

**Solutions to HWS-4
Class Tests-3 & 4**

Reactions of Aldehydes & Ketones

I. Typical (Direct) Nucleophilic Addition :

1. Of Hydride ion (H^-) : LiAlH_4 / ether or NaBH_4 / H_2O
2. Of Alkynide ion ($\text{R}-\text{C}\equiv\text{C}^- \text{Na}^+$)
3. Of $\text{H}_2\text{O}/\text{H}^+$ (Hydration)
4. (a) Of ROH/H^+ (b) Of Glycols (c) Of 1,3 Diols
5. Of HCN/KOH
6. Of NaHSO_3 (Bisulphate addition)
7. Of Grignard Reagent
8. Of Ylides (Wittig Reaction)
9. Of Ammonia & its derivatives

(a) of ammonia	(b) of Amines (RNH_2 & RNHR)
(c) of special derivatives (NH_2Y)	(d) Reductive amination

II. Special Reactions :

1. Beckmann Rearrangement
2. Cannizzaro Reaction
3. Tischenko Reaction
4. Reformatsky Reaction
5. Benzoin Condensation

III. Aldol Reaction & Condensation

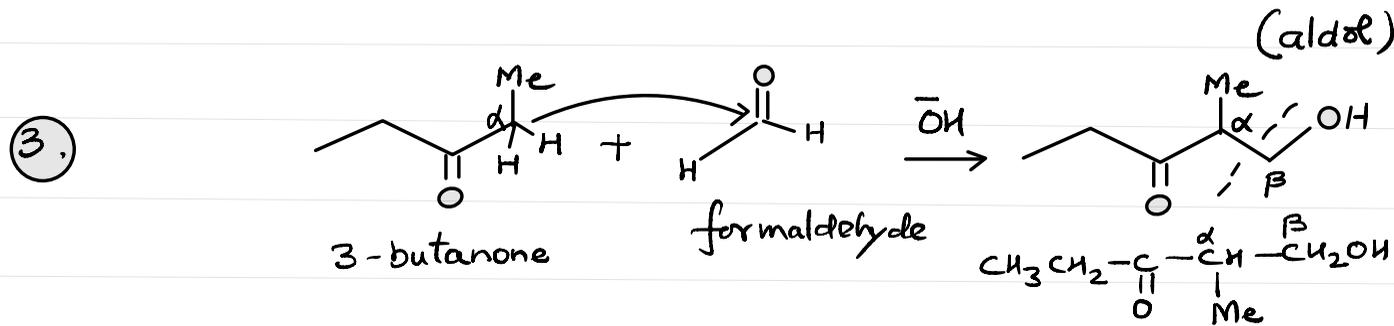
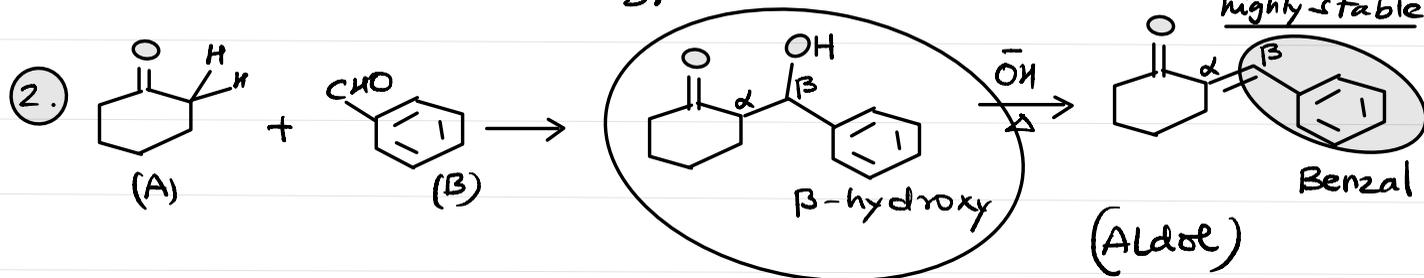
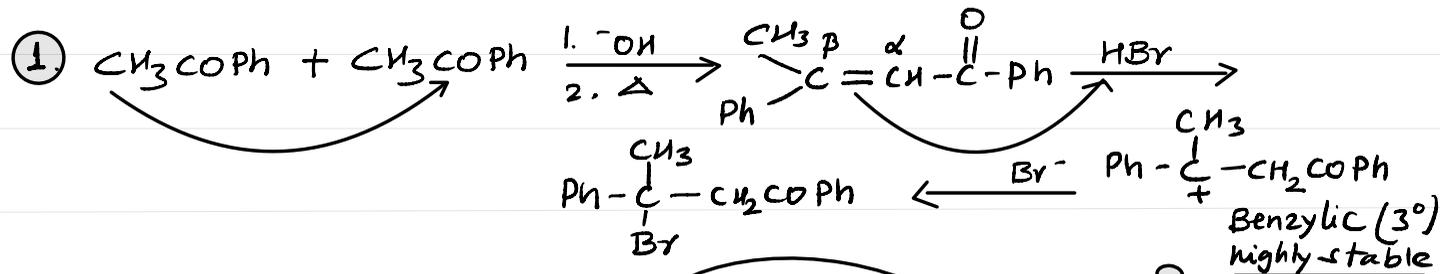
- (i) Self Aldol**
- (ii) Cross Aldol**
- (iii) Internal Aldol(Intramolecular)**

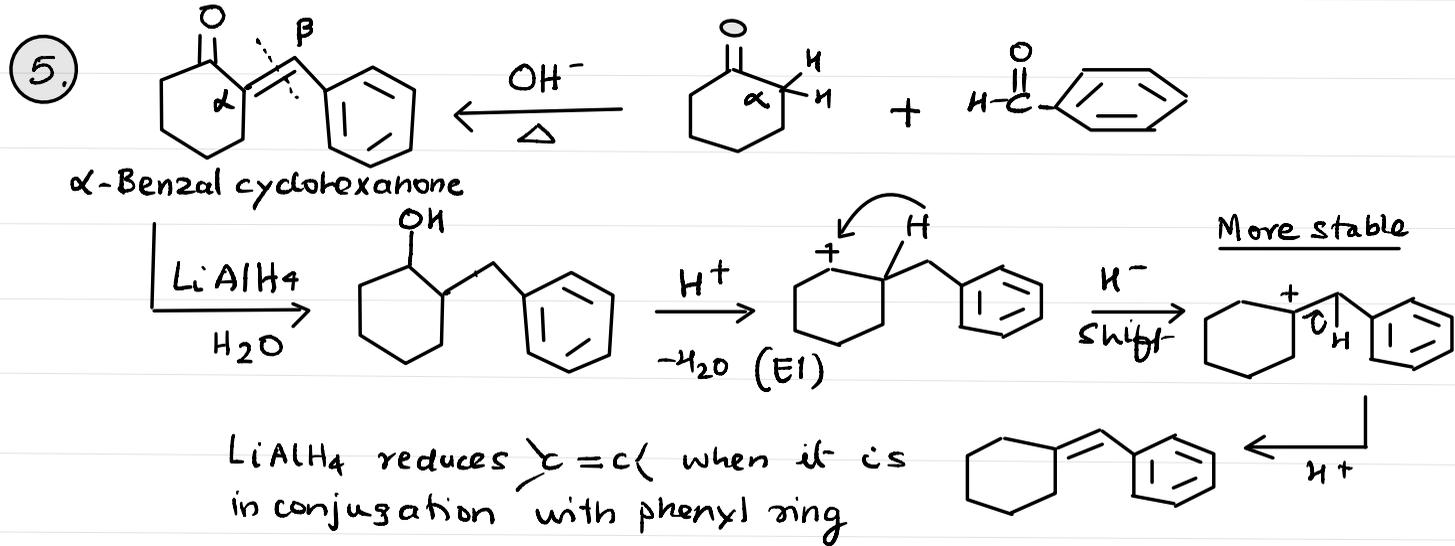
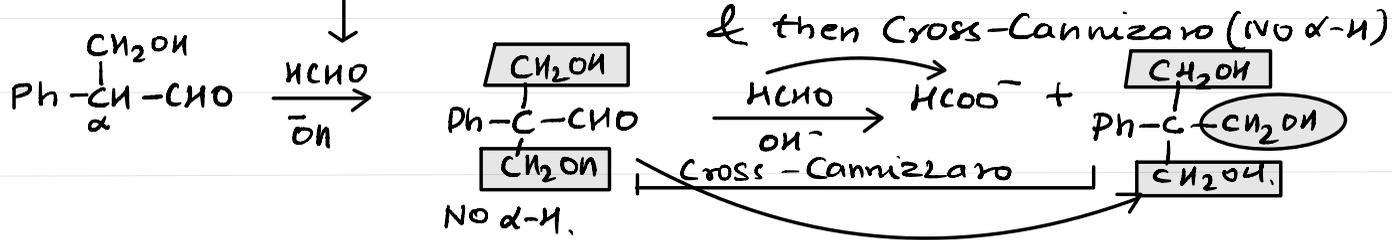
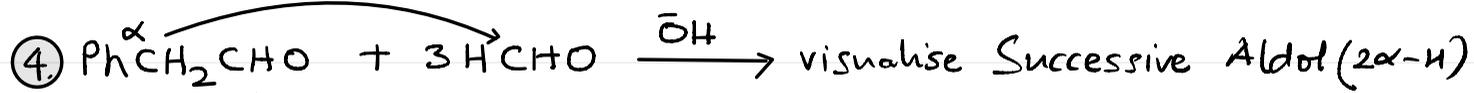
IV. Special Cross-Aldol type other Condensations

