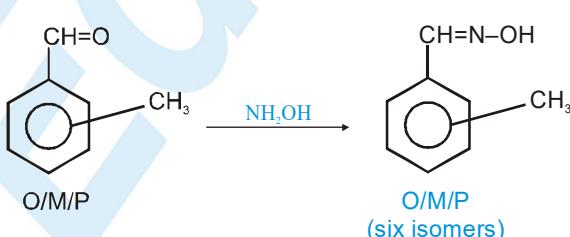
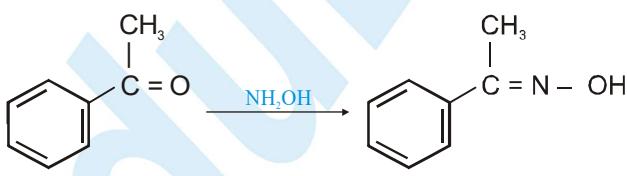
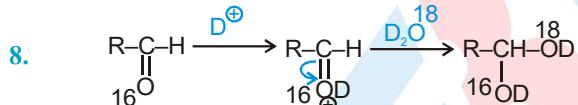
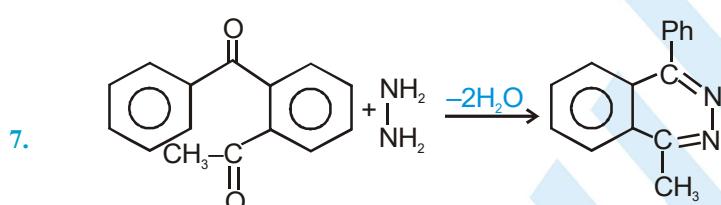
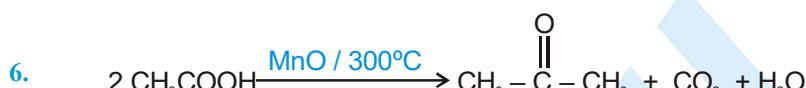
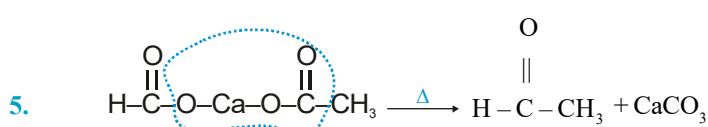
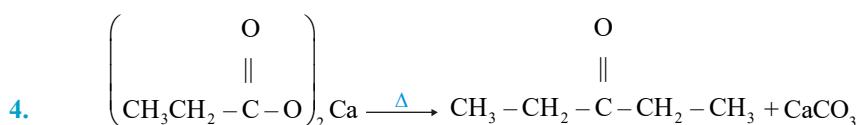
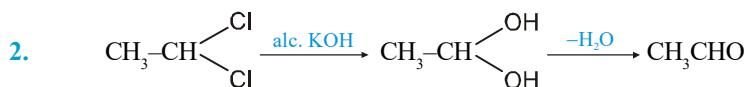
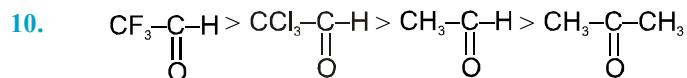


HINTS & SOLUTIONS

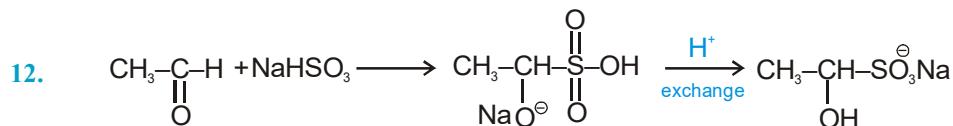
EXERCISE - 1

Single Choice



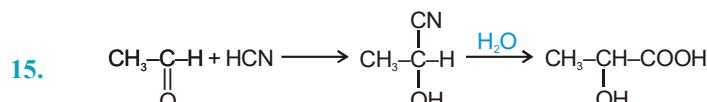


11. $-\text{I}$ and $-\text{M}$ group increase electrophilicity on $-\text{CHO}$ group so rate of addition reaction increase and also increases equilibrium constant.

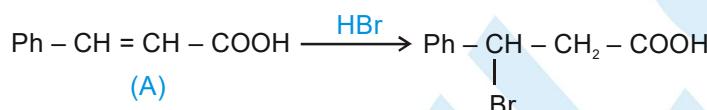


13. It is protection of carbonyl compound.

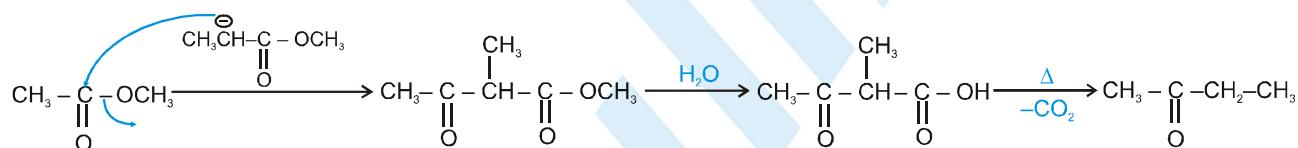
14. As the positive charge decreases and steric hindrance increases on carbonyl group the rate of nucleophilic addition reaction decreases.



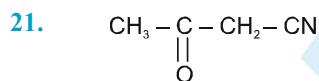
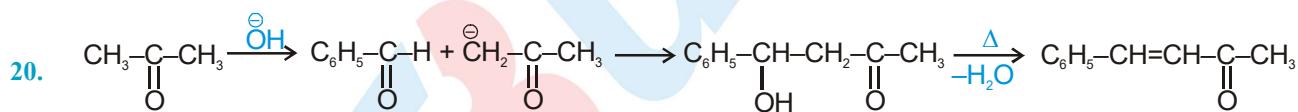
16. Perkin reaction



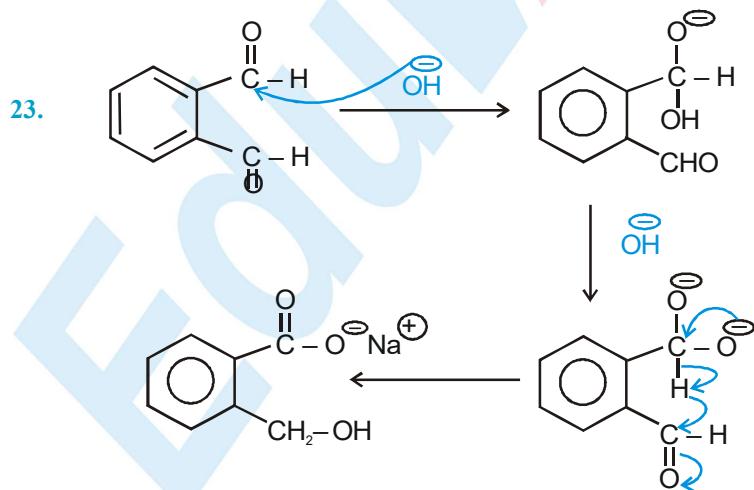
17.

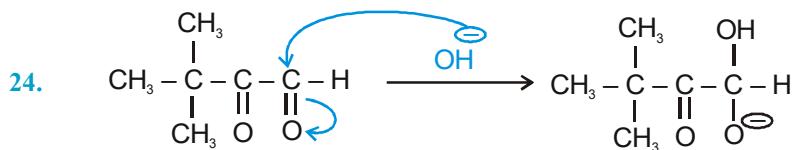


18. Compound which have α -hydrogen gives aldol condensation reaction.

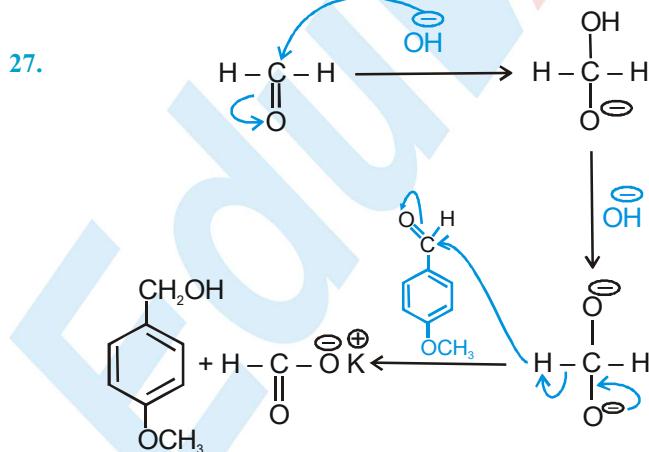
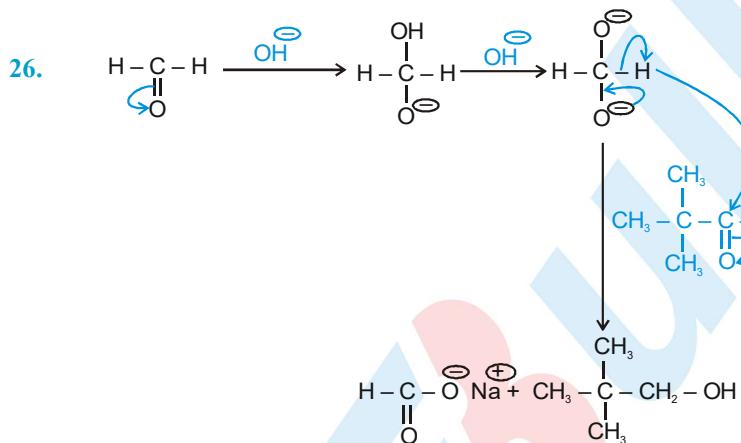


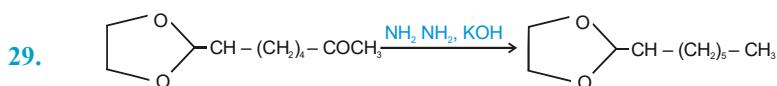
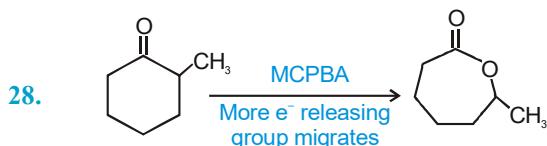
22. Dioxide anion is a better hydride donor, and presence of $-\text{OCH}_3$ group further increases the electron density.





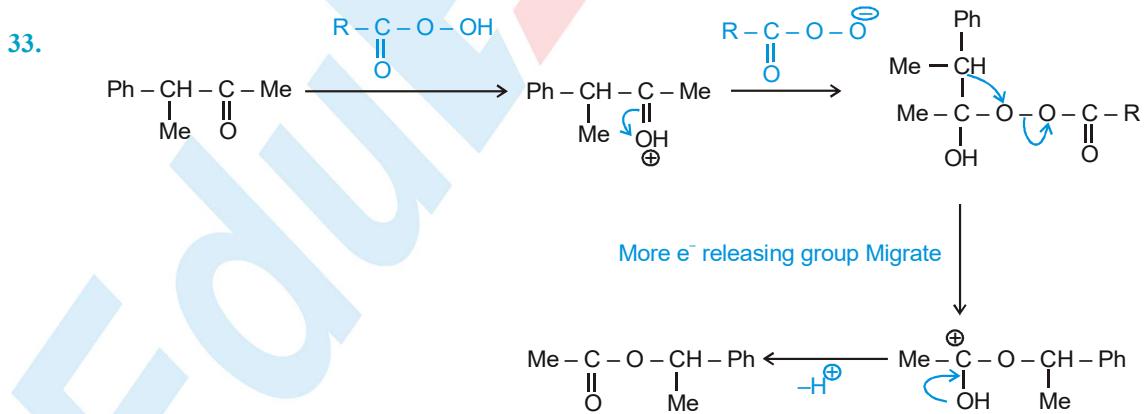
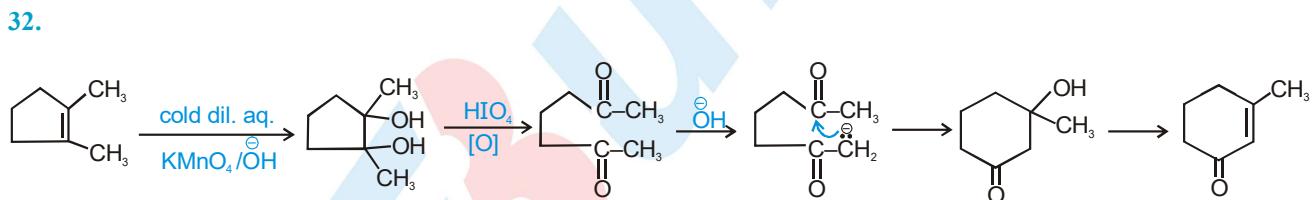
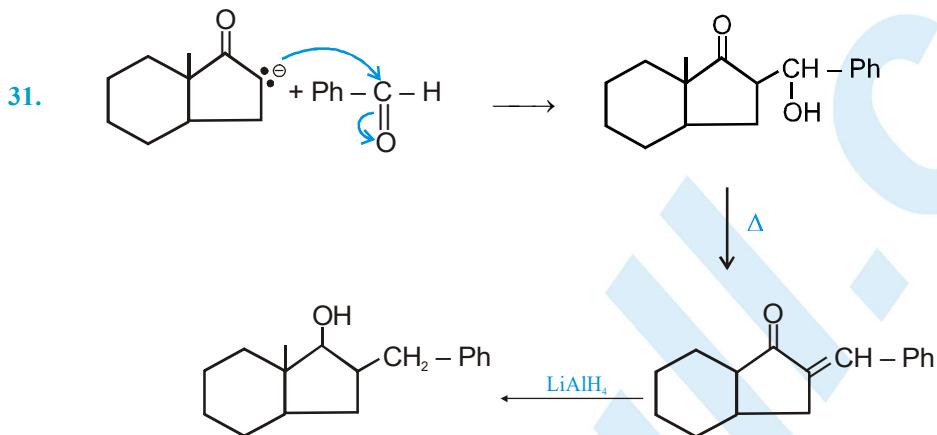
25. $\text{CH}_3 - \text{CHO}$ (α -Hydrogen is present).





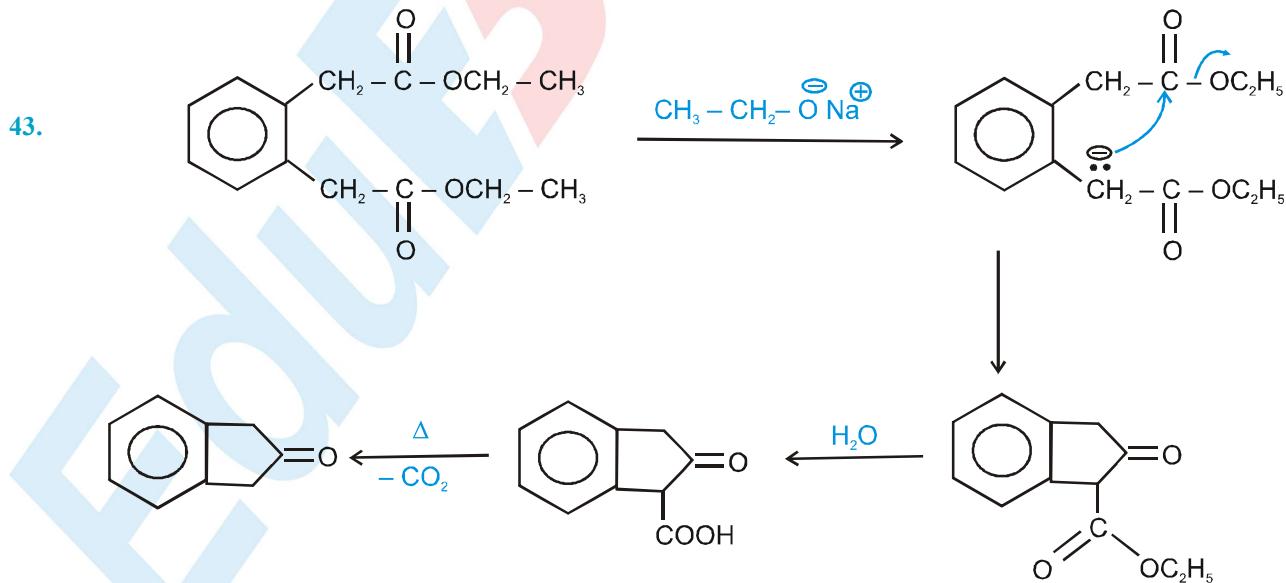
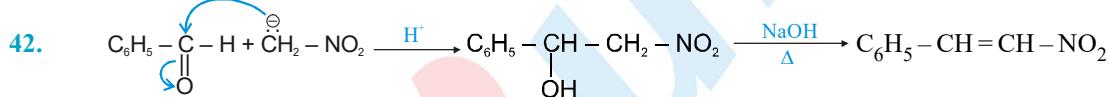
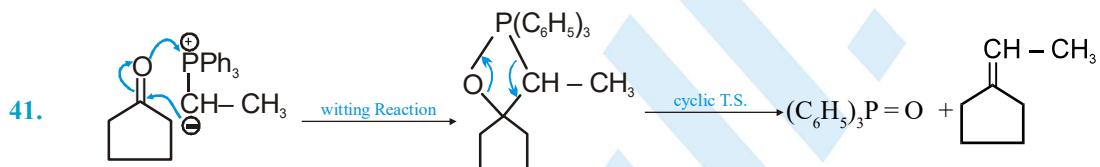
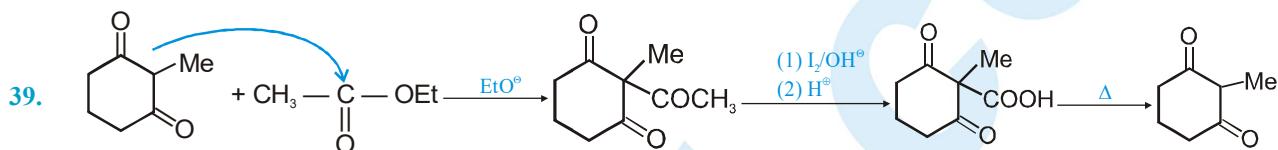
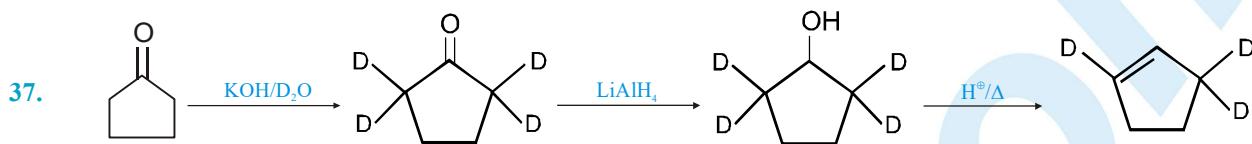
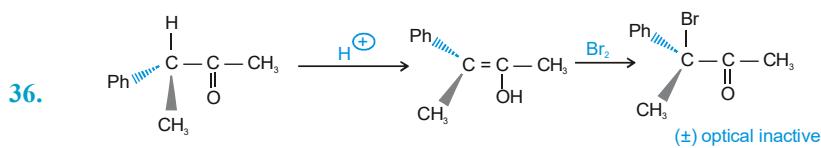
Acetal is hydrolysed in acidic Medium so Clemmensen reduction is not used.

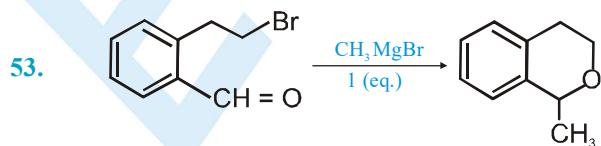
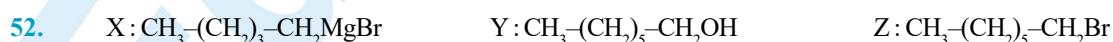
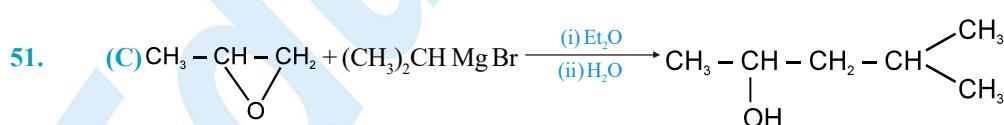
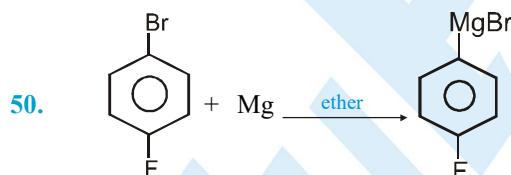
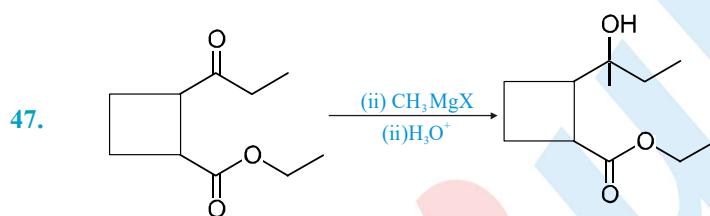
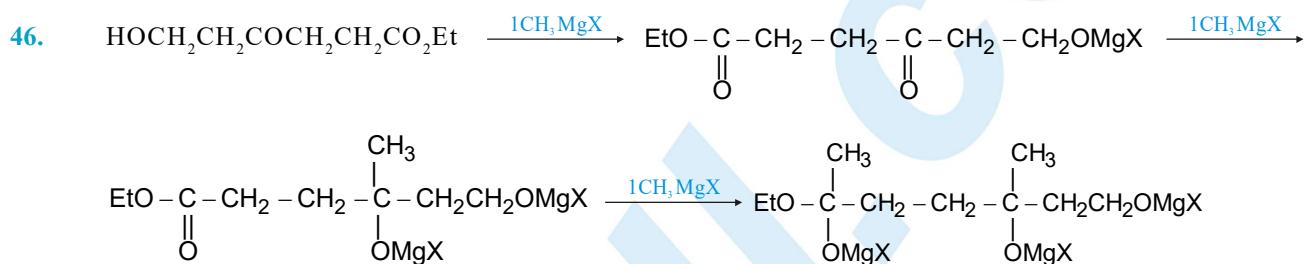
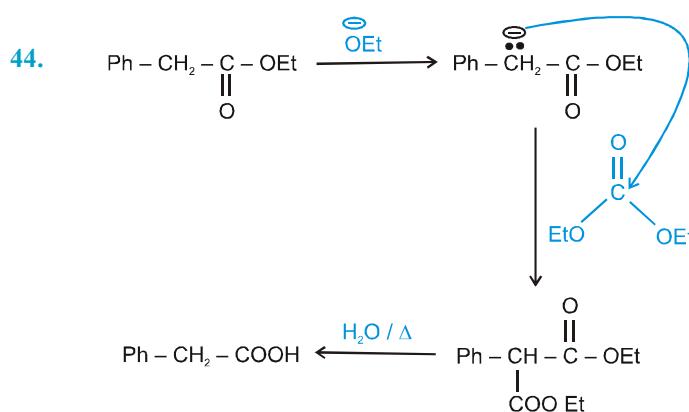
30. If base sensitive group is present on carbonyl compound then Clemmensen reduction is used.



