

## CARBONYL COMPOUNDS

Carbonyl compounds are divided into two classes i.e Aldehydes ( $\overset{\text{O}}{\parallel}\text{RCH}$ ) and

Ketones ( $\overset{\text{O}}{\parallel}\text{RCR}$ ). They have a general molecular formula  $\text{C}_n\text{H}_{2n}\text{O}$ .

Their functional group is the carbonyl group,  $-\overset{\text{O}}{\parallel}\text{C}-$

### Nomenclature of carbonyl compounds.

#### 1. Aldehydes

They are named by replacing the ending "e" in the corresponding alkane with "al" in the corresponding aldehydes.

Examples



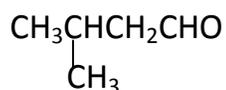
Methanal



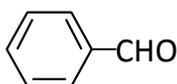
Ethanal



Propanal



3-methylbutanal



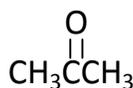
Benzaldehyde (Phenylmethanal)

#### 2. Ketones

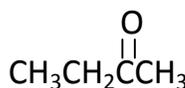
They are named by replacing the ending "e" in the corresponding alkane with "one" in the corresponding ketones.

The position of carbonyl group should be specified and should be given the lowest number possible when either left to right or right to left numbering is followed.

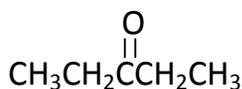
Examples



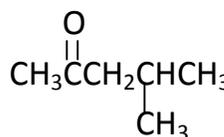
propanone



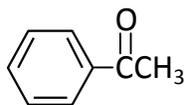
Butanone



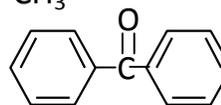
pentan-3-one



4-methylpentan-2-one



Phenylethanone (Acetophenone)



Diphenylmethanone (Benzophenone)

### Physical properties of carbonyl compounds.

- Methanal is a gas at room temperature and other lower molecular weight ketones and aldehydes are colourless liquids.
- Lower molecular weight carbonyl compounds are soluble in water due to their ability to form hydrogen bonds with water molecules. Higher members are insoluble in water.

N.B

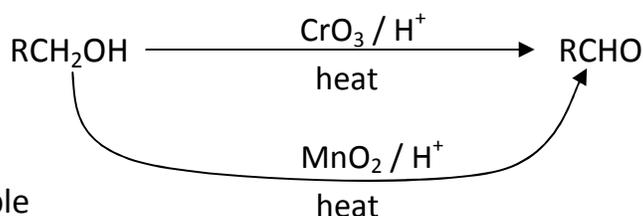
Solutions of carbonyl compounds are neutral to litmus.

- Boiling points of carbonyl compounds increases with increase in molecular weight. This is because the magnitude of the vander waals forces of attraction increases with increase in the molecular weight of the compounds and the energy required to break these forces also increases.

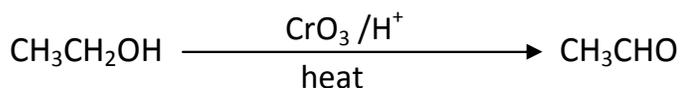
### METHODS OF PREPARATION OF CARBONYL COMPOUNDS

#### 1. Oxidation of alcohols

(a) Primary alcohols are oxidised to aldehydes when mild oxidizing agent like acidified chromium (VI) oxide or acidified manganese (IV) oxide are used. i.e

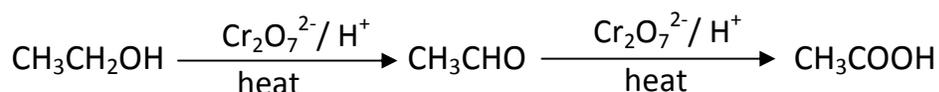


Example

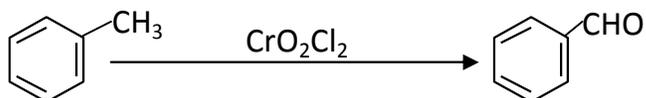


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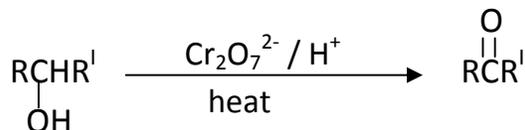
When a strong oxidising agent is used in limited amount, the alcohols is oxidised to an aldehydes. However when the oxidising agent is used in excess the aldehydes is further oxidised to a carboxylic acid. i.e.



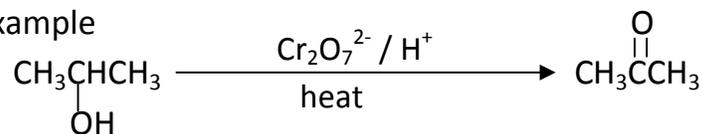
Methylbenzene is oxidised to Benzaldehyde using mild oxidizing agent like chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ), acidified chromium (VI) oxide and acidified manganese (IV) oxide.



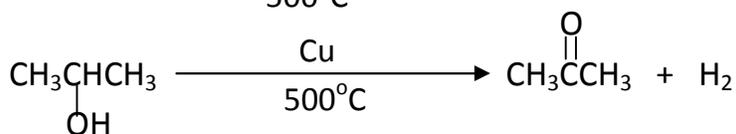
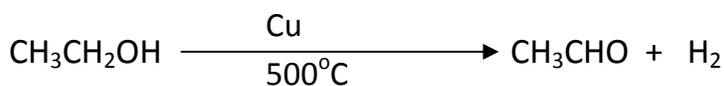
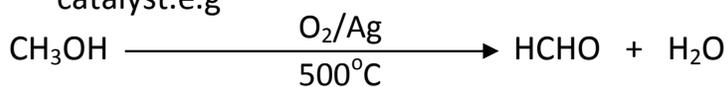
(b) Secondary alcohols are oxidised to ketones. i.e



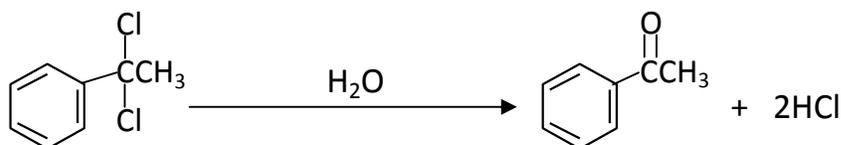
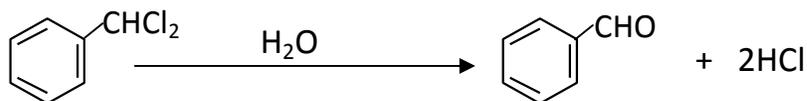
Example



(c) Alcohols are also oxidised by passing their vapour over silver or copper catalyst. e.g



2. Hydrolysis of geminal dihalides.



NOTE

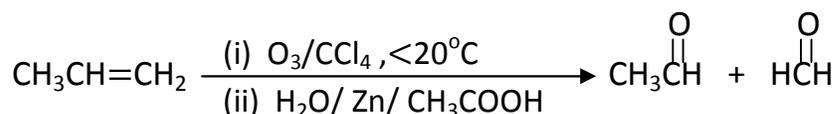
This method is of limited use for aliphatic compounds because it is very difficult to prepare geminal dihalides. However is very convenient for aromatic dihalides because it is easy to obtain them by halogenation of methylbenzene in presence of ultra violet light.

