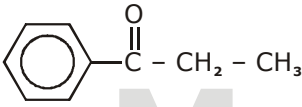
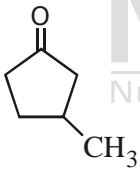
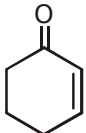


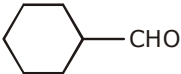
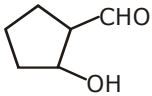
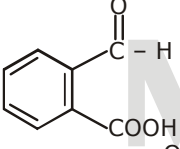
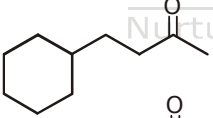
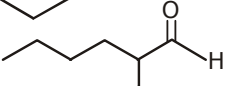
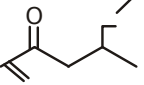
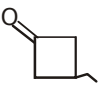
CARBONYL COMPOUNDS**1. Introduction**

These have general formula $C_nH_{2n}O$ and contains $>C=O$ group which is present in aldehyde $\begin{array}{c} R \\ \diagdown \\ C = O \\ \diagup \\ H \end{array}$

and $\begin{array}{c} R \\ \diagdown \\ C = O \\ \diagup \\ R \end{array}$ ketone. Thus aldehydes and ketones are collectively called as carbonyl compounds

5. IUPAC Nomenclature of Aldehydes and Ketones

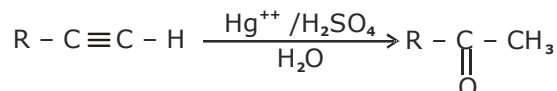
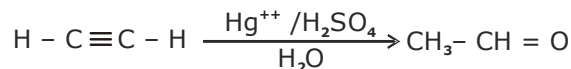
	Ketones	IUPAC name
1.	$CH_3 - \overset{\overset{O}{\parallel}}{C} - CH_3$	Propanone
2.	$CH_3 - \overset{\overset{O}{\parallel}}{C} - CH_2 - CH_3$	Butanone
3.	$CH_3 - \overset{\overset{O}{\parallel}}{C} - CH_2 - CH_2 - CH_3$	Pentan-2-one
4.	$CH_3 - \overset{\overset{O}{\parallel}}{C} - \overset{\overset{O}{\parallel}}{C} - CH_3$	Butanedione
5.	$CH_3 - \overset{\overset{CH_3}{\mid}}{CH} - \overset{\overset{O}{\parallel}}{C} - \overset{\overset{CH_3}{\mid}}{CH} - CH_3$	2, 4-Dimethyl pentan-3-one
6.		1-Phenylpropan-1-one
7.		3-Methylcyclopentanone
8.		Cyclohex-2-en-1-one or 2-Cyclohexenone
9.	$CH_3 - \overset{\overset{O}{\parallel}}{C} - CH_2 - \overset{\overset{OH}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}} - CH_3$	4-Hydroxy-4-methyl pentan-2-one

	Ketones	IUPAC name
10.	$\text{CH}_3 - \overset{\text{O}}{\underset{\text{ }}{\text{C}}} - \text{H}$	Ethanol
11.	$\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\underset{\text{ }}{\text{C}}} - \text{H}$	Propanol
12.	$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \overset{\text{O}}{\underset{\text{ }}{\text{C}}} - \text{H}_3$	Butanol
13.	$\text{CH}_3 - \overset{\text{OH}}{\underset{ }{\text{CH}}} - \text{CH}_2 - \overset{\text{O}}{\underset{\text{ }}{\text{C}}} - \text{H}$	3-Hydroxybutanal
14.	$\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH} - \text{CHO}$	Pent-2-en-1-el or Pen-2-enal
15.	$\text{CH}_2\text{CH}_2\text{CH}_2 - \overset{\text{Br}}{\underset{ }{\text{CH}}} - \overset{\text{CH}_3}{\underset{ }{\text{CH}}} - \text{CH}_2 - \overset{\text{O}}{\underset{\text{ }}{\text{C}}} - \text{H}$	4-Bromo-3-methyl heptanal
16.		Cyclohexanecarbaldehyde
17.		2-Hydroxycyclopentane -1-carbaldehyde
18.	$\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\underset{\text{ }}{\text{C}}} - \text{CH}_2 - \text{CHO}$	3-Oxopentanal
19.	$\text{CH}_3 - \overset{\text{O}}{\underset{\text{ }}{\text{C}}} - \text{CH}_2 - \text{COOH}$	3-Oxobutanoic acid
20.		2-Formylbenzoic acid
21.		2-(3-oxobutyl)-cyclohexanone
22.		2-ethylhex-2-en-1-al
23.		2,5-dimethylheptan-3-one
24.	$\text{CH}_3 - \underset{\text{Cl}}{\underset{ }{\text{CH}}} - \underset{\text{CH}_3}{\underset{ }{\text{CH}}} - \text{CH} = \text{O}$	3-chloro-2-methylbutanal
25.		3-ethylcyclobutanone

8. General methods of preparation of Aldehyde and Ketones

(I) Hydration of Alkyne :

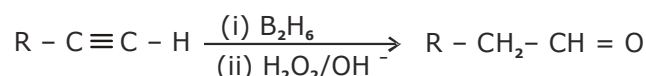
It is addition of water in the presence of heavy metal ion. acetylene on hydration gives aldehyde while any higher alkyne gives ketone.



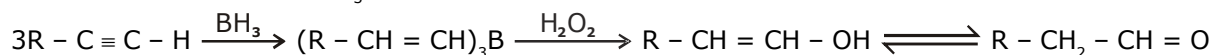
The preparation of carbonyl compounds from alkyne depends upon R part of (A) and also presence of inductive effect group attached to R.

(II) Hydroboration of alkyne :

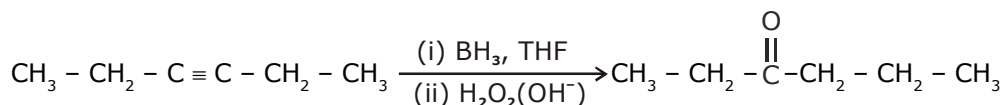
It is used to get aldehyde from alkyne-1. Here reagent is (i) diborane (B_2H_6) (ii) $\text{H}_2\text{O}_2(\text{OH}^-)$



In this reaction Borane (BH_3) is electrophile.

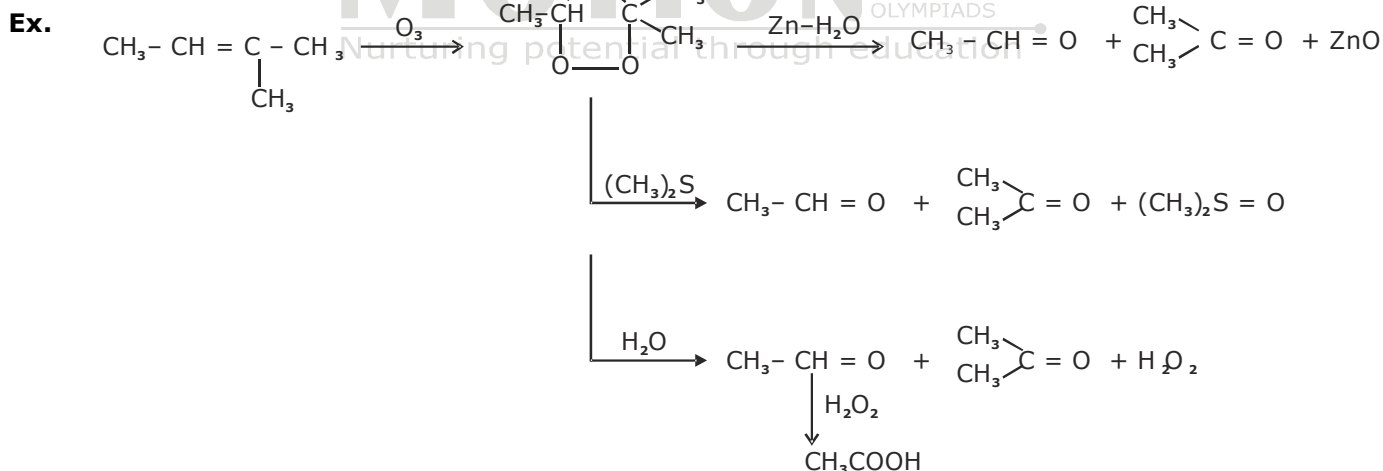
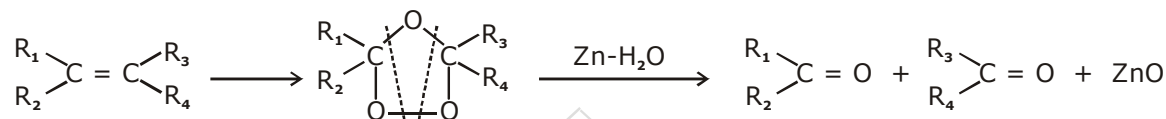


Higher alkyne except alkyne-1 will give ketone during hydroboration



(III) Ozonolysis of alkene :

It is used to get carbonyl compounds from alkene. The reaction is



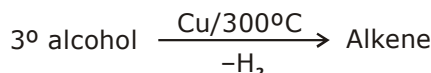
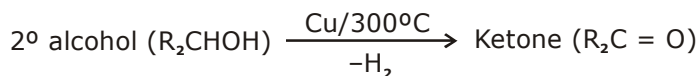
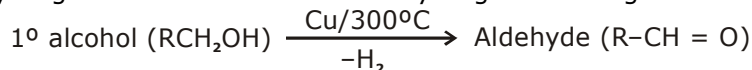
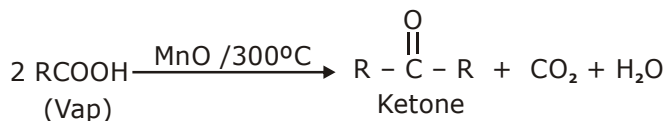
Note :

(I) During the cleavage of ozonide Zn is used to check further oxidation of aldehyde into acid.

