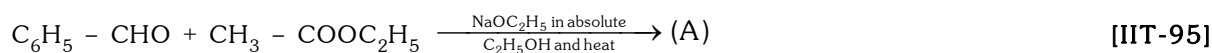
30. Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide. Why ? [IIT-91]

31. An organic compound 'A' on treatment with ethyl alcohol gives a carboxylic acid 'B' and compound 'C'. Hydrolysis of 'C' under acidic conditions gives 'B' and 'D'. Oxidation of 'D' with KMnO_4 also gives 'B'. 'B' on heating with Ca(OH)_2 gives 'E' ($\text{C}_3\text{H}_6\text{O}$). E does not give Tollen's test and does not reduce Fehling's solution but form a 2,4-dinitrophenyl hydrazone. Identify (A), (B), (C), (D) and (E). [IIT-92]

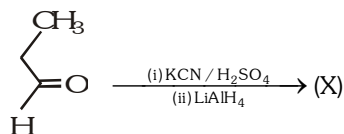
32. Complete the following :



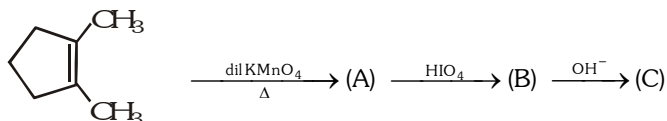
33. Complete the following :



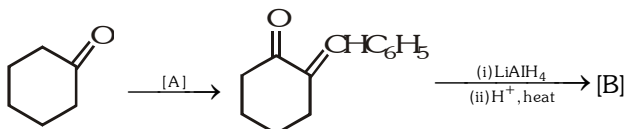
34. Complete the following reaction with appropriate structure : [IIT-96]



35. Suggest appropriate structures for the missing compounds. (The number of carbon atoms remains the same throughout the reactions). [IIT-96]

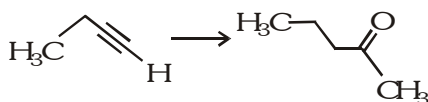


36. Complete the following : [IIT-98]



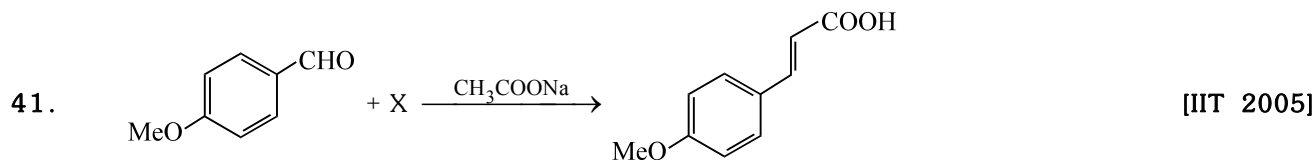
37. Compound 'A' ($\text{C}_8\text{H}_8\text{O}$) on treatment with $\text{NH}_2\text{OH} \cdot \text{HCl}$ gives 'B' and 'C'. 'B' and 'C' rearrange to give 'D' and 'E', respectively, on treatment with acid. B, C, D and E are all isomers of molecular formula ($\text{C}_8\text{H}_9\text{NO}$). When 'D' is boiled with alcoholic KOH an oil 'F' ($\text{C}_6\text{H}_7\text{N}$) separates out. 'F' reacts rapidly with CH_3COCl to give back 'D'. On the other hand, 'E' on boiling with alkali followed by acidification gives a white solid 'G' ($\text{C}_7\text{H}_6\text{O}_2$). Identify 'A' to 'G'. [IIT-99]

38. Carry out the following transformation in not more than three steps. [IIT-99]



39. An organic compound (A), $\text{C}_6\text{H}_{10}\text{O}$, on reaction with CH_3MgBr followed by acid treatment gives compound (B). The compound (B) on ozonolysis gives compound (C), which in presence of a base give 1-acetyl cyclopentene (D). The compound (B) on reaction with HBr gives compound (E). Write the structures of (A), (B), (C) and (E). Show how (D) is formed from (C). [IIT-2000]

40. An organic compound (A) reacts with H_2 to give (B) and (C) successively. On ozonolysis of (A), two aldehydes (D) $\text{C}_2\text{H}_4\text{O}$ and (E) $\text{C}_2\text{H}_2\text{O}_2$ are formed. On ozonolysis of (B) only propanal is formed. What are (A) to (E)? [IIT-01]

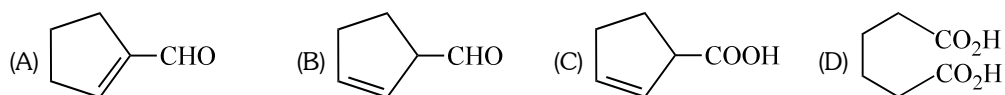


What is X?