34. Those carbonyl compound in which α -hydrogen is present show deuterium exchange.

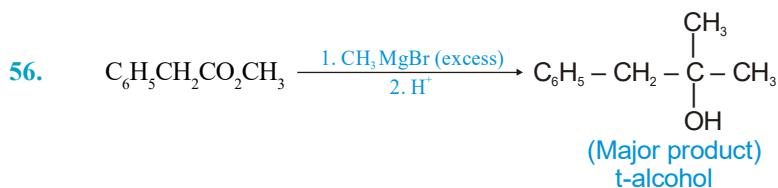
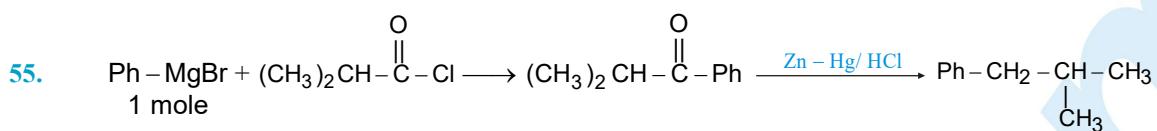
35. α -Hydrogen is absent so deuterium exchange is not observed in A and C.



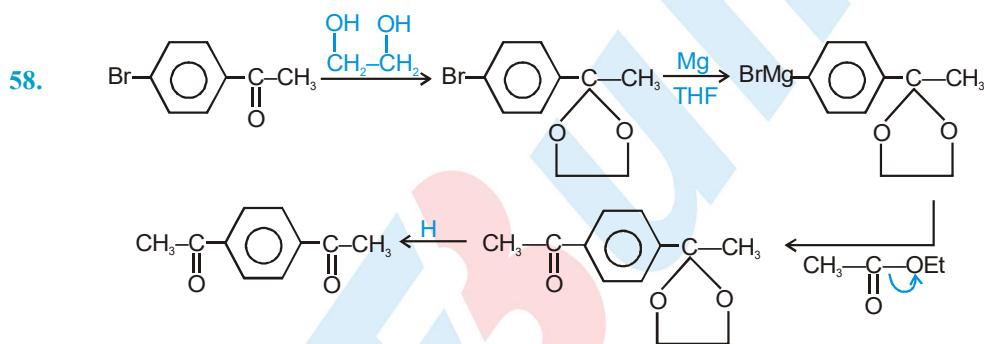
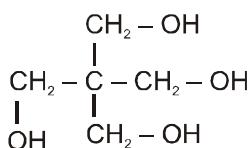


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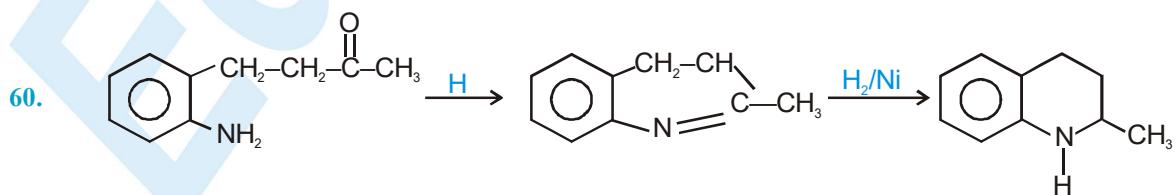
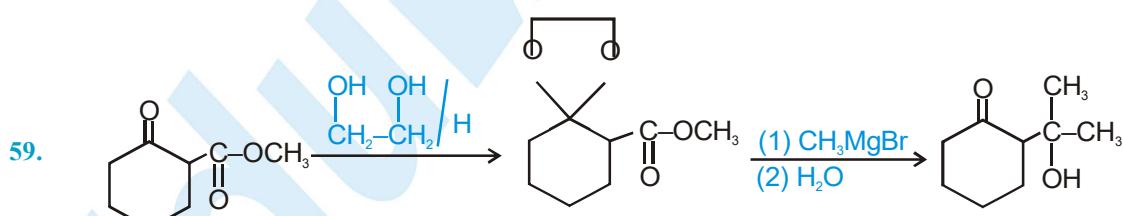
54. Active hydrogen containing functional group release CH_4 gas with CH_3MgBr . (i.e. OH, COOH, SO_3H)

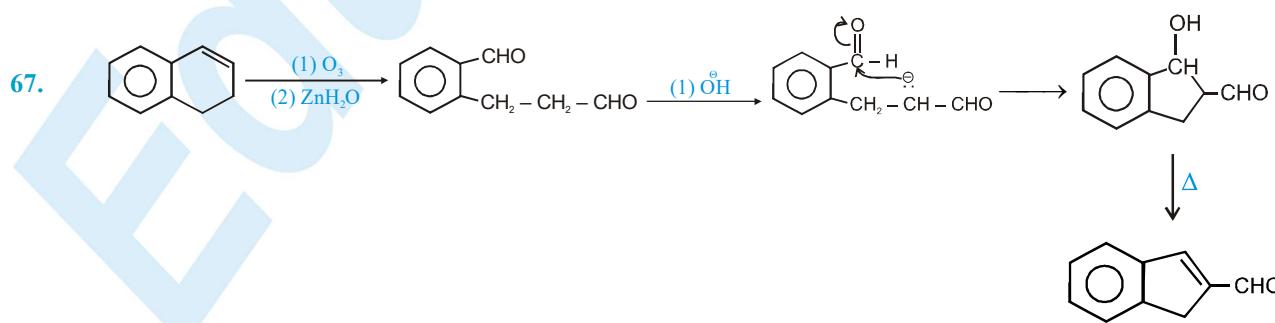
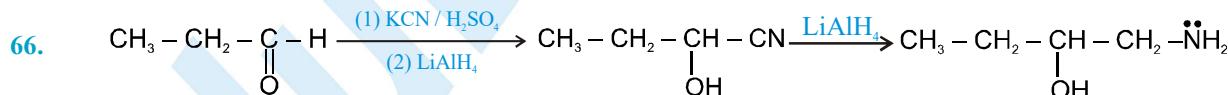
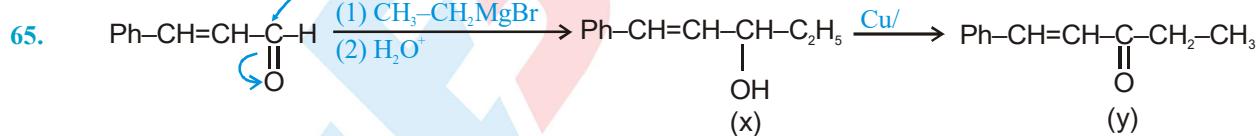
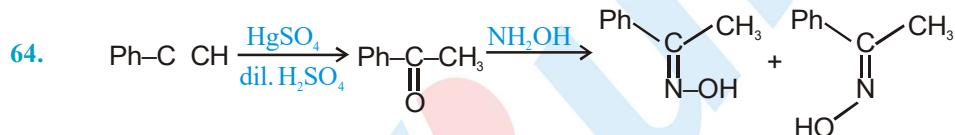
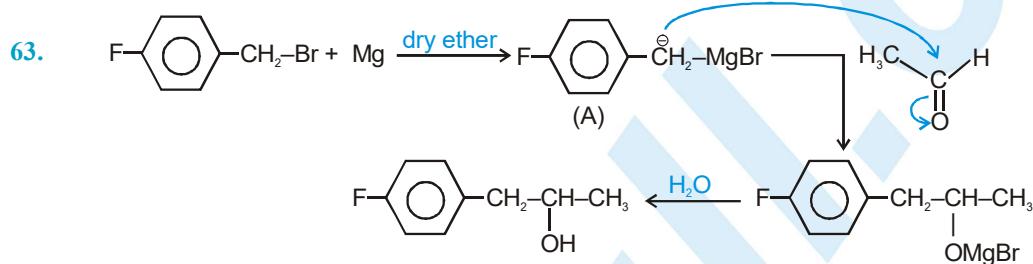
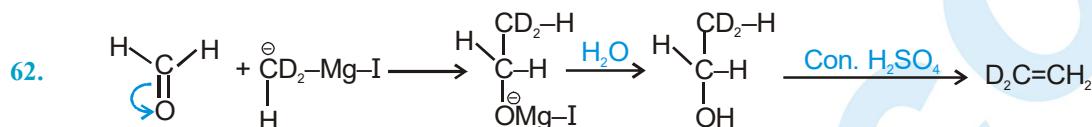
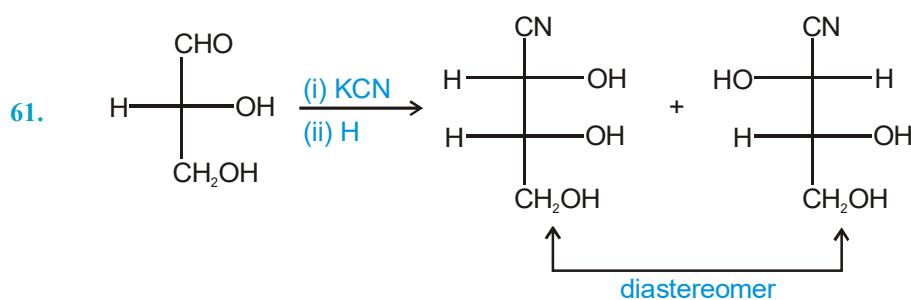


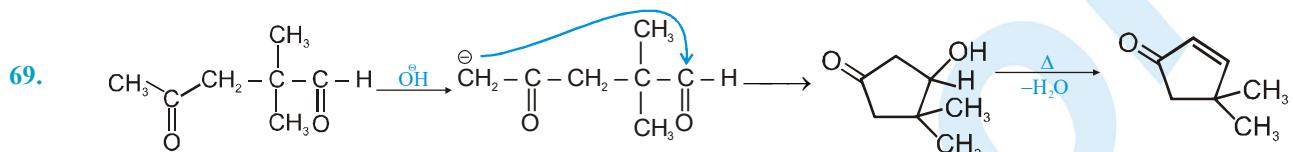
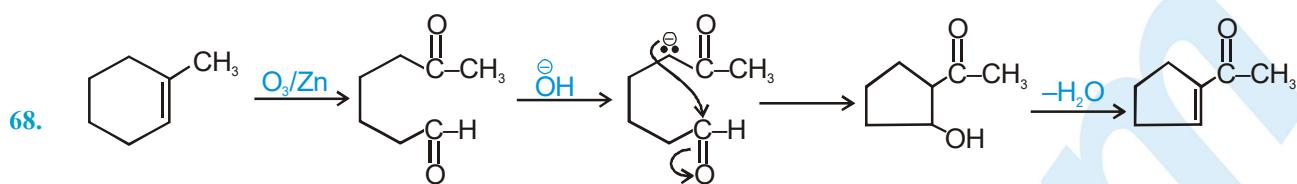
57. $\text{C}_5\text{H}_{12}\text{O}_4 \xrightarrow{\text{CH}_3\text{MgBr}} 4\text{CH}_4 \uparrow$.
It means compound (X) contains 4 acidic hydrogen.



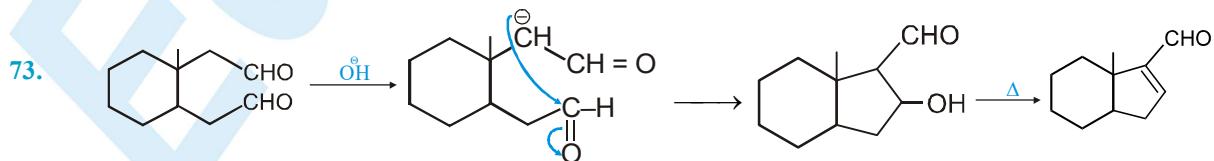
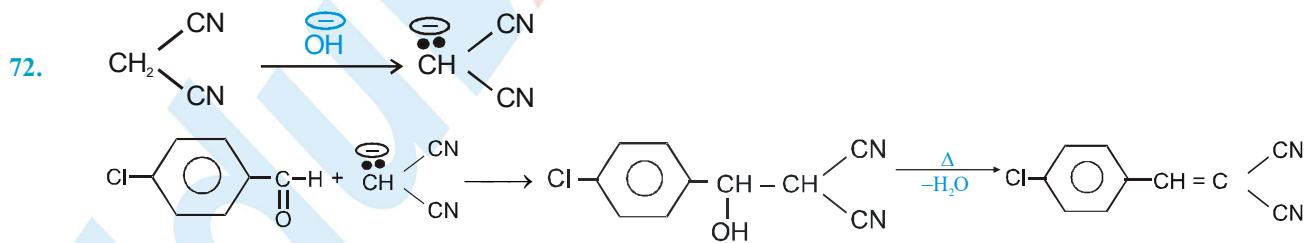
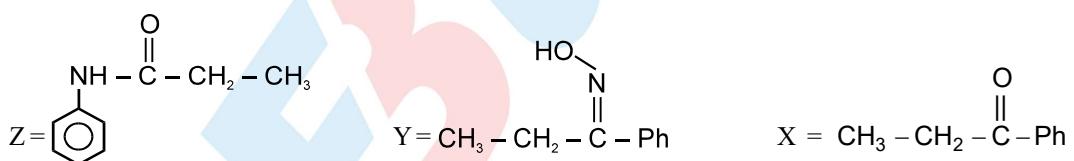
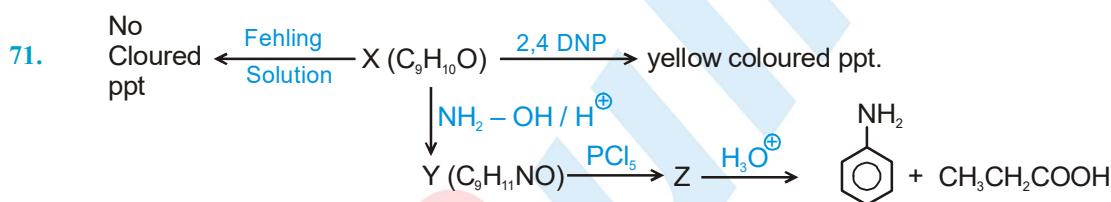
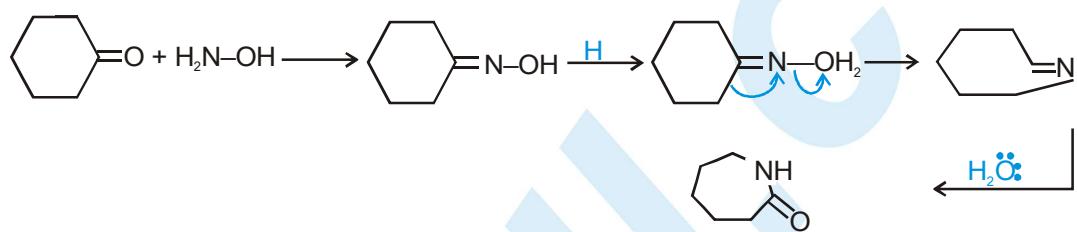
Grignard reagent is stable in THF. Grignard reagent reacts with epoxide hence (B) can't be the answer.

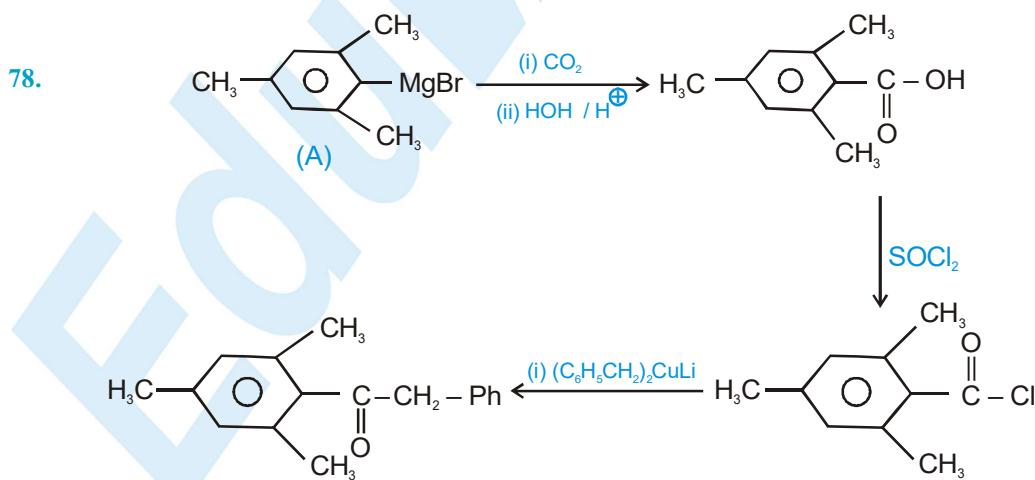
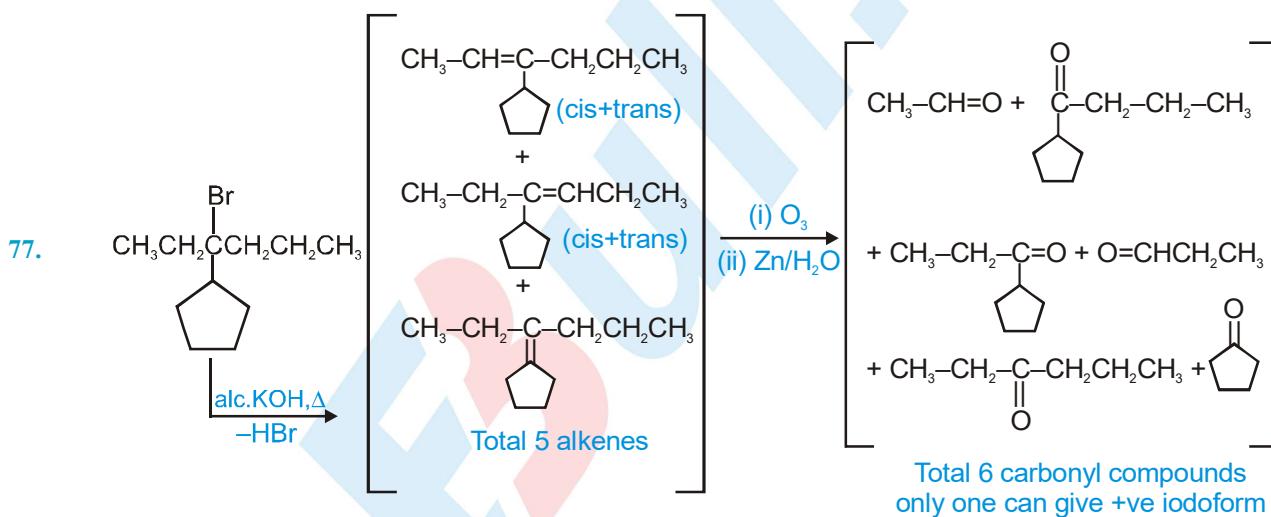
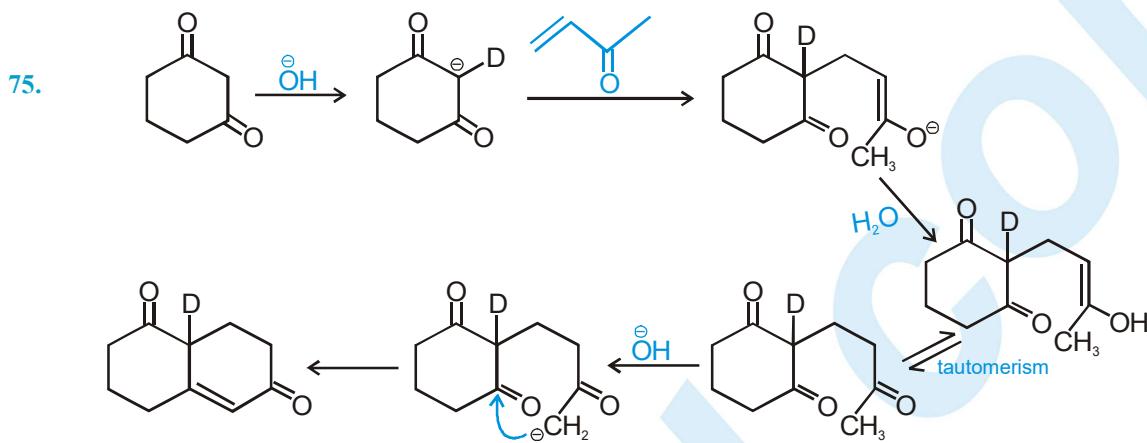
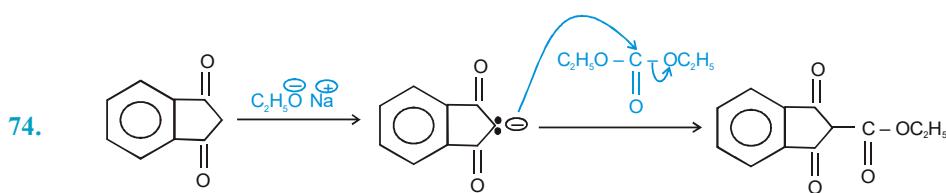