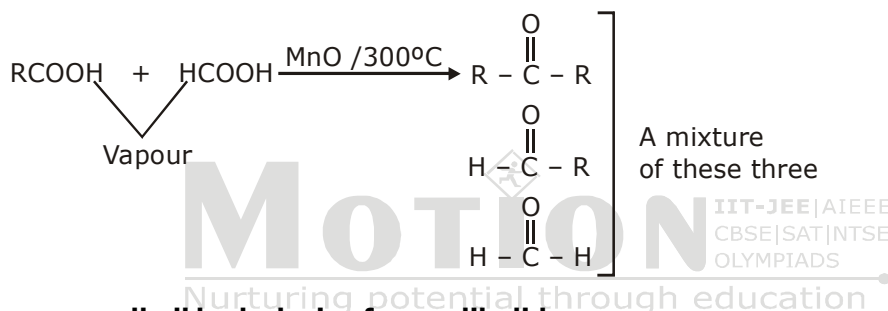
(II) By this method we can locate double bond in olefin or exact structure of hydrocarbon can be determined by knowing ozonolysis product i.e. by placing double bond at the place of two carbonyl oxygen of two carbonyl compounds.

(V) Dehydrogenation of Alcohol :

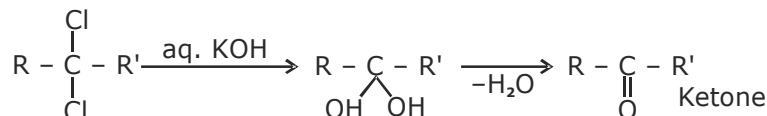
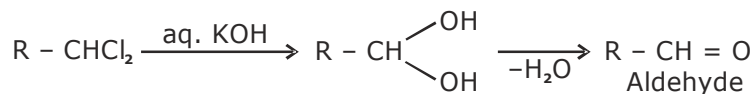
Dehydrogenation means removal of hydrogen and reagent used is heated copper.

**(VI) Dry distillation of Calcium salt of acid :****(VII) On passing vapours of fatty acids over Magnous oxide at 300°C.**

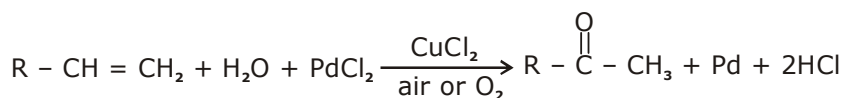
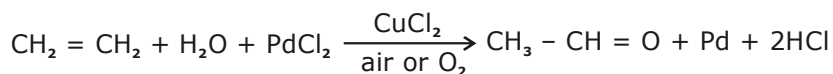
On passing mixture of vapours of fatty acid with formic acid we get a mixture of aldehyde, ketone and formaldehyde.

**(VIII) On aqueous alkali hydrolysis of gem-dihalides :**

Terminal gemdihalides will give aldehyde while non-terminal will give ketones as follows

**(IX) Wacker Process :**

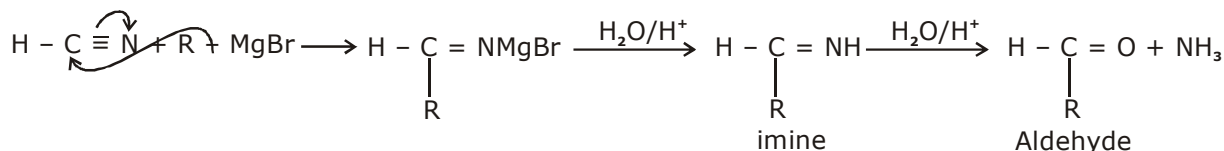
Alkenes can directly be oxidised to corresponding aldehydes or ketone by treating them with a solution of PdCl_2 containing a catalytic amount of CuCl_2 in presence of air or O_2 . Except ethene any higher alkene will give ketone.



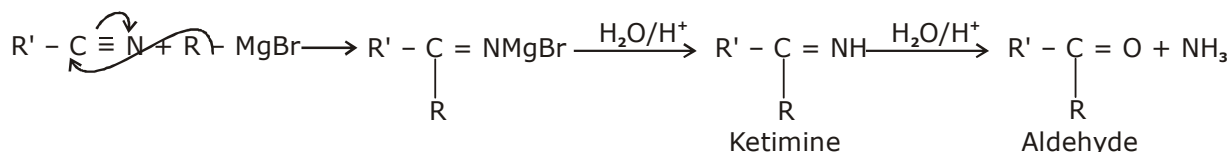
Note : During the reaction PdCl_2 is reduced to Pd and CuCl_2 is reduced to Cu(1)

(X) Preparation of Carbonyl compounds using Grignard's Reagent :

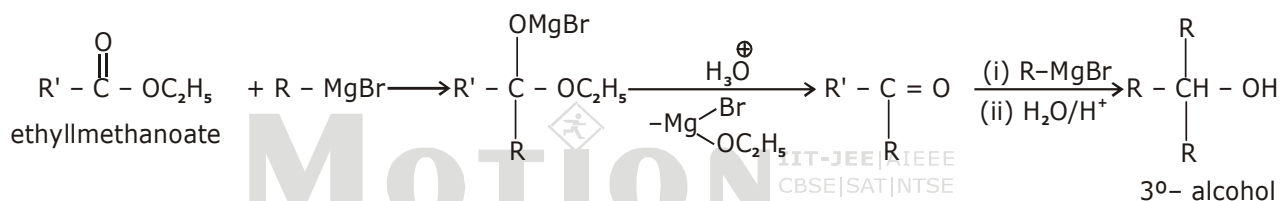
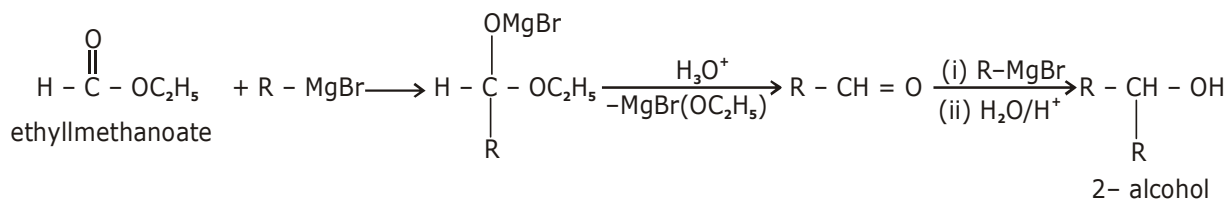
(a) Hydrogen cyanide on treating with Grignard reagent followed by double decomposition with water gives aldehyde via imine.



Alkylcyanide by using above process gives ketone via ketimine



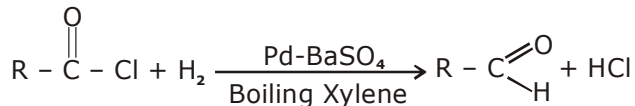
(b) Alkylformate with Grignard reagent gives 2° alcohol via aldehyde while alkyl alkanoate under similar condition gives 3° alcohol via ketone



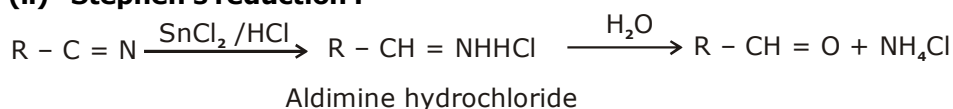
(A) Methode used for the preparation of Aldehydes only.

(i) Rosenmund's reaction :

Here acid chlorides are reduced to aldehyde with H_2 in boiling xylene using palladium as a catalyst supported on barium sulphate.

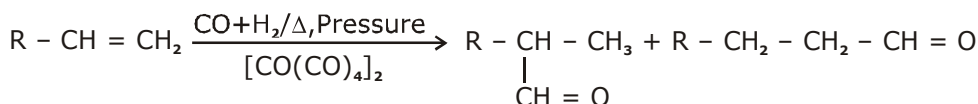


(ii) Stephen's reduction :

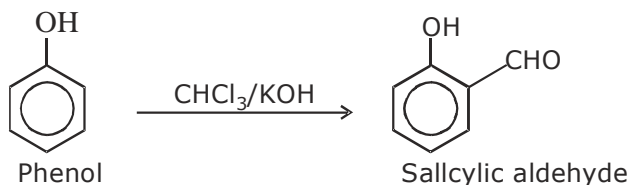
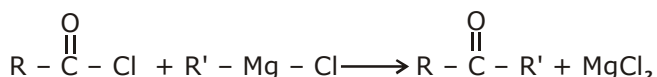
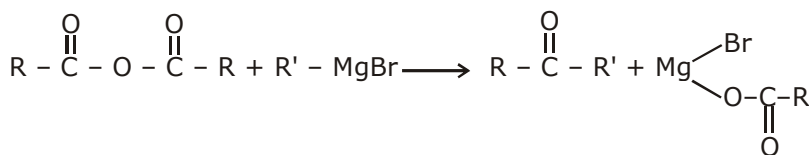
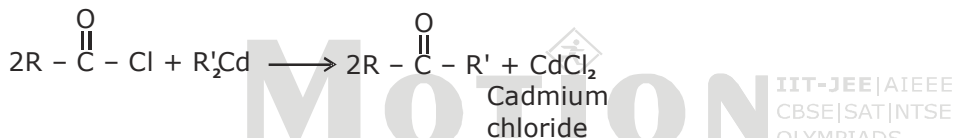
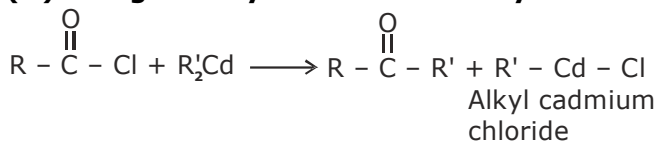
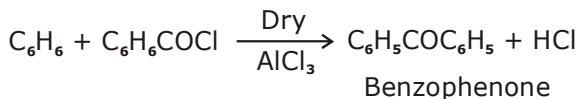
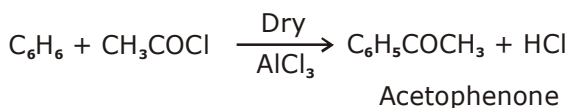
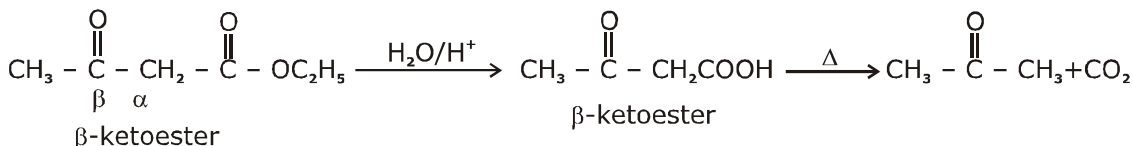


(iii) Oxo-process :

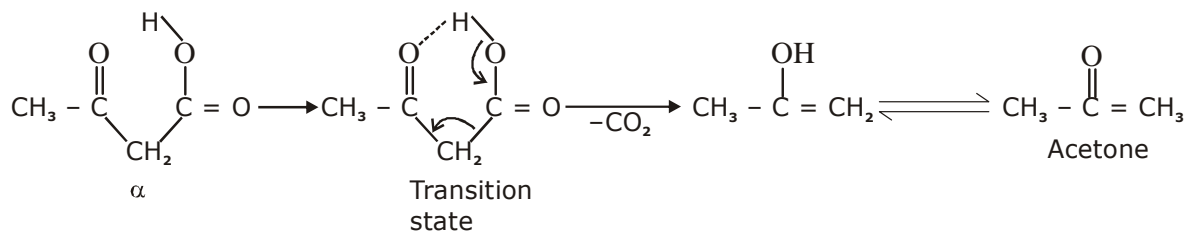
It is also called as carbonylation here alkene reacts with water gas at high temperature and pressure in the presence of cobalt carbonyl catalyst to give aldehyde.