- (A) CH_3COOH (B) BrCH_2COOH (C) $(\text{CH}_3\text{CO})_2\text{O}$ (D) $\text{CHO}-\text{COOH}$

42. 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 [JEE 2006]

43. 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 [JEE 2007]



44. **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.

[JEE 2007]

45. 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.

[JEE 2007]

Column I

(A) C_6H_5CHO

(B) $CH_3C\equiv CH$

(C) CN^-

(D) I^-

Column II

(P) gives precipitate with
2,4-dinitrophenylhydrazine

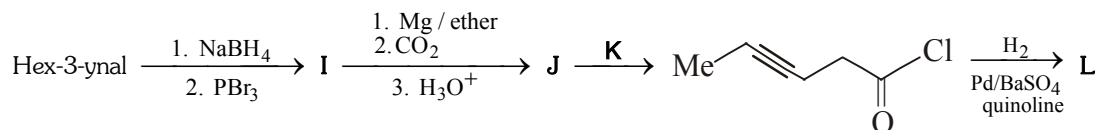
(Q) gives precipitate with $AgNO_3$

(R) is a nucleophile

(S) is involved in cyanohydrin formation

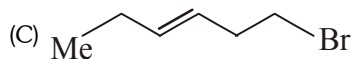
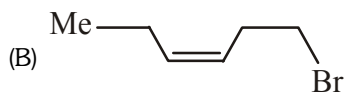
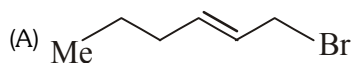
Paragraph for Question No. 46 to 48

In the following reaction sequence, products **I**, **J** and **L** are formed. **K** represents a reagent.



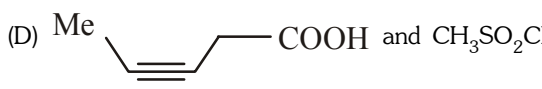
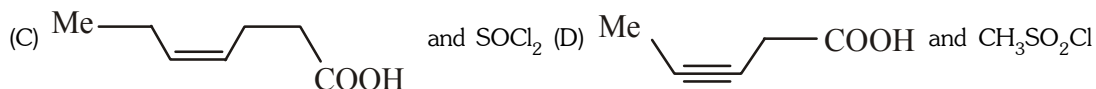
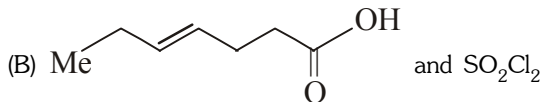
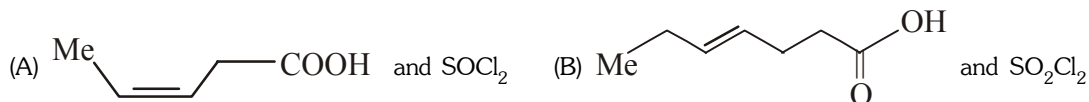
46. The structure of the product **I** is

[JEE 2008]



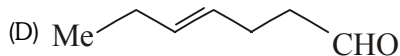
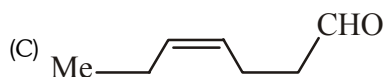
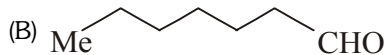
47. The structures of compounds **J** and **K**, respectively, are

[JEE 2008]



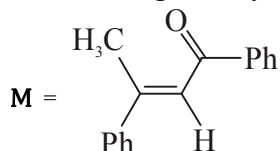
48. The structure of product **L** is

[JEE 2008]