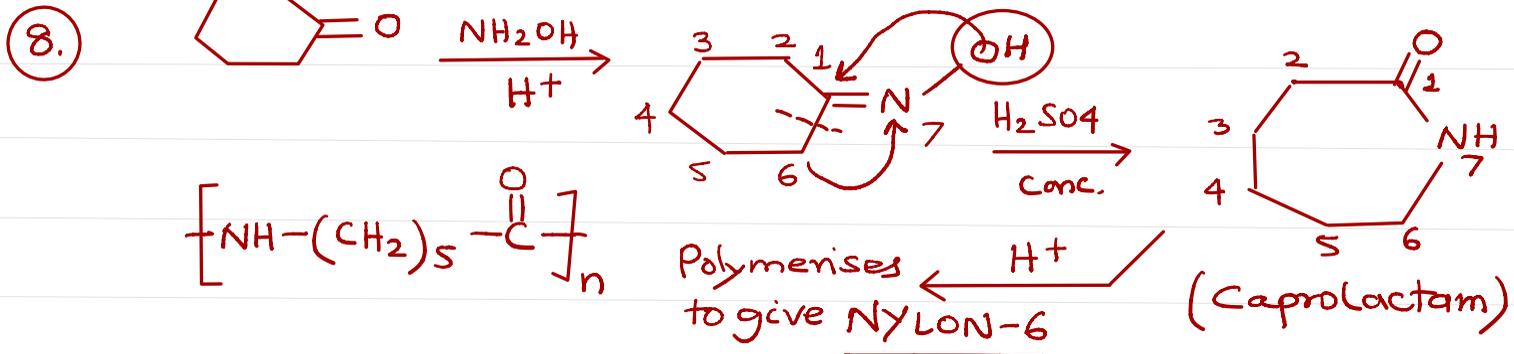
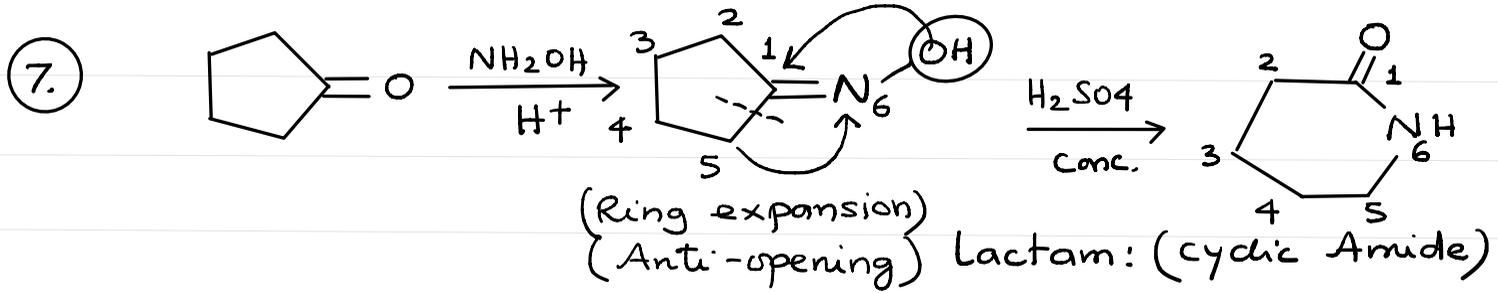
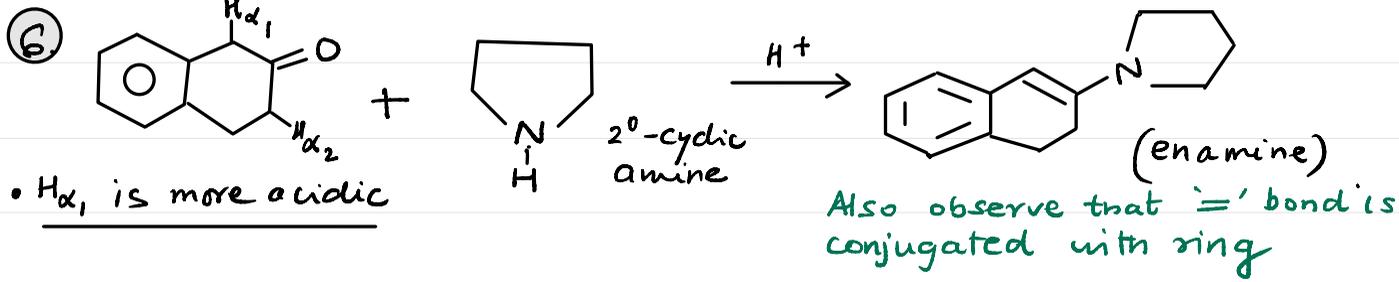
- 1. With Nitro-Alkanes**
- 2. With Alkyl Nitriles**
- 3. With Esters**
- 4. Perkin Condensation**
- 5. Knoevenagel Condensation**

V. Other Reactions

- 1. (a) With PCl_5**
 - (b) Chlorination & Bromination**
 - (c) Action of Heat on Keto Acids**
- 2. Reduction**
 - (a) Hydride Addition**
 - (b) Reductive Hydrolysis**
 - (c) Using Red P/HI**
 - (d) Clemmensen's Reduction**
 - (e) Wolf Kishner Reduction**
- 3. Oxidation**
 - (a) Simple Oxidation**
 - (b) Abnormal Oxidation**
 - (c) Oxidation using SeO_2**
 - (d) Baeyer Villiger Oxidation**



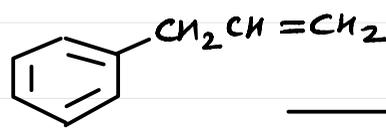
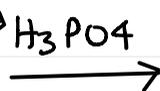




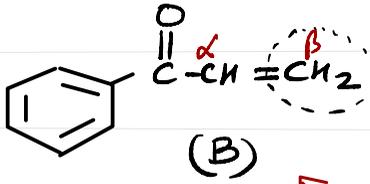
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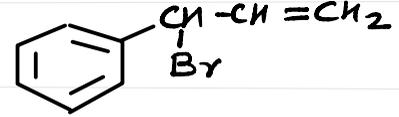
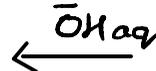
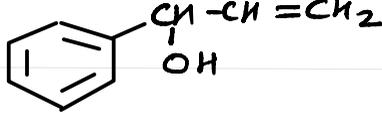
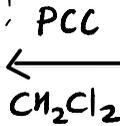
+ FC Alkylation



Allyl benzene

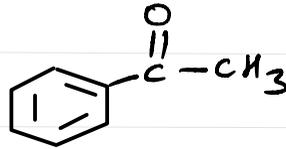
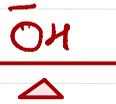


(B)



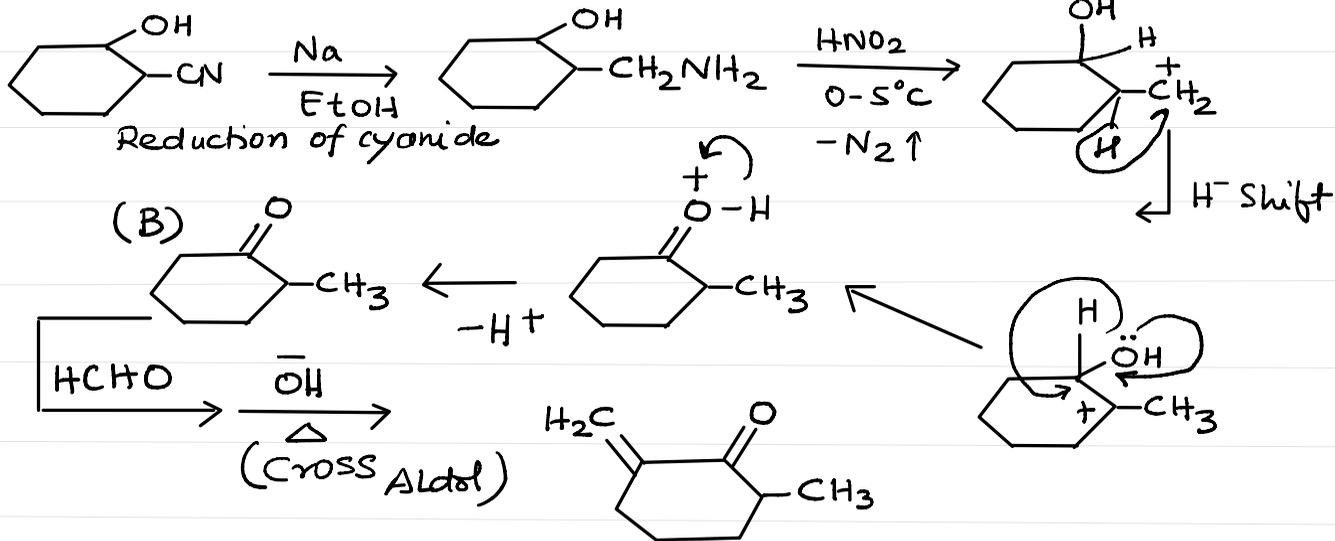
alpha-Methylene
acetophenone

10.