**(iv) Reimer-Teimann Reaction :**

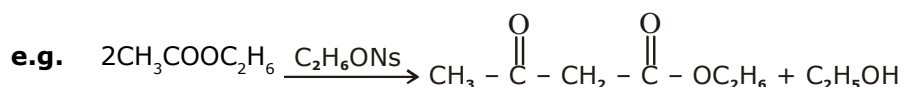
By this method phenolic aldehyde is prepared

**(B) Methods used for the preparation of Ketones only****(i) Using alkanoyl chloride and Grignard reagent****(ii) Using alkanoyl anhydride and Grignard reagent****(iii) Using alkanoyl chloride and dialkyl cadmium****(iv) By acylation or benzylation of aromatic hydrocarbon (Friedel-Carft Reaction)****(v) By Acid hydrolysis followed by heating of β -Ketoester.**

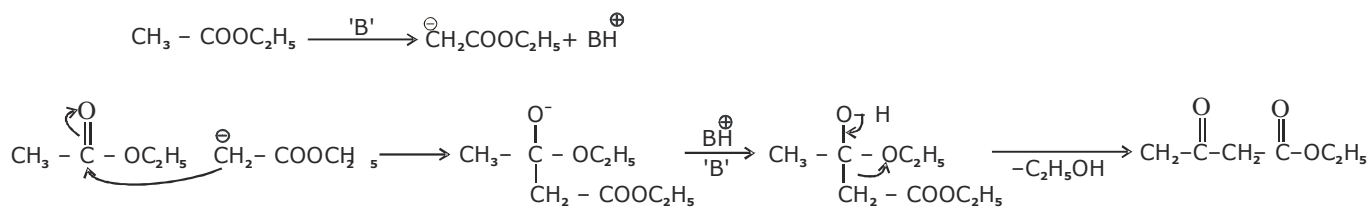
Note : (i) It is β -ketoacid which decarboxylate more readily as it proceeds via six membered cyclic



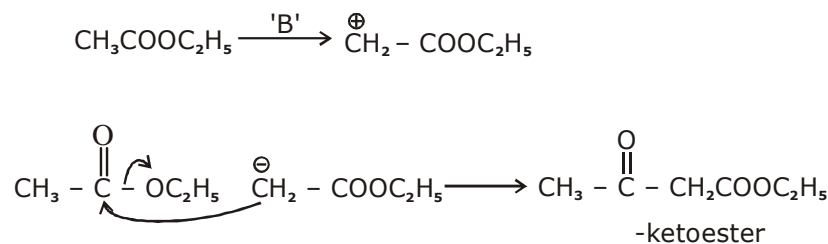
Note : (ii) β -ketoester is obtained by claisen ester condensation of two moles of ester using sodium ethoxide as a base.



Mechanism :

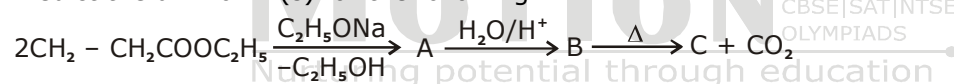


The product β ketoester can be easily obtained by placing anion of one ester at the place of ethoxy part of other ester as –

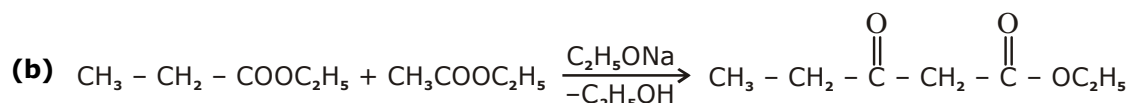
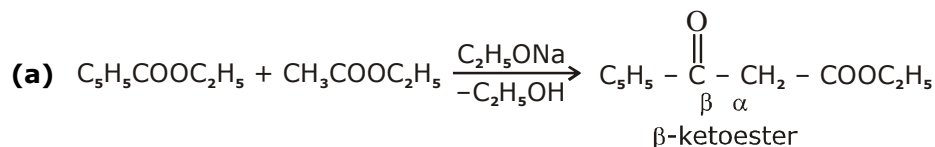


Note : (iii) If two ester units are same then it is inter molecular claisen ester condensation

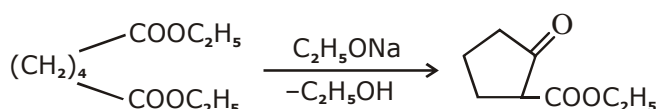
Q. Predict the unknown (s) for the following :



Note : (iv) If two ester units are different then it is crossed Claisen ester condensation



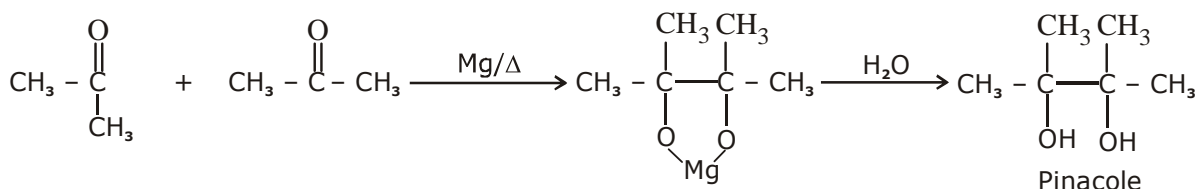
Note : (v) If two ester units are present with in the same molecule then we get cyclic β -ketoester and the reaction is intramolecular Claisen ester condensation.



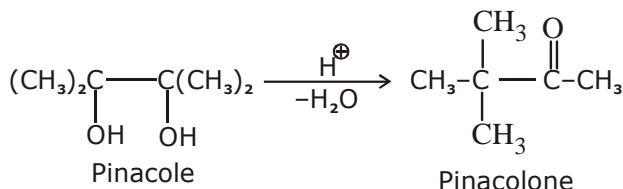
Note : (vi) Active methylene group hydrogen is too acidic that it can be replaced by alkyl of arylalkyl halide in the presence of base like sodium ethoxide.

(C) Pinacol-Pinacolone rearrangement :

Pinacole is obtained when 2 moles of acetone are heated with divalent active metal magnesium followed by treating with water.



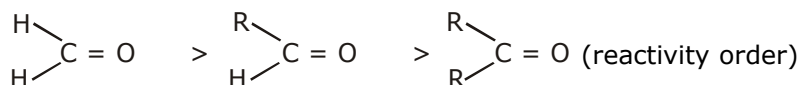
Pinacole undergoes rearrangement in acidic media to give pinacolone



9. Chemical Reactions of Carbonyl Compounds :

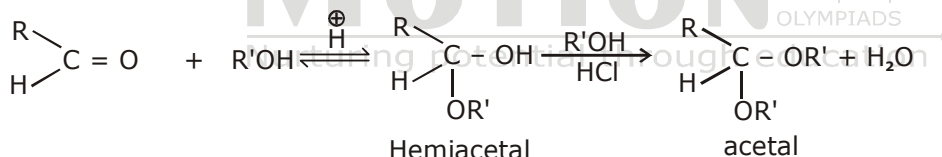
Carbonyl compounds undergo nucleophilic addition reaction and reactivity order will be :

(I) Nucleophilic Addition Reaction :



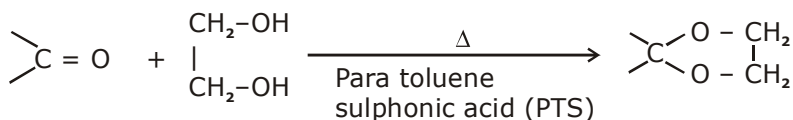
(i) Reaction with alcohol :

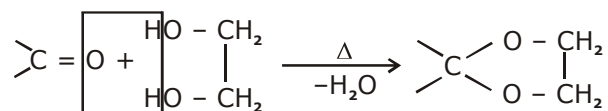
Carbonyl compounds react with alcohols in the presence of dry HCl gas to give acetal (if aldehyde) and ketal if ketone via formation of unstable hemiacetal and hemiketal respectively.



Note :

- (i) Acetal is formed to protect aldehyde for a long time.
- (ii) Acetal has functional groups ether.
- (iii) Acetal formed can be decomposed to original aldehyde by dilute acid.
- (iv) On treating with ethyleneglycol we get cyclic acetal or ketal (1, 3-dioxolans)

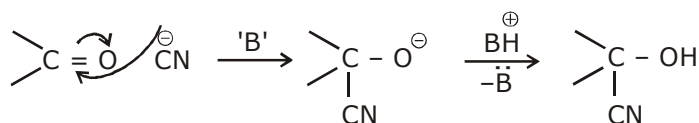
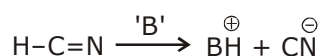
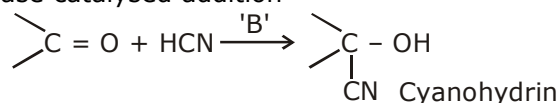


Mechanism :

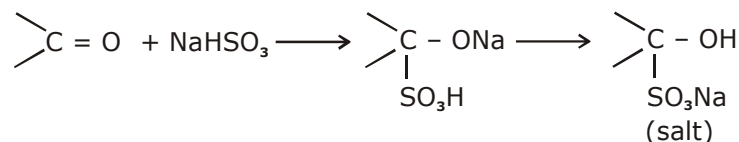
(v) Acetal formation is found to be more favourable than ketal formation. If both the carbonyl groups are present within the molecule.