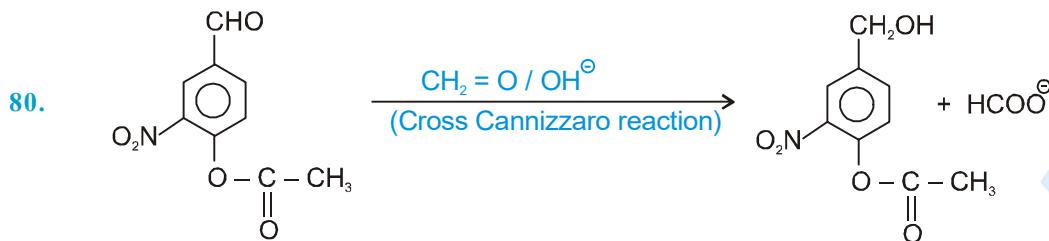




70. Beckmanns rearrangement

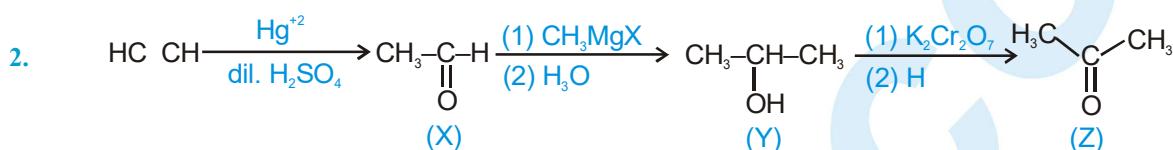




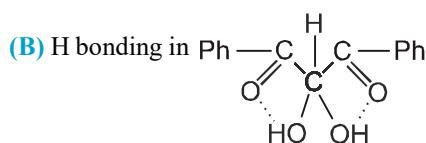


EXERCISE - 2

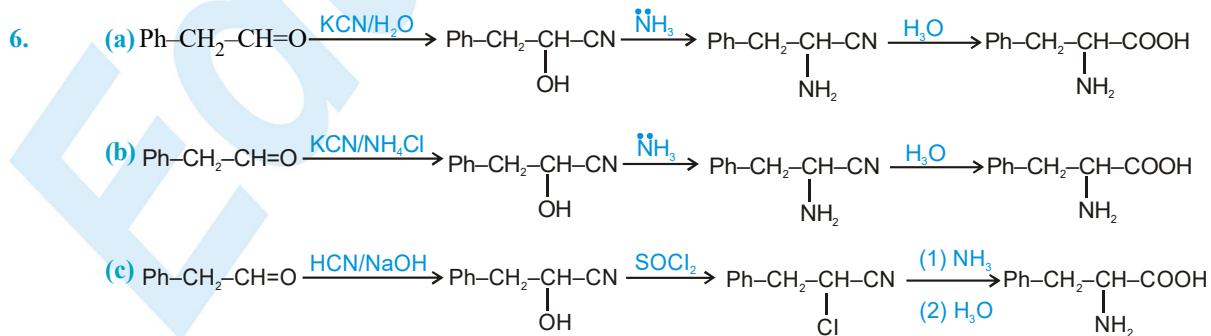
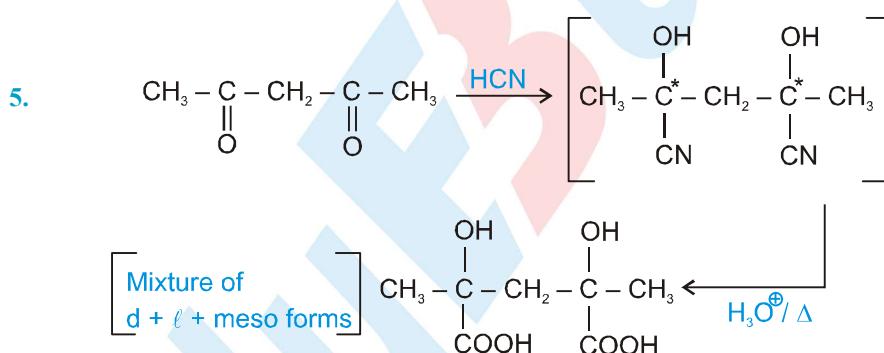
Part # I : Multiple Choice

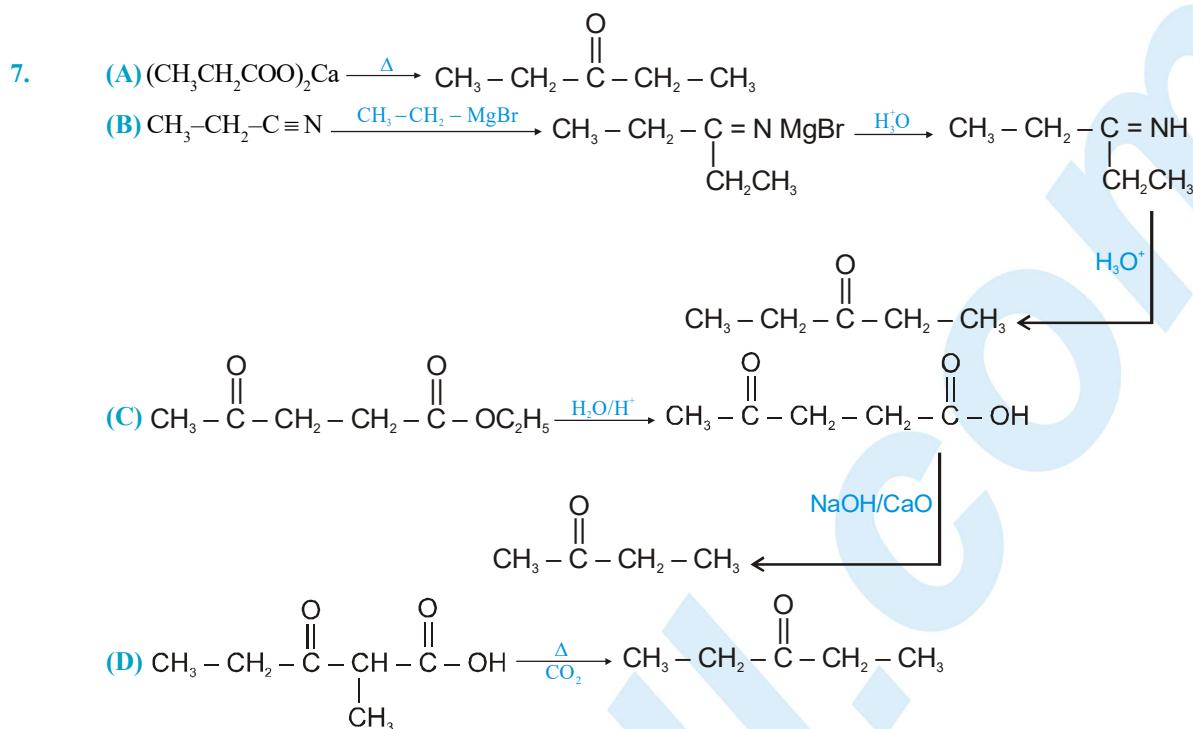


4. (A) Due to substrate (steric factor)

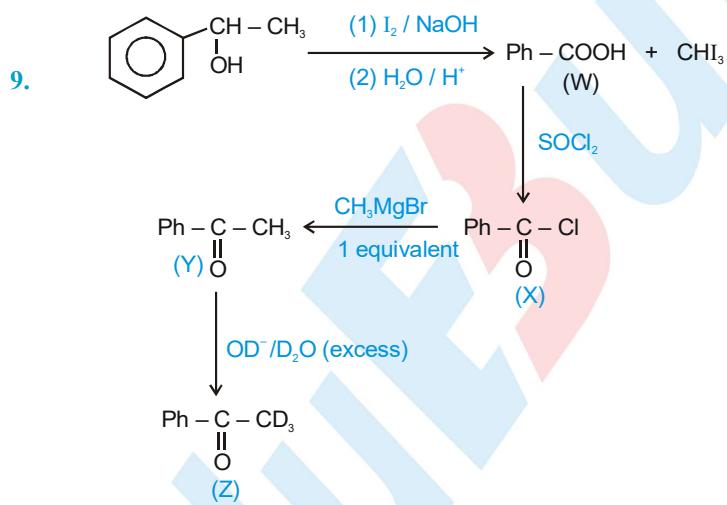


(C) Cyanohydrin formation is usually reversible

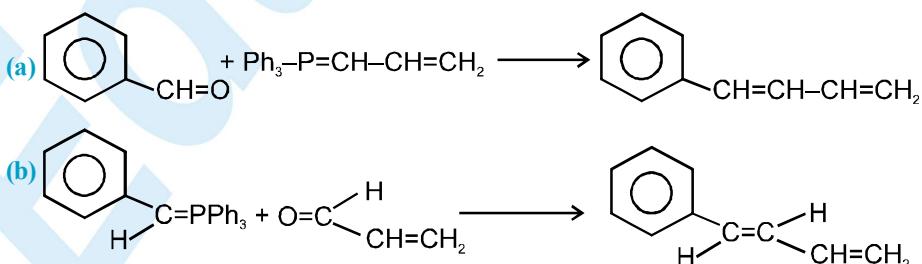




8. (A) Perkin reaction (B) Knoevenagel reaction (D) Reformatsky reaction

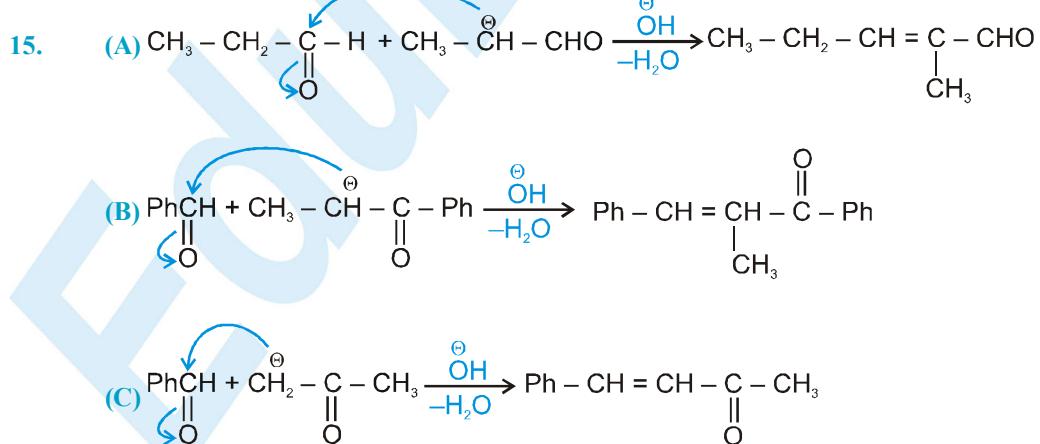
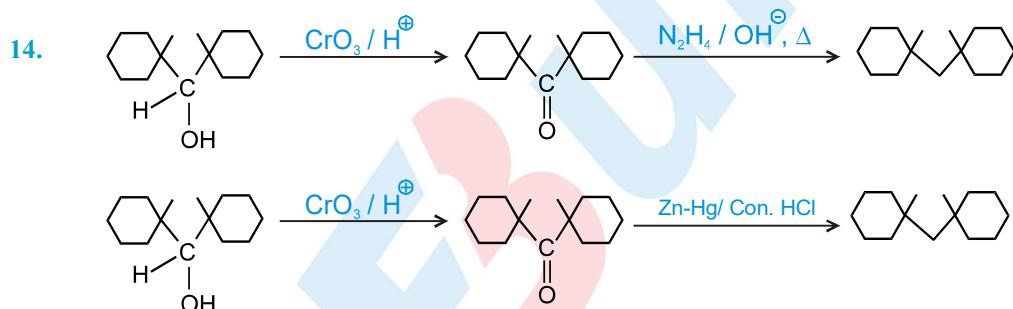
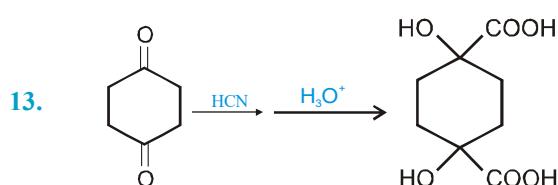
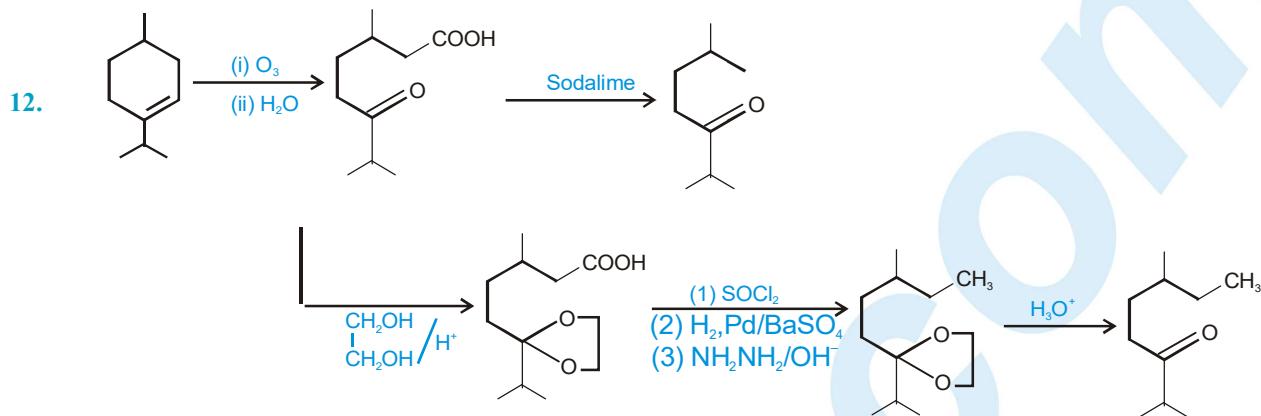


10. Wittig reaction.

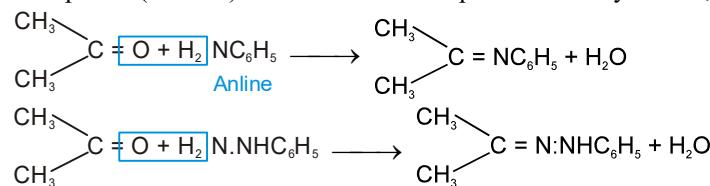


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11. Stability of hydrates of carbonyl compound depends on steric hindrance, presence of -I group on gemdiol. Intramolecular H-bonding and angle strain in carbonyl compound.

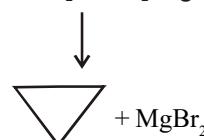


16. Carbonyl compound (acetone) forms condensation product with hydrazine, phenyl hydrazine aniline etc.

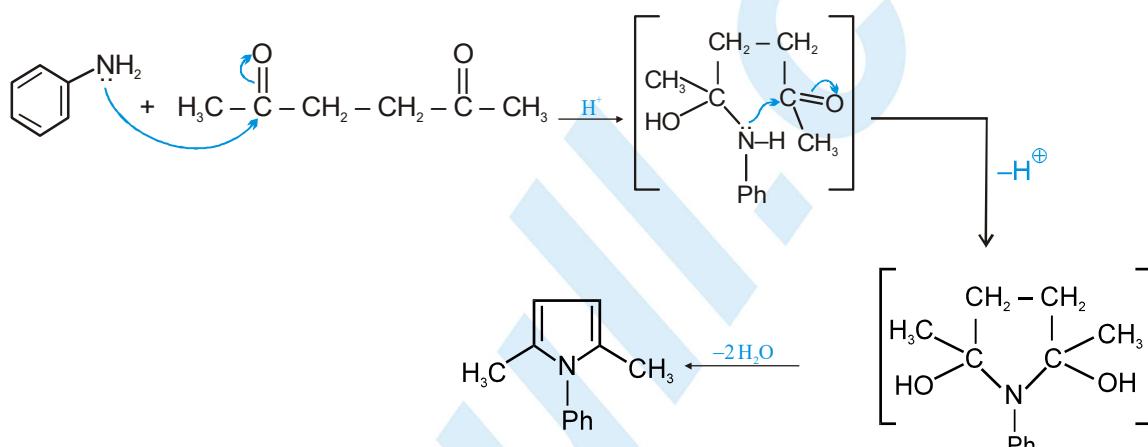


Hence in these reaction $>\text{C}=\text{N}$ bonds are formed in products.

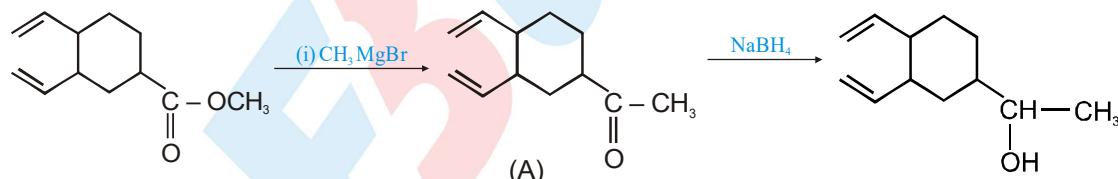
18. (C) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{Mg} \xrightarrow{\text{Et}_2\text{O}} \text{Br}-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{MgBr}$



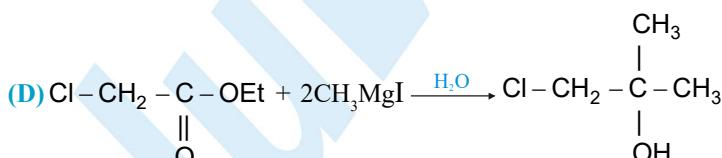
19.



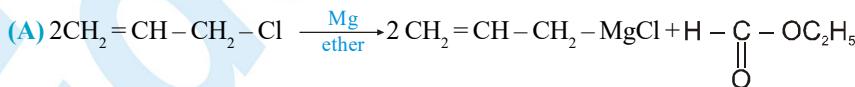
20.



21.



22.



$$(\text{CH}_2 = \text{CH} - \text{CH}_2)_2 \text{CH} - \text{OH} + \text{CH}_3 - \text{CH}_2 - \text{OH}$$

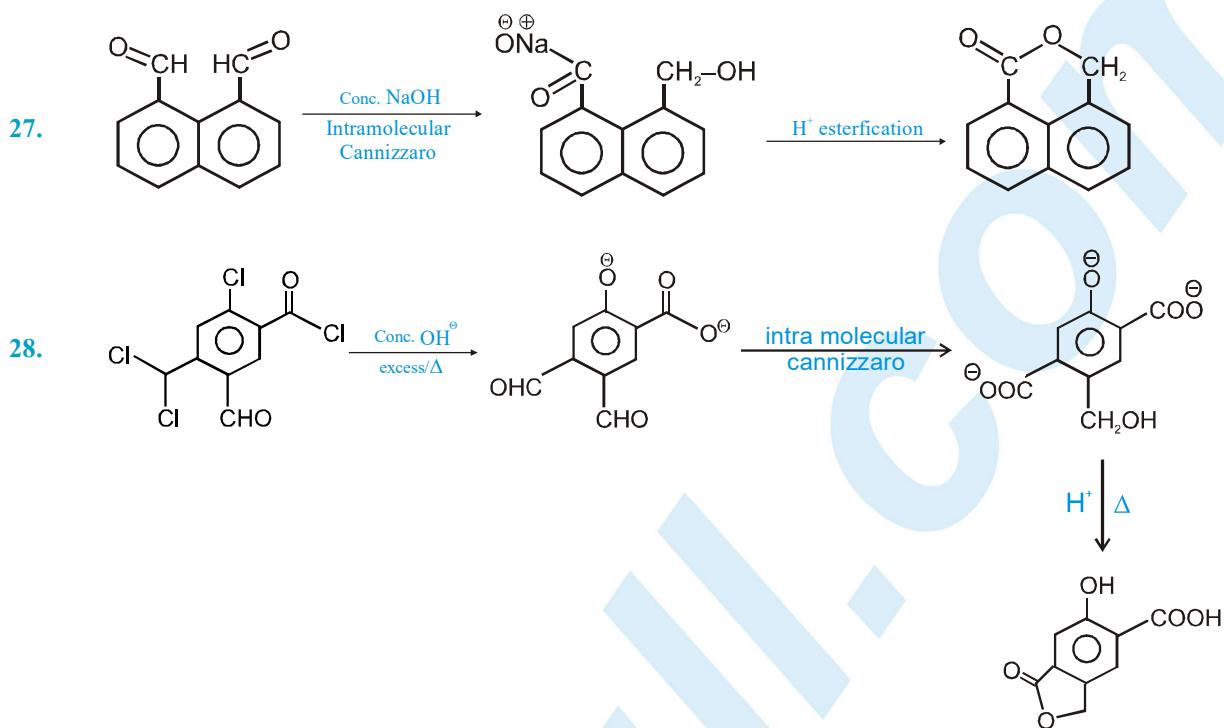
- 23.** It is cannizzaro reaction.

- 24.** In Wolf-Kishner reduction carbonyl compound is converted to hydrocarbon.