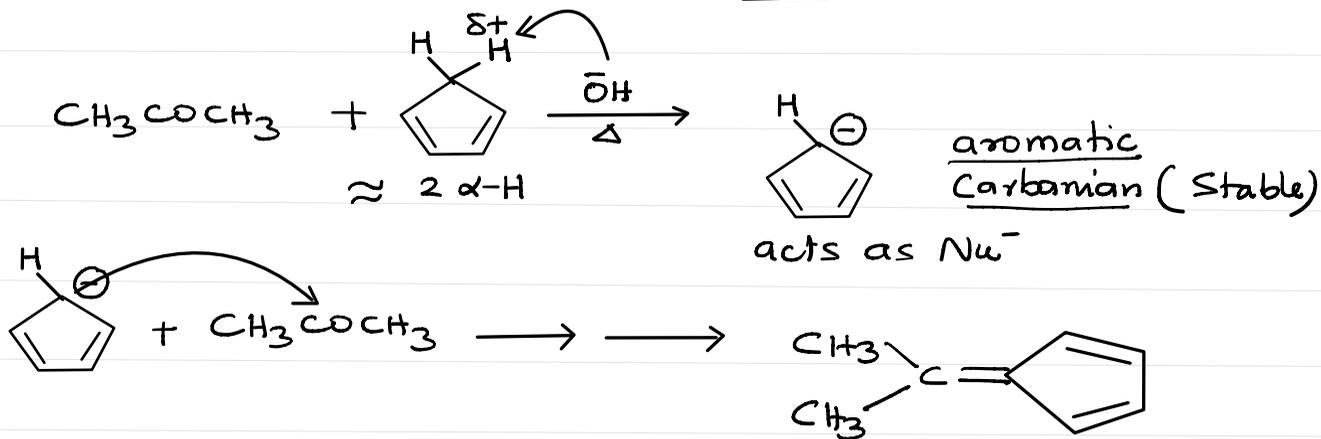


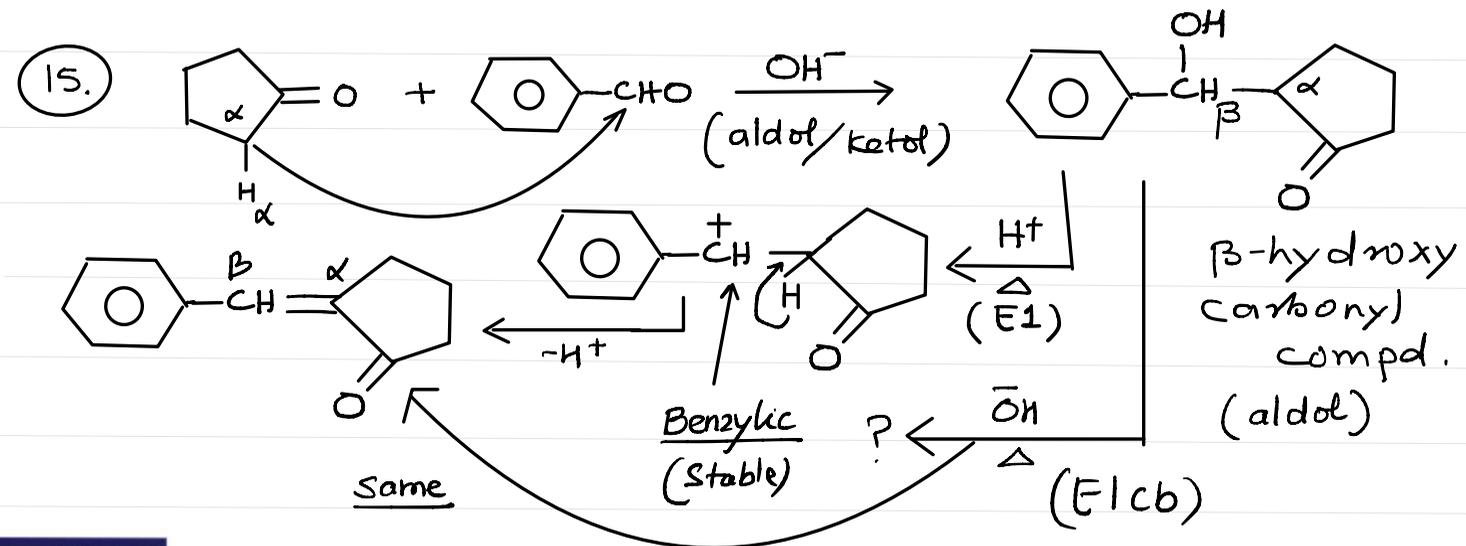
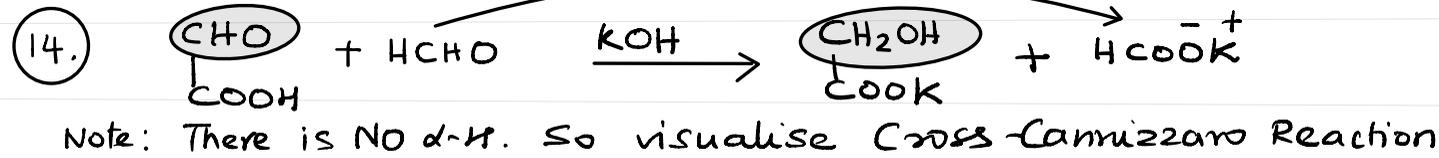
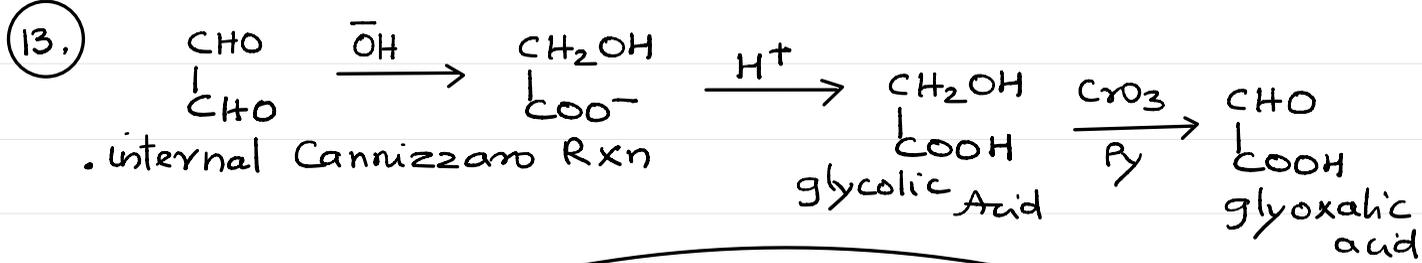
+ HCHO

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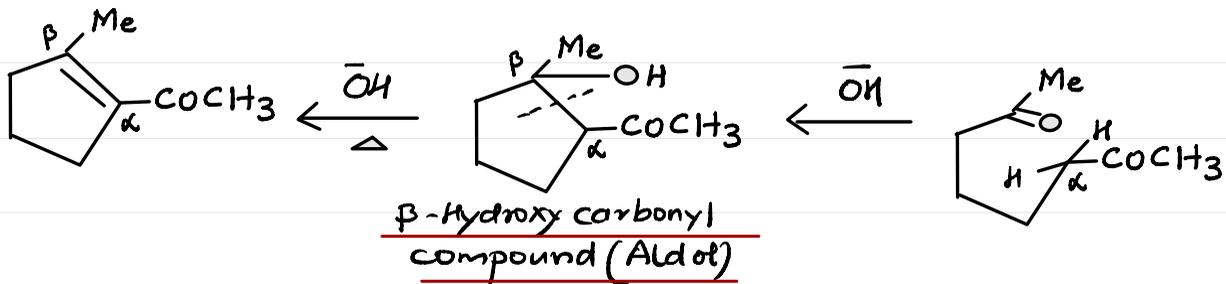


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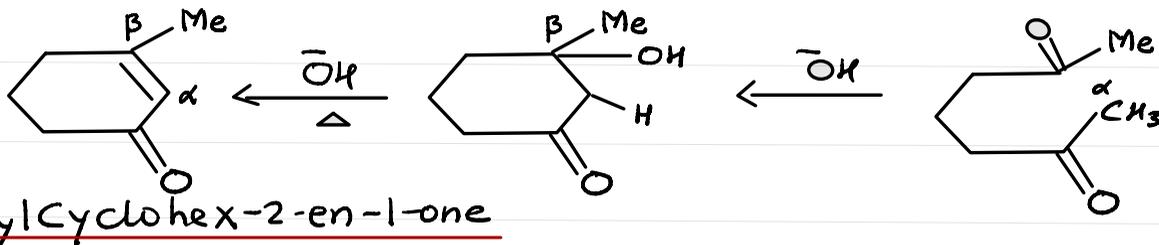