### 3. From ozonolysis of alkenes.

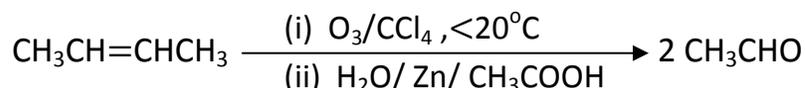
Alkenes react with ozone ( $O_3$ ) to form ozonide. The ozonide is unstable and very explosive and so the reaction is carried out in carbon tetrachloride solvent ( $CCl_4$ ) because it is inert and at temperatures less than  $20^\circ C$ .

The ozonide is then hydrolysed in presence of zinc and ethanoic acid to form carbonyl compounds.

(a) If the alkene is unsymmetrical, two different carbonyl compounds are formed on ozonolysis followed by hydrolysis. e.g.

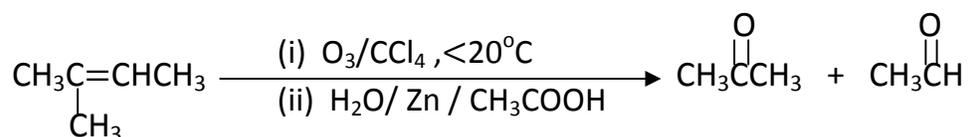


(b) If the alkene is symmetrical, one type of carbonyl compound is formed on ozonolysis followed by hydrolysis. e.g.

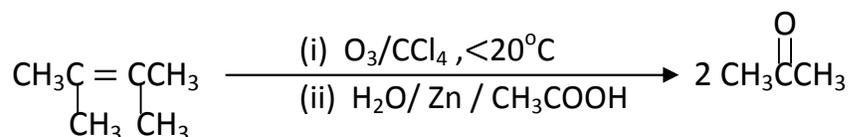


(c) If the alkene has side chains (branched alkene), ozonolysis followed by hydrolysis forms ketones. i.e.

(i) Alkenes with one side branch forms a ketone and an aldehydes. e.g.

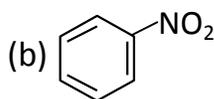


(ii) Alkene with two side branches on adjacent carbon atoms next to the double bond forms ketones. e.g.

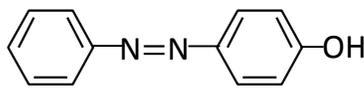


Qn. Use equations only to show how the following conversions can be made.

(a)  $CH_3CH_2CH_2CH_2OH$  to  $CH_3CH_2Cl$

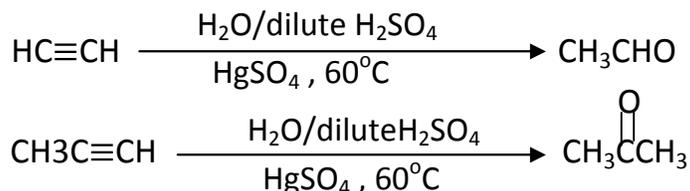


to

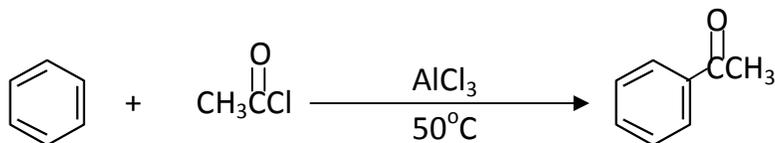


#### 4. Hydration of alkynes

Alkynes react with water in presence of sulphuric acid and mercury (II) sulphate at 60°C to form carbonyl compounds. Ethyne forms ethanal while other alkynes form ketones. E.g

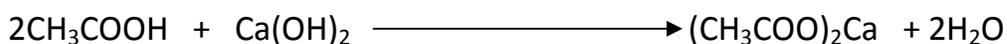


#### 5. Friedel craft acylation.

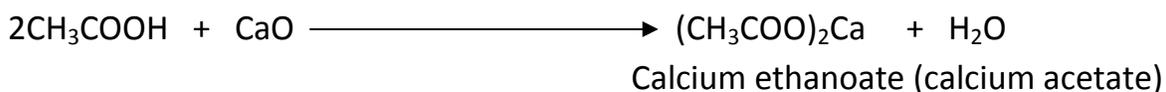


#### 6. From decarboxylation of calcium salts of carboxylic acids.

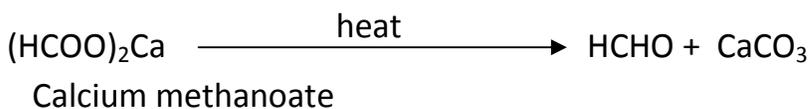
Calcium salts of carboxylic acids are formed by reacting a carboxylic acid with either calcium hydroxide, calcium oxide or calcium carbonate. i.e



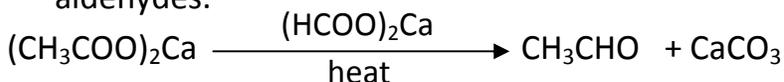
Or



(a) Heating calcium methanoate alone yields methanal.



(b) Heating calcium salts of carboxylic acids with calcium methanoate yields other aldehydes.

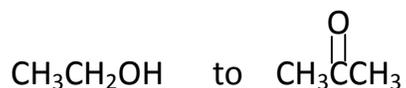


(c) Heating calcium salts of carboxylic acids alone yields ketones.

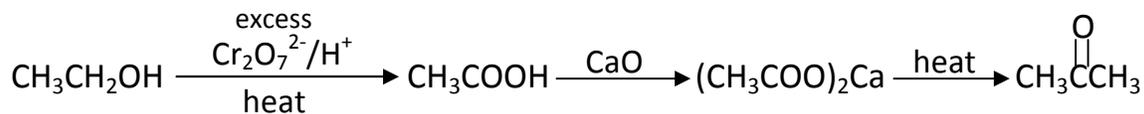


### Worked example

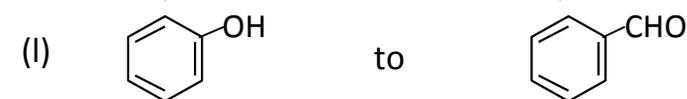
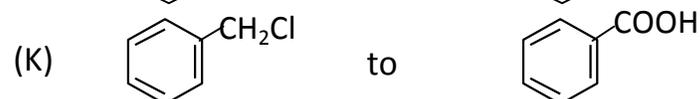
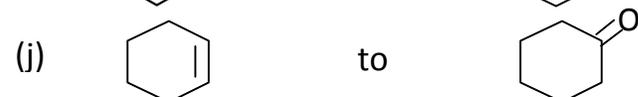
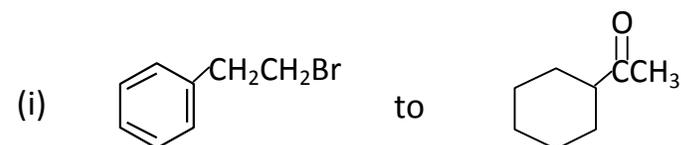
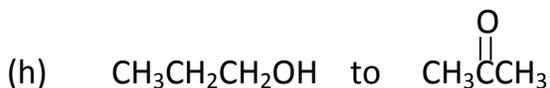
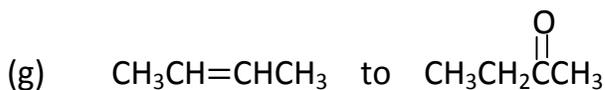
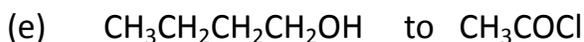
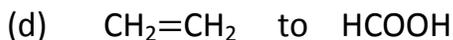
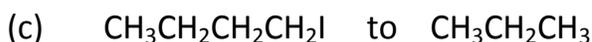
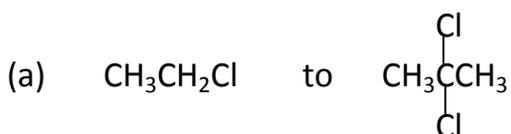
Using equations only show how the following compound can be synthesised.