(ii) Addition of HCN :

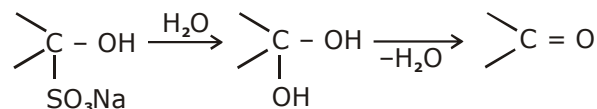
If is base catalysed addition

**(iii) Addition of sodiumbisulphite (NaHSO₃) :**

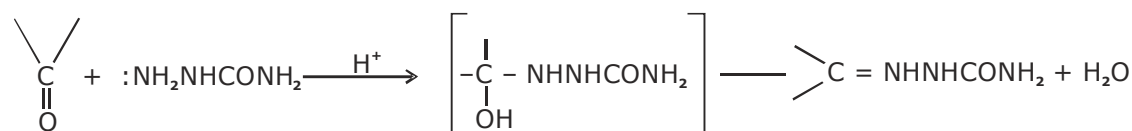
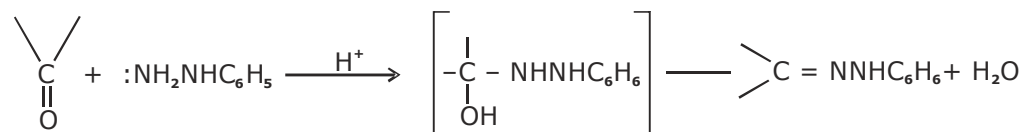
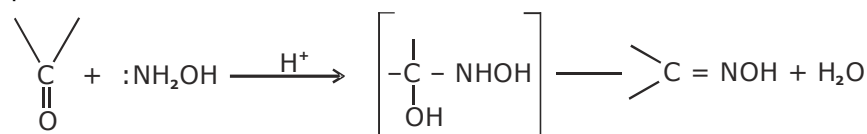
This addition is used to isolate carbonyl compounds from the mixture as we get salt.



Salt on acidification gives carbonyl compounds again.

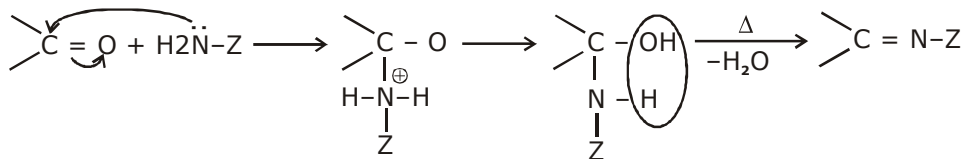
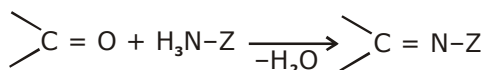
**(II) Addition elimination reactions :**

Certain compounds related to ammonia add to the carbonyl group to form derivatives that are important chiefly for the characterization and identification of aldehydes and Ketones the product contain a carbon nitrogen double bond resulting from elimination of a molecule of water from the initial addition products.

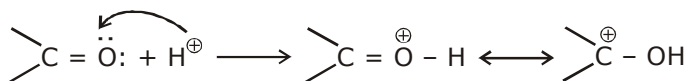


(i) Reaction with ammonia derivatives ($\text{H}_2\ddot{\text{N}}-\text{Z}$) :

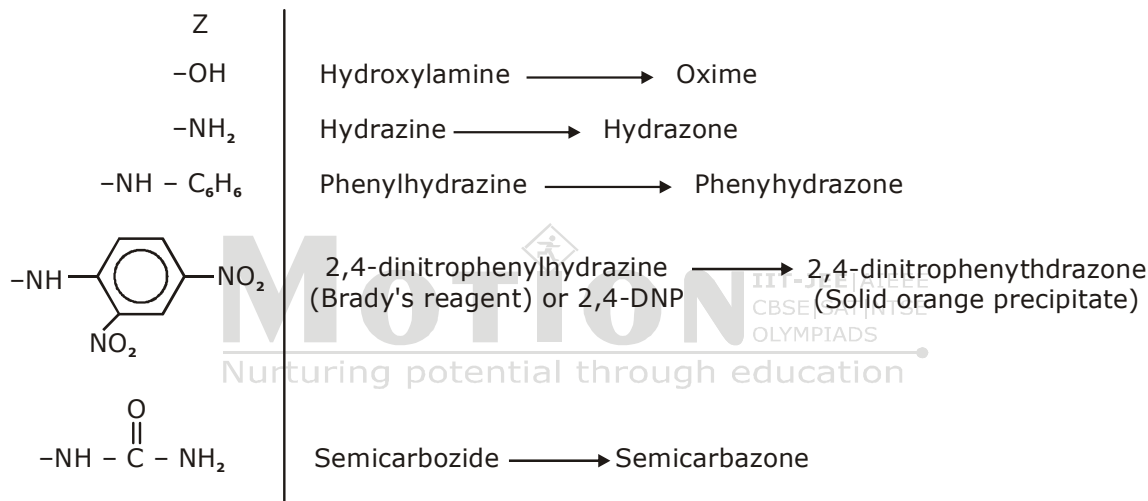
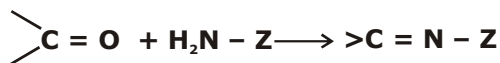
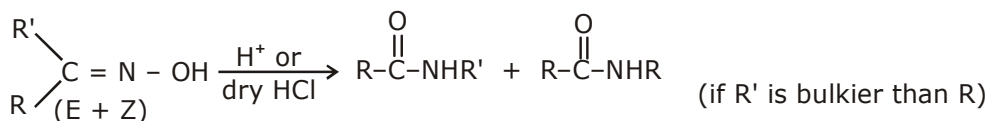
This reaction is nucleophilic followed by water elimination :

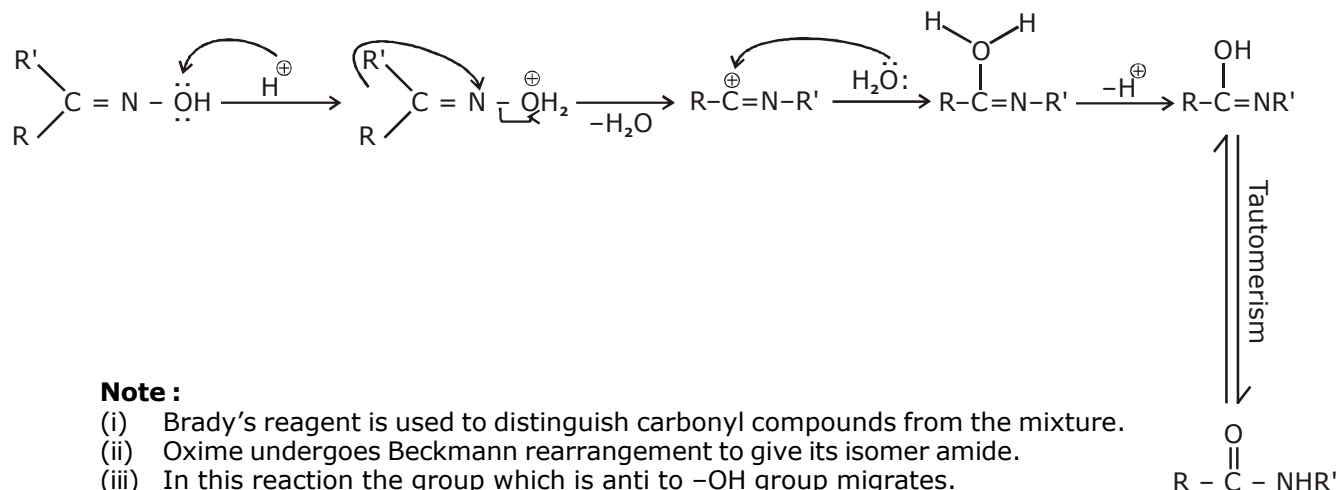


This reaction is carried out in slightly acidic media which will generate a nucleophilic centre for weak base ammonia derivatives.

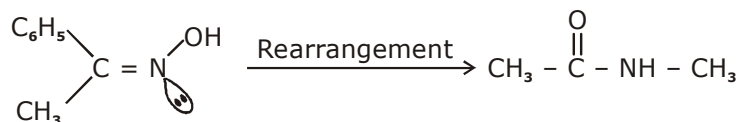
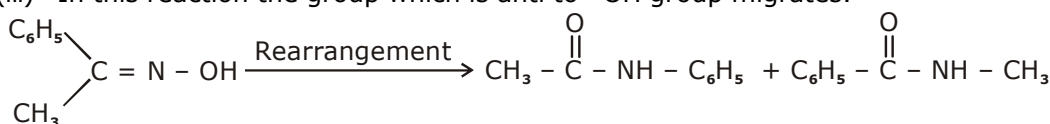


On using strong acidic media lone pair of electrons present at N-atom of ammonia derivatives will accept proton forming protonated ammonia derivatives which can not act as nucleophile for carbonyl carbon.

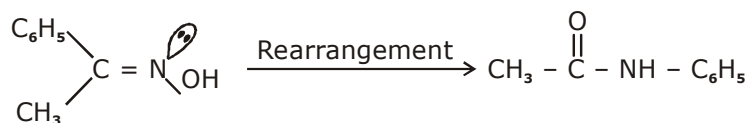
**(III) Beckmann Rearrangement in Oxime :**

Mechanism :**Note :**

- Brady's reagent is used to distinguish carbonyl compounds from the mixture.
- Oxime undergoes Beckmann rearrangement to give its isomer amide.
- In this reaction the group which is anti to -OH group migrates.