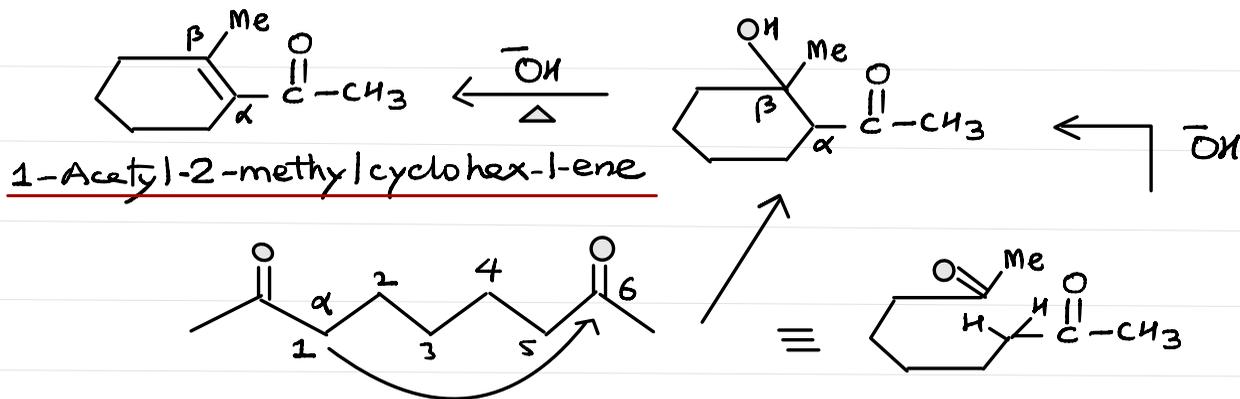
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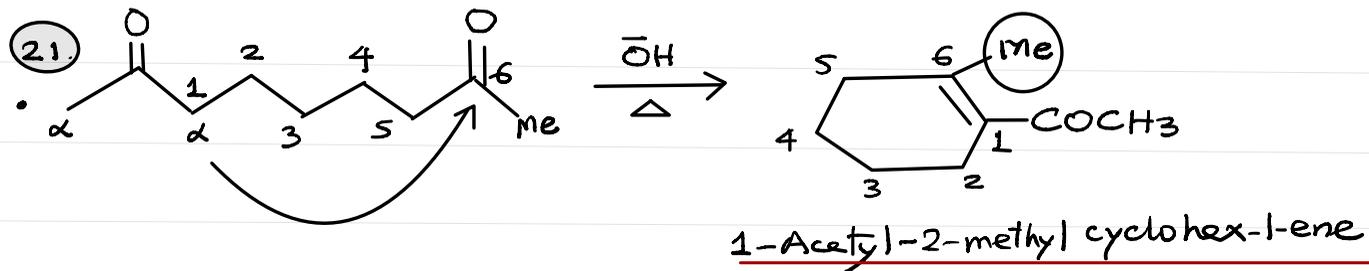
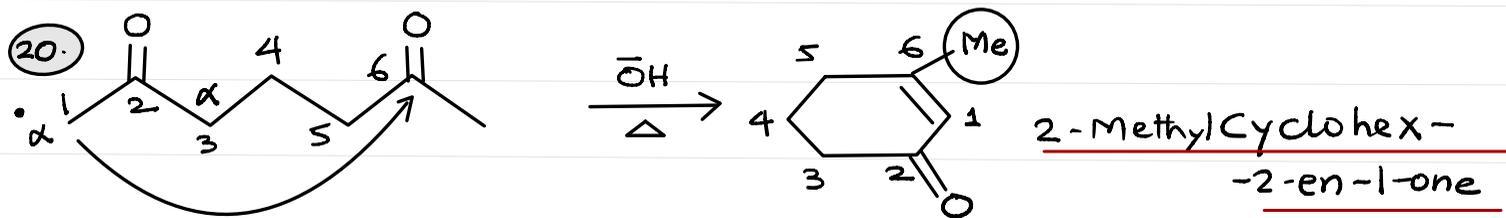
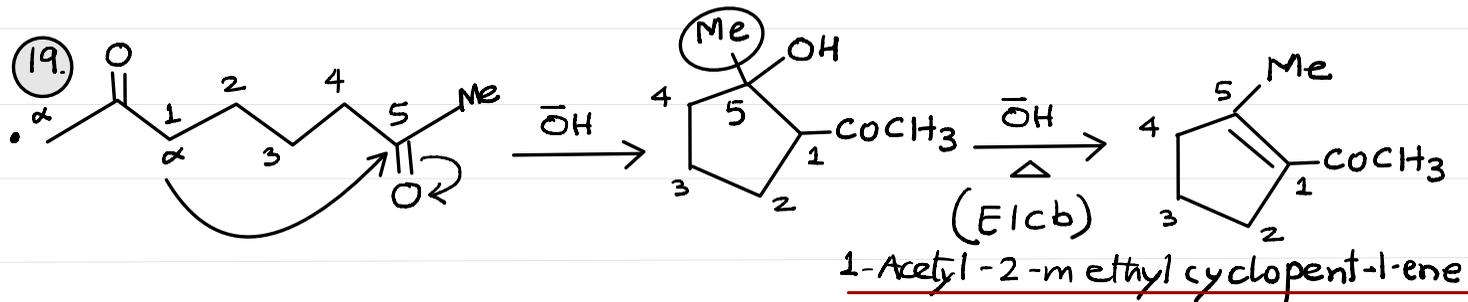


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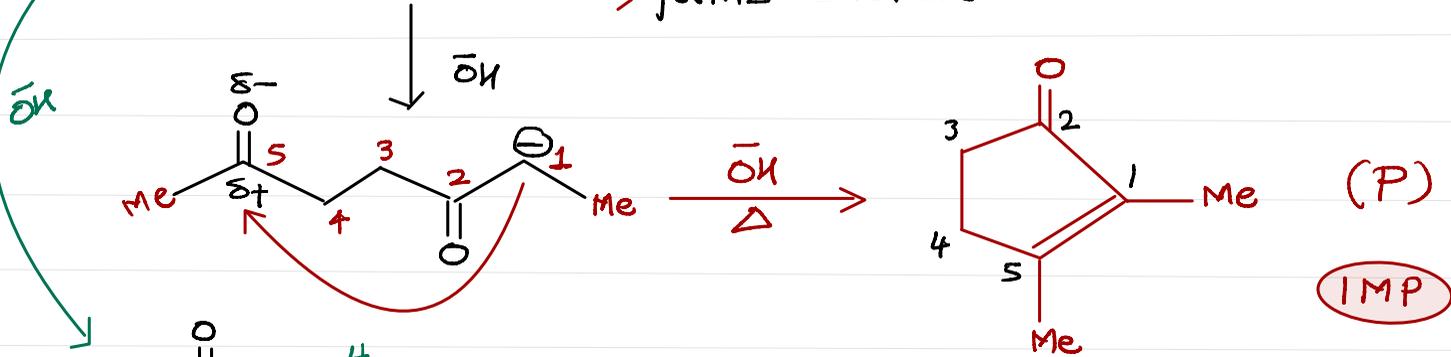
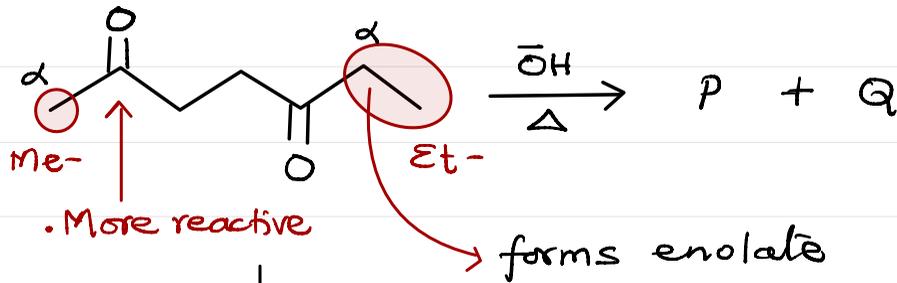


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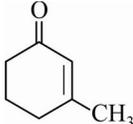


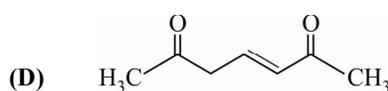
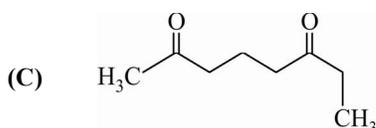
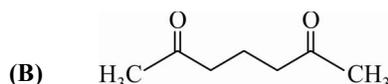
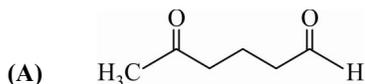


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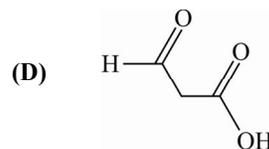
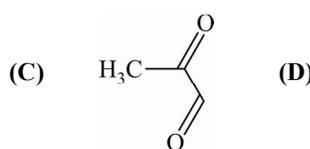
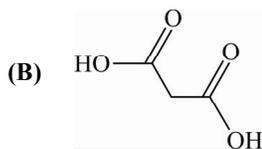
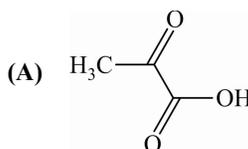
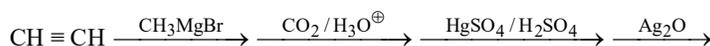


Choose the correct Alternatives for each of the following questions. Each Question has ONE correct Alternative, however those marked with (*) may have MORE THAN ONE correct Alternatives.