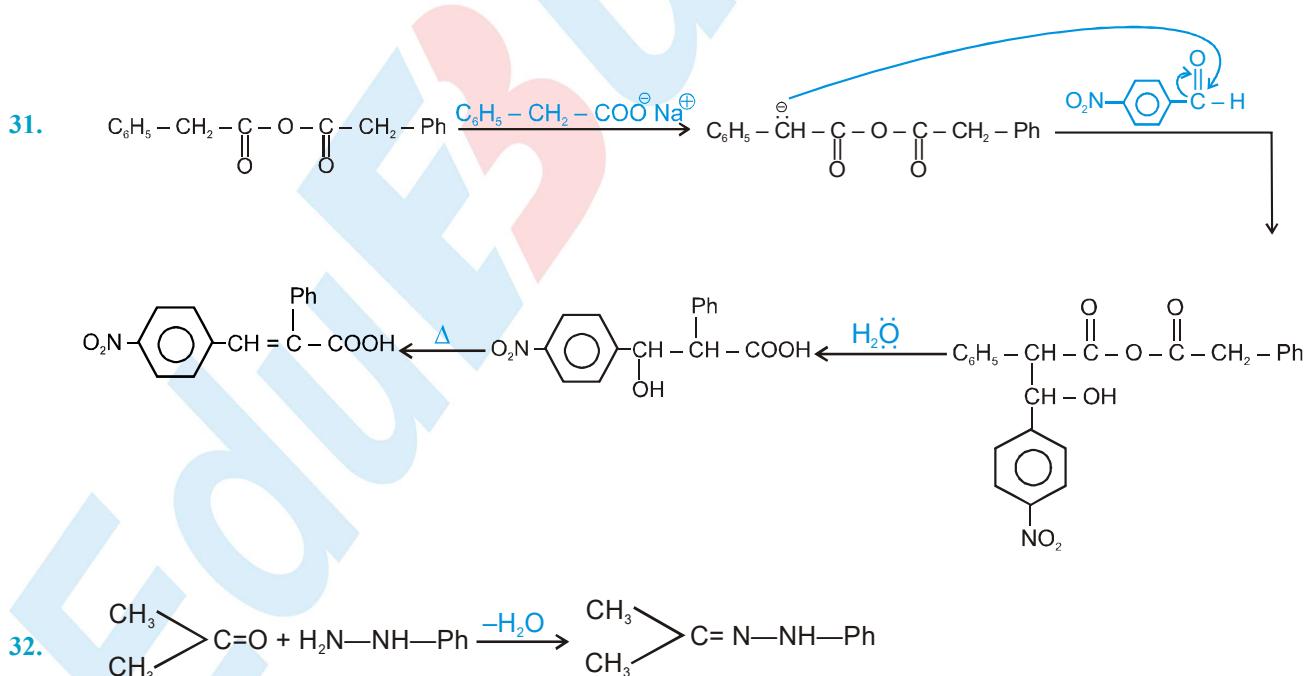
25. $\text{C}_6\text{H}_5 - \underset{\text{O}}{\overset{||}{\text{C}}} - \text{Cl} \xrightarrow[\text{Rossenmund's reduction}]{\text{H}_2, \text{Pd/BaSO}_4} \text{C}_6\text{H}_5 - \underset{\text{O}}{\overset{||}{\text{C}}} - \text{H}$

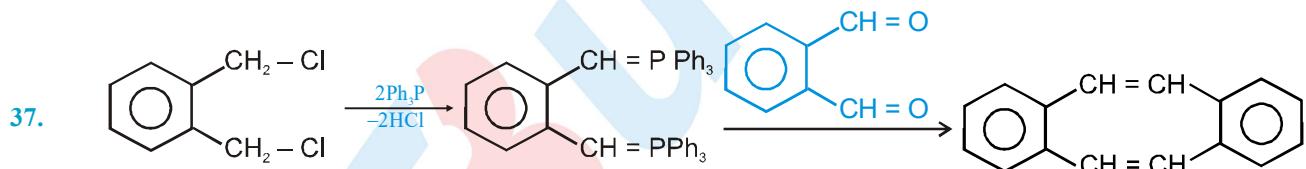
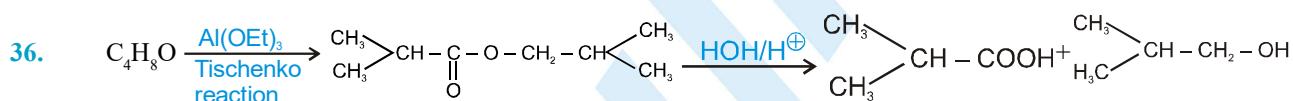
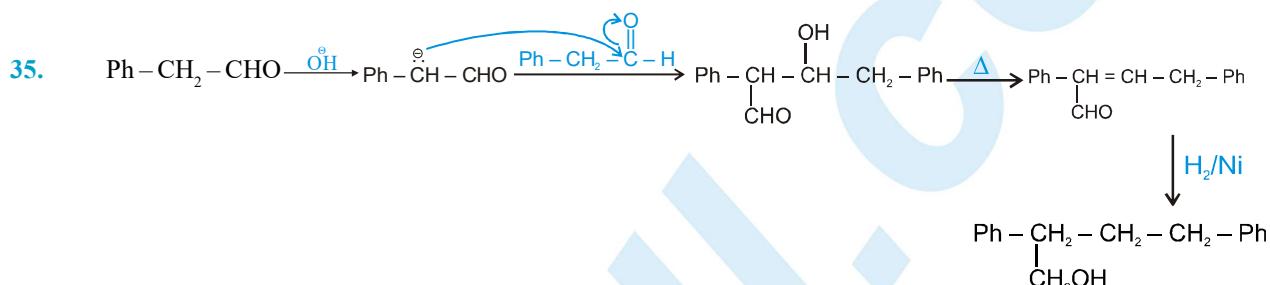
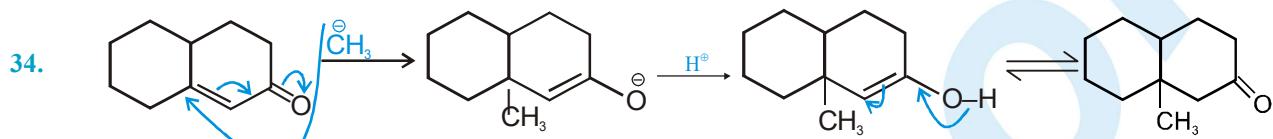
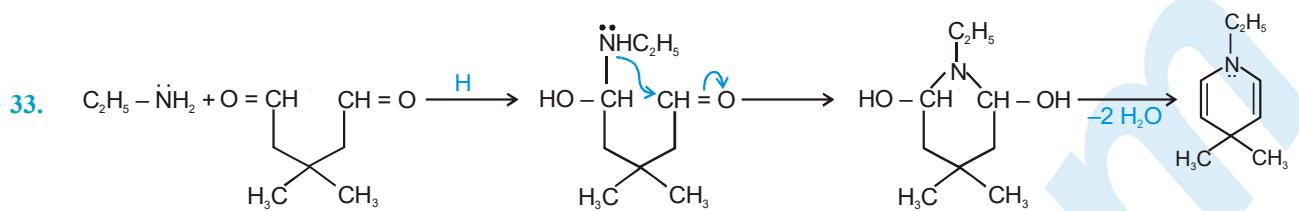
CHEMISTRY FOR JEE MAIN & ADVANCED

26. It is a protection of carbonyl group.

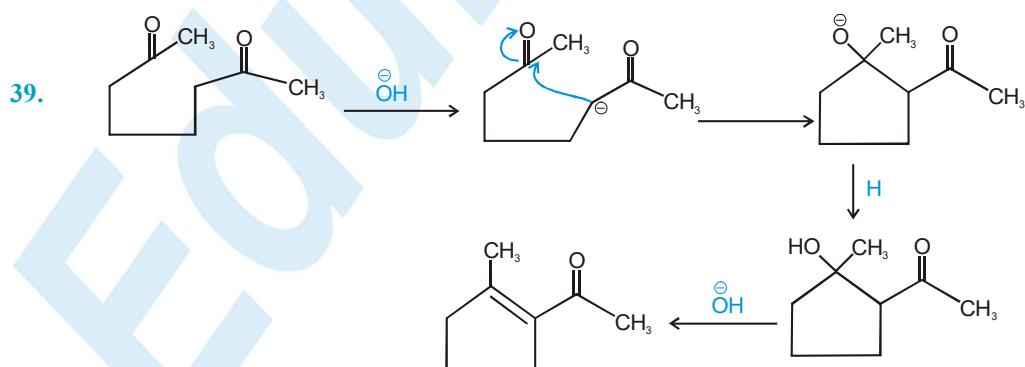
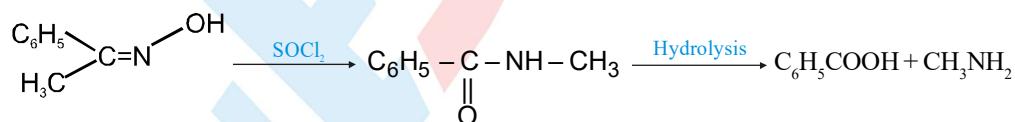


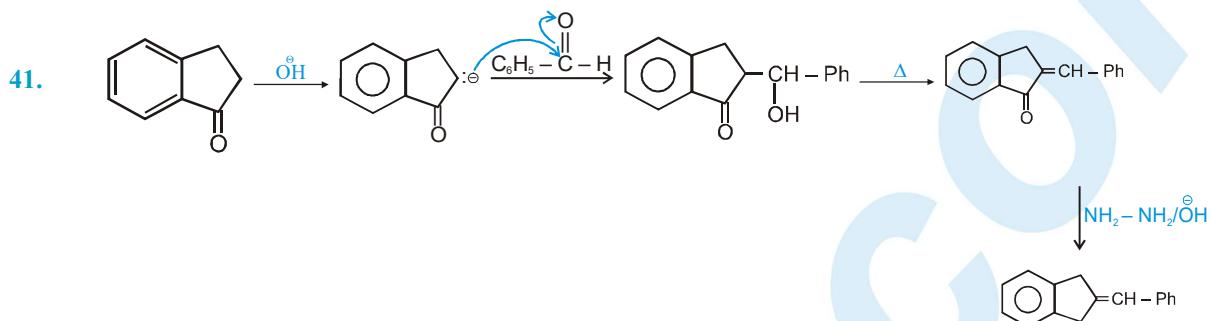
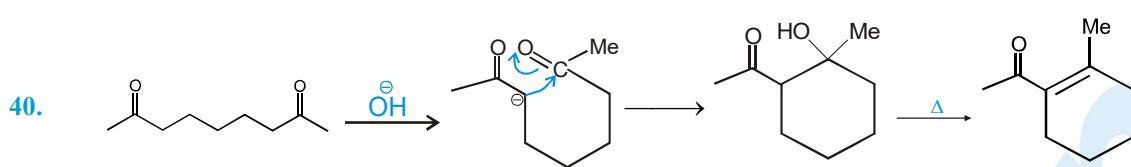
29. Rate of nucleophilic attack \propto amount of +ve charge at carbonyl carbon.





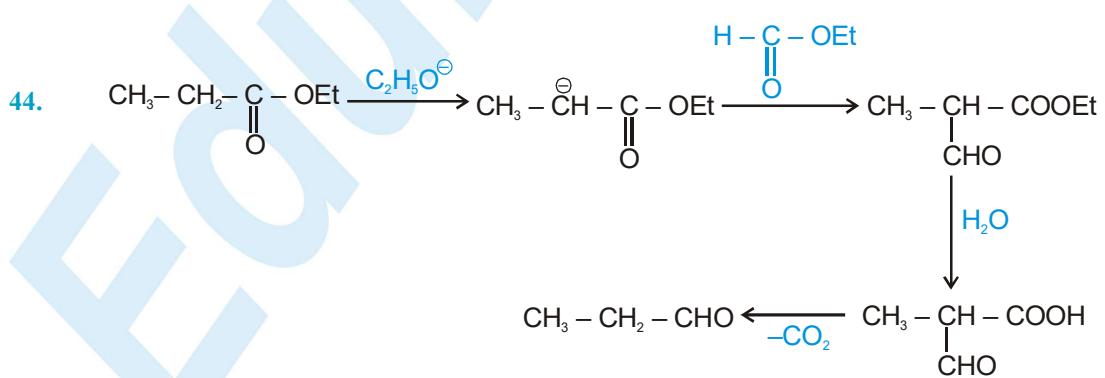
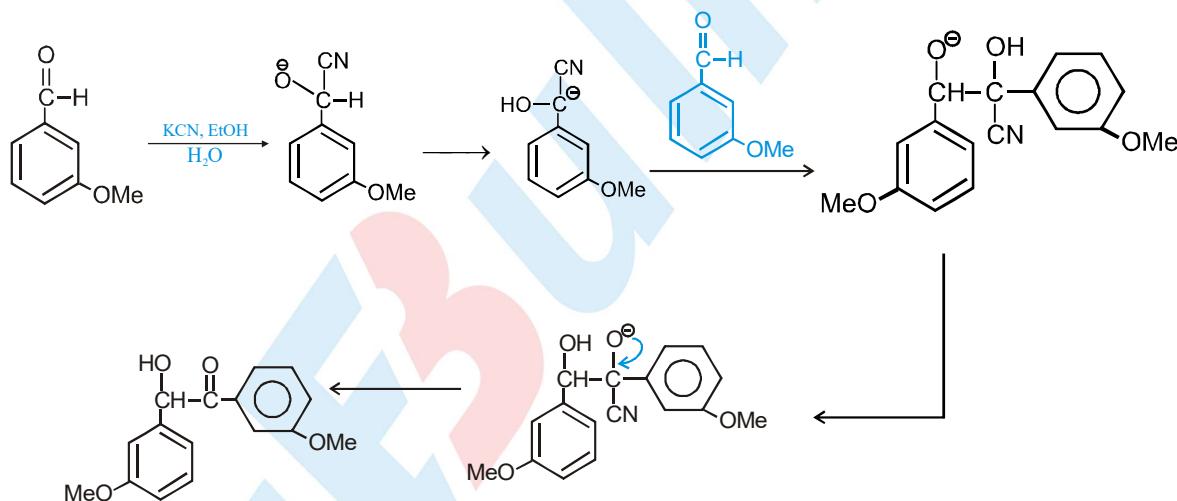
38. Beckmann rearrangement (anti group of -OH migrates)

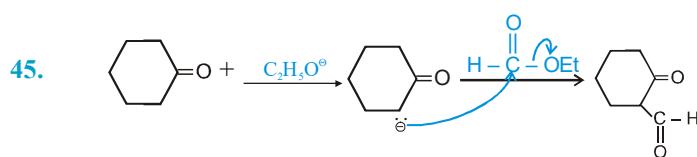




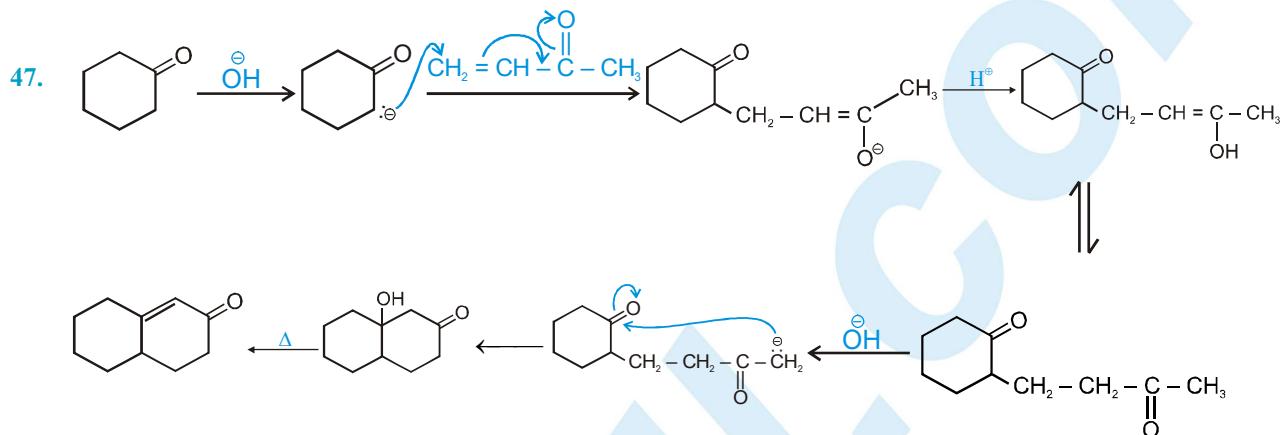
42. $-I$ and $-M$ group increase electrophilicity on carbonyl group so rate of addition reaction increase and also increases equilibrium constant.

43. Benzoin condensation

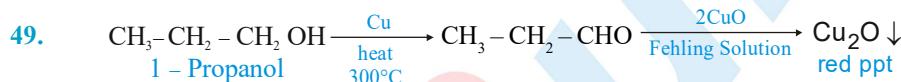




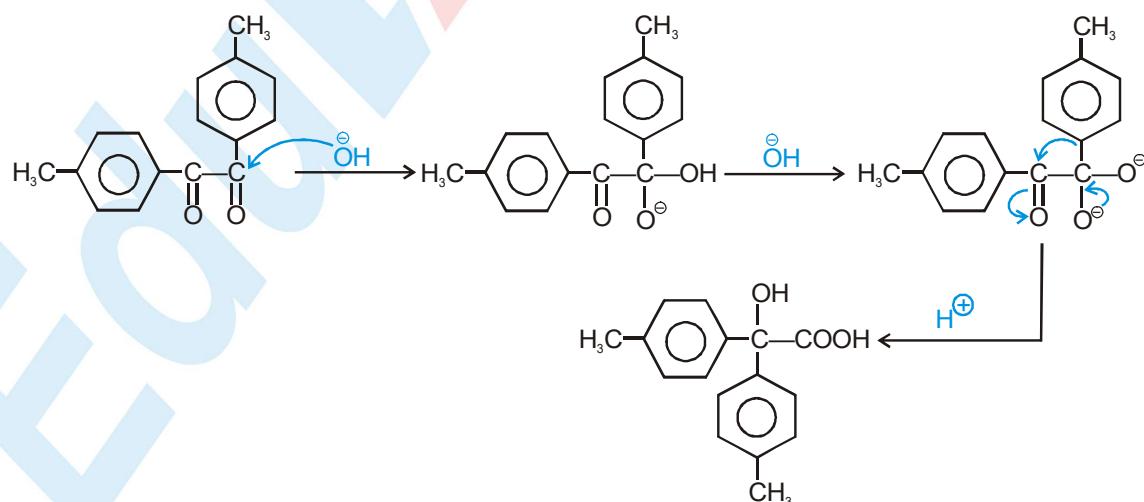
46. $\text{K}_2\text{Cr}_2\text{O}_7$ oxidised secondary alcohol which gives iodoform test.

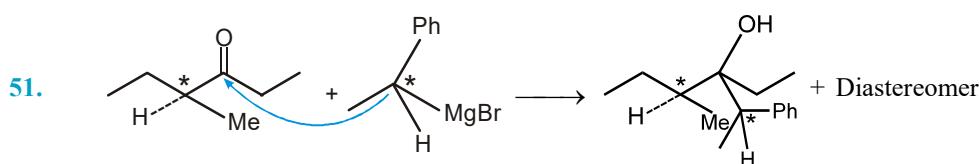


It is crossed Cannizzaro's reaction.



50. It is benzil-benzyllic acid rearrangement





52. Transfer of hydride ion

Part # II : Assertion & Reason

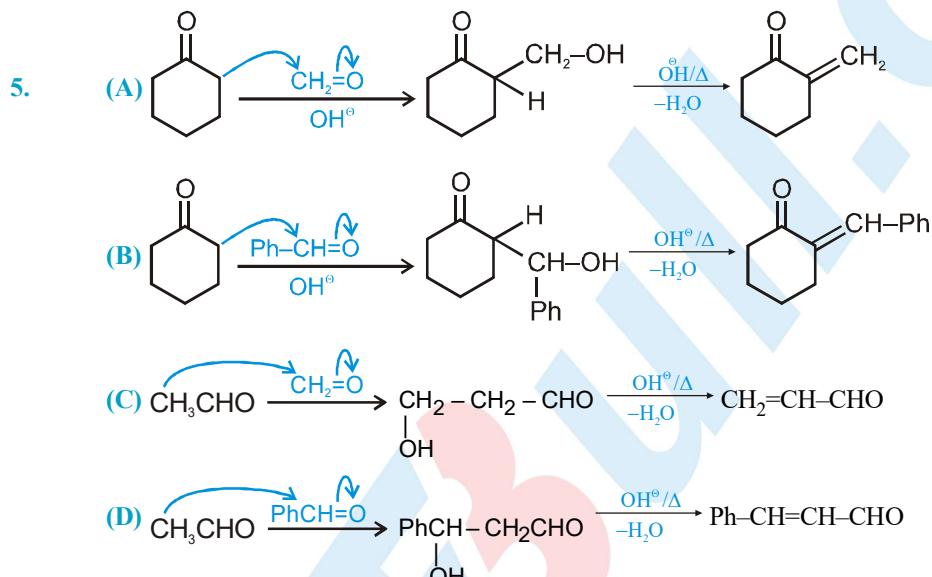
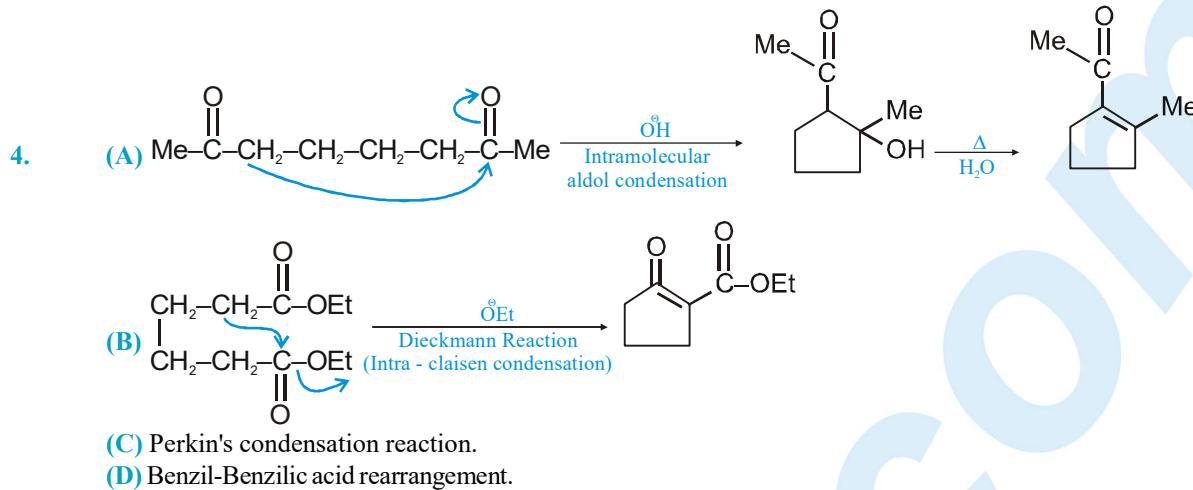
1. NaHSO_3 on addition of carbonyl compound forms a salt.
5. Base will decrease the rate of reaction.
7. Grignard reagent can not be prepared in all nonpolar solvent, it can prepare only in ether solvent.
8. G.R. can not be prepared in aqueous solution due to acid base reaction.
10. In weakly acidic medium nucleophile is not affected.
12. Acetals are not hydrolysed in basic medium.
13. Hydrogen of nitromethane is more acidic as $\text{CH}_2^{\ominus}-\text{NO}_2$ is more stable.