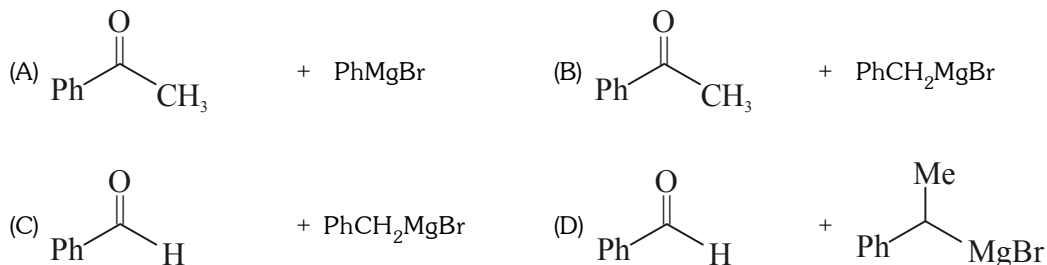
Paragraph for Question No. 49 to 51

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**.



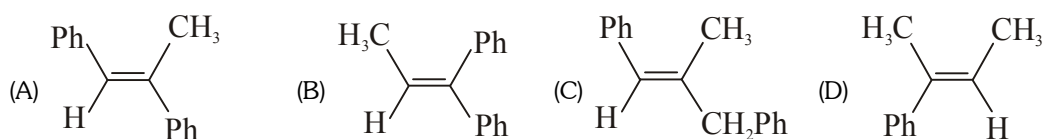
49. Compound **H** is formed by the reaction of

[JEE 2008]



50. The structure of compound **I** is

[JEE 2008]



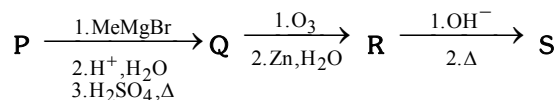
51. The structures of compounds **J**, **K** and **L**, respectively, are

[JEE 2008]

- (A) PhCOCH₃, PhCH₂COCH₃ and PhCH₂COO K⁺
 (B) PhCHO, PhCH₂CHO and PhCOO K⁺
 (C) PhCOCH₃, PhCH₂CHO and CH₃COO K⁺
 (D) PhCHO, PhCOCH₃ and PhCOO K⁺

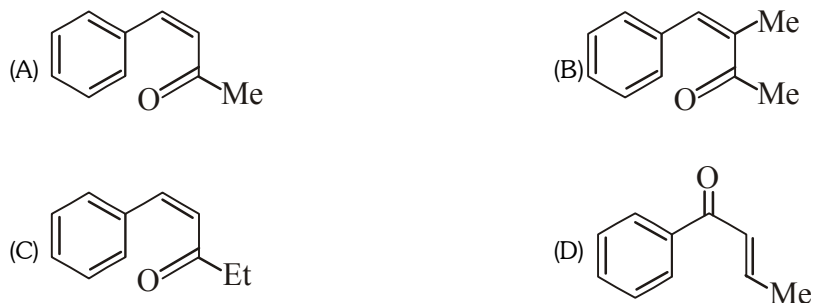
Paragraph for Question Nos. 52 to 54

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**.



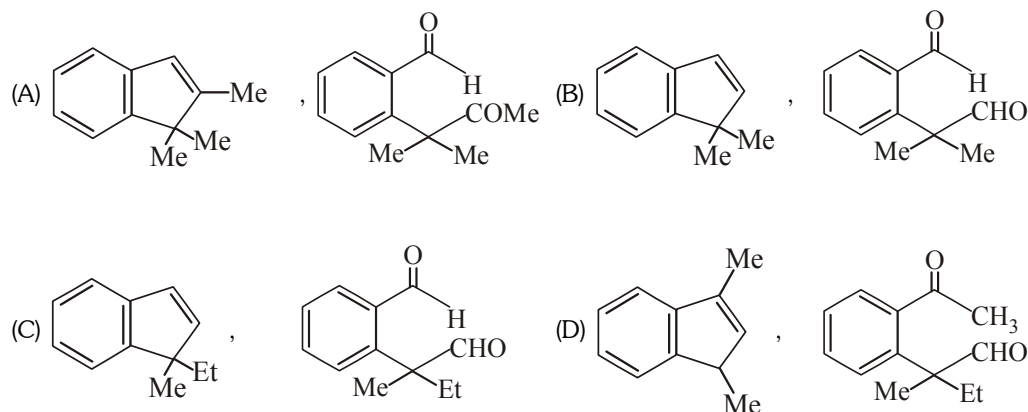
52. The structure of the carbonyl compound **P** is