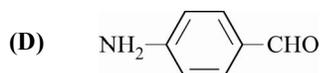
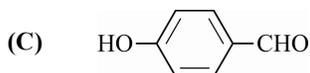
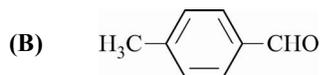
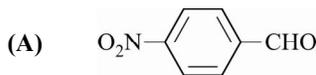
1.  is the final product obtained when one of the following is reacted with base :



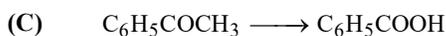
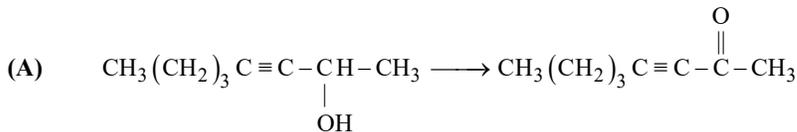
2. End product of the following sequence of reactions is :



3. In which of the following substrates, rate of Benzoin condensation will be maximum ?



- *4. Which of the following oxidation reaction(s) can be carried out with chromic acid in aqueous acetone at 5-10°C ?



- *5. $3\text{HCHO} + \text{CH}_3\text{CHO} \xrightarrow{\text{NaOH}} \text{P}$. Which of the following is/are true for P ?

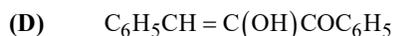
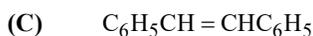
(A) Reduces Tollen's reagent

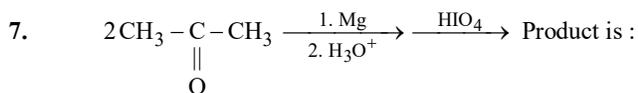
(B) Gives Cannizaro reaction

(C) Reacts with Na

(D) Gives green colour with $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$

6. Benzaldehyde on reaction with acetophenone in the presence of sodium hydroxide and heat gives :





- (A) $\text{H}_3\text{C} - \underset{\text{OH}}{\underset{|}{\text{C}}} - \underset{\text{OH}}{\underset{|}{\text{C}}} - \text{CH}_3$ (B) $\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3$
 (C) $\text{CH}_3 - \underset{\text{OH}}{\underset{|}{\text{CH}}} - \underset{\text{OH}}{\underset{|}{\text{CH}}} - \text{CH}_3$ (D) CH_3COOH

*8. Which of the following can undergo aldol condensation reaction ?

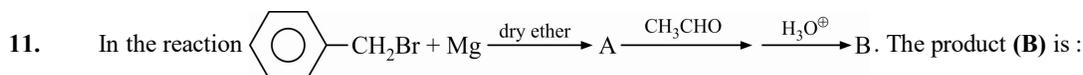
- (A) HCHO (B) CH_3CHO (C) $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ (D) $\text{CH}_3\text{CH}_2\text{CHO}$

*9. Cannizzaro reaction can be given by :

- (A) Trimethylacetaldehyde (B) Acetaldehyde
 (C) Benzaldehyde (D) Chloral

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

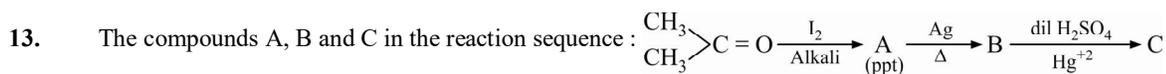
- (A) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_3$ (B) $\text{CH}_3\text{CH}_2\text{CD}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_3$
 (C) $\text{CH}_3\text{CH}_2\text{CH}(\text{OD})\text{CH}_2\text{CH}_2\text{CH}_3$ (D) $\text{CH}_3\text{CH}_2\text{CD}(\text{OD})\text{CH}_2\text{CH}_2\text{CH}_3$



- (A) $\text{CH}_3\text{CH}(\text{OH}) - \text{C}_6\text{H}_4 - \text{CH}_2\text{Br}$ (B) $\text{C}_6\text{H}_5 - \text{CH}_2\text{CH}(\text{OH})\text{CH}_3$
 (C) $\text{CH}_3\text{CH}(\text{OH}) - \text{C}_6\text{H}_4 - \text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ (D) $\text{CH}_2=\text{CH} - \text{C}_6\text{H}_4 - \text{CH}_2\text{Br}$

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



- (A) Iodoform, ethylene, ethyl alcohol (B) Iodoform, acetylene, acetaldehyde
 (C) Iodoform, acetylene, ethanol (D) Iodoform, 2-propanol, propanone

14. In the reaction sequence : $\text{RCOCl} + \text{H}_2 \xrightarrow{\text{Pd} + \text{BaSO}_4} \text{A} \xrightarrow{\text{KCN}} \text{B} \xrightarrow{\text{H}_3\text{O}^{\oplus}} \text{C}$. A, B and C are given by the set :

- (A) RCHO, $\text{RCH}(\text{OH})\text{CN}$, $\text{RCH}(\text{OH})\text{CH}_2\text{NH}_2$ (B) RCHO, $\text{RCH}(\text{OH})\text{CN}$, $\text{RCH}(\text{OH})\text{COOH}$
 (C) RCHO, $\text{R} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \underset{\text{CN}}{\underset{|}{\text{C}}} - \text{H}_2$, $\text{R} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_2 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{H}$ (D) RCHO, $\text{R} - \text{CH}_2 - \text{CN}$, $\text{R} - \text{CH}_2 - \text{COOH}$

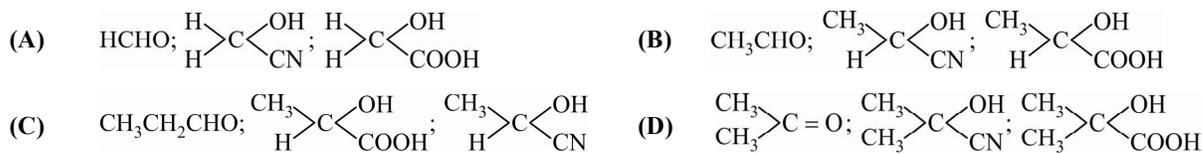
15. Oxidation of 2-methyl propane-1, 2-diol with periodic acid gives :

- (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 and with a methyl side chain. The compound is :

- (A) Acetaldehyde (B) Propionaldehyde (C) Acetone (D) 3-Pentanone

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. The compound 'A', 'B' and 'C' are :

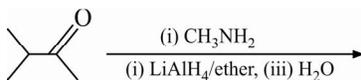


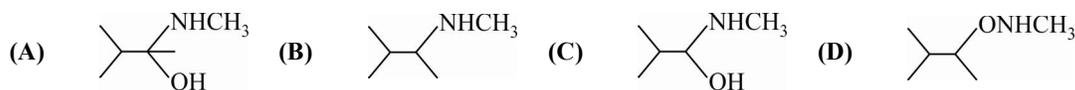
*18. In which of the following reactions aldehydes and ketones react similarly ?

- (A) Reaction with phenyl hydrazine (B) Reaction with hydroxylamine
(C) Reaction with semicarbazide (D) Reaction with silver nitrate mixed with ammonia

*19. Cyanohydrin of the following compound on hydrolysis gives optically active product :

- (A) Cyclohexanone (B) CH_3CHO (C) CH_3COCH_3 (D) $\text{C}_6\text{H}_5\text{CHO}$

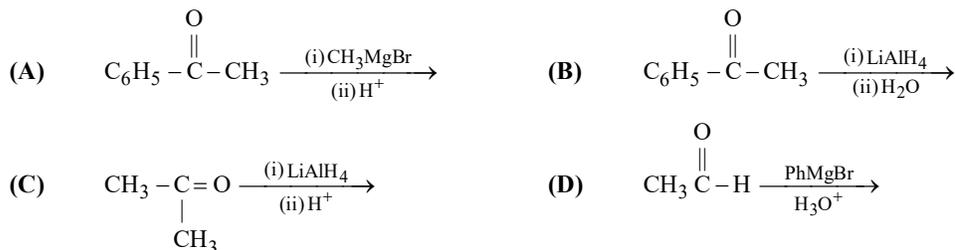
20. The major organic product formed in given reaction is : 



*21. Which of the following compound(s) give orange precipitate with 2, 4-dinitro phenyl hydrazine ?

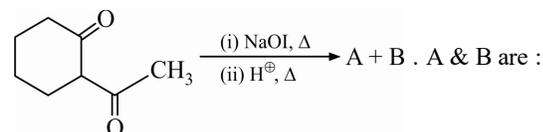
- (A) CH_3COCH_3 (B) $\text{CH}_2=\text{CHOH}$ (C) HCHO (D) CH_3COCl

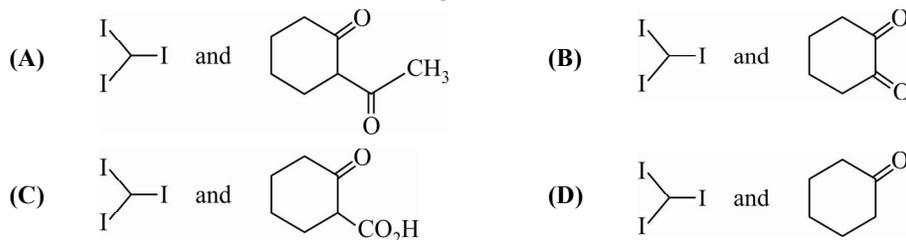
*22. Which of the following reaction leads to the formation of secondary alcohol ?