EXERCISE - 3

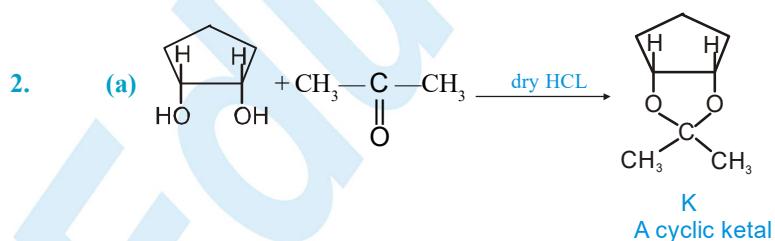
Part # I : Matrix Match Type

- | | | | | |
|----|-----|--|---|---|
| 1. | (A) | $\text{Ph}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{CH}=\text{CH}_2$ | - | 1, 4-addition.
Shows tautomerism as it has two α -H.
Gives +ve 2, 4-DNP test as the carbonyl group is present. |
| | (B) | | - | Gives 1, 4-addition.
Shows tautomerism as it has two α -H.
Gives +ve tollen's test as it has aldehyde groups.
+ve 2, 4-dNP test. |
| | (C) | $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ | - | It is a conjugated diene and gives 1, 4-addition. |
| | (D) | $\text{CH}_3-\overset{\text{ }}{\underset{\text{O}}{\text{C}}}-\text{CH}_2-\overset{\text{ }}{\underset{\text{O}}{\text{C}}}-\text{H}$ | - | Shows tautomerism as it has active methylene group (α -H).
+ve tollen's test since $-\text{CHO}$ group is present.
+ve 2, 4-DNP test. |
| 3. | (A) | $\text{RMgI} + \text{CH}_3-\text{C}\equiv\text{N} \longrightarrow \text{CH}_3-\overset{\text{R}}{\underset{\text{C}}{\text{C}}}=\text{NMgI} \xrightarrow{\text{H}_2\text{O}^+} \text{CH}_3-\overset{\text{R}}{\underset{\text{C}}{\text{C}}}-\text{C}(=\text{O})-\text{R}$ (Alkanone) | | |
| | (B) | $\text{RMgI} + \text{S}=\text{C}=\text{S} \longrightarrow \text{R}-\overset{\text{S}}{\underset{\text{C}}{\text{C}}}-\text{S}-\text{MgI} \xrightarrow{\text{H}_2\text{O}^+} \text{R}-\overset{\text{R}}{\underset{\text{C}}{\text{C}}}-\text{SH}$ (Dithionic acid) | | |
| | (C) | $\text{RMgI} + \text{CH}_3\text{CH}_2\text{O}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{Cl} \longrightarrow \text{CH}_3-\text{CH}_2-\text{O}-\overset{\text{R}}{\underset{\text{C}}{\text{C}}}-\text{Cl} \longrightarrow \text{CH}_3-\text{CH}_2-\text{O}-\overset{\text{R}}{\underset{\text{C}}{\text{C}}}-\text{OMgI} + \text{MgCl}$ (Ester) | | |
| | (D) | $\text{RMgI} + \text{CH}_2-\overset{\text{O}}{\text{C}}-\text{CH}_2 \longrightarrow \text{R}-\text{CH}_2-\text{CH}_2-\text{OMgI} \xrightarrow{\text{H}_2\text{O}^+} \text{R}-\text{CH}_2-\text{CH}_2-\text{OH}$ (Alcohol) | | |

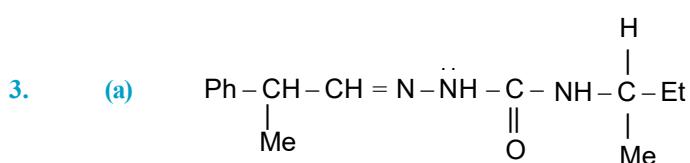




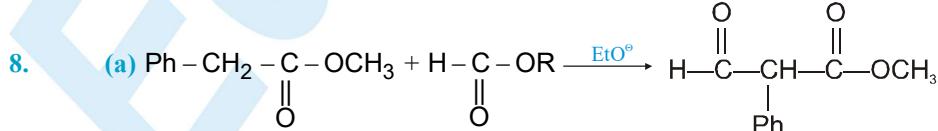
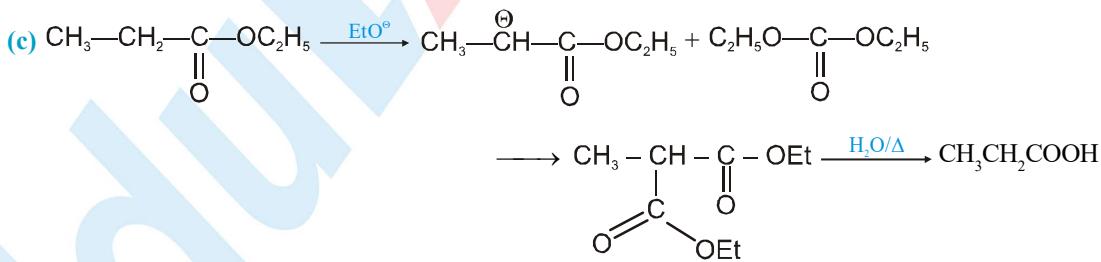
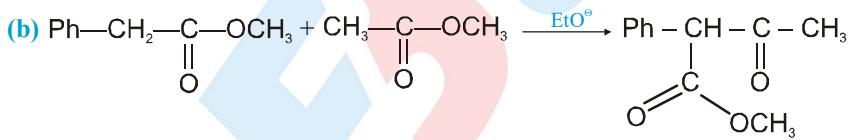
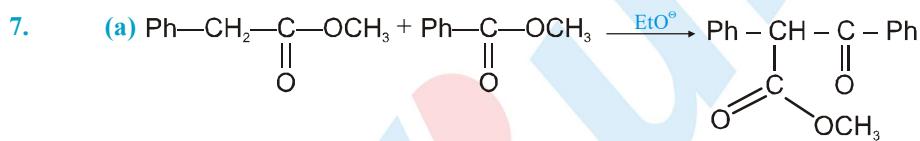
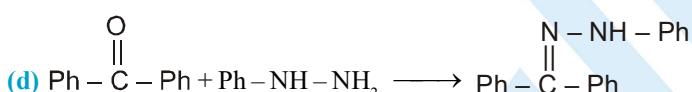
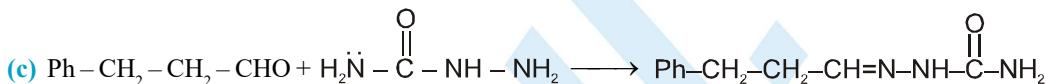
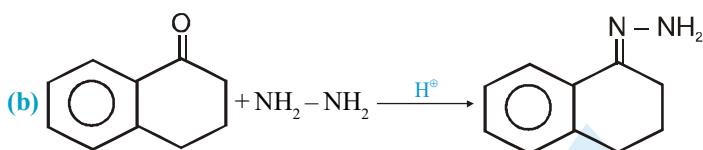
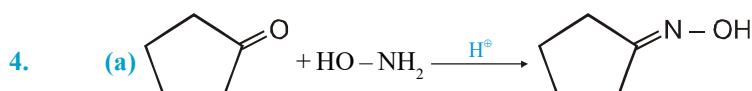
EXERCISE - 4
Subjective Type

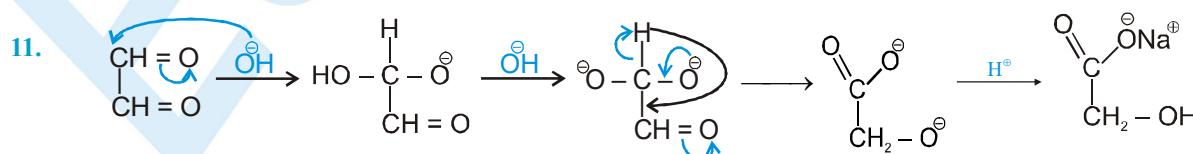
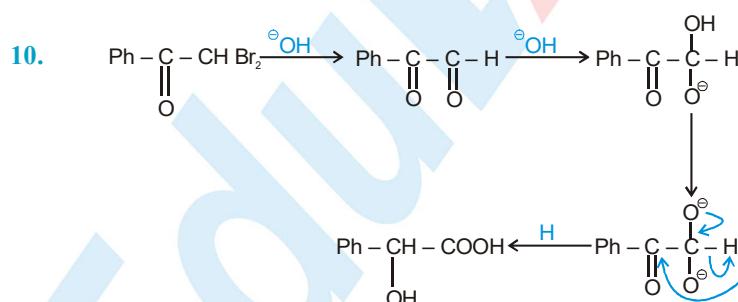
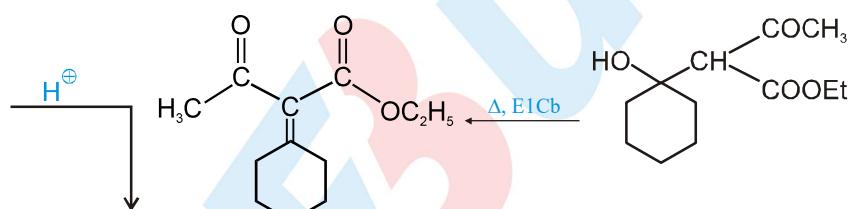
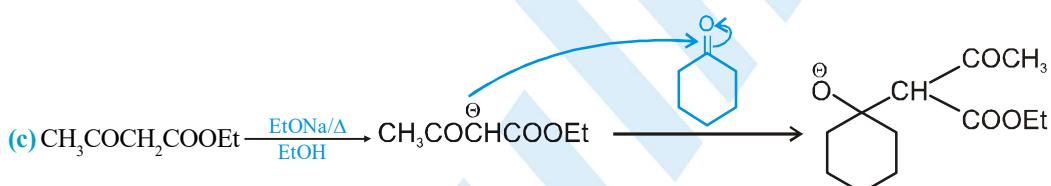
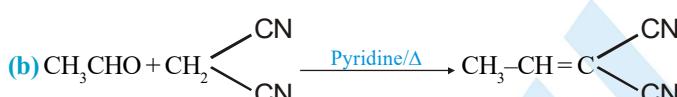
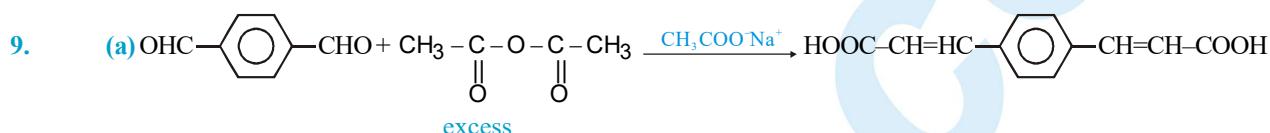
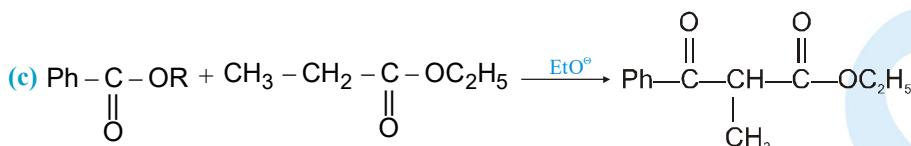
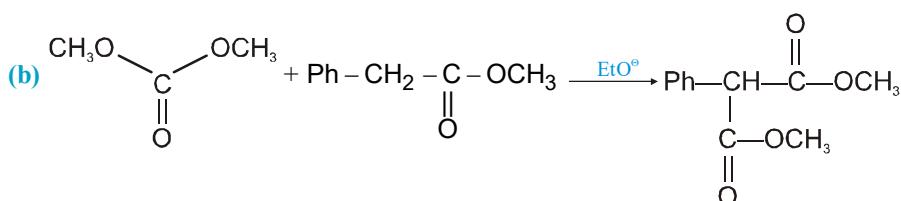


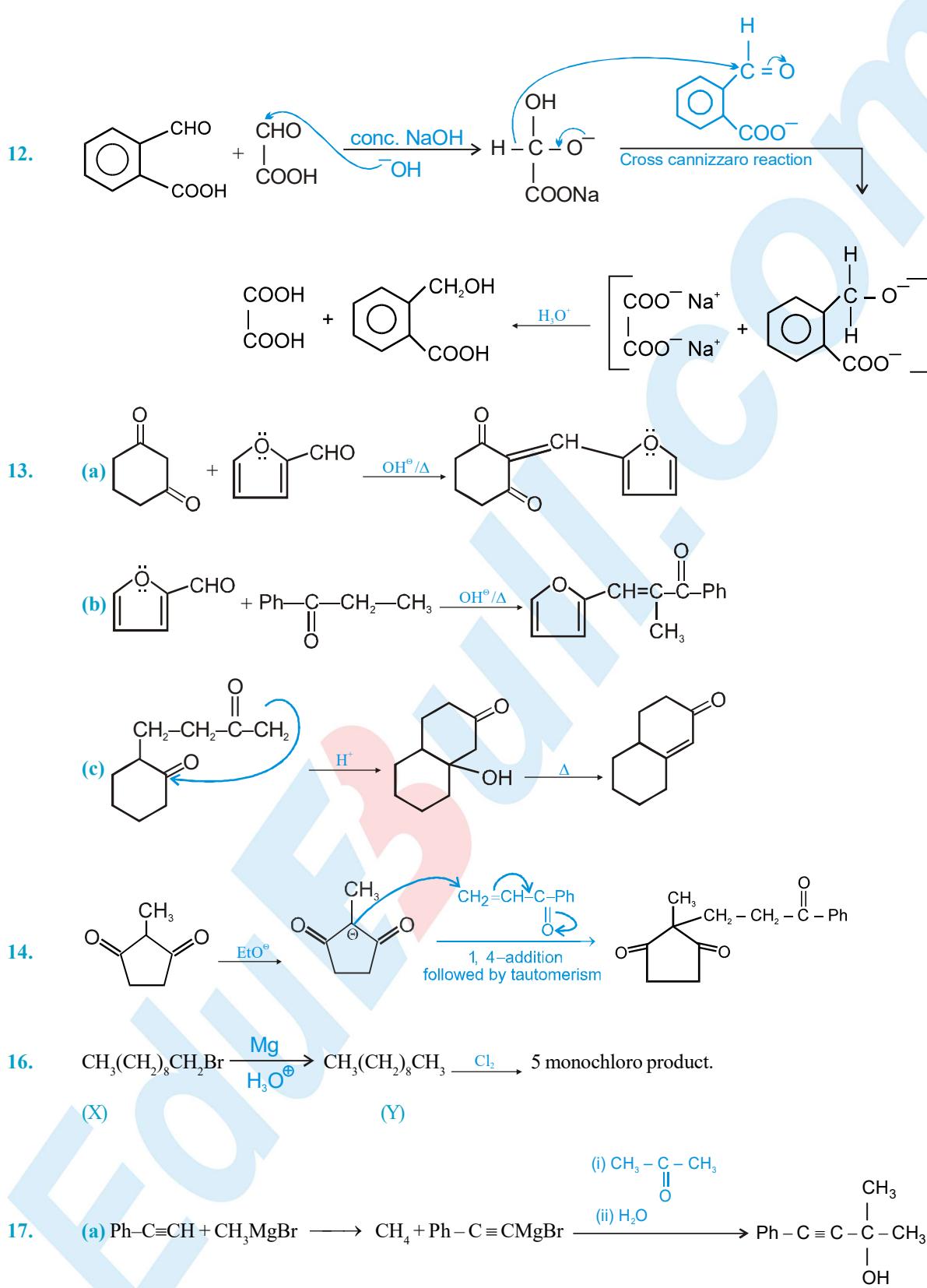
(b) The –OH groups in the trans isomer are too far apart to form cyclic structure.

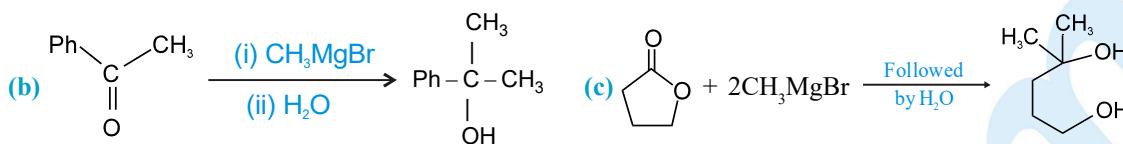


- (R, syn)
- (R, anti)
- (S, syn)
- (S, anti)

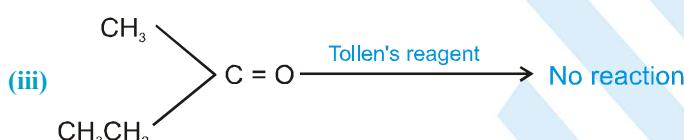
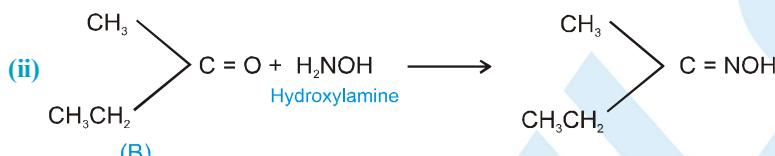
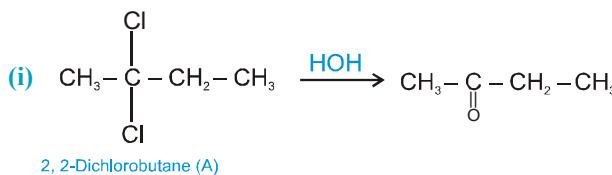








18. (i) (B) reacts with hydroxyl amine and thus (B) has carbonyl group, i.e., $>C=O$ group ketonic or aldehyde ($-CH=O$) group.
 (ii) (B) gives negative test with Tollen's reagent and thus (B) is ketone.
 (iii) (B) is obtained by hydrolysis of (A) and thus both Cl atoms should be on same carbon atoms, i.e., (A) must be gem dihalide as well as not on terminals. Thus, only possibility of (A) is $CH_3CCl_2CH_2CH_3$.

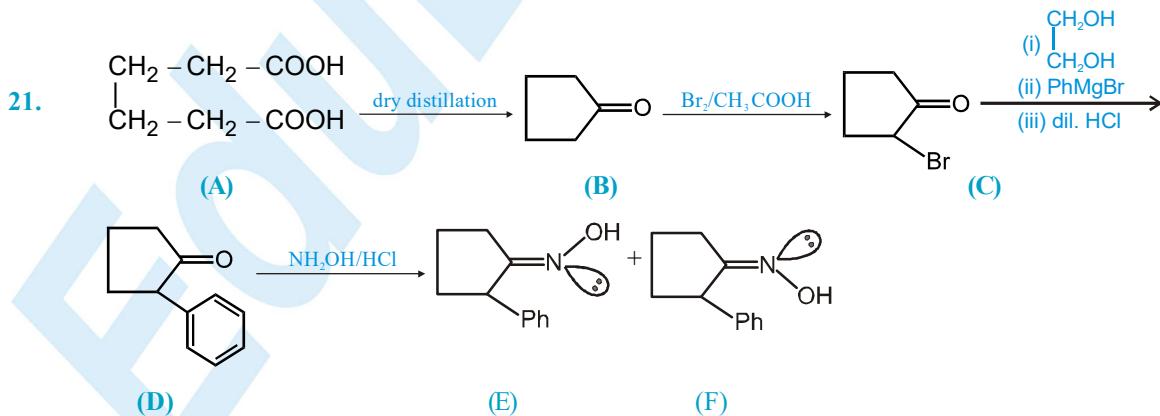


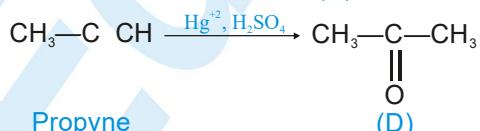
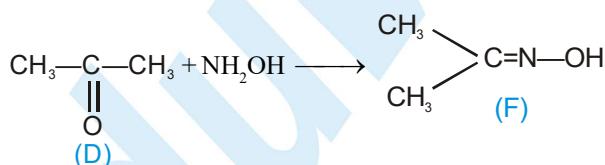
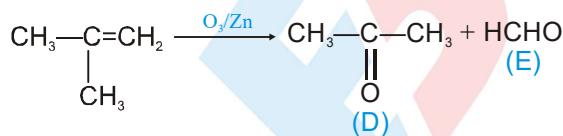
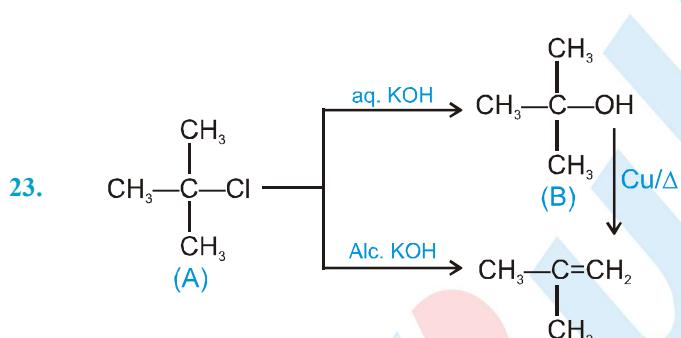
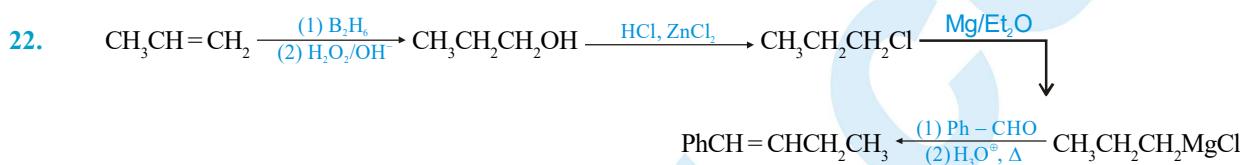
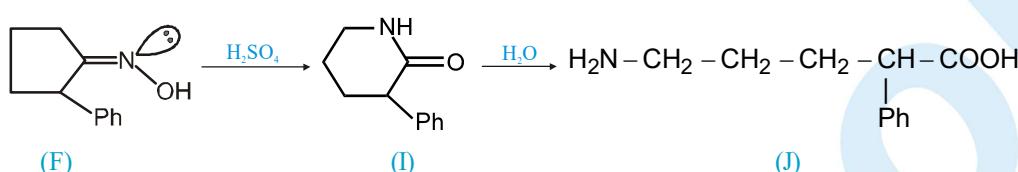
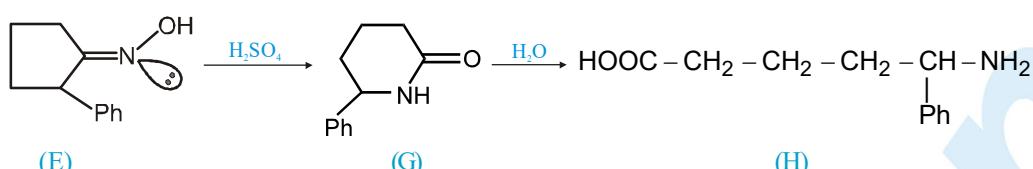
20. $ROH + CH_3MgX \rightarrow CH_4 + ROMgX$
 Let molecular mass of alcohol is M

$$\frac{56}{22400} = \frac{0.22}{M}$$

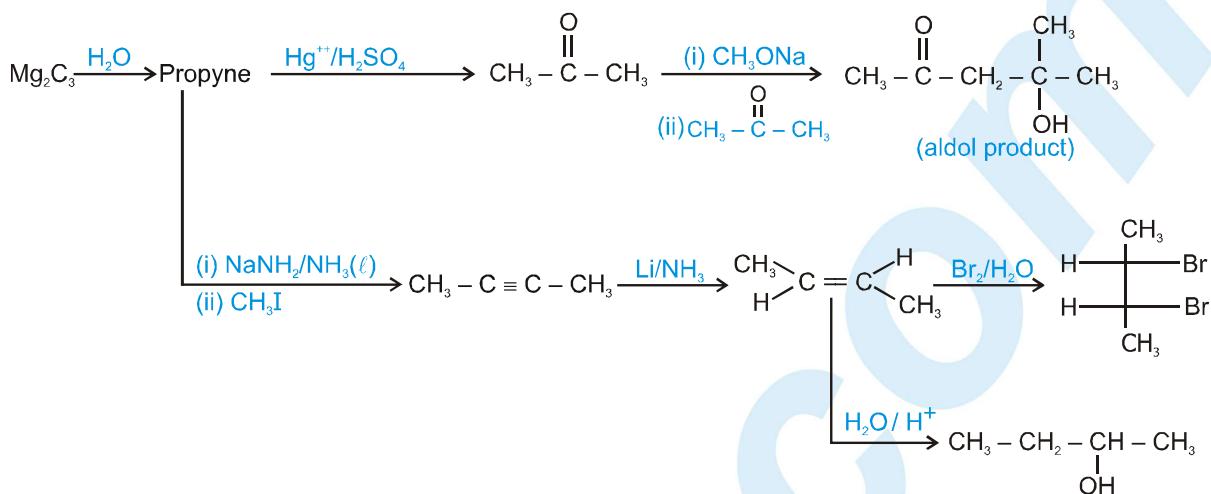
$$M = \frac{22400 \times 0.22}{56} = 88 \text{ gm}$$

General formula of alcohol is $C_nH_{2n+1}OH$ which correspond to the molecular mass 88. Hence value of n = 5. So molecular formula of alcohol is $C_5H_{11}OH$.