[JEE 2009]



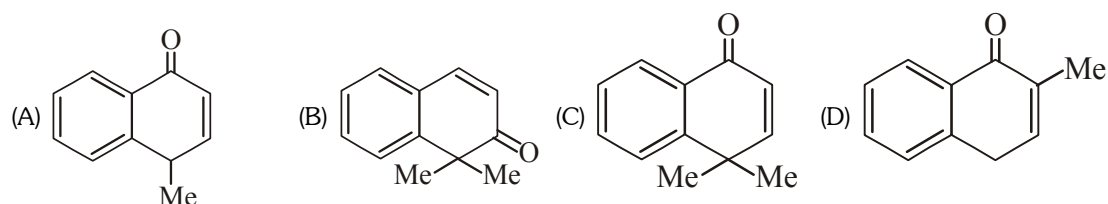
53. The structure of the products **Q** and **R**, respectively, are

[JEE 2009]



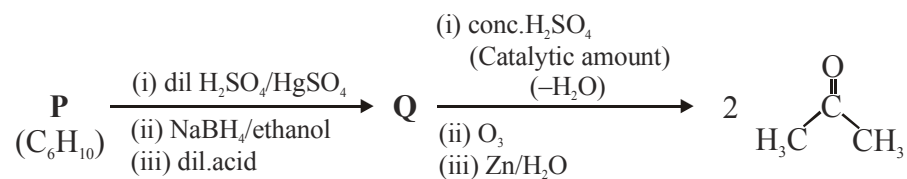
54. The structure of the product **S** is

[JEE 2009]



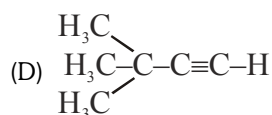
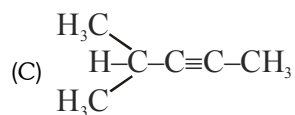
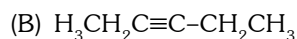
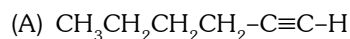
Paragraph for Questions Nos. 55 to 56

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.

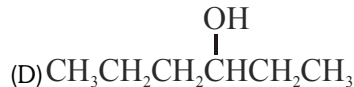
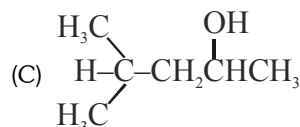
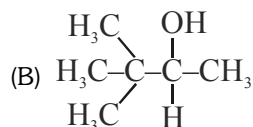
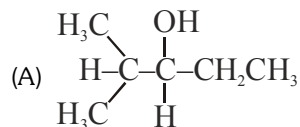


[JEE 2011]

55. The structure of compound **P** is -

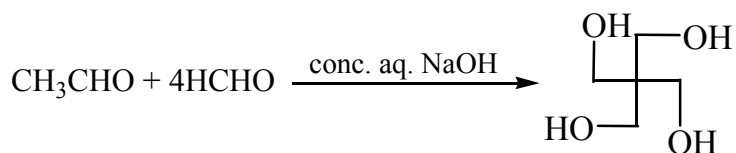


56. The structure of the compound **Q** is -



57. The number of aldol reaction(s) that occurs in the given transformation is

[JEE 2012]



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

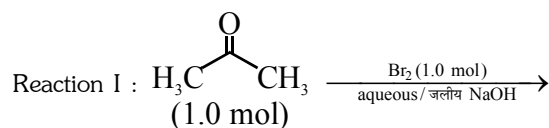
58. Among P, Q, R and S, the aromatic compound(s) is / are :

[JEE 2013]