*23. Which of the following compound(s) will react with NaHSO_3 ?

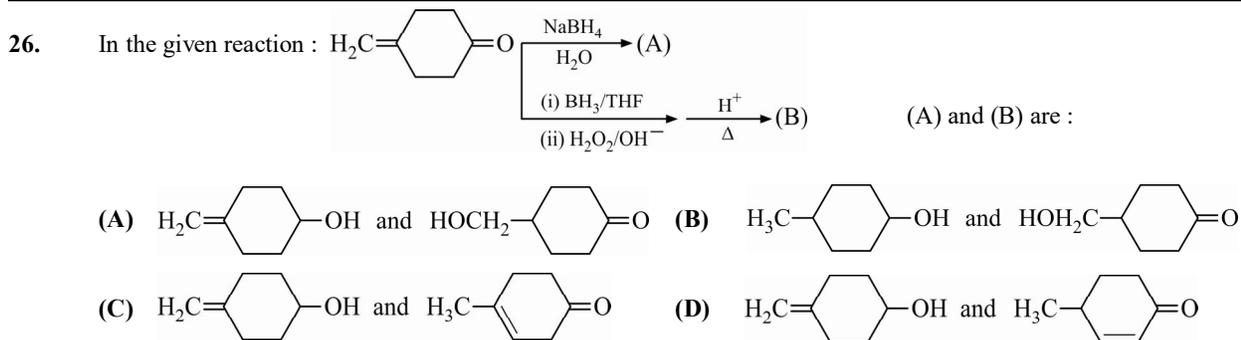
- (A) CH_3CHO (B) $(\text{CH}_3)_2\text{CHCO}-\text{CH}_2\text{CH}_2\text{CH}_3$
(C) $\text{CH}_3-\text{COCH}_3$ (D) HCHO

24. End products of the reaction is :  . A & B are :

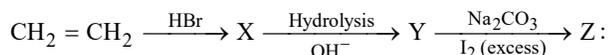


*25. Which of the following compound(s) on treatment with LiAlH_4 will give a product that will give positive iodoform test?

- (A) $\text{CH}_3\text{CH}_2\text{CHO}$ (B) $\text{CH}_3\text{COOC}_2\text{H}_5$
(C) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ (D) CH_3COCH_3



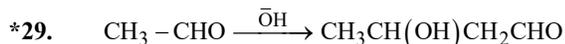
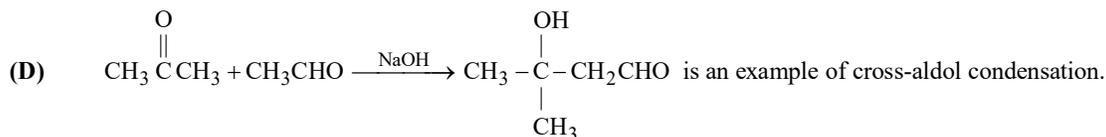
*27. Which of the given compound(s) will be formed in the following sequence of reaction ?



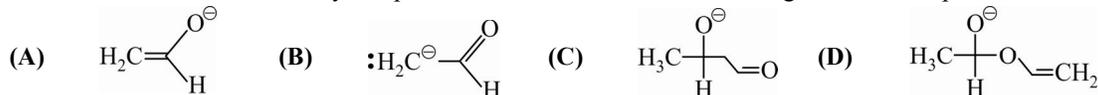
- (A) $\text{C}_2\text{H}_5\text{Br}$ (B) $\text{C}_2\text{H}_5\text{OH}$ (C) CHI_3 (D) CH_3CHO

*28. Which of the following statement(s) is/are correct ?

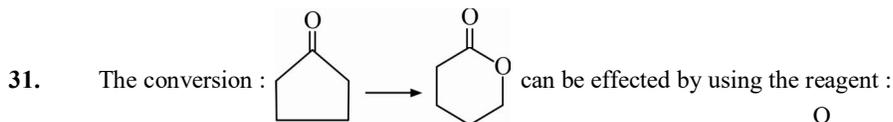
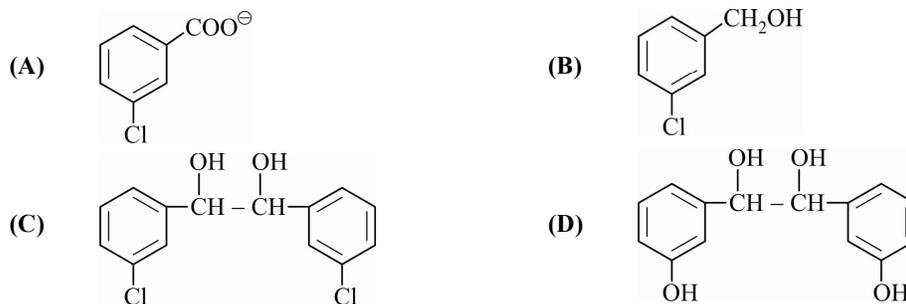
- (A) Benzaldehyde reduces Tollen's reagent.
 (B) $\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CHO} \xrightarrow{\text{NaOH}} \text{C}_6\text{H}_5\text{CH} = \text{CHC}_6\text{H}_5 + \text{O}_2$ is Claisen-Schmidt reaction.
 (C) Formaldehyde reduces Fehling's solution.



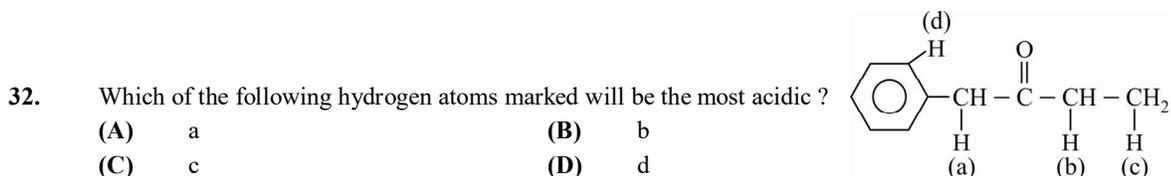
In the condensation of acetaldehyde represented above, which of the following intermediate species are obtained ?



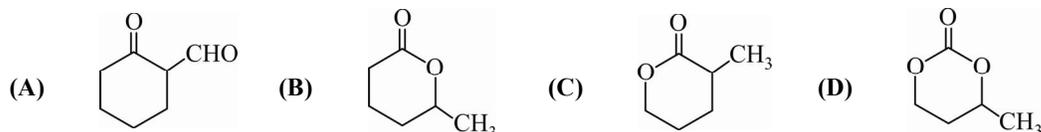
*30. When m-Chlorobenzaldehyde is treated with 50% KOH solution, the product obtained is (are) :



- (A) $\text{H}_2\text{O}, \text{H}_2\text{SO}_4$ (B) O_2 (C) $\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}\text{OOH}$ (D) $\text{CrO}_3, \text{H}_2\text{SO}_4$



33. 2-Methylcyclopentanone is allowed to react with m-Cpba. The major product formed in the reaction is :



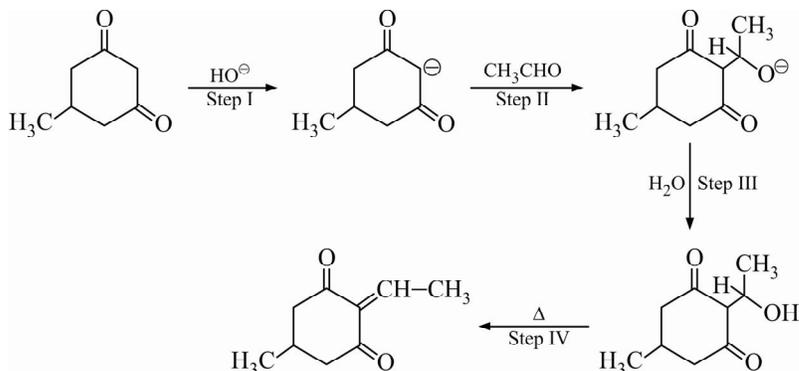
ASSERTION & REASON QUESTION :

These question 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

34. **Statement I :** Benzaldehyde does not undergo aldol condensation.
Statement II : Benzaldehyde does not contains acidic α -Hydrogen.
35. **Statement I :** Rate of addition of HCN on carbonyl compounds increases in presence of NaCN.
Statement II : Reaction involved the addition of CN^- in rate determining step.
36. **Statement I :** Fehling's solution can be used to distinguish benzaldehyde from acetaldehyde.
Statement II : Both benzaldehyde and acetaldehyde reduces Tollen's reagent.
37. **Statement I :** 2, 2-dimethyl propanal undergoes Cannizaro reaction with concentrated NaOH.
Statement II : Cannizaro reaction is a disproportionation reaction.
38. **Statement I :** In formaldehyde all four atoms are in same plane.
Statement II : The carbon atom in formaldehyde is sp^2 hybridised.

*39. Consider the following sequence :



Which of following statement(s) is/are correct for reaction sequence ?

- (A) Step I is acid-base reaction
 (B) Step II is nucleophilic addition reaction
 (C) Step III is acid-base reaction
 (D) Step IV is E1-cb elimination reaction
40. Which of the benzaldehyde(s) is most reactive towards KCN/H^+ ?