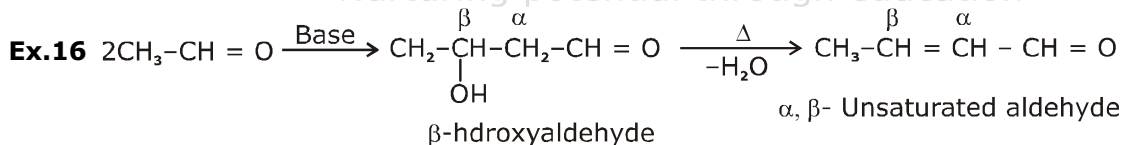
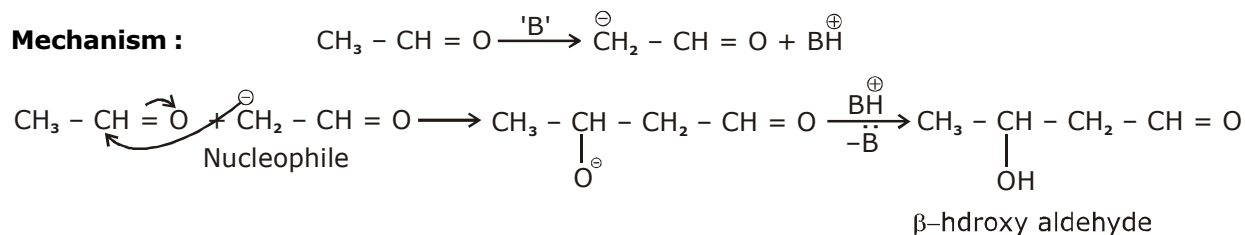
(-CH₃ is anti -OH)



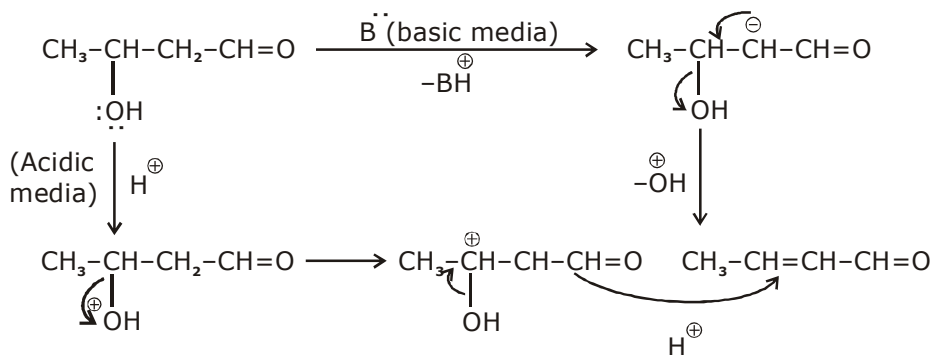
(-C₆H₅ is anti -OH)

(IV) Aldol Condensation :

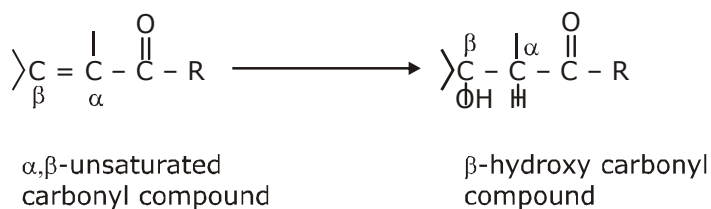
It is condensation between two moles of carbonyl compounds among which at least one must have α-hydrogen atom in dilute basic media to get α,β-unsaturated aldehyde / ketone via the formation of β-hydroxy aldehyde / ketone.

**Mechanism :**

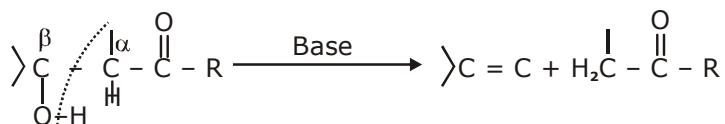
from β -hydroxy aldehyde / ketone, water is eliminated on using either acidic or basic media as –



Now try to get carbonyl compounds from α, β -unsaturated carbonyl compounds as – keep 'H' at α -position and $-\text{OH}$ at β -position of α, β unsaturated carbonyl compounds to get β -hydroxy carbonyl compounds.

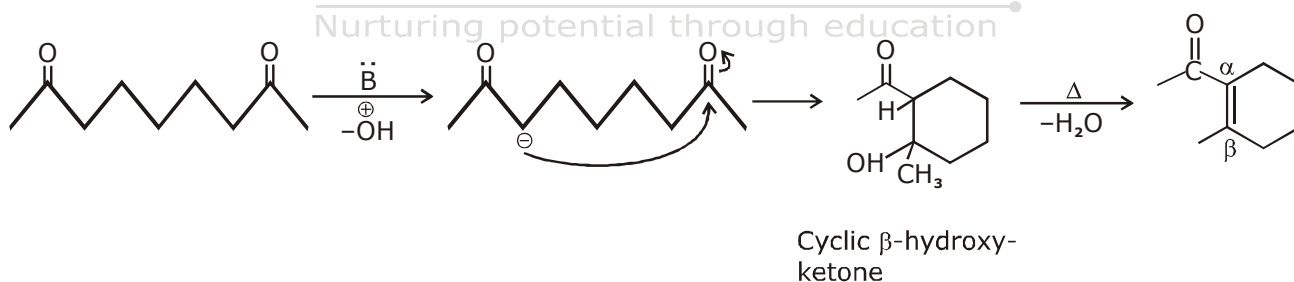


Now break α and β carbon as shown below to get carbonyl compound.



These two carbonyl compounds can be obtained on ozonolysis of hydrocarbon $\text{>C} = \underset{\text{R}}{\text{C}} + \text{CH}_2$ if it is asked.

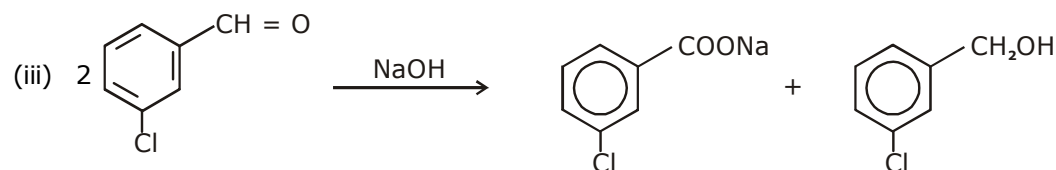
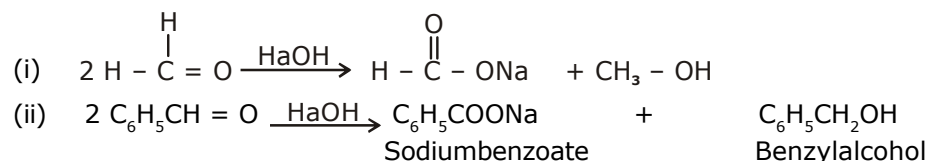
Intramolecular aldol condensation :



By knowing product we can get reactant as in case of intermolecular aldol condensation :

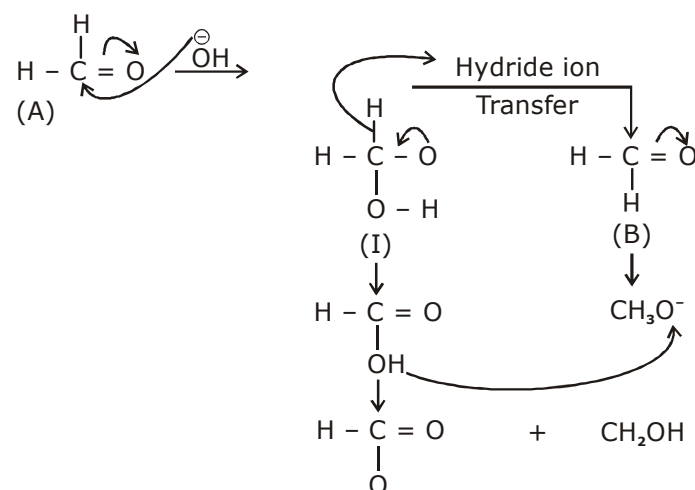
(V) Cannizzaro reaction :

Carbonyl compounds not having α -hydrogen atom undergo disproportionation or redox reaction in strong basic media.



These reaction are intermolecular cannizzaro reaction :

Mechanism :

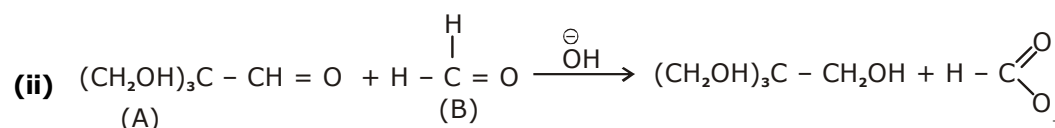
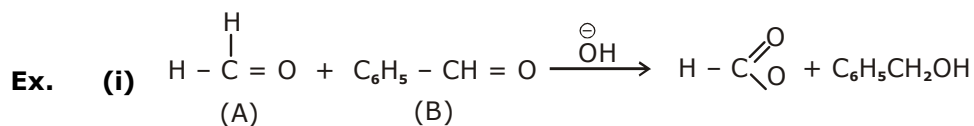


By this mechanism it clear that acid is corresponding to that carbonyl compound over which OH is going easily as nucleophile.

Note : It is observed that hydride ion transfer from (I) to Carbonyl compound (B) is rate determining step.

Crossed Cannizzaro reaction :

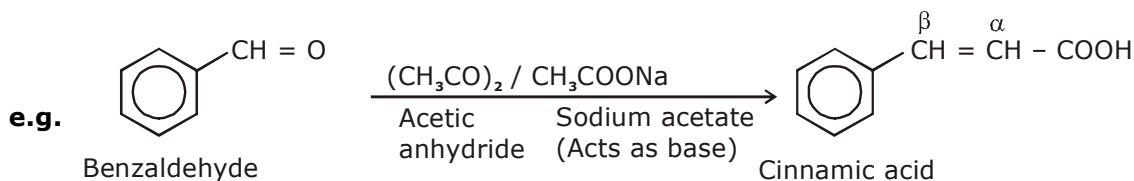
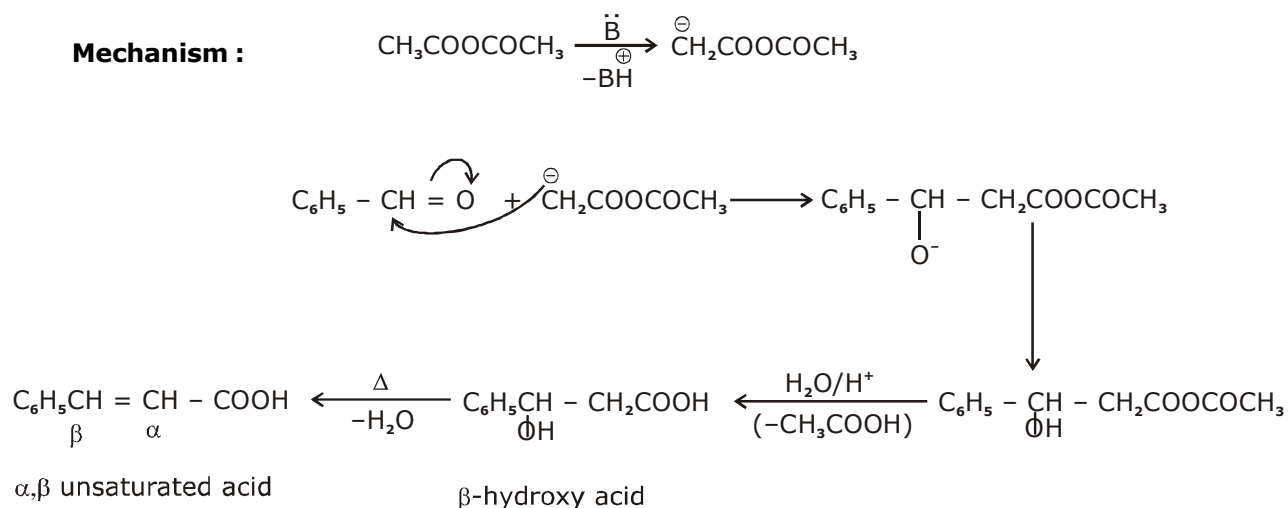
On using two types of carbonyl compounds not having α -hydrogen atom, acid will be corresponding to that aldehyde over which OH will approach without any hindrance.