Solution



Qn. Using equations only show how the following conversions can be made.



## CHEMICAL PROPERTIES OF CARBONYL COMPOUNDS

Qn. Explain the following observations.

1. Both aldehydes and ketones undergo nucleophilic addition reaction.

Explanation

This is because both aldehydes and ketones have the same carbonyl group that is polarized since the oxygen atom is more electronegative than the carbon atom. The oxygen atom attracts electrons of the bond more towards itself thus acquiring a partial negative charge and leaving a partial positive charge on the carbon atom. Therefore nucleophiles attack the electron deficient carbon atom.

2. Aldehydes are more reactive towards nucleophilic reagents than ketones.

Explanation

Ketones have two alkyl groups bonded to the carbonyl group. Each alkyl group has a positive inductive effect and pushes electrons of the bond towards the partially positive carbonyl carbon. This increases the electron density on the carbonyl carbon and thus the positive charge on the carbonyl carbon is more reduced in ketones than in aldehydes with only one alkyl group bonded to the carbonyl group. Therefore nucleophiles are less attracted in ketones than in aldehydes.

3. Reactivity of carbonyl compound increases if an electron attracting group is attached on the alpha carbon (carbon atom adjacent to the carbonyl group) i.e 2-chloropropanal ( $\text{CH}_3\underset{\text{Cl}}{\text{CH}}\text{CHO}$ ) is more reactive than Propanal ( $\text{CH}_3\text{CH}_2\text{CHO}$ )

Explanation

This is because the chlorine atom on the alpha carbon withdraws the bond pair of electrons in the carbon-chlorine bond more towards itself. This reduces the electron density on the alpha carbon thus the alpha carbon also withdraws electrons away from the carbonyl carbon. The electron density on the carbonyl carbon decreases while the positive charge increases. Therefore nucleophiles are more attracted to the carbonyl carbon. Propanal has an ethyl group with a positive inductive effect and pushes electrons towards the carbonyl carbon thus the electron density is increased on the carbonyl carbon and the positive charge is more reduced. Therefore nucleophiles are less attracted at the carbonyl carbon

4. Propanone is more reactive towards nucleophilic reagents than pentan-3-one.  
Explanation

The ethyl group attached on the carbonyl group in pentan-3-one is larger than the methyl group attached on the carbonyl group in propanone and since the ethyl group is larger, it offers a greater steric hindrance to the incoming nucleophile from approaching the carbonyl group than the methyl group which is small (the ethyl group hinders the approach of the nucleophile to the carbonyl group) and hence the less reactivity of pentan-3-one than propanone.

## REACTIONS OF CARBONYL COMPOUNDS

Reactions of carbonyl compounds are divided into three types:

- (a) Reactions of the carbonyl group.
- (b) Reactions of the alkyl group(s) adjacent to the carbonyl group.
- (c) Oxidation reactions.

### (a) REACTIONS OF THE CARBONYL GROUP

These are divided into two;

- (i) Addition reactions.
- (ii) Condensation reactions.

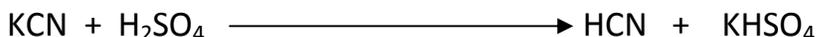
### (i) ADDITION REACTIONS

Both ketones and aldehydes undergo addition reactions and these include;

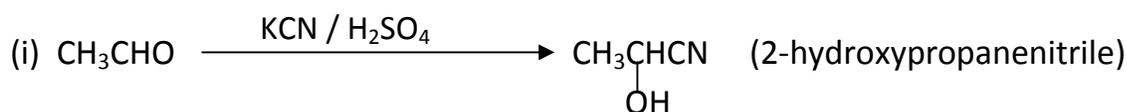
#### (1) Reaction with hydrogen cyanide (HCN)

Aldehydes and ketones react with hydrogen cyanide to form 2-hydroxynitriles (Cyanohydrins).

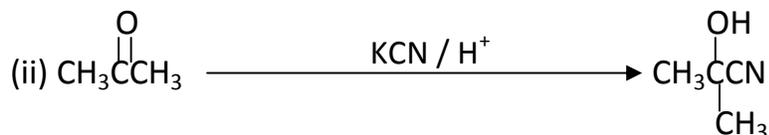
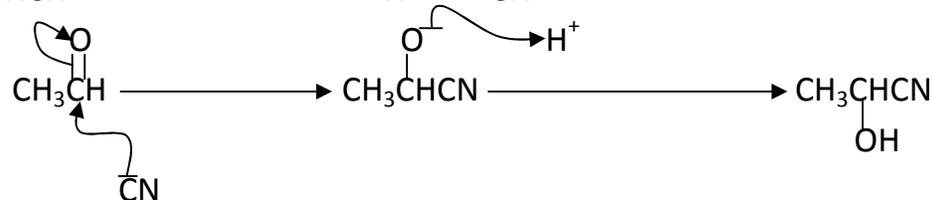
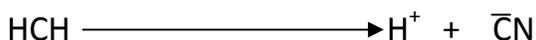
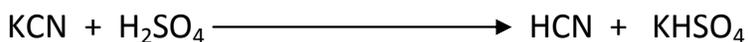
Hydrogen cyanide is formed in situ from the reaction between potassium cyanide or sodium cyanide with sulphuric acid. i.e



Examples

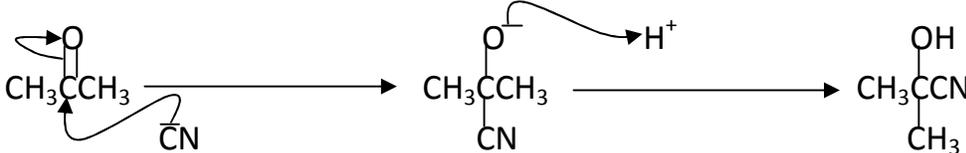
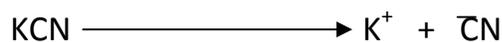


Mechanism

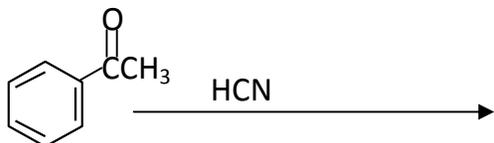


2-hydroxy-2-methylpropanenitrile

Mechanism



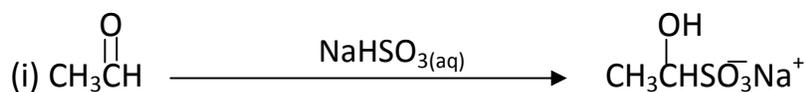
Qn. Complete the following equation and outline the mechanism.



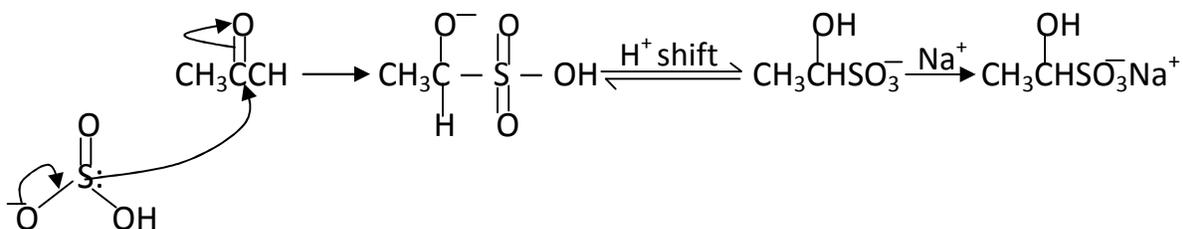
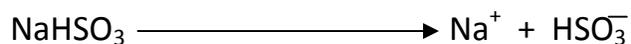
2. Reaction with sodium hydrogen sulphite solution.