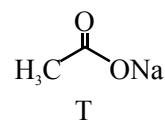
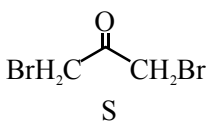
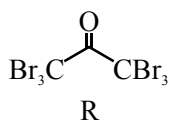
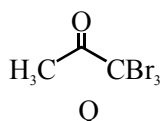
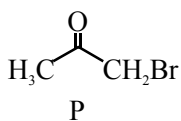
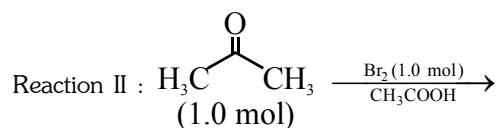


(A) P (B) Q (C) R (D) S

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



[JEE 2013]



- (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

PREVIOUS YEARS QUESTIONS				ANSWER KEY			EXERCISE -5	
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1. (B)	2. (A)	3. (D)	4.(B)	5. (C, D)	6. (D)	7.(A)	8. (B)	9. (A)
10. (A)	11. (D)	12. (B)	13. (A)	14. (A)	15. (C)	16. (B)	17. (C)	18. (B)
19. (B)	20. (A)	21. (A)	22. (A)	23. (C)	24. (D)	25. (A)	26. (A)	27. (C)

28. (A)

29. (i) For empirical formula

Element	%	Relative no. of atoms	Simplest ratio
C	69.77	5.76	5
H	11.63	11.63	10
O	19.20	1.2	1

∴ Empirical formula of compound is $C_5H_{10}O$.

and Empirical formula wt. = 86

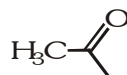
Also Molecular wt. = 86

∴ Molecular formula of compound is $C_5H_{10}O$.

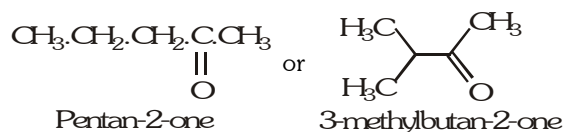
(ii) Compound form bisulphate addition compound and thus, has carbonyl group. i.e., aldehyde or ketone.

(iii) It does not reduce Fehling solution and thus, it is not aldehyde but it is ketone.

(iv) It gives positive iodoform test and thus, it has



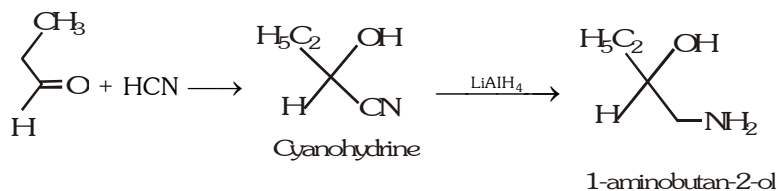
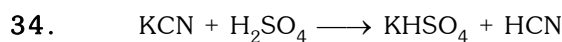
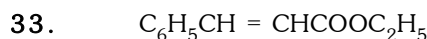
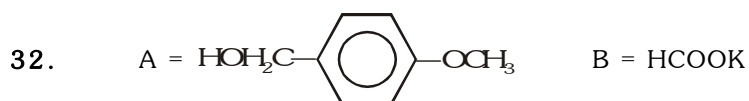
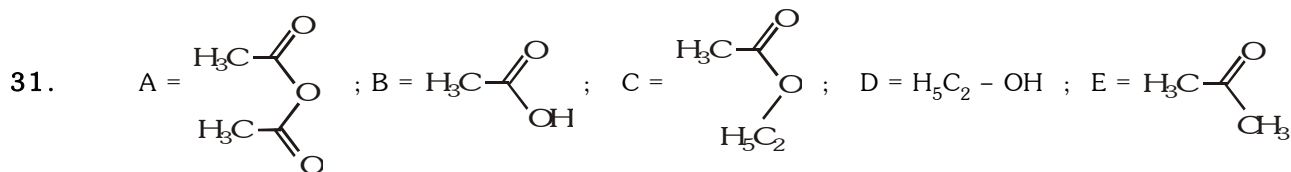
(v) Above facts reveals that compound is