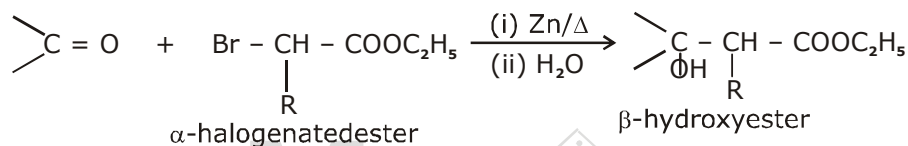
in case (i) OH will easily go to (A) and in case (ii) it will go to (B) hence acid will be formate ion in both the cases.

(VI) Perkin reaction :

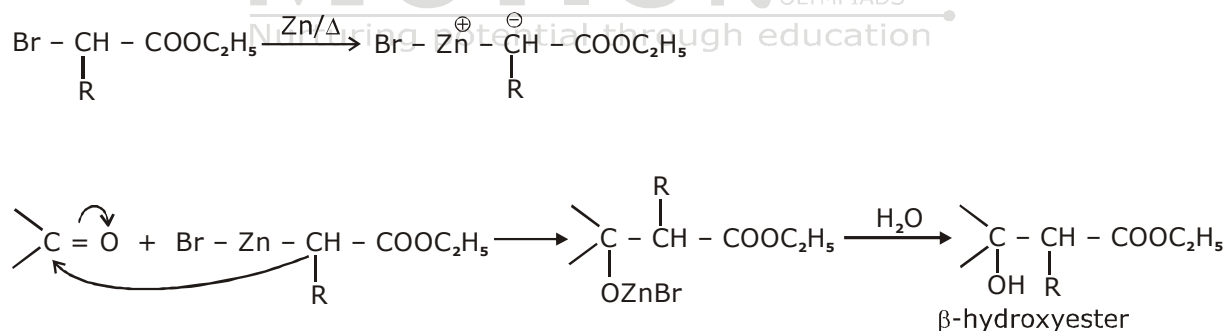
When aromatic aldehyde like benzaldehyde is treated with anhydride in the presence of sodium salt of acid from which anhydride is derived we get α, β -unsaturated acid.

**Mechanism :****(VII) Reformatsky reaction :**

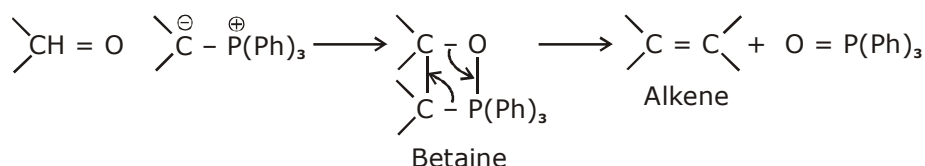
When carbonyl compound and α -halogenated ester are heated with zinc followed by treating with water we get β -hydroxyester.



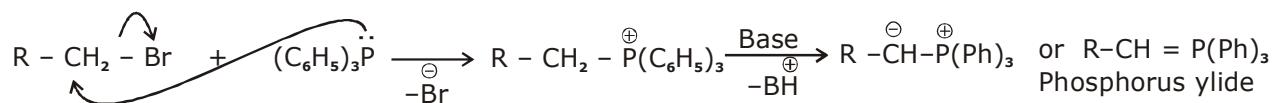
This reaction can be represented as –

**(VIII) Wittig reaction :**

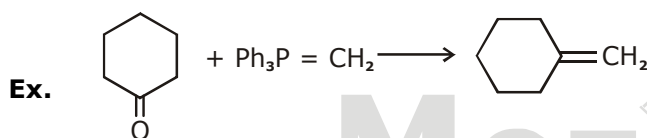
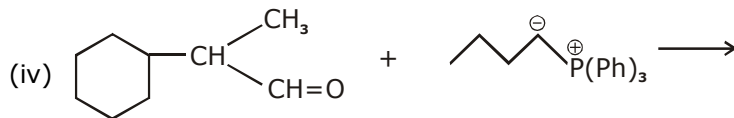
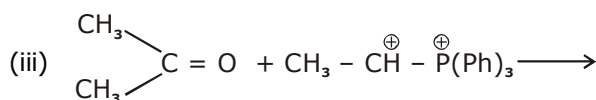
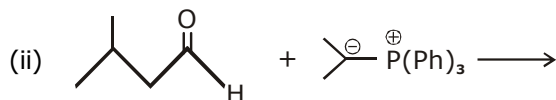
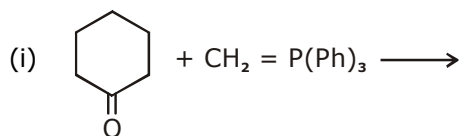
It is used to get alkene from carbonyl compound using phosphorus ylide via the formation of cyclic structure betaine.



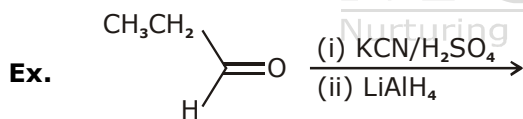
Note : Phosphorus ylides are prepared from alkylhalide and triphenylphosphine in the presence of base like sodium ethoxide as –



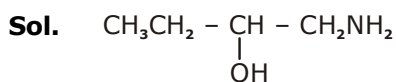
Q. Predict the product for the following :



[JEE-96]

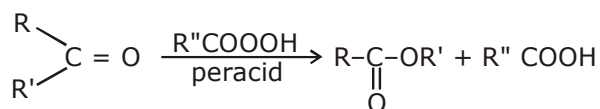


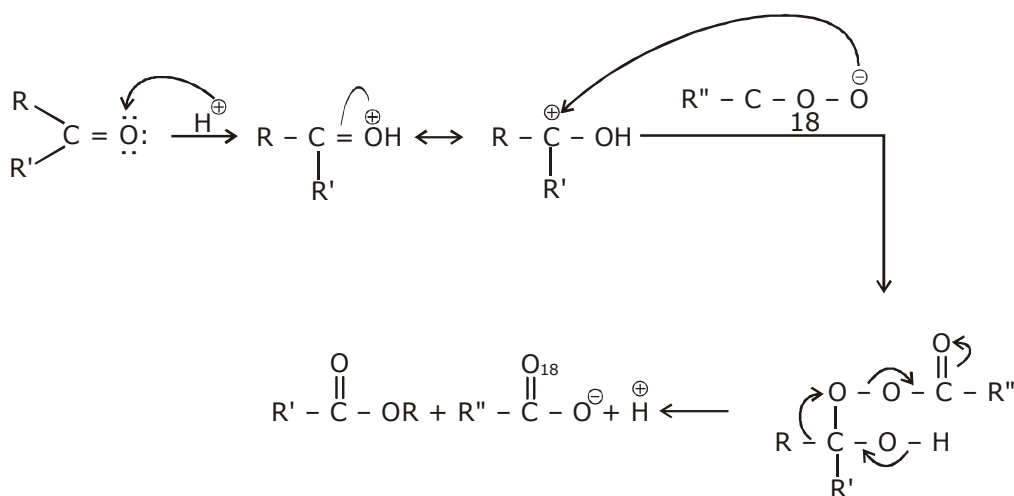
[JEE-96]



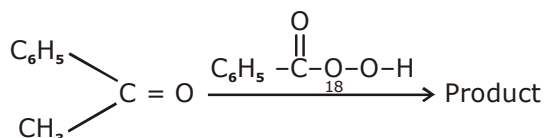
(IX) Baeyer-Villiger oxidation :

It is preparation of ester from ketone using peracid.

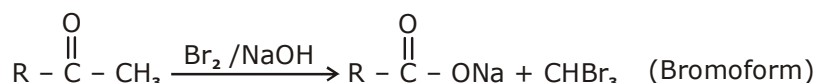


Mechanism :

Q. Predict product for the following

**(X) Haloform reaction :**

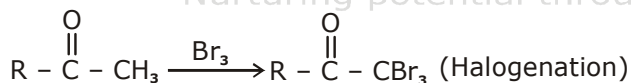
Acetaldehyde and methylalkyl ketones react rapidly with halogen (Cl_2 , Br_2 or I_2) in the presence of alkali to give haloform and acid salt.



In this reaction $-\text{CH}_3$ of $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$ group is converted into haloform as it contains acidic hydrogen atom and rest-part of alkyl methyl ketone gives acid salt having carbon atom corresponding to alkyl ketone.