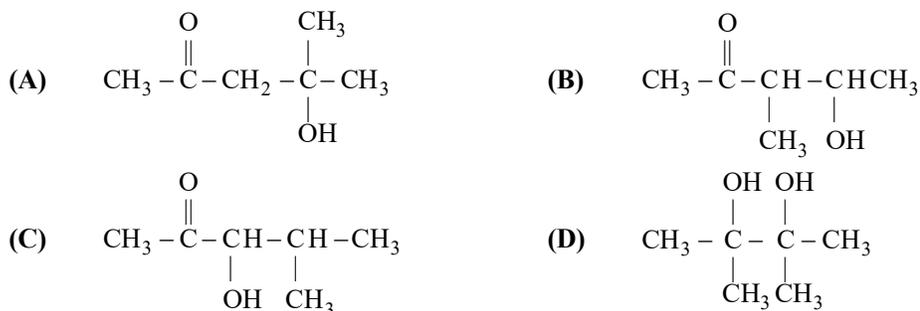


ANSWER KEY FOR CLASS TEST-3
ALDEHYDES & KETONES

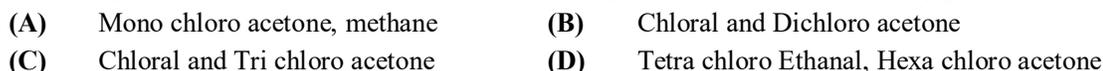
1	2	3	4	5	6	7	8	9	10
B	B	A	ABD	ABCD	A	B	BCD	AC	C
11	12	13	14	15	16	17	18	19	20
B	B	B	B	B	C	B	ABC	BD	B
21	22	23	24	25	26	27	28	29	30
ABC	BCD	ACD	D	BD	C	ABC	ACD	ABC	AB
31	32	33	34	35	36	37	38	39	40
C	A	B	A	A	B	B	A	ABCD	D

For each question choose the correct alternative Only One choice is correct. However, questions marked with '*' may have More than One correct option :

1. Which of the products is formed when acetone reacts with barium hydroxide solution ?



2. Acetaldehyde and Acetone on reaction with chlorine in presence of NaOH respectively gives :



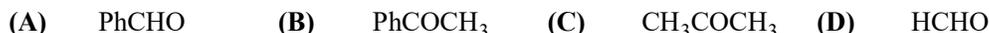
3. An organic compound readily undergoes Cannizzaro reaction but does not react with Fehling's solution is :



- *4. An organic compound give haloform test but does not react with Tollen's reagent is(are) :



- *5. An organic compound gives 2, 4-DNP test but does not react with Fehling's solution is(are) :



- *6. Aldol condensation can occur between :



7. The reagent which gives the same reduction product with propionaldehyde and acetone is :



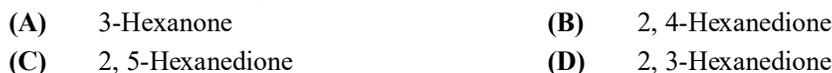
- *8. Which of the following can undergo aldol formation ?

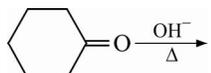
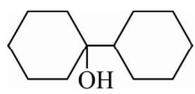
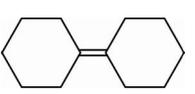
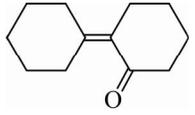
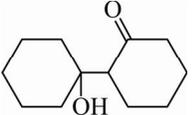


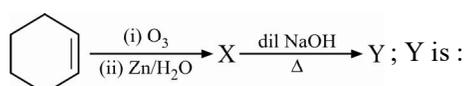
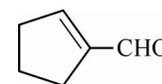
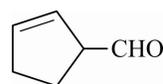
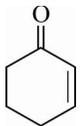
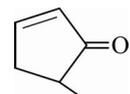
- *9. Which of the following gives Tollen's test ?

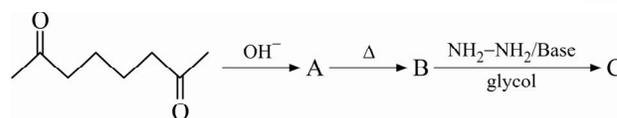
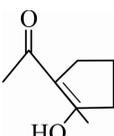
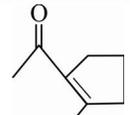
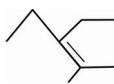
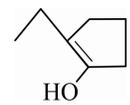


10. Which of the following has the most acidic hydrogen ?



11. Identify the product of the following condensation reaction : 
- (A)  (B)  (C)  (D) 
12. On oxidation by permanganate solution, $(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}_2-\text{CHO}$ gives :
- (A) $(\text{CH}_3)_2\text{CO}$ and $\text{OHC}-\text{CH}_2-\text{CHO}$ (B) $(\text{CH}_3)_2-\text{C}(\text{OH})-\text{CH}(\text{OH})-\text{CH}_2-\text{CHO}$
 (C) $(\text{CH}_3)_2\text{CO}$ and $\text{OHC}-\text{CH}_2-\text{COOH}$ (D) $(\text{CH}_3)_2\text{CO}$ and $\text{CH}_2(\text{COOH})_2$
13. 4-heptanone $\xrightarrow{\text{KMnO}_4/\text{H}^+/\Delta}$ A + B. Identify A and B :
- (A) Ethanoic acid pentanoic acid (B) Ethanal and butanone
 (C) Butanoic acid and propanoic acid (D) Acetic acid and pentanoic acid

14.  ; Y is :
- (A)  (B)  (C)  (D) 

15. Identify C in the following : 
- (A)  (B)  (C)  (D) 

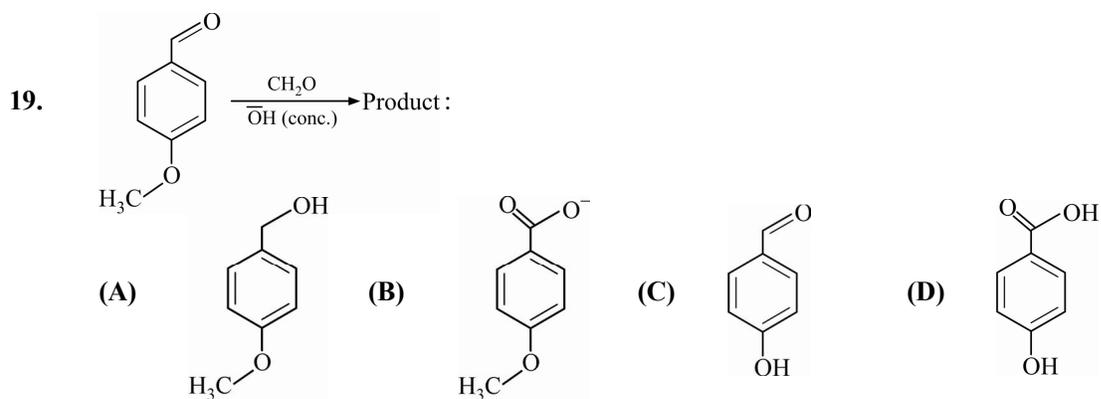
16. $\text{---CHO} + \text{X} \xrightarrow[\text{KOH}]{\text{conc.}}$ $\text{---CH}_2\text{OH} + \text{HCOOK}$. X is :
- (A) Formic acid (B) Formaldehyde (C) Acetaldehyde (D) Methanol
17. Aldol condensation between which of the following compounds followed by dehydration gives methyl vinyl ketone ?
- (A) Formaldehyde and acetone (B) Formaldehyde and acetaldehyde
 (C) Two molecules of acetaldehyde (D) Two molecules of acetone

18. Match the following columns : (Identify x, y, z, w)

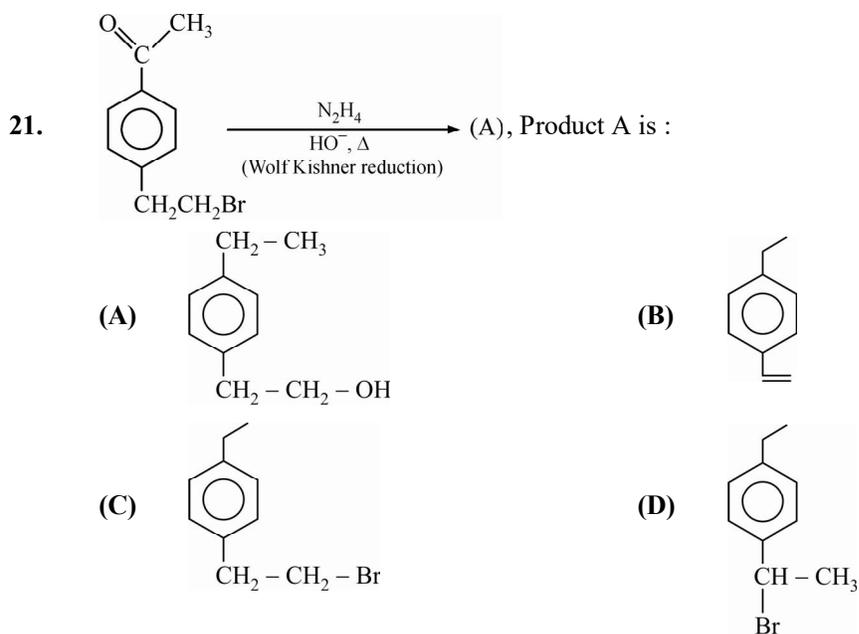
Column I		Column II	
(P)	$\text{PhMgBr} + (\text{x}) \xrightarrow{\text{H}^+} 1^\circ \text{ alcohol}$	1	Formaldehyde
(Q)	$\text{PhMgBr} + (\text{y}) \xrightarrow{\text{H}^+} 2^\circ \text{ alcohol}$	2	Propanaldehyde
(R)	$\text{PhMgBr} + (\text{z}) \xrightarrow{\text{H}^+} 3^\circ \text{ alcohol}$	3	Acetone
(S)	$\text{PhMgBr} + (\text{w}) \xrightarrow{\text{H}^+} \text{Benzene}$	4	Ethyl alcohol