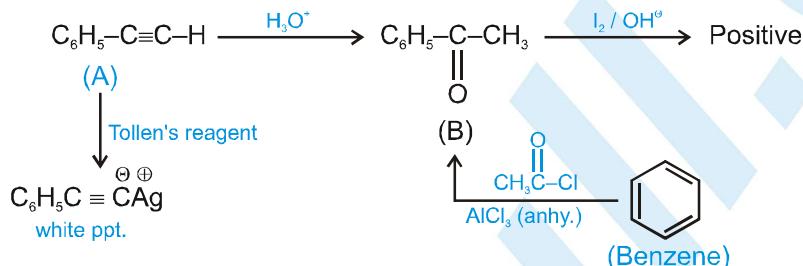




24.

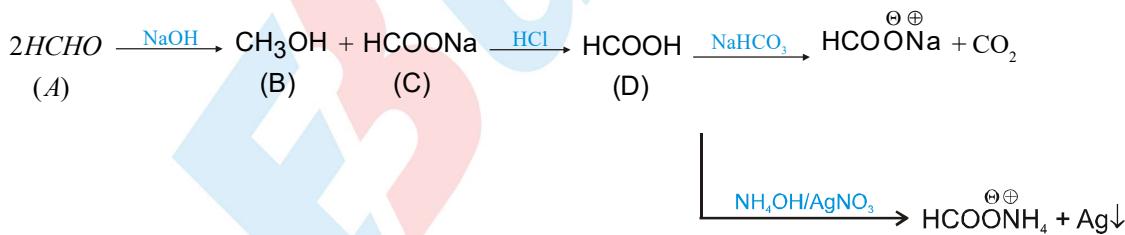


25.

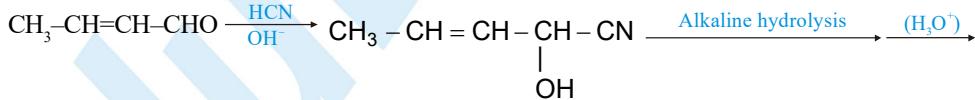


27.

Empirical formula of (A) \Rightarrow CH₂O
 Molecular formula of (A) \Rightarrow HCHO

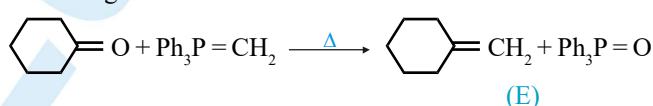


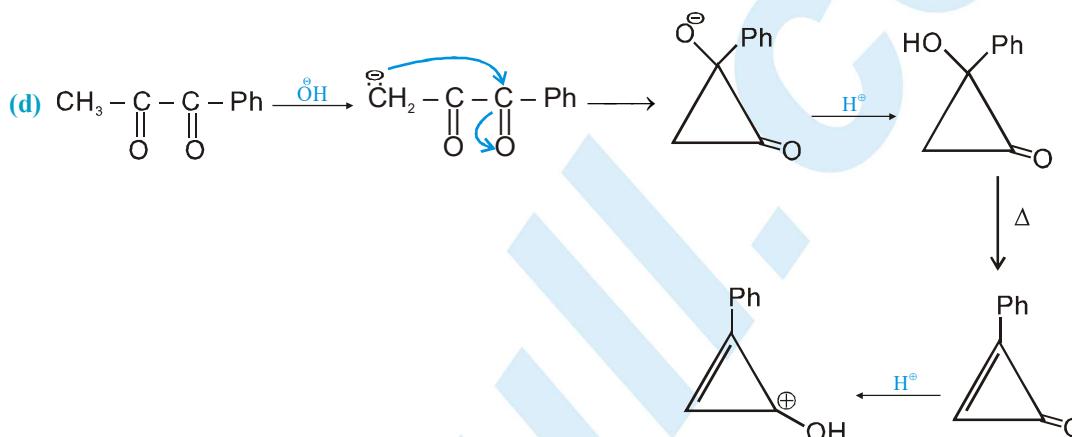
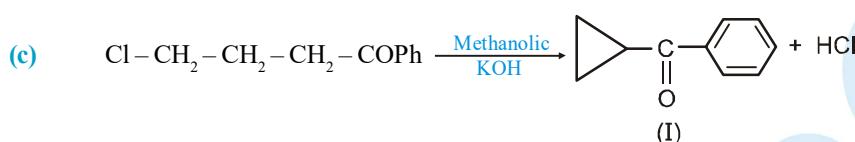
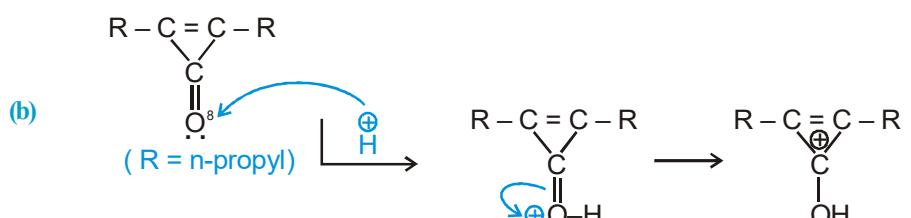
28.



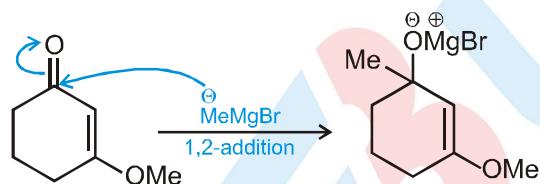
30.

(a) It is Wittig reaction.

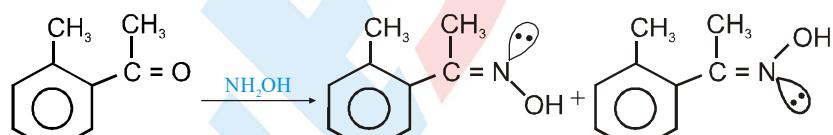




32.



33.



(A)

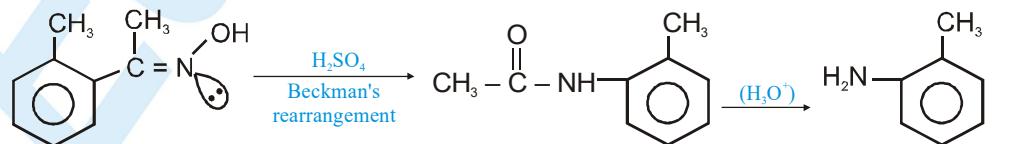
(B)

(C)



(C)

(D)



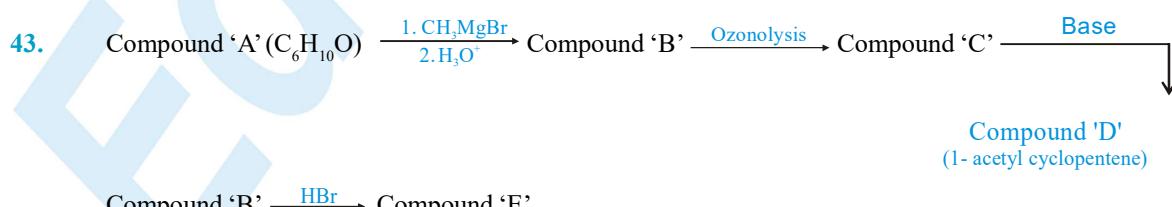
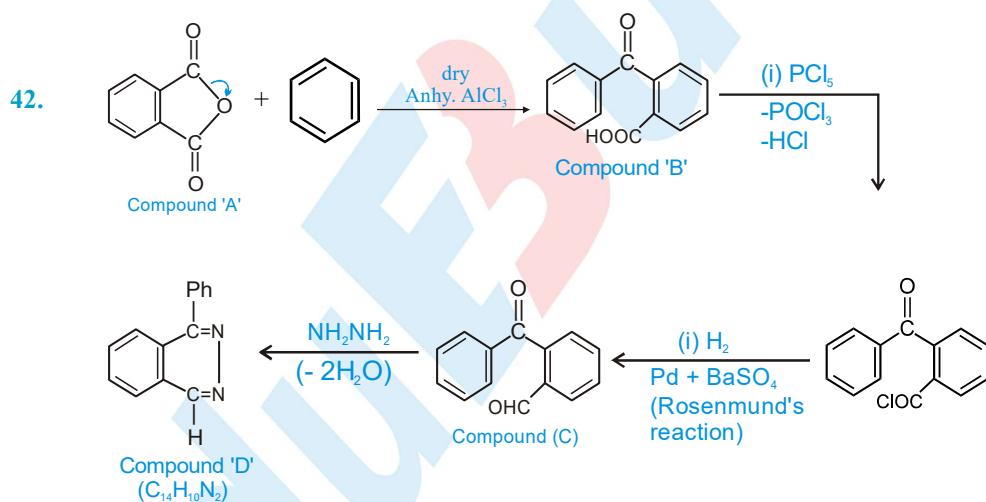
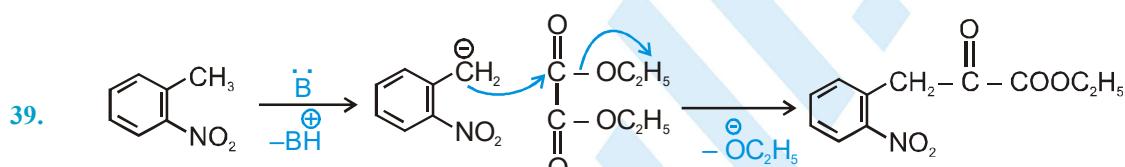
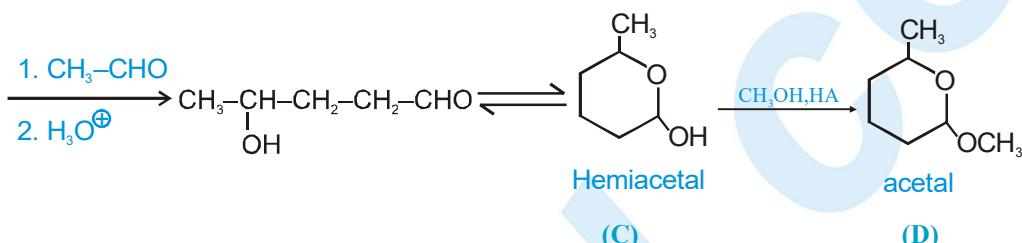
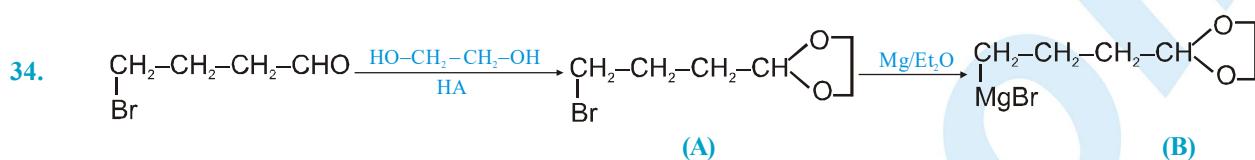
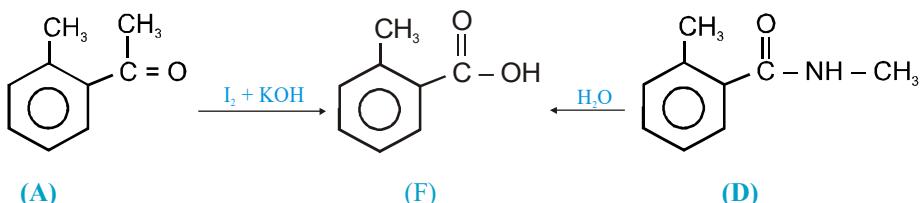
(B)

(E)

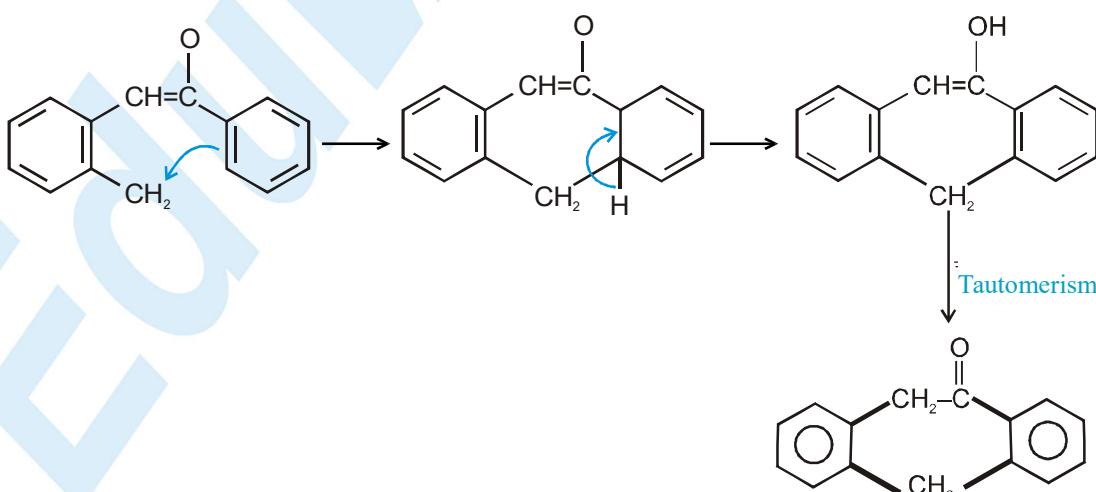
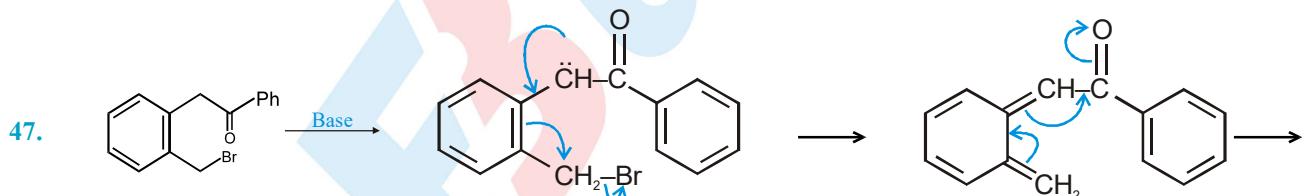
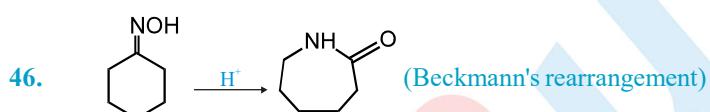
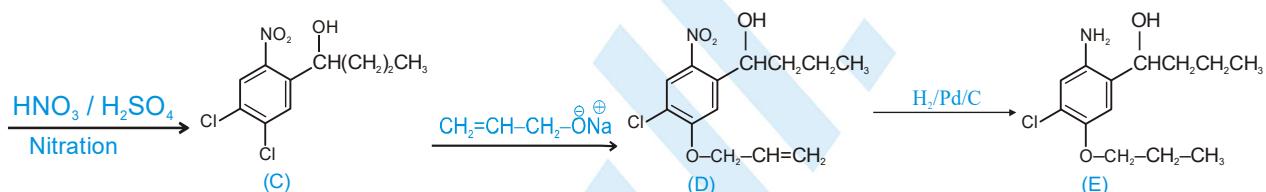
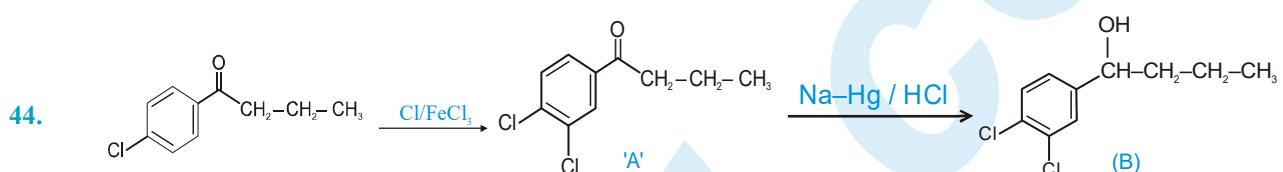
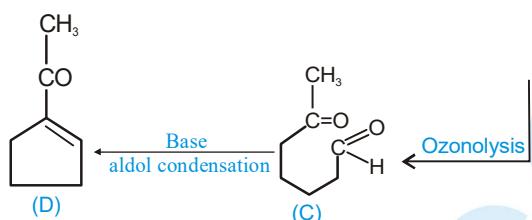
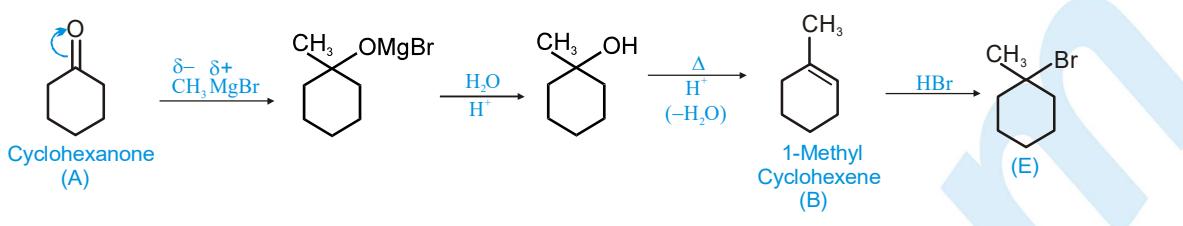


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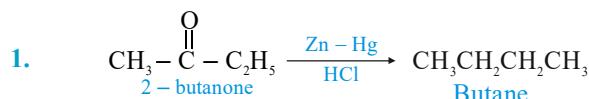


Compound 'A' is cyclic carbonyl compound which gives following reaction according to given problem.

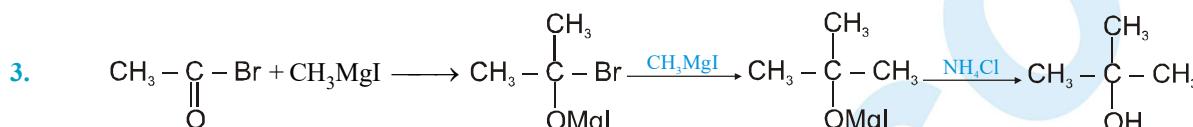
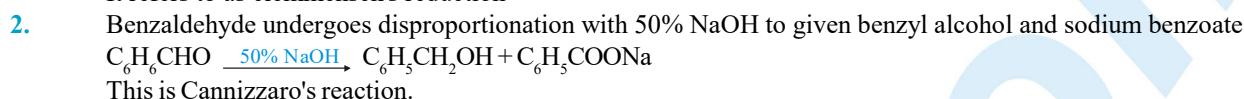


EXERCISE - 5

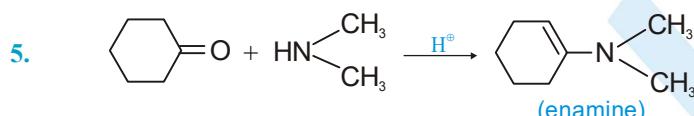
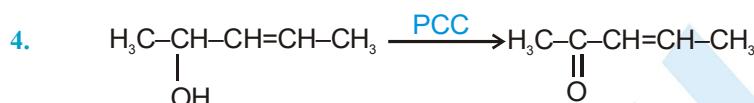
Part # I : AIEEE/JEE-MAIN



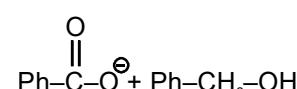
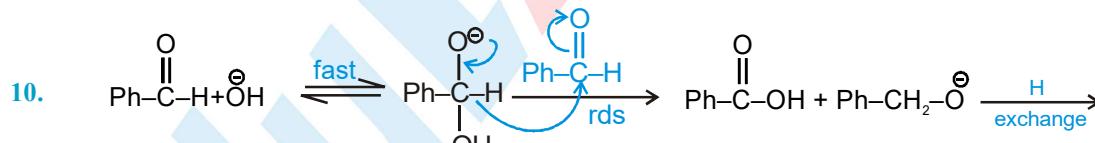
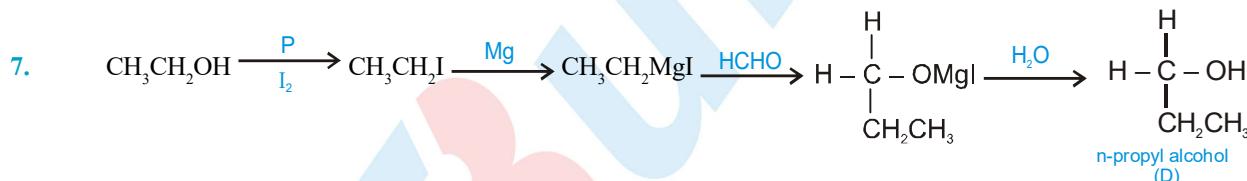
It refers to as clemmensen's reduction



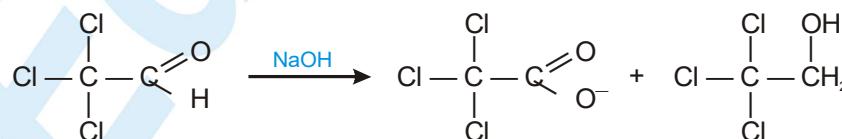
2-Methyl-2-propanol

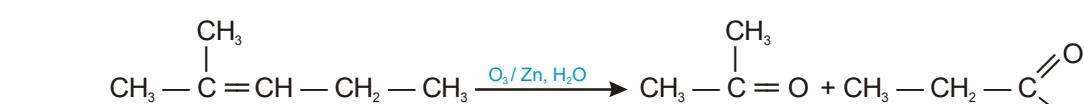


6. As increase steric hinderance around carbonyl group then rate of nucleophilic addition reaction decreases.



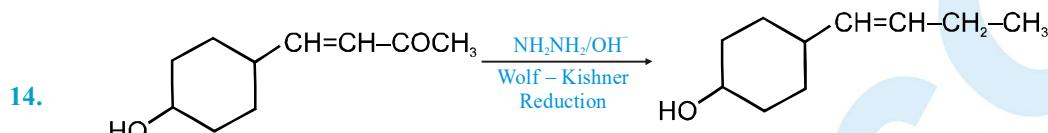
11. The cannizzaro product of given reaction yields 2, 2, 2-trichloroethanol.