(a) Halogenation

(b) Alkali hydrolysis



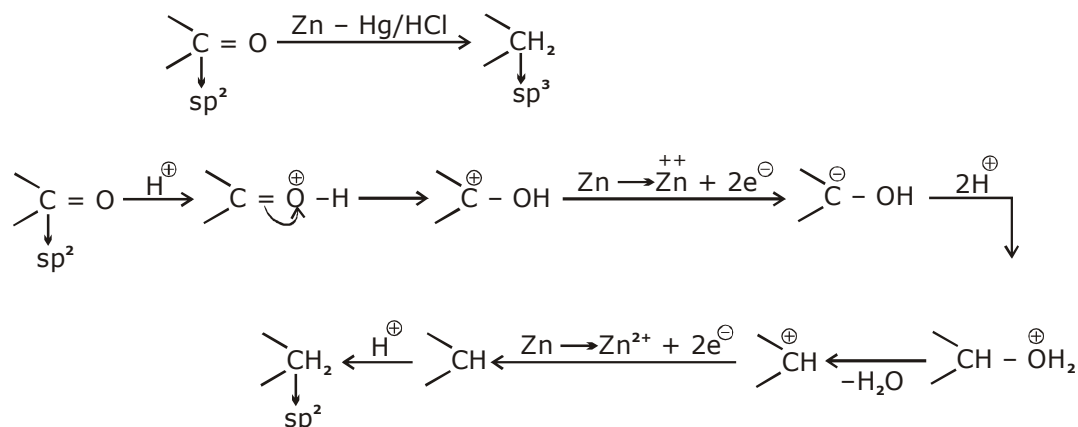
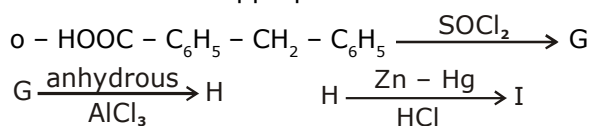
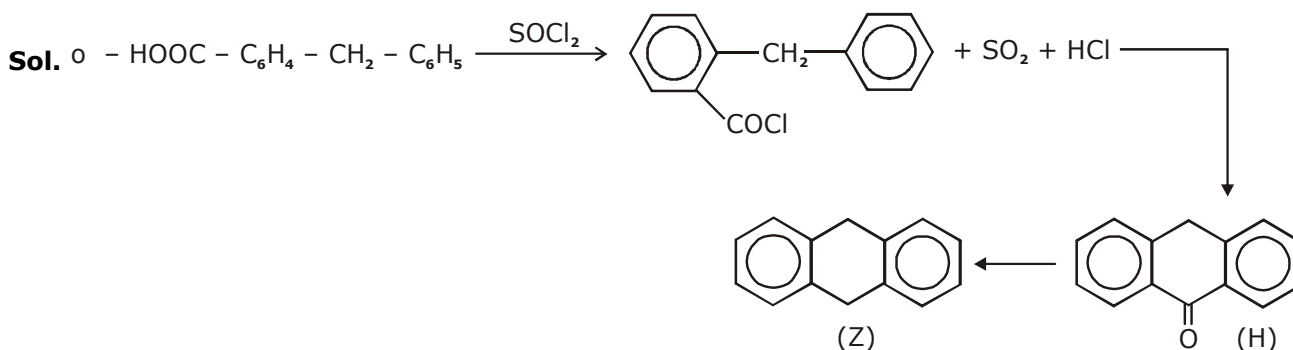
Note : This reaction is used to distinguish the presence of $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$ group.

Q.21 Which of the following is correct order of rate of halogenation of acetone ?

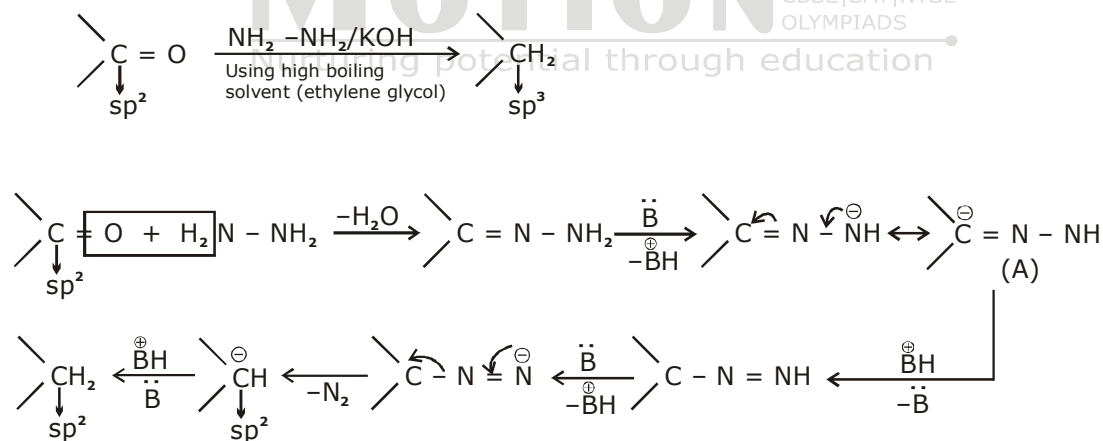
- (a) $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$ (b) $\text{Br}_2 > \text{I}_2 > \text{Cl}_2$ (c) $\text{I}_2 > \text{Cl}_2 > \text{Br}_2$ (d) $\text{Cl}_2 = \text{Br}_2 = \text{I}_2$

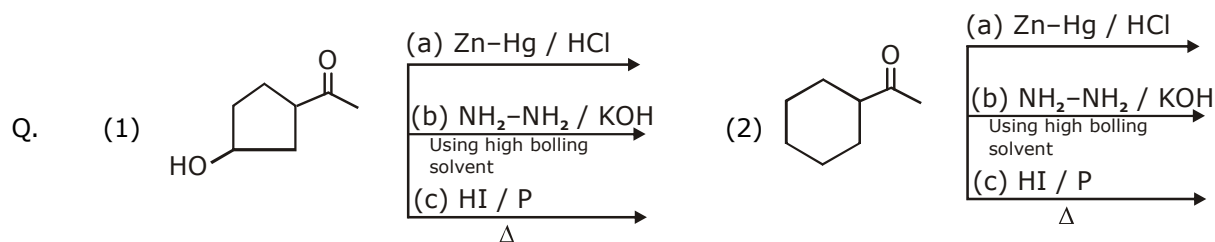
(XI) Clemmensen reduction :

Used to get alkane from carbonyl compounds.

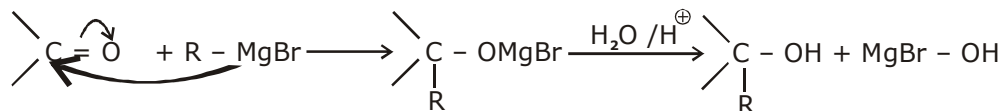
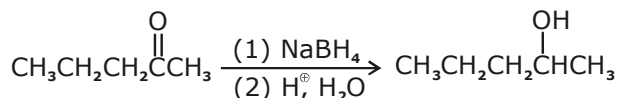
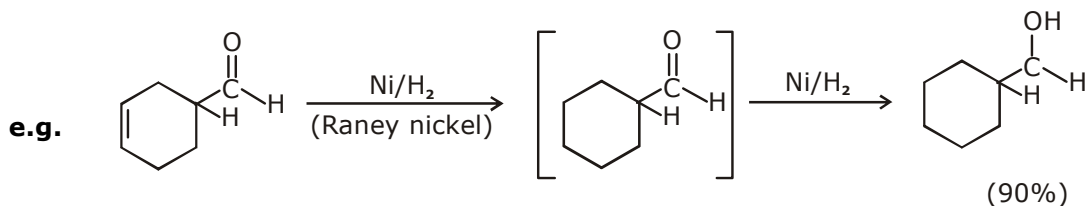
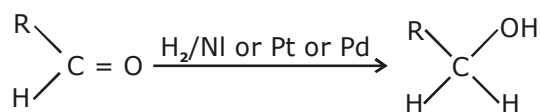
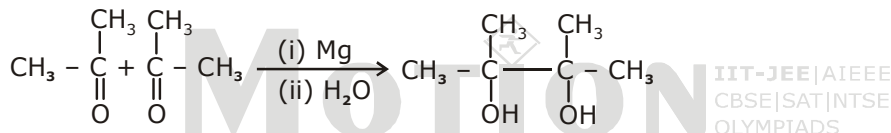
**Ex.** Fill in the blanks with appropriate structures of reaction products in the following transformations**[JEE-95]****(XII) Wolf-Kishner reduction :**

(Used to get alkane from carbonyl compounds)

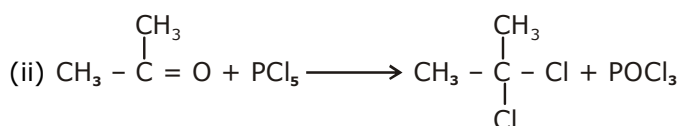
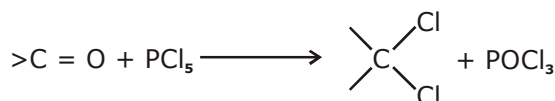


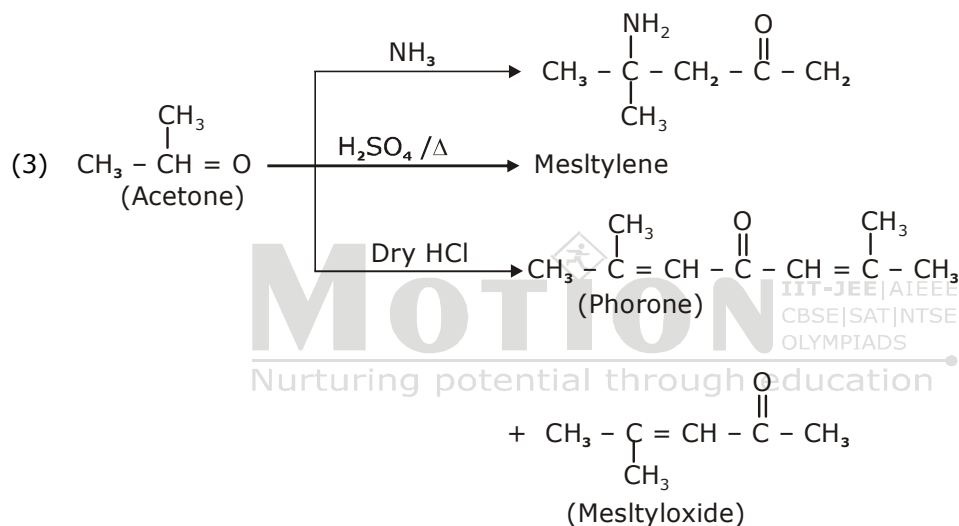
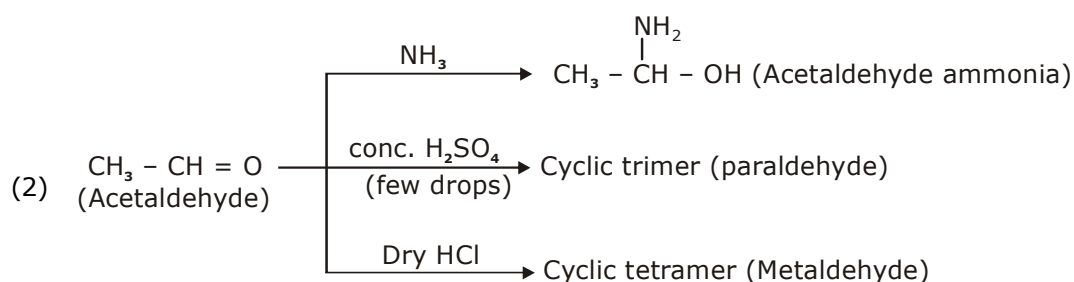
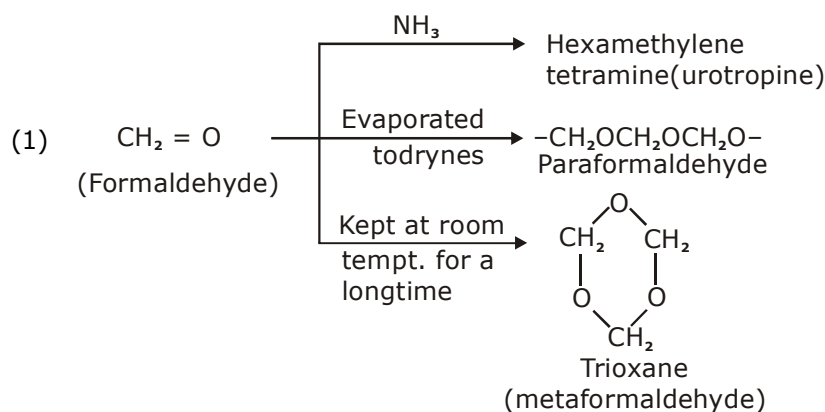
**(XIII) Addition of Grignard reagent over Carbonyl compound :**