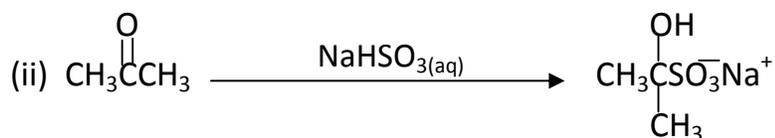
Both aldehydes and ketones react with a saturate solution of sodium hydrogen sulphite to form white crystalline solids.

Examples

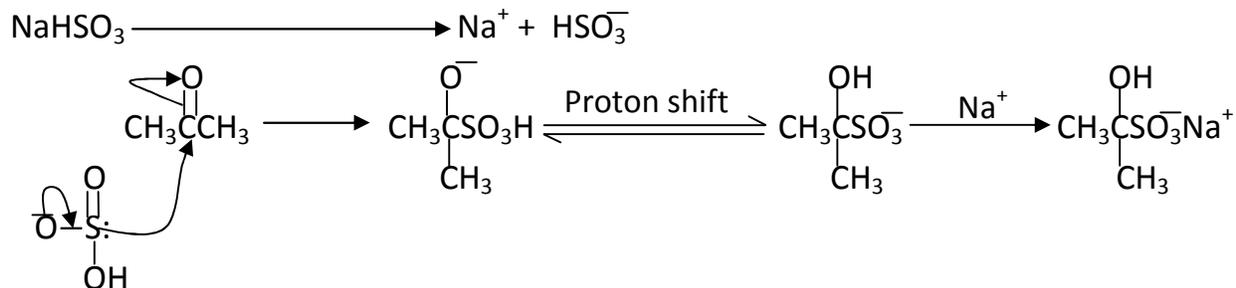


Mechanism



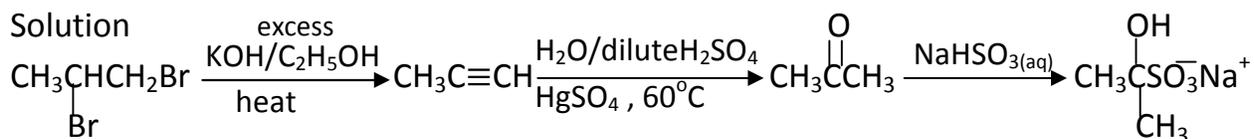
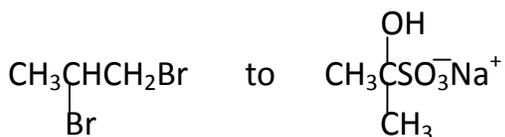


Mechanism

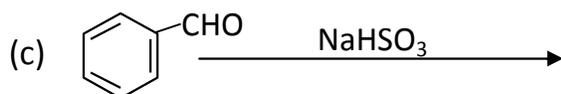
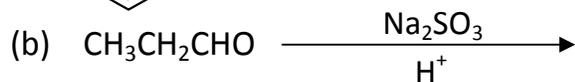
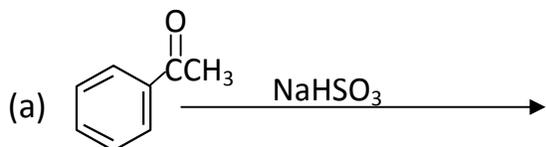


Worked example

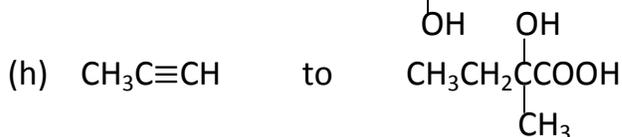
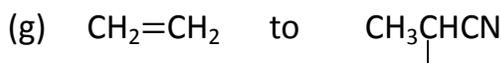
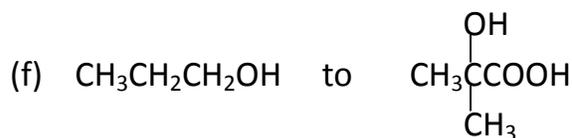
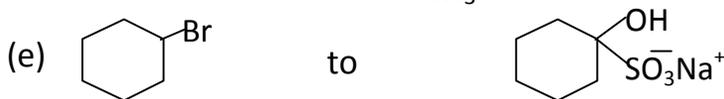
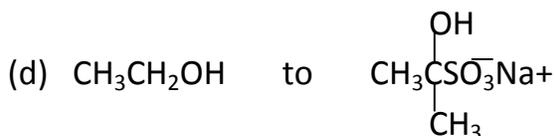
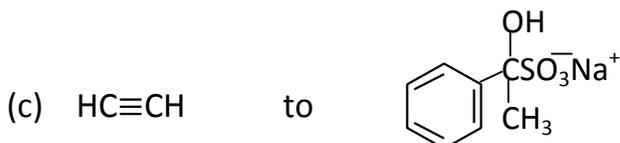
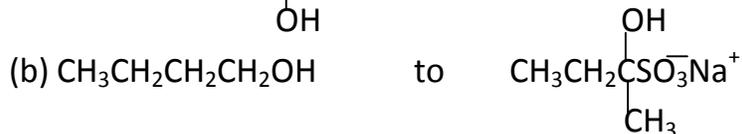
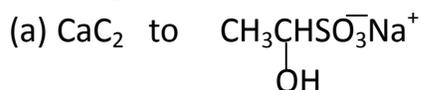
Using equations only show how the following conversion can be effected.



Qn 1. Complete the following equations and in each case outline a mechanism for the reaction.

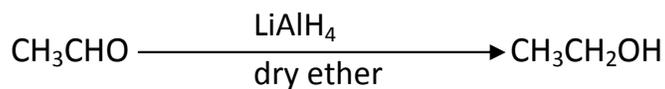


Qn 2. Using equations only show how the following compounds can be synthesised.

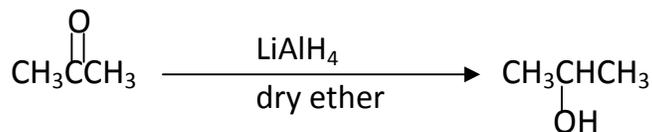


3. Carbonyl compounds are reduced to alcohols by treatment with lithium aluminium hydride in dry ether ( $\text{LiAlH}_4/\text{dry ether}$ ), sodium amalgam and water ( $\text{Na}/\text{Hg}/\text{H}_2\text{O}$ ), sodium in ethanol ( $\text{Na}/\text{C}_2\text{H}_5\text{OH}$ ), zinc and ethanoic acid ( $\text{Zn}/\text{CH}_3\text{COOH}$ ) or hydrogen in presence of heated nickel catalyst.e.g

(a) Aldehydes are reduced to primary alcohol.