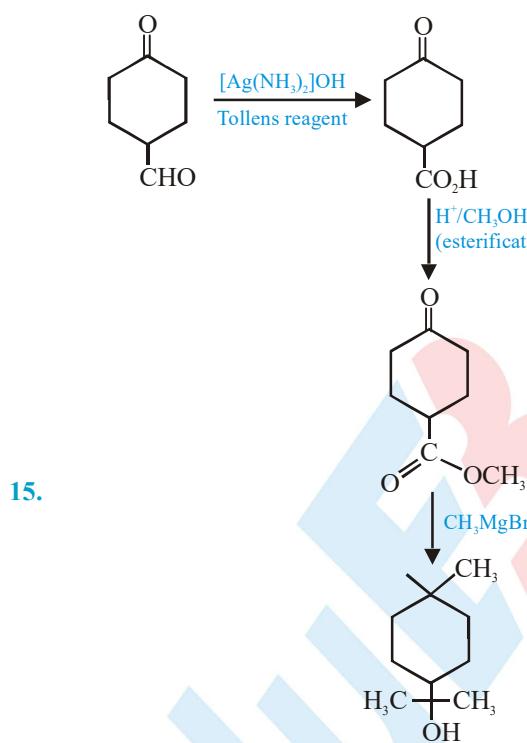


12. (2-Methyl-2-pentene)
(A)

13. $\begin{array}{c} \text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{OH} \end{array}$ isobutyl alcohol does't give positive iodoform test.



-OH group and alkene are acid-sensitive groups so clemmensen reduction can not be used.

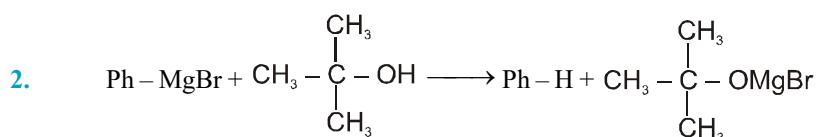


15.

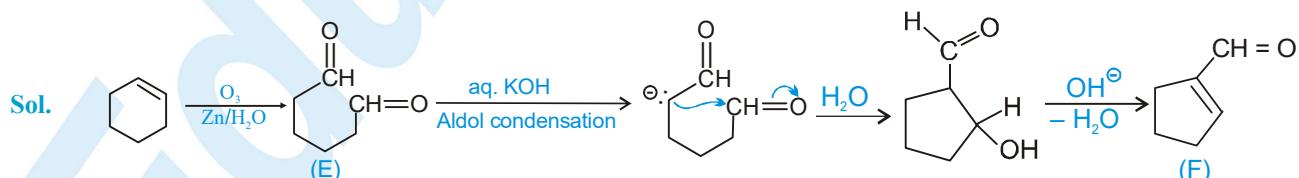
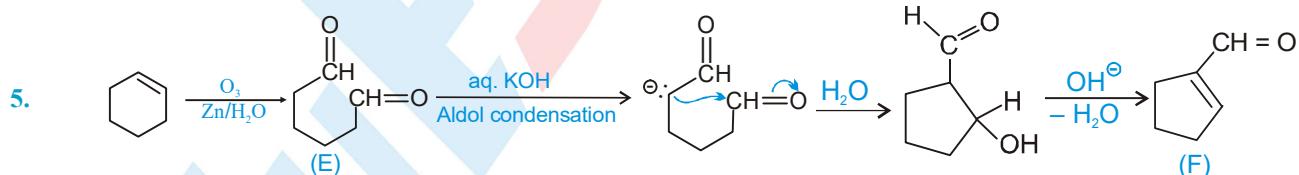
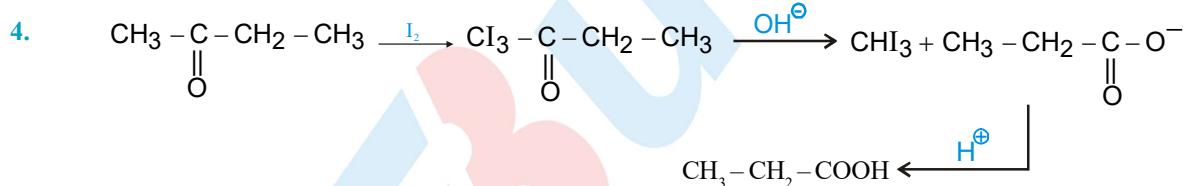
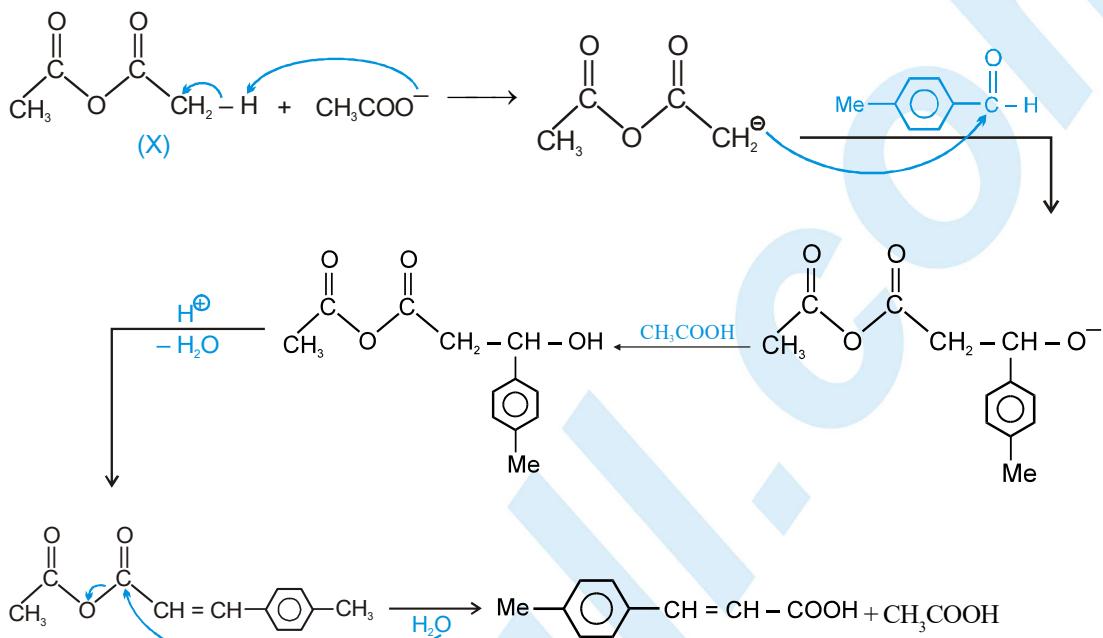
Part # II : IIT-JEE ADVANCED

1. $\text{Ph}-\text{C}(=\text{O})-\text{Ph} < \text{CH}_3-\text{C}(=\text{O})-\text{CH}_3 < \text{CH}_3-\text{C}(=\text{O})\text{H}$





3. This is Perkin reaction



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

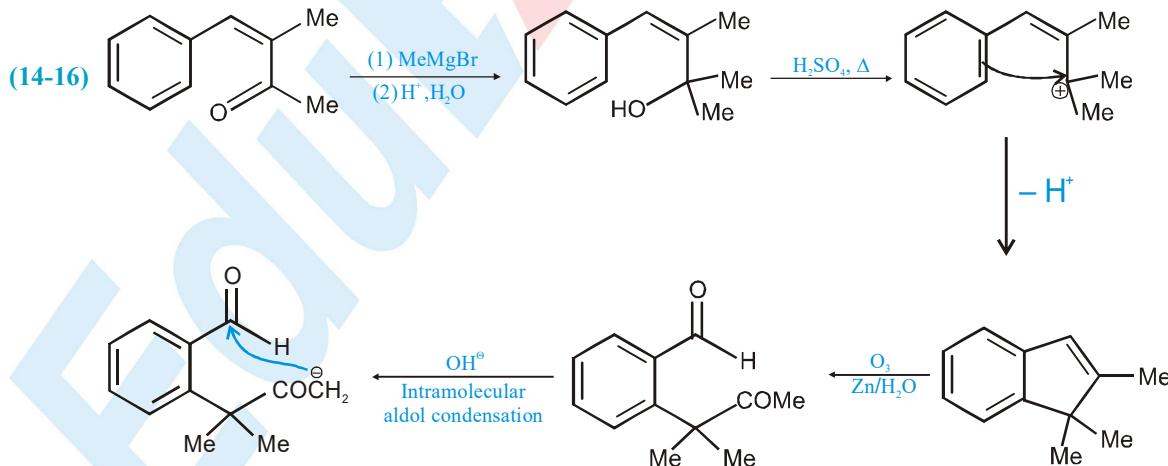
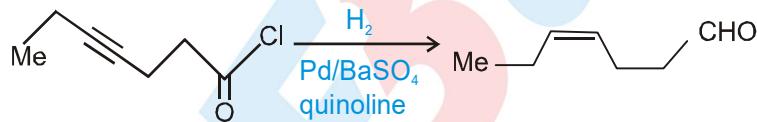
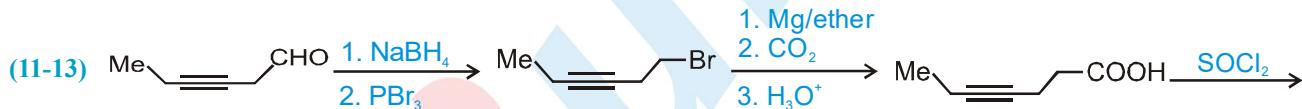
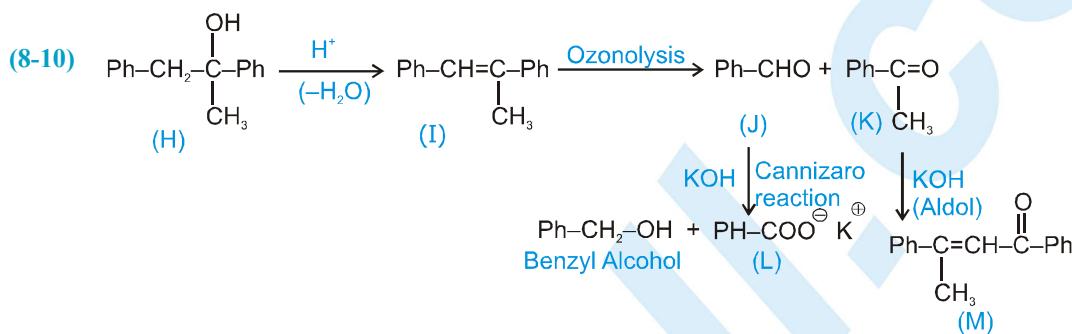
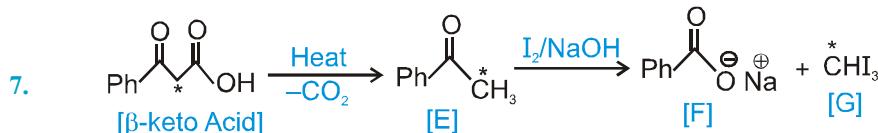
6. (p) 2,4-DNP (2,4-dinitrophenyl hydrazine) is used to distinguish carbonyl compounds as it gives solid orange precipitate of 2,4-dinitrophenyl hydrazone.

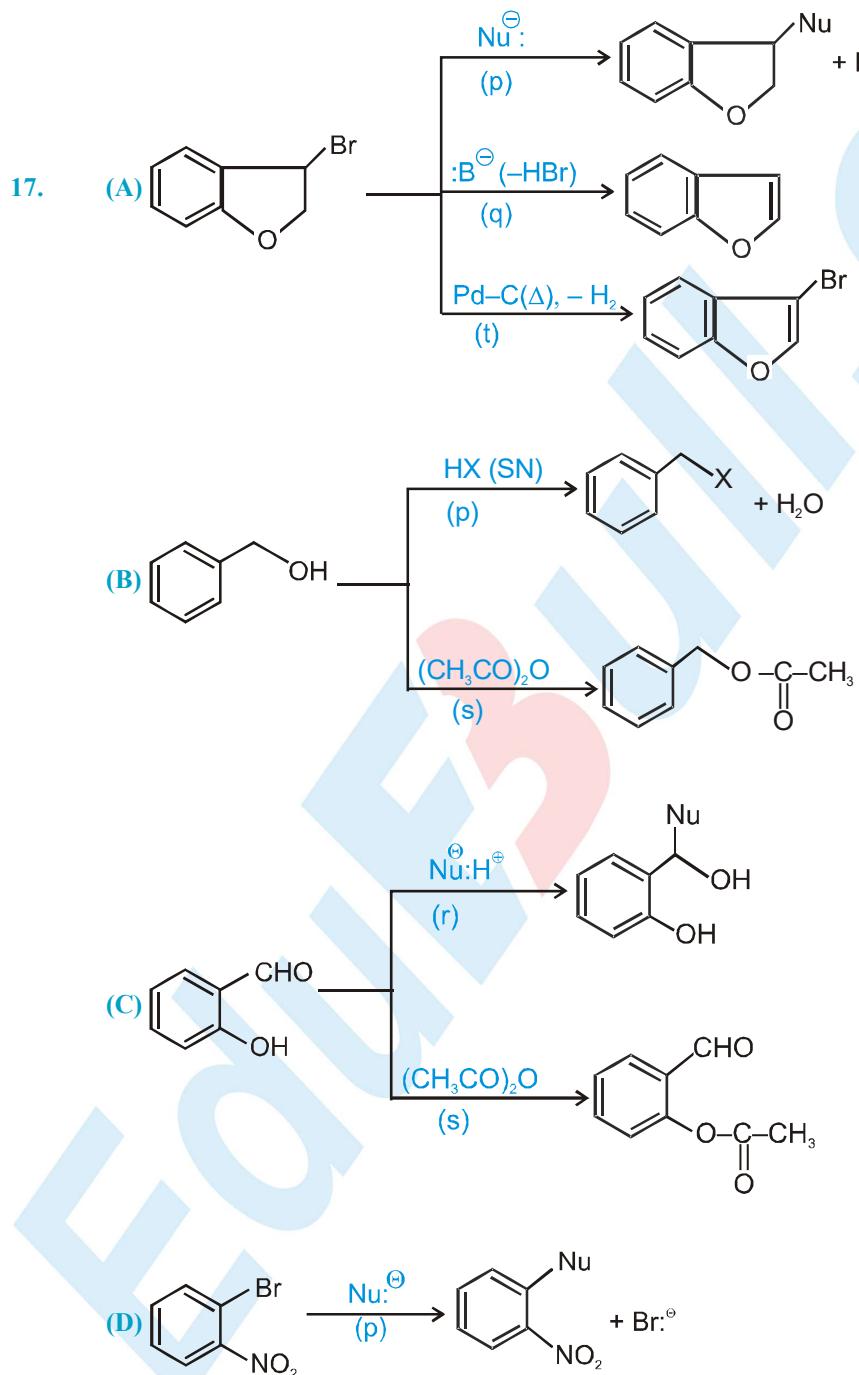
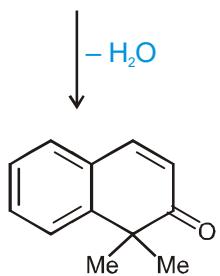
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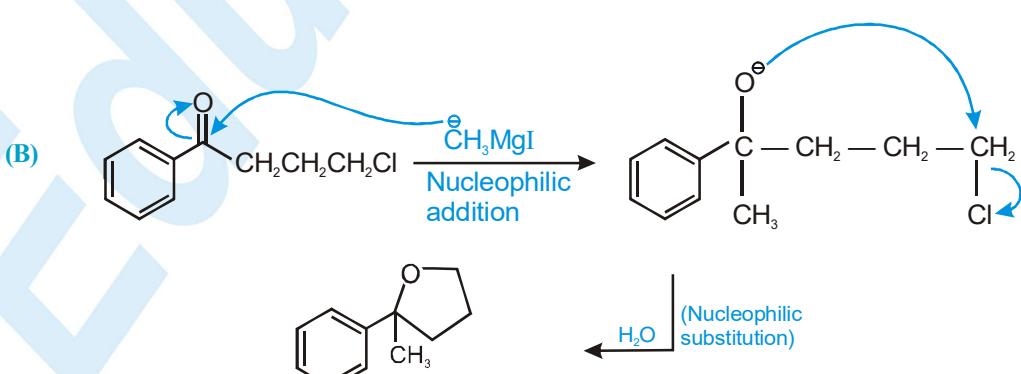
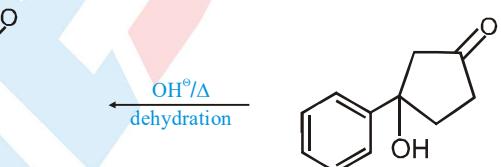
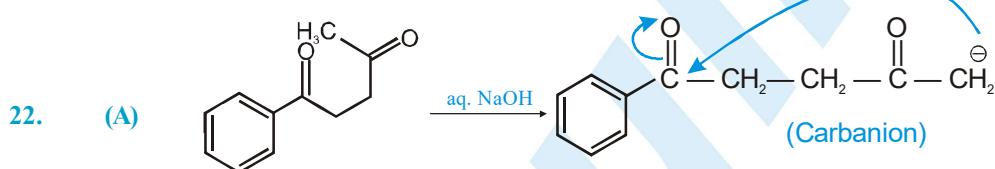
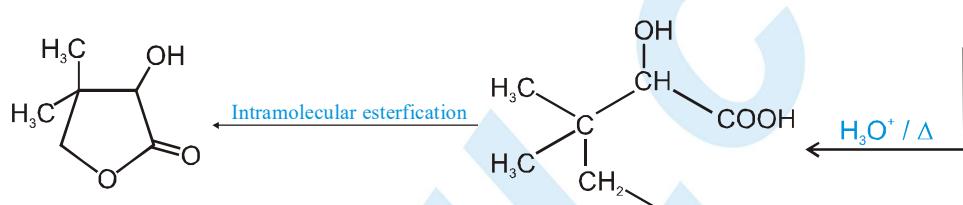
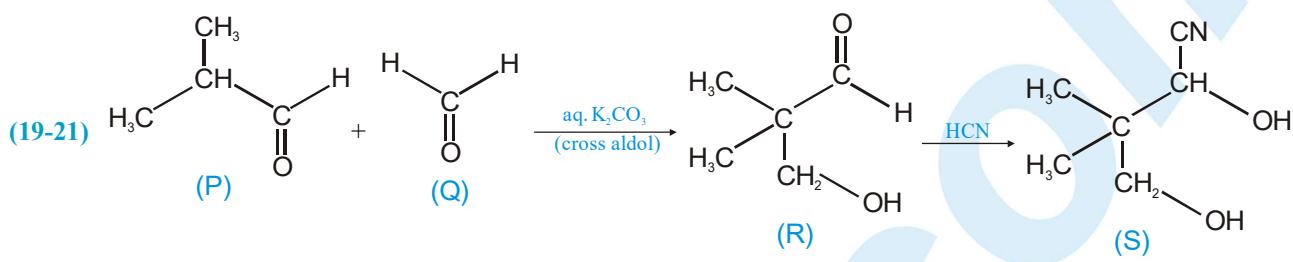
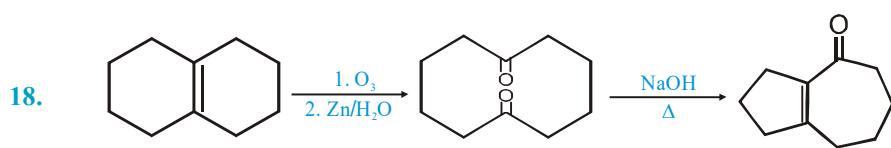
(q) Tollen's reagent (ammonical silver nitrate solution) gives white precipitate with alkyne and silver mirror test with aldehyde.