Codes

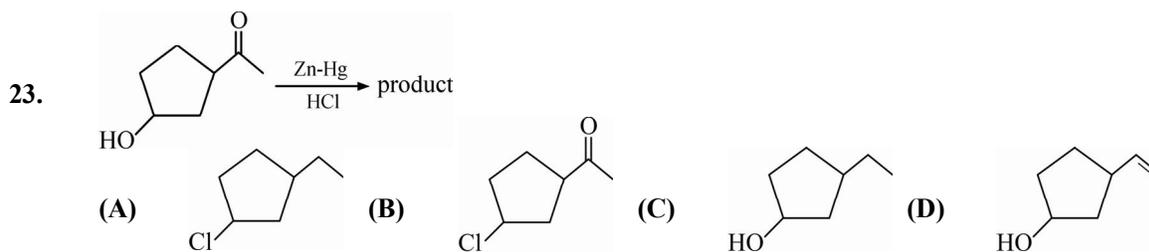
	P	Q	R	S		P	Q	R	S
(A)	1	2	4	3	(B)	1	4	2	3
(C)	1	3	2	4	(D)	1	2	3	4



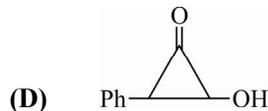
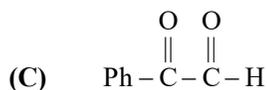
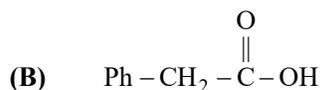
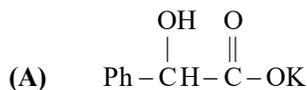
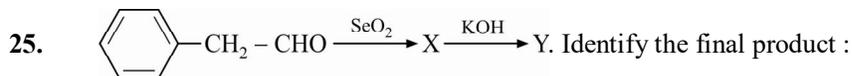
20. The synthesis of crotonaldehyde from acetaldehyde is an example of.... reaction :
- (A) Nucleophilic addition (B) Elimination
(C) Electrophilic addition (D) Nucleophilic addition – elimination



22. $A + B \xrightarrow{\text{dil OH}^-} \text{Ph} - \text{CH} = \text{CH} - \text{CO} - \text{CH}_3$. Identify A and B in the given reaction :
- (A) Acetophenone, Acetone (B) Acetophenone, Benzaldehyde
(C) Acetone, Benzaldehyde (D) Acetaldehyde, Benzoic acid



- *24. Which statement about the aldol condensation is correct ?
- (A) A Lewis acid is commonly used as a catalyst
(B) The initial step is the formation of a carbanion
(C) A new carbon-carbon bond is formed
(D) The last step involves E1cB



Statement Type Questions

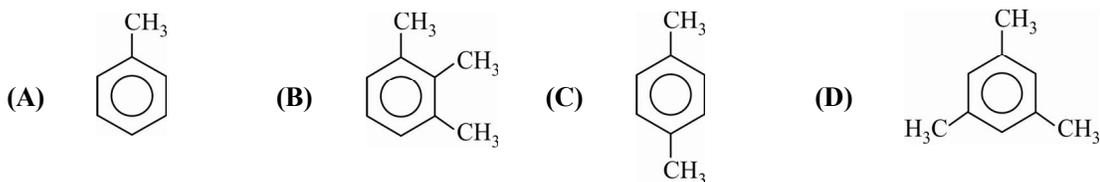
- (A) Both the statements are true and statement-II is the correct explanation of statement I.
 (B) Both the statements are true but statement-II is not the correct explanation of statement I.
 (C) Statement-I is true but statement-II is false.
 (D) Statement-I is false but statement-II is true.
26. **Statement-I :** Crossed Cannizzaro reaction between formaldehyde and benzaldehyde gives benzyl alcohol and formate ion.
Statement-II : Formaldehyde is a better hydride donor than benzaldehyde.
27. **Statement-I :** The addition of ammonia derivatives on carbonyl compound is carried in weakly acidic medium.
Statement-II : In weakly acidic medium attacking Nucleophile is also protonated.
28. **Statement-I :** Fehling's reagent is a test for all aliphatic aldehydes.
Statement-II : Aliphatic aldehydes can be easily oxidised even with mild oxidising agents.
29. **Statement-I :** Formaldehyde is a polar molecule.
Statement-II : Carbon atom in formaldehyde is sp^2 -hybridized.
30. **Statement-I :** Nitromethane can give aldol condensation.
Statement-II : α -hydrogen of nitromethane is acidic.
31. **Statement-I :** Lower aldehydes and ketones are soluble in water. The solubility decreases as the molecular mass increases.
Statement-II : Distinction between aldehydes and ketones can be made by Tollen's reagent.
32. **Statement-I :** The solubility of aldehydes and ketones in water decreases with increase of size of alkyl group.
Statement-II : Alkyl groups are electron releasing groups.
33. **Statement-I :** The B.P's aldehydes and ketones are higher than those of ethers of comparable molecular masses.
Statement-II : Aldehydes and ketones undergo intermolecular association due to dipole-dipole interactions.
34. During formation of trihalo ketone, which halogen is introduced most easily ?
 (A) First (B) Second (C) Third (D) All at the same rate

41. Match the reactions given in Column I with the suitable reagents given in Column II.

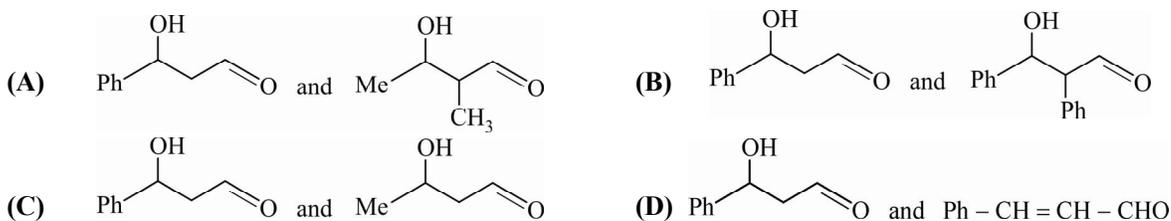
Name of the reaction		Reagent used	
(P)	Benzophenone → Diphenylmethane	I	LiAlH ₄
(Q)	Benzaldehyde → 1-Phenylethanol	II	DIBAL-H
(R)	Cyclohexanone → Cyclohexanol	III	Zn(Hg)/ Conc. HCl
(S)	Phehyl benzoate → Benzaldehyde	IV	CH ₃ MgBr

Codes

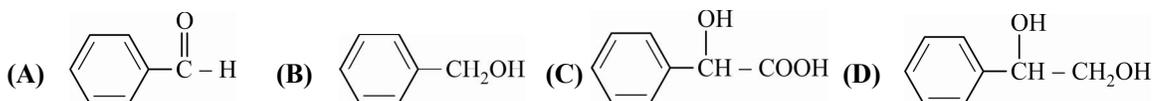
- (A) P → III, Q → IV, R → I, S → II (B) P → IV, Q → III, R → I, S → II
 (C) P → I, Q → IV, R → III, S → II (D) P → III, Q → IV, R → II, S → I
42. $(\text{CH}_3)_2\text{C} = \text{CHCOCH}_3 \xrightarrow[\text{HCl}]{(\text{CH}_3)_2\text{CO}}$ 'X'. Here 'X' is :
 (A) Mesityl oxide (B) Phorone (C) Acetic acid (D) Mesitylene
43. Acetone is distilled with concentrated H₂SO₄. The resultant product obtained is :



44. The product obtained by reaction of PhCHO & MeCHO in basic medium and on base catalysed heating is



45. In the reaction $\text{C}_6\text{H}_5\text{COCHO} \xrightarrow{\text{NaOH}/200^\circ\text{C}} \xrightarrow{\text{H}^+/\text{H}_2\text{O}}$ the major product is :



ANSWER KEY FOR CLASS TEST-4/Aldehydes & Ketones (Review Test)

1	2	3	4	5	6	7	8	9	10
A	C	C	ABC	ABC	ABC	D	ACD	ABCD	B
11	12	13	14	15	16	17	18	19	20
C	D	C	A	C	B	A	D	A	D
21	22	23	24	25	26	27	28	29	30
B	C	A	BCD	A	A	C	A	B	A
31	32	33	34	35	36	37	38	39	40
B	B	A	C	B	A	C	C	B	A
41	42	43	44	45					
A	B	D	D	C					

A wooden clothespin is attached to a piece of light-colored paper with a red and blue striped border. The paper is pinned to a dark wooden surface. The words "THANK YOU" are written in a bold, black, sans-serif font on the paper.

THANK YOU