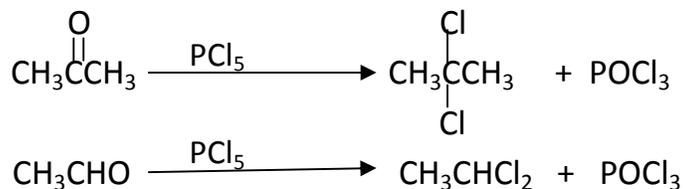


(b) Ketones are reduced to secondary alcohols



#### 4. Reaction with phosphorus pentachloride (PCl<sub>5</sub>)

Aldehydes and ketones react with phosphorus pentachloride to form geminal dichlorides.e.g



#### (ii) CONDENSATION REACTIONS

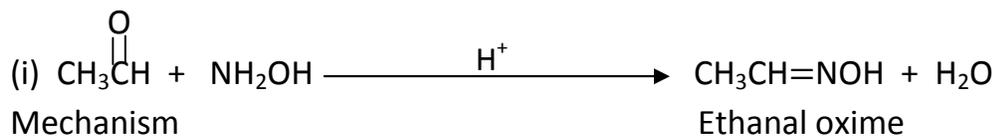
Both aldehydes and ketones react with compounds containing the -NH<sub>2</sub> group (derivatives of ammonia, XNH<sub>2</sub>) with elimination of water.

These reactions can occur either in presence or in absence of mineral acids.

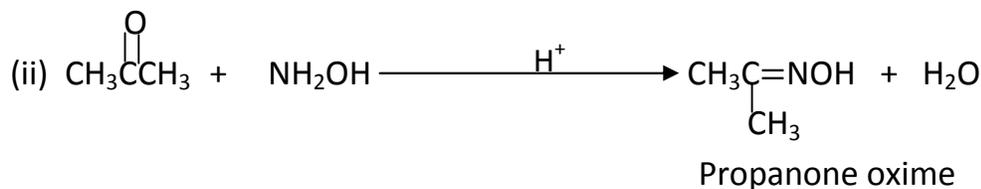
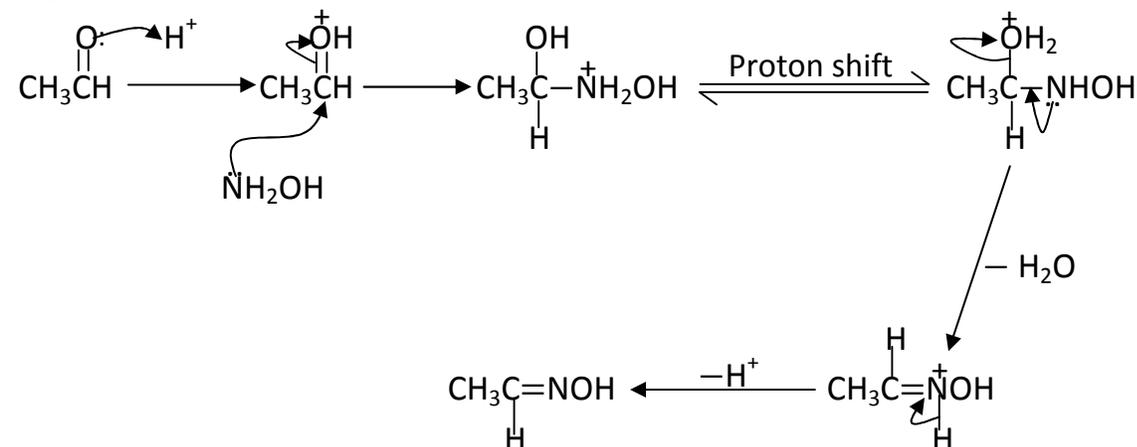
These reactions include;

##### 1. Reaction with hydroxylamine (NH<sub>2</sub>OH)

In these reactions Oximes are formed. e.g.



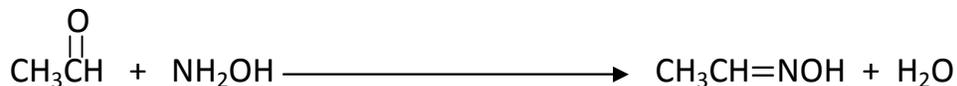
Mechanism



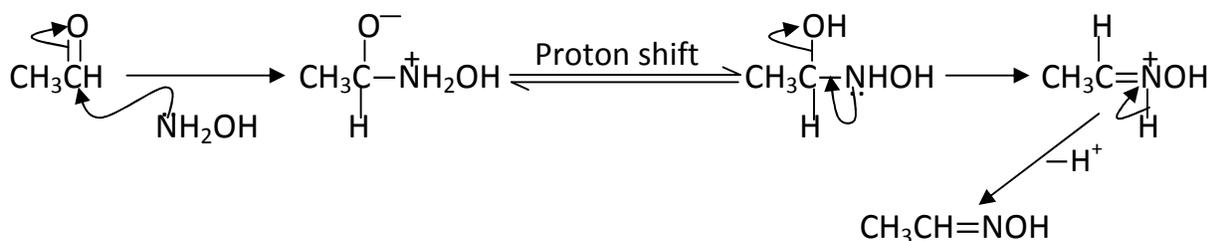
Outline the mechanism for reaction (ii) above

## NOTE

In absence of a mineral acid ( $H^+$ ), the mechanism proceeds as shown below.

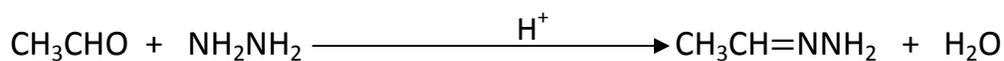


Mechanism

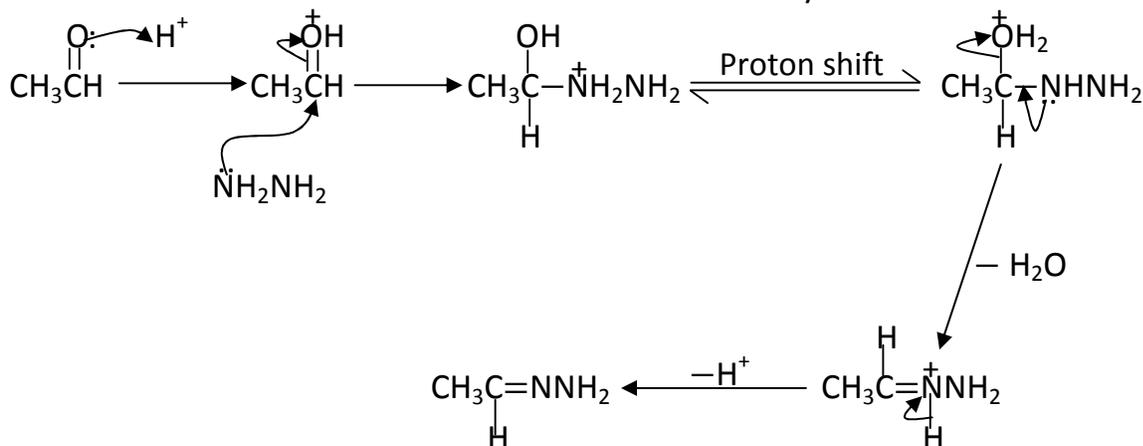


## 2. Reaction with hydrazine ( $NH_2NH_2$ ).

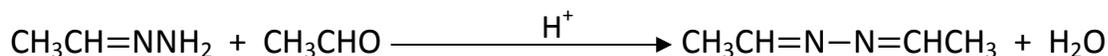
In this reaction hydrazones are formed.