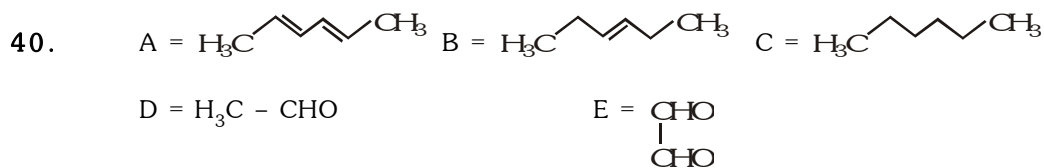
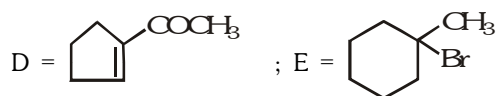
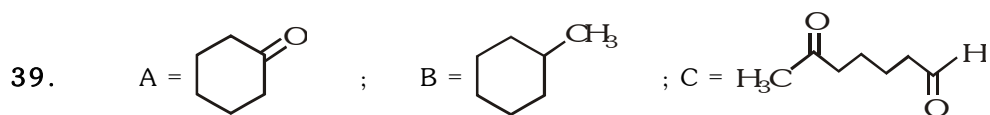
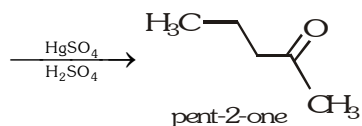
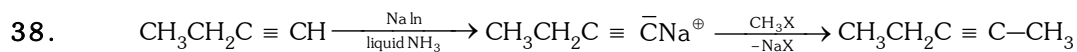
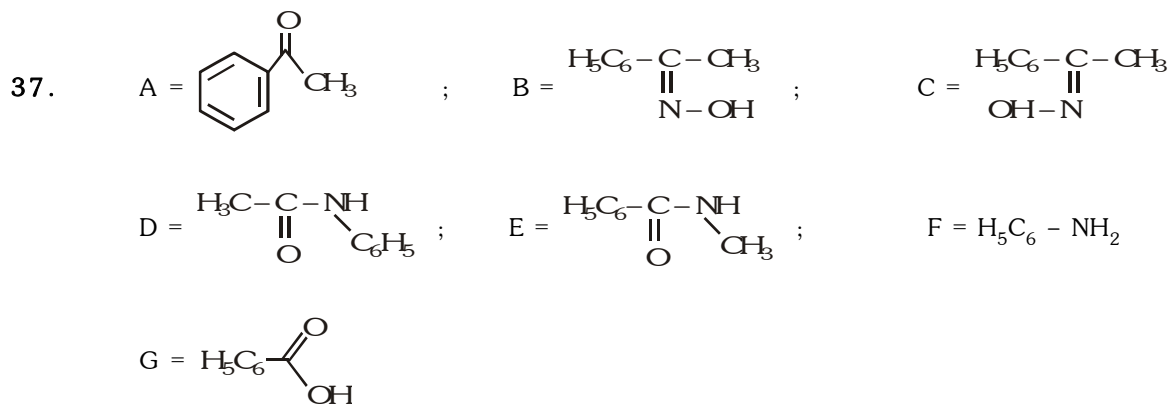
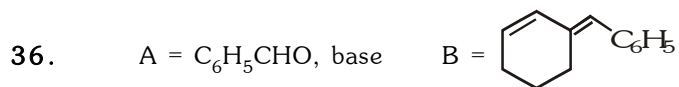
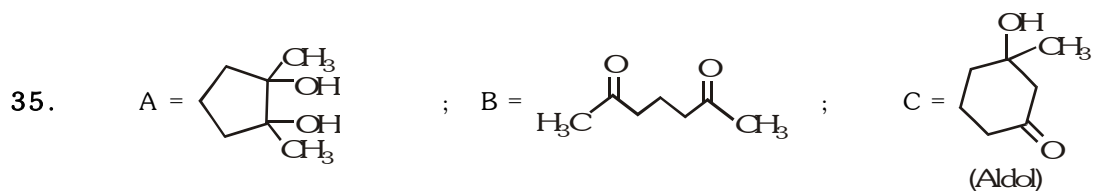


30. The formation of CHI_3 takes place as follows :



I^- cannot bring about this reaction. The active species is OI^- , OI^- is an oxidant and an iodinating agent.





41. C 42. B 43. A 44. C 45. (A) P, S; (B) Q; (C) Q, R, S; (D) Q, R
46. D 47. A 48. C 49. B 50. A 51. D 52. B
53. A 54. B 55. D 56. B 57. C 58. A, B, C, D 59. C