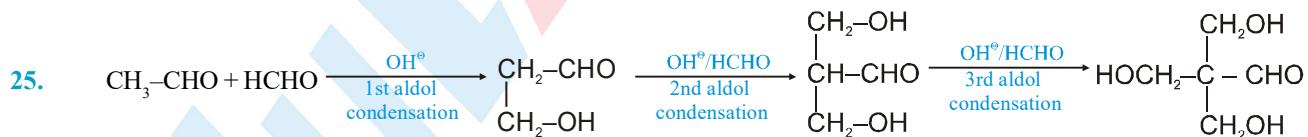
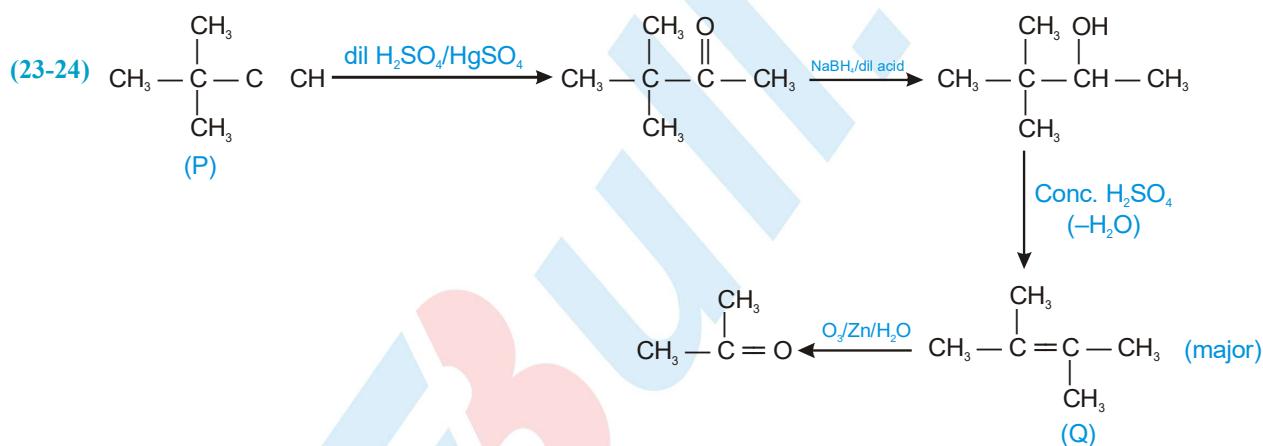
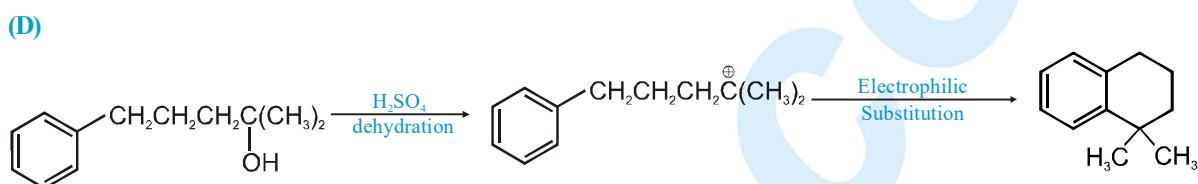
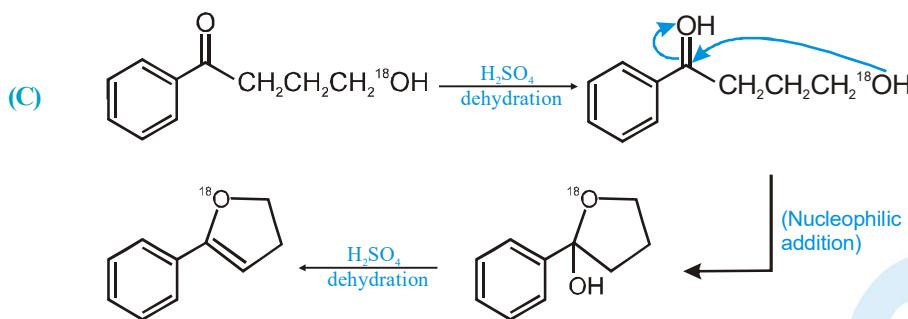
(r) (i) CN^- will give AgCN with AgNO_3 (ii) is nucleophile (iii) forms cyanohydrin

(s) (i) I^- will give AgI with AgNO_3 (ii) is nucleophile



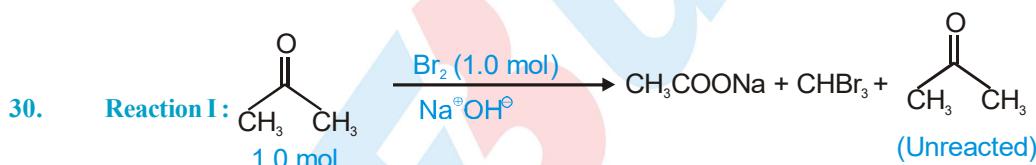
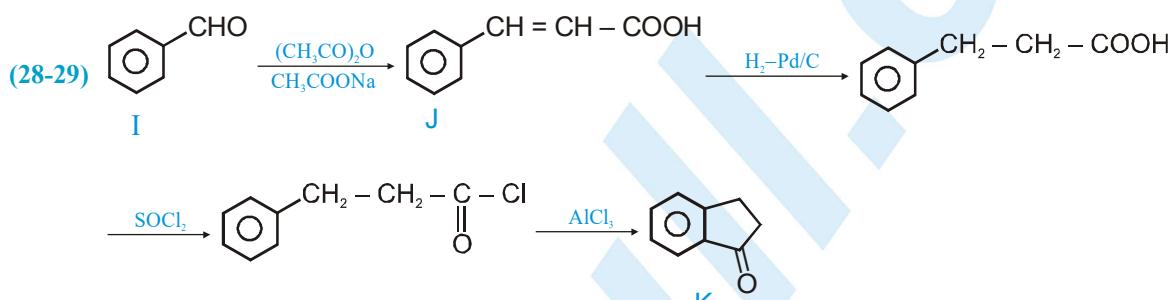
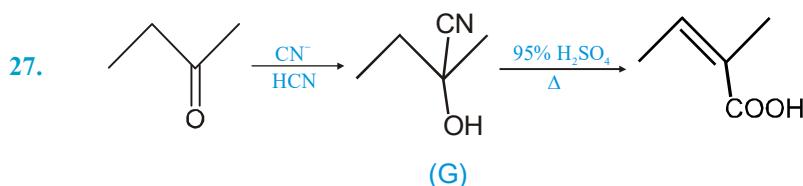
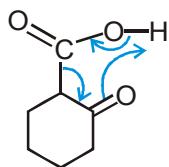




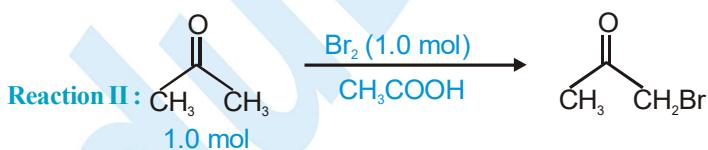


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26. In decarboxylation, β -carbon acquires $\delta-$ charge. Whenever $\delta-$ charge is stabilized, decarboxylation becomes simple. In (B), it is stabilized by $-m$ & $-I$ of $C=O$, which is best amongst the options offered,



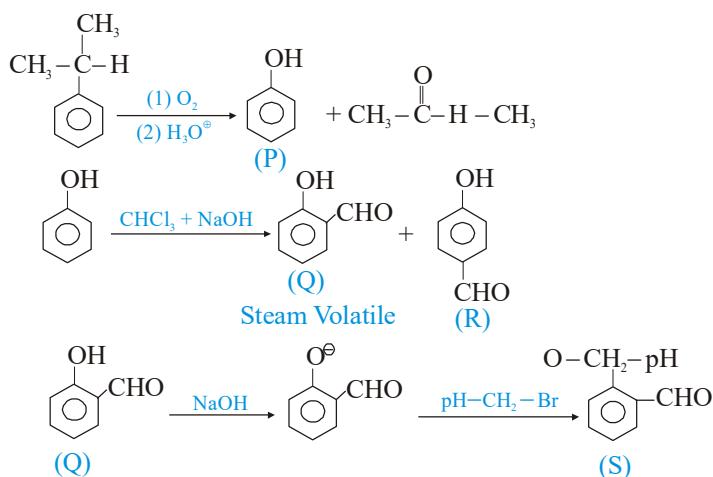
(In basic medium complete haloform reaction takes place since the rate of reaction increases with each α -halogenation)



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

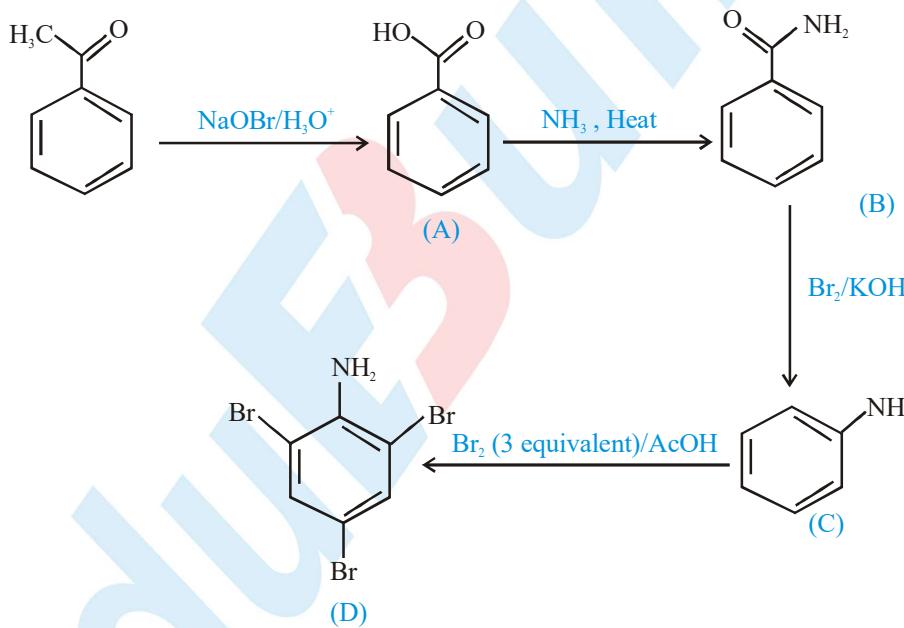
31. B, C





32. A, B, C

$\text{CH}_2 = \text{CH} - \text{CHO}$, and gives positive test with Tollen's reagent.

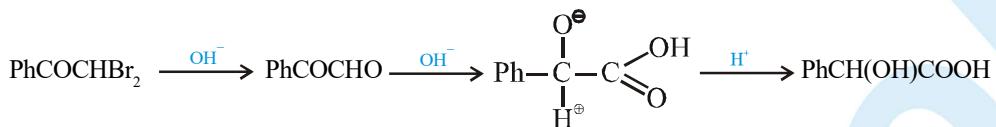


$$\text{Moles of D formed} = 10 \times 0.6 \times 0.5 \times 0.5 \times 1 = 1.5$$

$$\text{Mass of D formed} = 1.5 \times 330 = 495 \text{ gram}$$

MOCK TEST

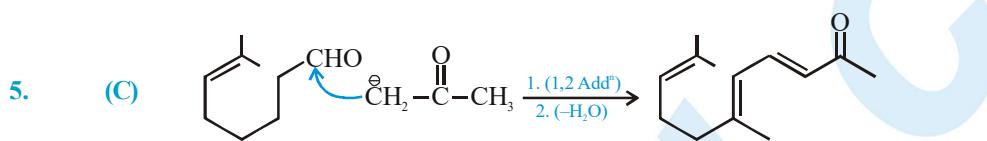
1. (B)



2. (D)

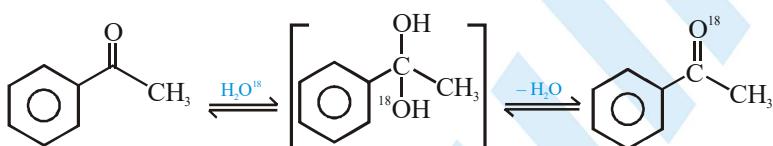
3. (B) Benzoin condensation

4. (C) Intramolecular adol condensation take place.



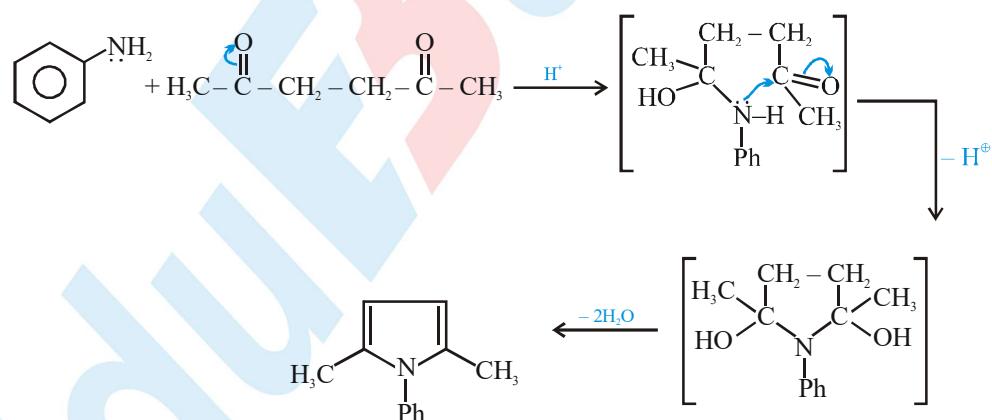
6. (D) :NH₂NH₂ is most nucleophilic as compared others.

7. (D)

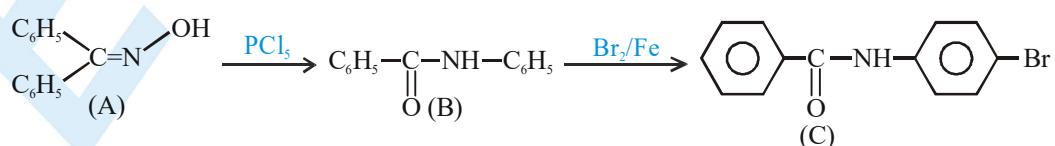


In water, carbonyl compounds form hydrates.

8. (B)

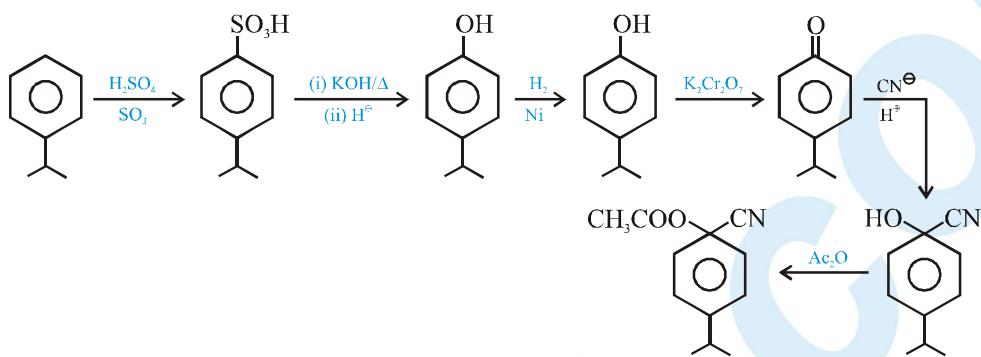


9. (C)

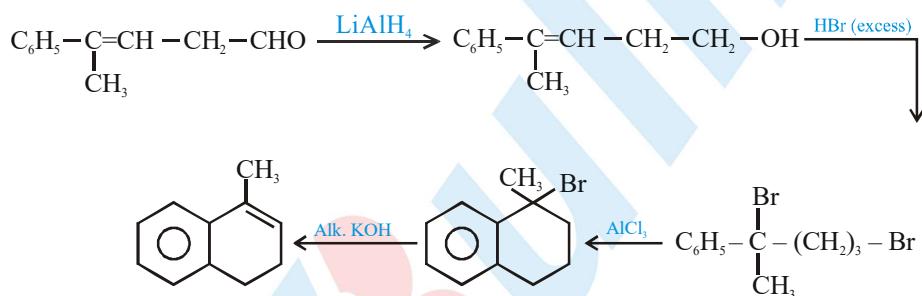


10. (C) I is conjugated system.

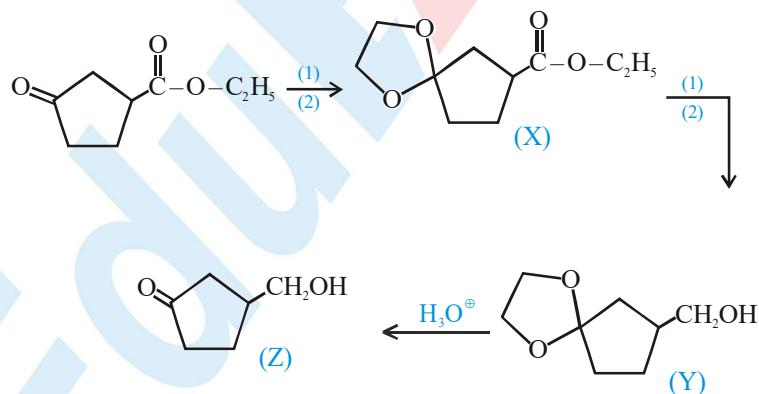
11. (D)



12. (C)



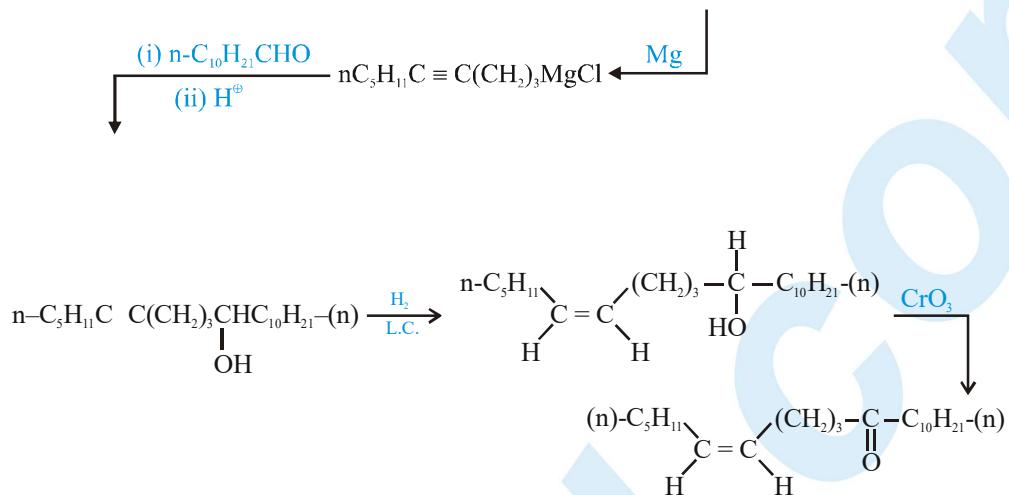
13. (C)



14. (C) Ag_2O oxidises the aldehyde selectively to the carboxylic acid.

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15. (A)

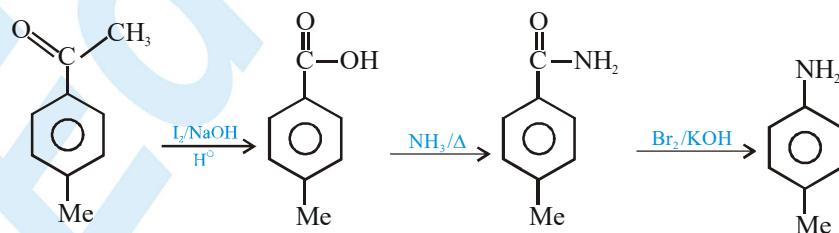
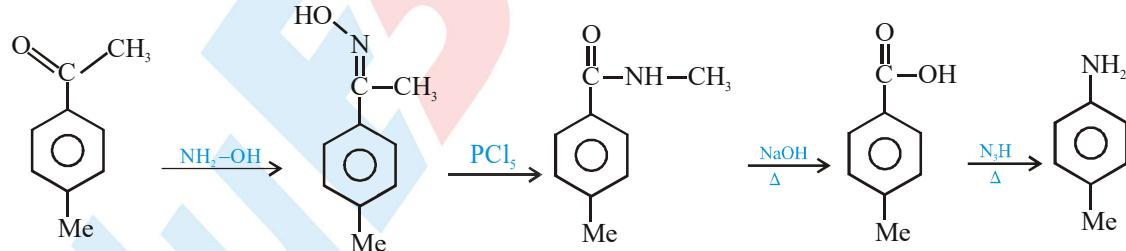


17. (A, B, C) Bakemann's rearrangement.

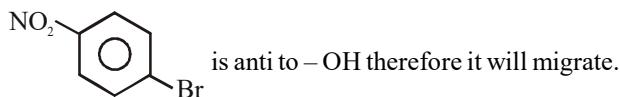


It is a **Cannizaro reaction**.

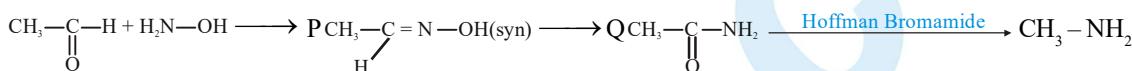
19. (B, C)



20. (A, B, C, D)
 21. (B, D)
 22. (C)
 23. (A)
 24. (A)
 25. (A)
 26. (A)
 27. (A)
 28. (A)



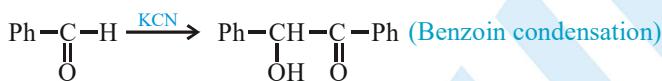
29. (B)



30. (B, D)

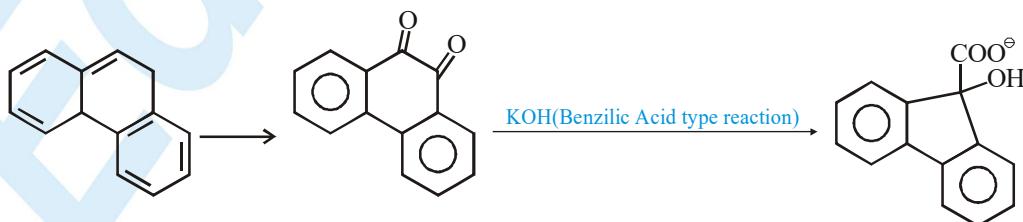
Shift is retentive therefore initial configuration will be maintained. Initially it is "S" and afterwards it will be "R" due to change in Priority of atoms not connected on dextro laevo can be made.

32. (A) \rightarrow p, q, s (B) \rightarrow r, s (C) \rightarrow q (D) \rightarrow r, s

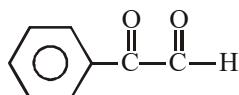


33. a \rightarrow s, b \rightarrow r, c \rightarrow q, d \rightarrow p

- 34.
- | | | |
|---|---|---|
| X | Y | Z |
| 7 | 3 | 2 |



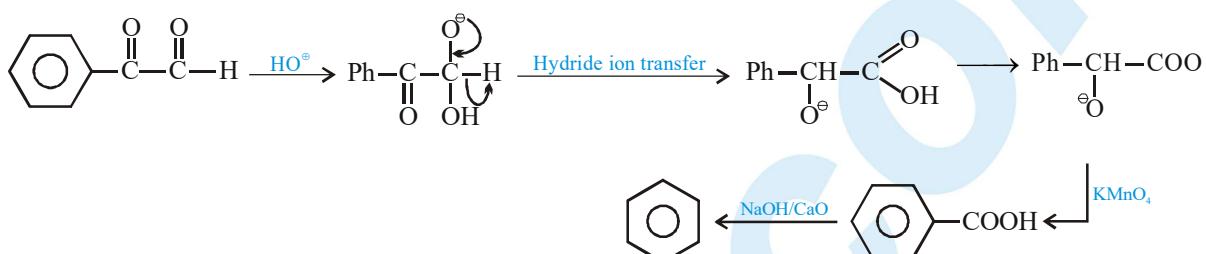
35. 72



or



Internal Cannizaro



36. **Tischenko reaction**