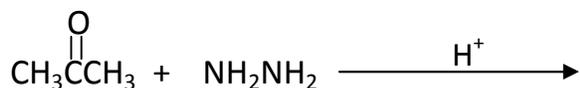
Mechanism



**N.B;** The hydrazone still contain the  $-NH_2$  group and can react with other carbonyl compounds to form azine. i.e

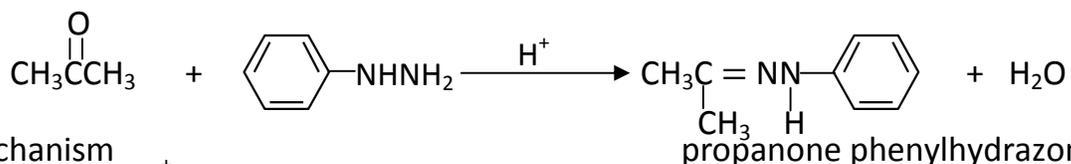


Qn. Complete the equation below and outline the mechanism.

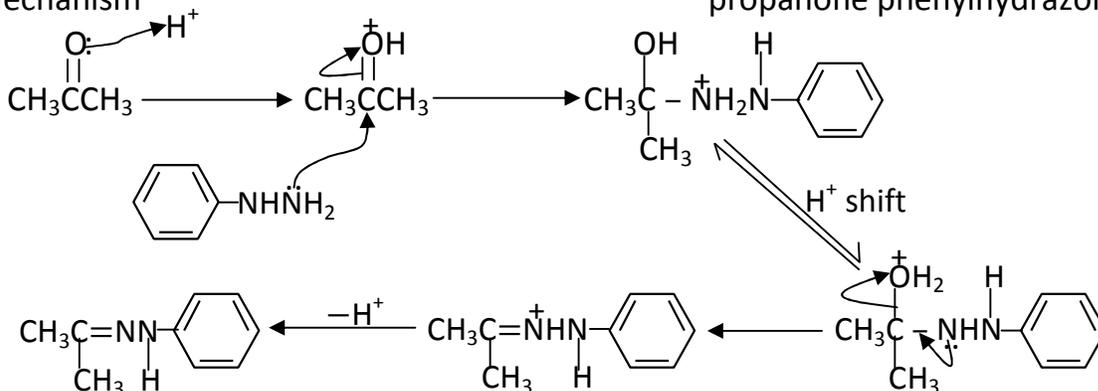


### 3. Reaction with phenyl hydrazine $\left(\text{C}_6\text{H}_5\text{NHNH}_2\right)$

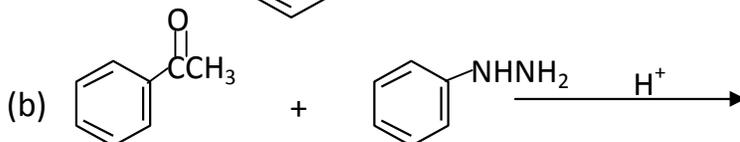
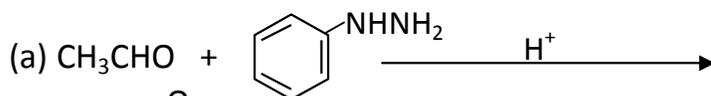
In this reaction phenyl hydrazones are formed. e.g



Mechanism



Qn. Complete the following equations and in each case outline the mechanism.



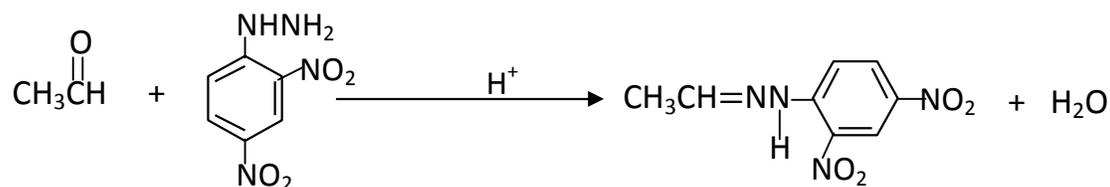
### 4. Reaction with 2,4-dinitrophenyl hydrazine (Brady's reagent), $\text{O}_2\text{N}-\text{C}_6\text{H}_3(\text{NO}_2)-\text{NHNH}_2$

In this reaction, 2,4-dinitrophenyl hydrazones are formed. These appear as yellow or orange precipitates.

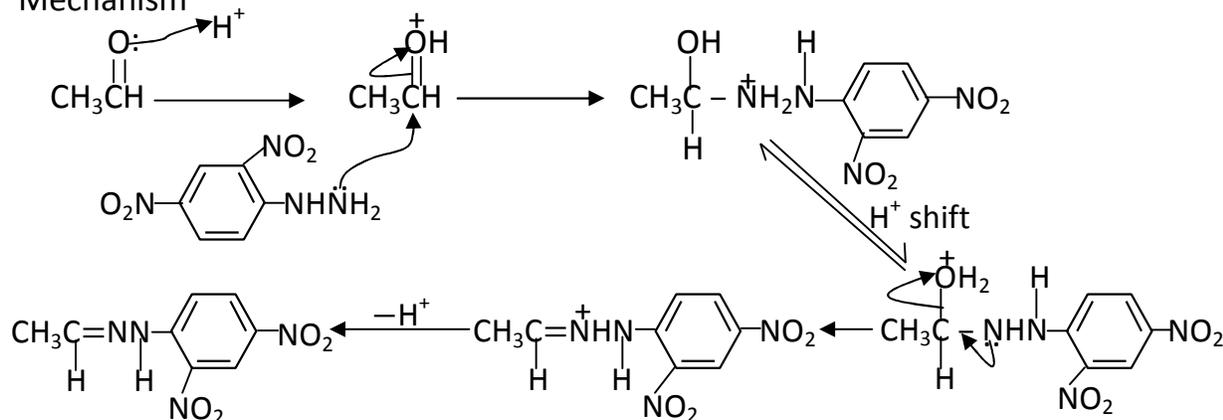
Therefore both aldehydes and ketones **form yellow or orange precipitates** when treated with 2,4-dinitrophenyl hydrazine solution (Brady's reagent). This reaction is used to distinguish carbonyl compounds from other organic compounds. i.e

The reagent is used to test for the presence of the carbonyl group in compounds.

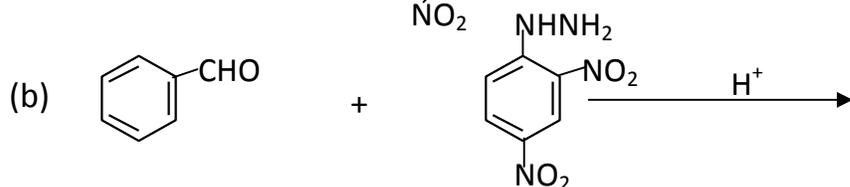
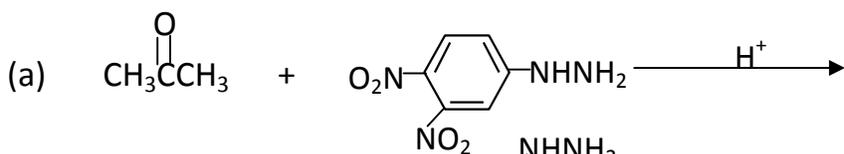
Example.



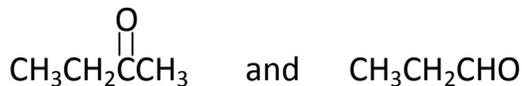
Mechanism



Qn. Complete the following equations and in each case outline the mechanism.



Qn. Name a reagent that can be used to test for the functional group in the following pair of compound. State what is observed when the reagent is treated with the reagent.