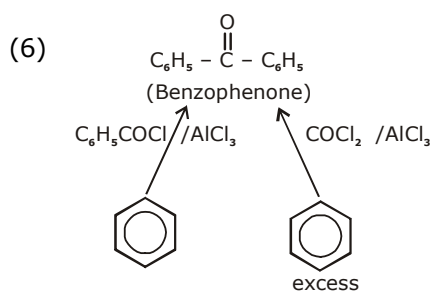
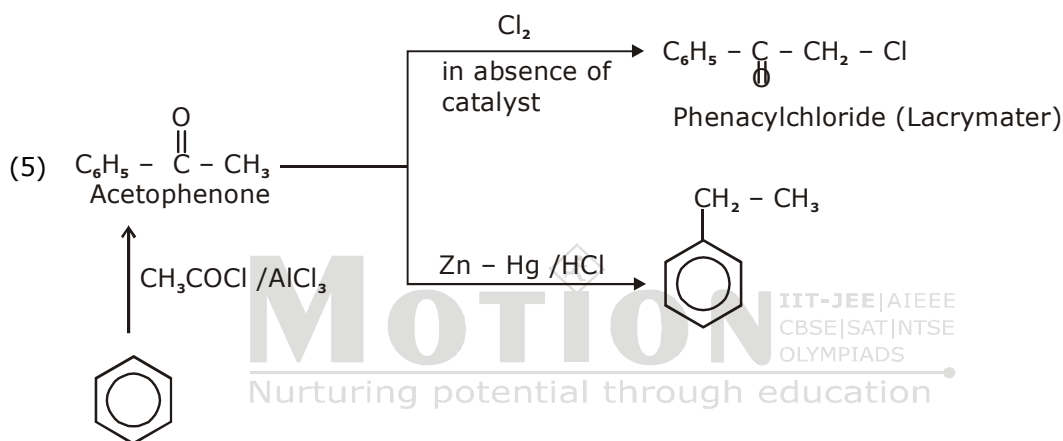
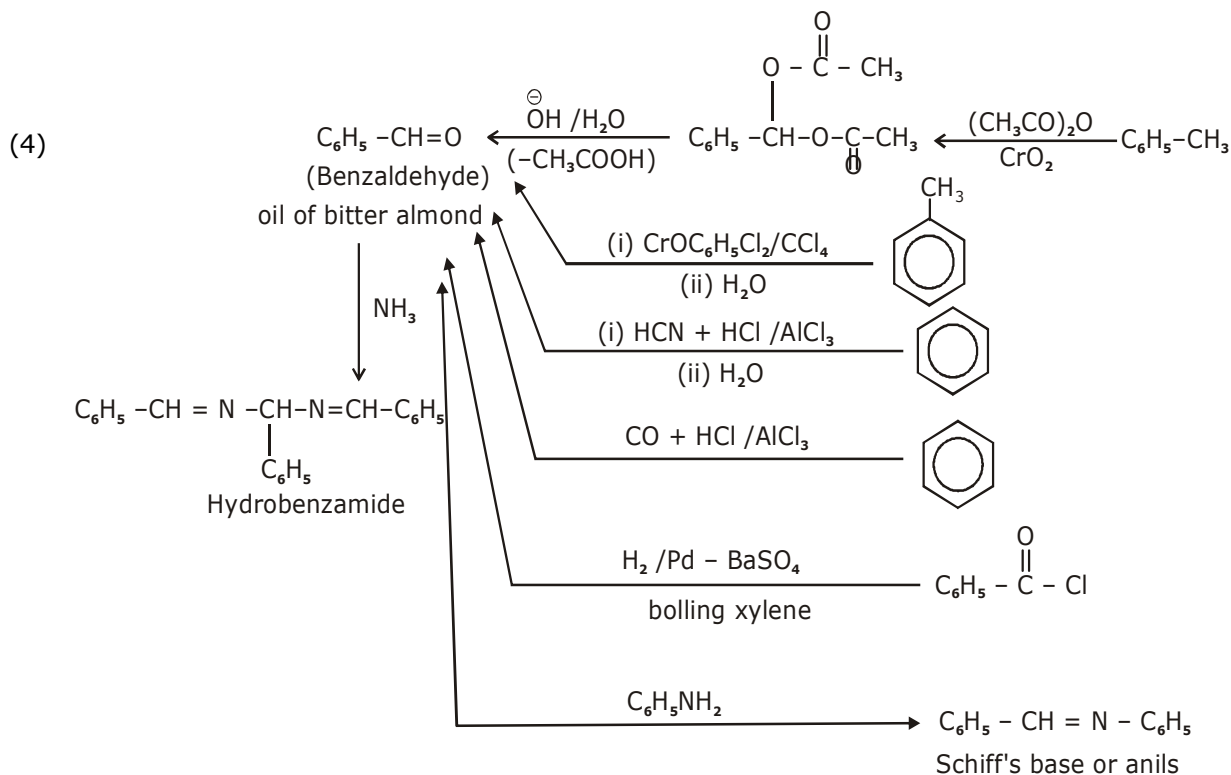
It gives alcohol

**(XIV) Reduction of Carbonyl Compounds :****(i) Reduction to alcohols****(ii) Reduction to pinacols****(XV) Reaction with PCl_5 :**

Carbonyl compounds give gemdihalides

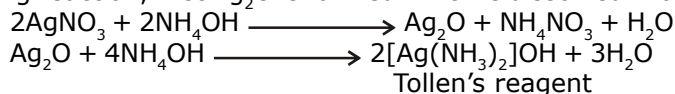


Other reaction :

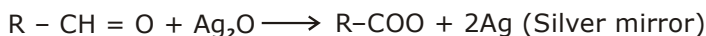
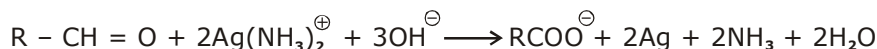


Some important reagents used for identification of aldehyde.**(i) Tollen's reagent :**

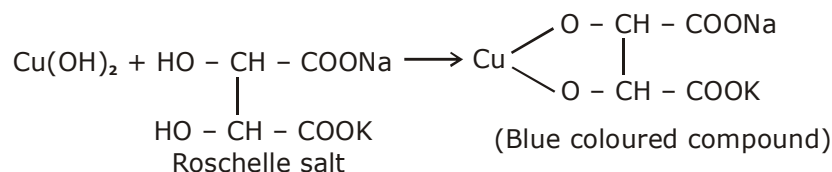
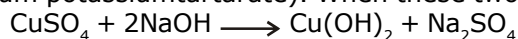
It is ammoniacal silver nitrate solution, prepared by adding ammonium hydroxide to AgNO_3 solution. During reaction, first Ag_2O is formed which is dissolved in ammoniumhydroxide to give Tollen's reagent.



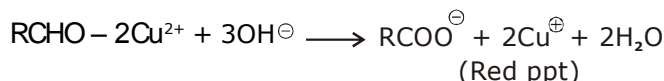
Tollen's reagent is weak oxidising agent, it gives Ag mirror test with aldehyde.

**(ii) Fehling's solution :**

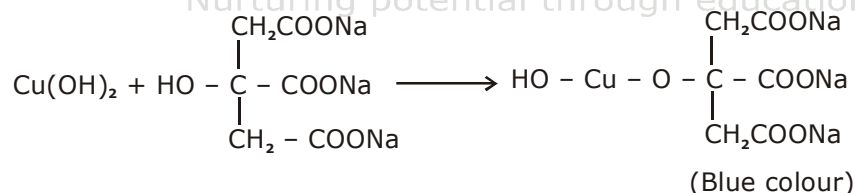
It is an alkaline solution of cupric ion complexed with sodium potassium tartarate. Two solutions are kept by naming Fehling solution (I) (CuSO_4 solution) and Fehling solution (II) (Alkaline solution of sodium potassium tartarate). When these two solutions are mixed we get deep blue coloured solution.



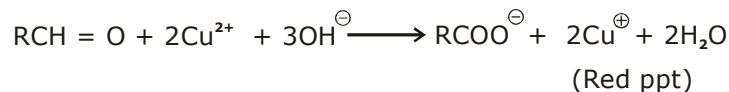
Equal volume of both the solution are heated with aldehyde to give red brown precipitate of cuprous oxide (Cu_2O) which confirms the presence of aldehyde.

**(iii) Banadict solution :**

It is solution of CuSO_4 , sodium citrate and sodium carbonate. It also consists of two solution. Solution (I) is alkaline solution of sodium citrate and solution (II) is CuSO_4 solution.



Aldehyde gives positive test with Benedict solution.

**(iv) Schiff's reagent :**

It is dilute solution of rosniline hydrochloride whose red colour has been discharged by passing SO_2 . Aldehyde reatored red colour when treated with schiff's reagent (Magenta solution in H_2SO_4).