**Reagent**

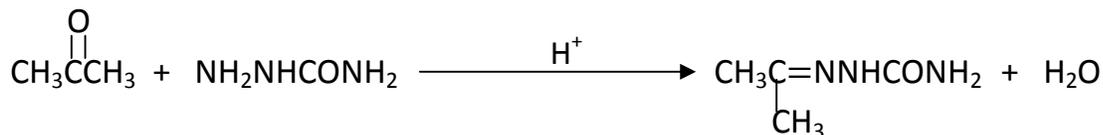
2,4-dinitrophenyl hydrazine solution (Brady's reagent)

**Observation**

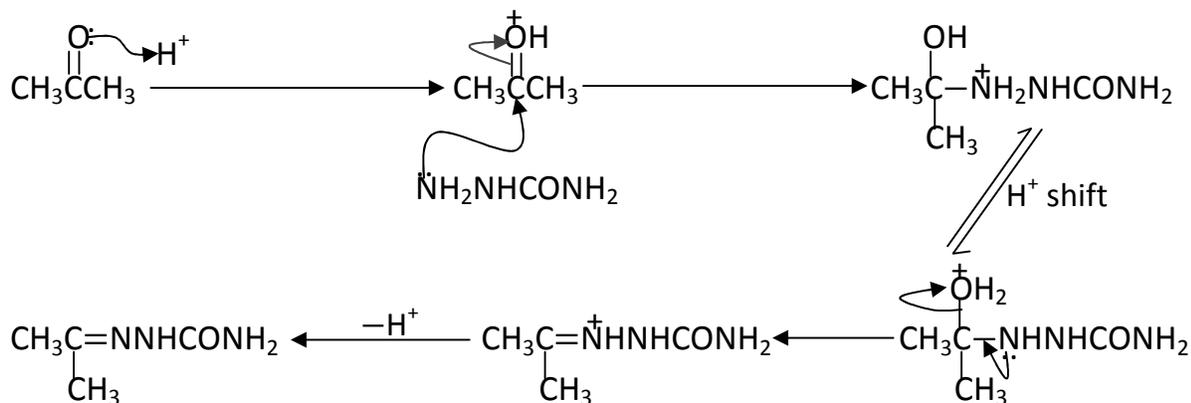
Both  $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{CHO}$  form a yellow precipitate (or orange precipitate) when treated with Brady's reagent.

5. Reaction with semi carbazines (NH<sub>2</sub>NHCONH<sub>2</sub>).

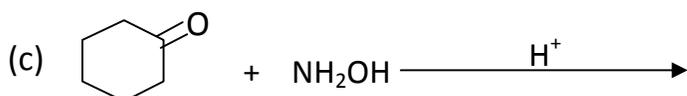
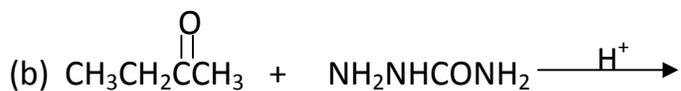
In this reaction semi carbazones are formed.i.e



Mechanism

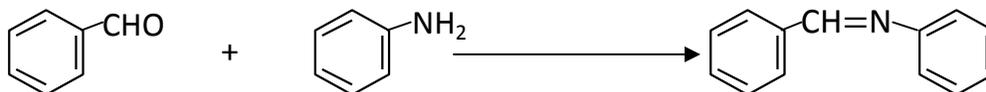


Qn. Complete the following equations and in each case outline the mechanism.

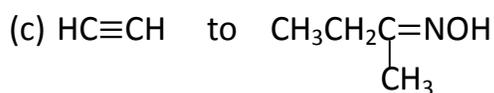
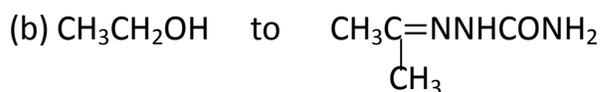


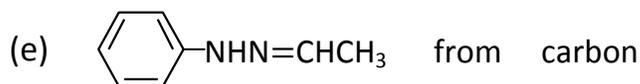
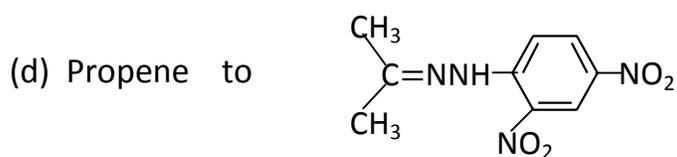
6. Reaction with primary amines.

In this reaction imines are formed.i.e



Qn. Using equations only show how the following conversions can be made.

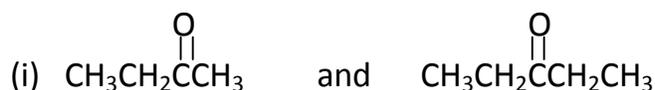




## (b) REACTIONS OF THE ALKYL GROUP(S)

### 1. Iodoform reaction.

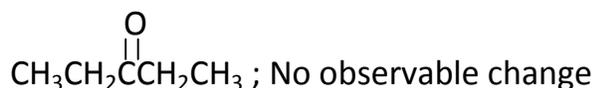
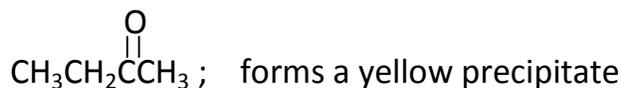
Ethanal and methyl ketones ( $\text{CH}_3\text{COR}$ ) reacts with iodine solution and sodium hydroxide solution forming a yellow precipitate of tri-iodomethane and hence Iodoform test can also be used to distinguish between;



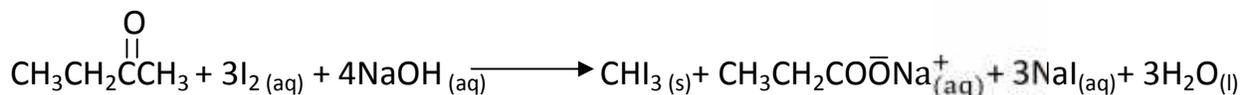
#### Reagent

Iodine solution in the presence of sodium hydroxide solution.

#### Observation



#### Equation



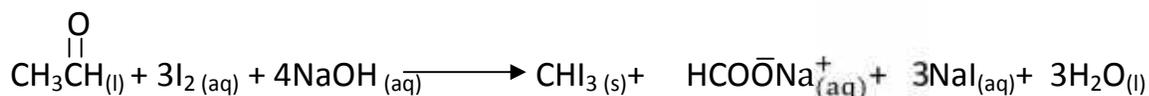
#### Reagent

Iodine solution in the presence of sodium hydroxide solution.

#### Observation

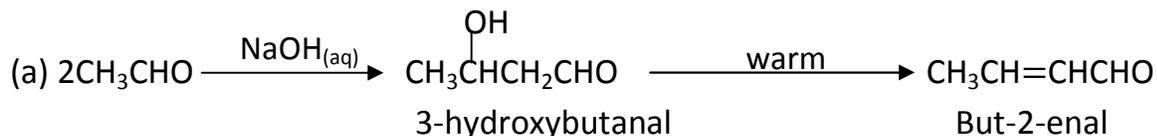


#### Equation

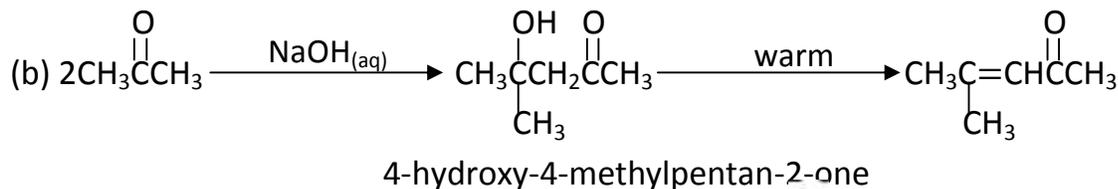
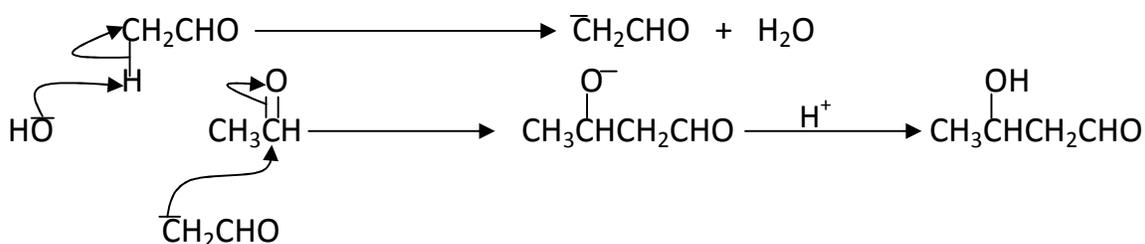
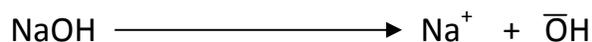


## 2. Aldo condensation reaction (reaction with dilute sodium hydroxide solution).

Aldehydes and ketones with at least one  $\alpha$  – hydrogen atom react with dilute sodium hydroxide solution to form aldol products (Compounds containing both hydroxyl group and carbonyl group) which on warming forms enal (compounds containing both a carbon to carbon double bond and the carbonyl group). E.g



Mechanism

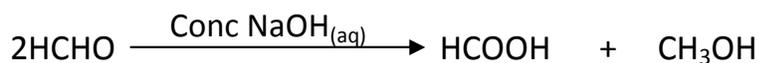


Outline the mechanism for reaction in (b) above.

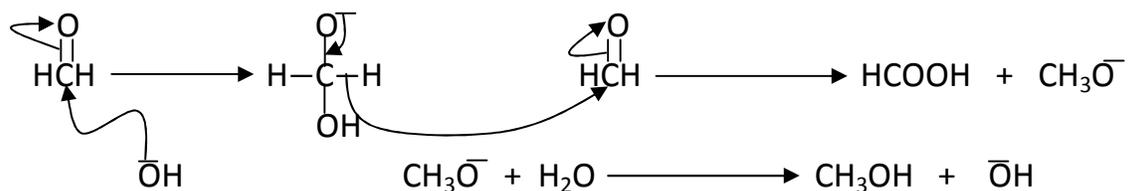
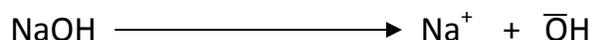
## 3. Cannizzaro reaction (reaction with concentrated sodium hydroxide solution).

This reaction is undergone by only aldehydes lacking  $\alpha$  –hydrogen atoms.e.g methanal ( $\text{HCHO}$ ) and Benzaldehyde ( $\text{C}_6\text{H}_5\text{CHO}$ )

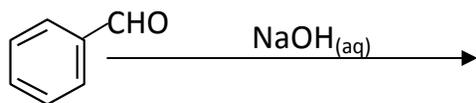
In this reaction half the quantity of aldehydes is oxidised to carboxylic acid and half is reduced to an alcohol. E.g



Mechanism

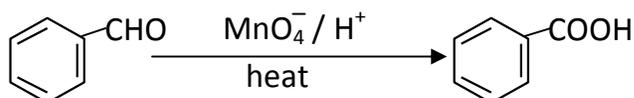
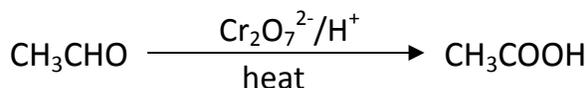


Qn. Complete the equation below and outline the mechanism of reaction.



(c) OXIDATION REACTIONS

Aldehydes are oxidised to carboxylic acids while ketones are not oxidised. E.g



**Distinguishing between aldehydes and ketones**

The following oxidation reactions are used to distinguish aldehydes from ketones.

**1. Ammoniacal silver nitrate solution (Tollen's reagent).**

The reagent consists of silver nitrate solution in aqueous ammonia solution.

The reagent oxidises the aldehydes to carboxylic acids and itself is reduced to silver.

Therefore aldehydes react with Ammoniacal silver nitrate solution on **warming to form a silver mirror (grey precipitate)** whereas **no observable change** with ketones.

Equation



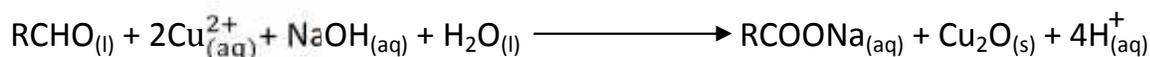
**2. Fehling's solution.**

Fehling's solution contains complexed copper (II) ions ( $\text{Cu}^{2+}$ ) which are reduced by the aldehydes on heating to a **reddish brown precipitate (red precipitate)** of copper (I) oxide ( $\text{Cu}_2\text{O}$ ).

Equation



Or



Or



**N.B.** Benzaldehyde forms a silver mirror (grey precipitate) when reacted with Ammoniacal silver nitrate solution (Tollen's reagent) but gives no observable change (does not form a reddish brown precipitate) when reacted with Fehling's solution.

**Qn.** Name a reagent that can be used to distinguish the following pair of compounds. Your answer should include the relevant observations and equation of reaction.



**Reagent:**

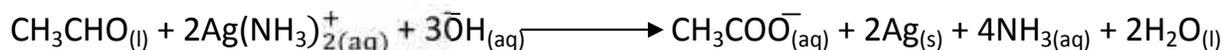
Ammoniacal silver nitrate solution (Tollen's reagent)

**Observation:**

$\text{CH}_3\text{CHO}$  forms a silver mirror (grey precipitate) on warming

$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_3$  No observable change

**Equation:**



OR

**Reagent**

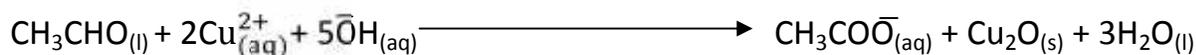
Fehling's solution

**Observation**

$\text{CH}_3\text{CHO}$  forms a reddish brown precipitate (red precipitate) on warming

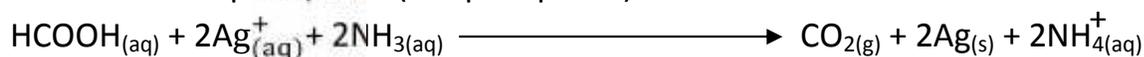
$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_3$  No observable change

**Equation**

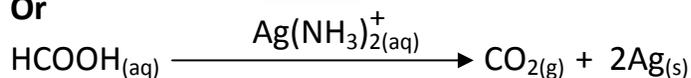


**NOTE**

Because methanoic acid ( $\text{HCOOH}$ ) has an aldehydes group, it forms a silver mirror (grey precipitate) with Ammoniacal silver nitrate solution (Tollen's reagent) and a reddish brown precipitate (red precipitate).



**Or**



**Qn.** Name a reagent that can be used to distinguish the following pair of compounds. In each case state what is observed when the reagent is treated with each member of the pair.



## CARBOXYLIC ACIDS AND THEIR DERIVATIVES