

Questions

Give names of the reagents to bring about the following transformations:

- (i) Hexan-1-ol to hexanal
(ii) Cyclohexanol to cyclohexanone
(iii) *p*-Fluor toluene to *p*-fluor benzaldehyde
(iv) Ethanenitrile to ethanal
(v) Allyl alcohol to propenal
(vi) But-2-ene to ethanal

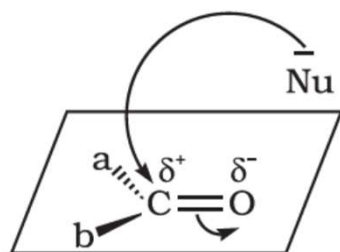
Solution

- (i) $C_5H_5NH+CrO_3Cl$ -(PCC)
(ii) Anhydrous CrO_3
(iii) CrO_3 in the presence of acetic anhydride/ 1. CrO_2Cl_2 2. HOH
(iv) (Di isobutyl) aluminium hydride (DIBAL-H)
(v) PCC
(vi) O_3/H_2O -Zn dust

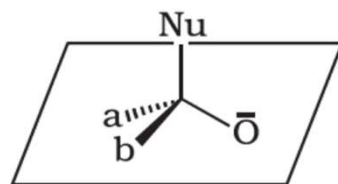
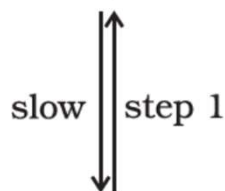
Chemical Reactions of Aldehydes and Ketones

1. Nucleophilic Addition Reactions

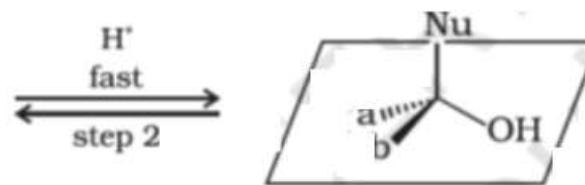
(i) Mechanism of Nucleophilic Addition Reactions



Planar



Tetrahedral intermediate



Addition product

1) **A nucleophile attacks the electrophilic carbon atom** of the polar carbonyl group from a direction approximately perpendicular to the plane of sp^2 hybridized orbitals of carbonyl carbon.

3) **This intermediate captures a proton from the reaction medium** to give the electrically neutral product.

2) **The hybridization of carbon changes from sp^2 to sp^3** ; a tetrahedral alkoxide intermediate is produced.

- The net result is addition of Nu^- and H^+ across the carbon oxygen double bond.

Chemical Reactions of Aldehydes and Ketones

1. Nucleophilic Addition Reactions

(ii) Reactivity

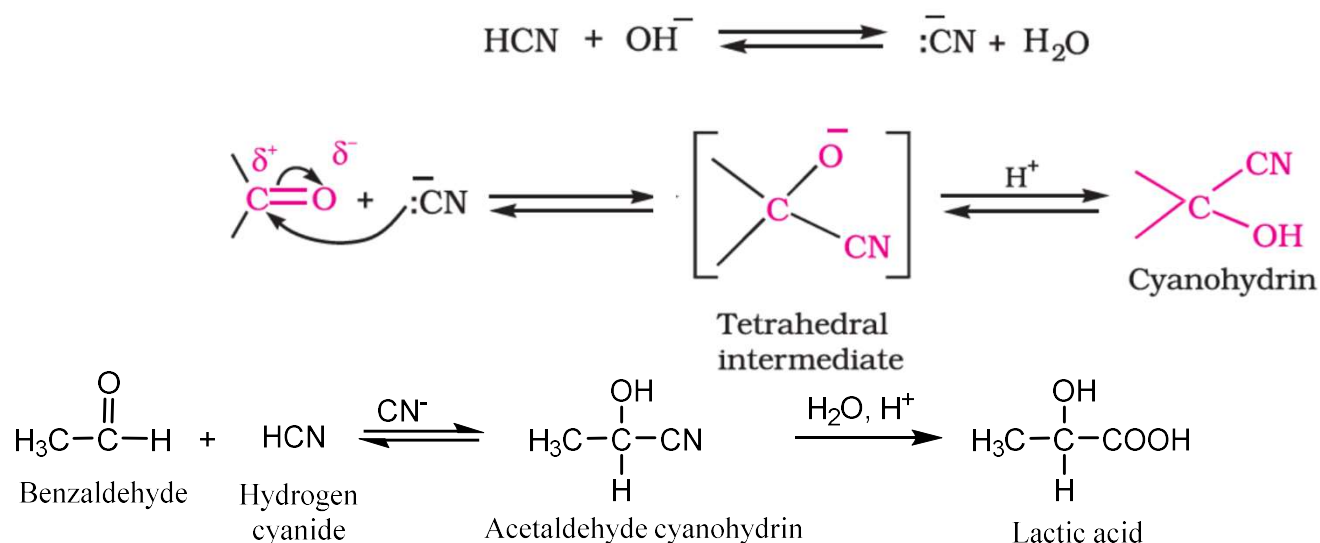
- *Aldehydes are generally more reactive than ketones* in nucleophilic addition reactions due to **steric** and **electronic reasons**.
 - **Sterically**, the presence of two relatively *large substituents in ketones hinders the approach of nucleophile to carbonyl carbon* than in aldehydes having only one such substituent.
 - **Electronically**, aldehydes are more reactive than ketones because *two alkyl groups reduce the electrophilicity of the carbonyl carbon* more effectively than in former.

Chemical Reactions of Aldehydes and Ketones

1. Nucleophilic Addition Reactions: **Examples**

(a) Addition of hydrogen cyanide (HCN):

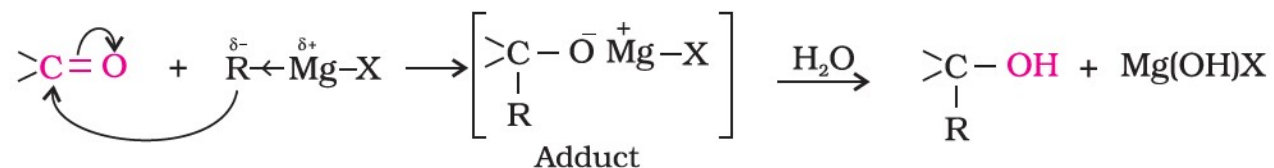
- Aldehydes and ketones react with hydrogen cyanide (HCN) to yield **cyanohydrins**.
- This reaction is catalyzed by a base and the generated cyanide ion (CN⁻) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrin.
- Cyanohydrins are useful synthetic intermediates.



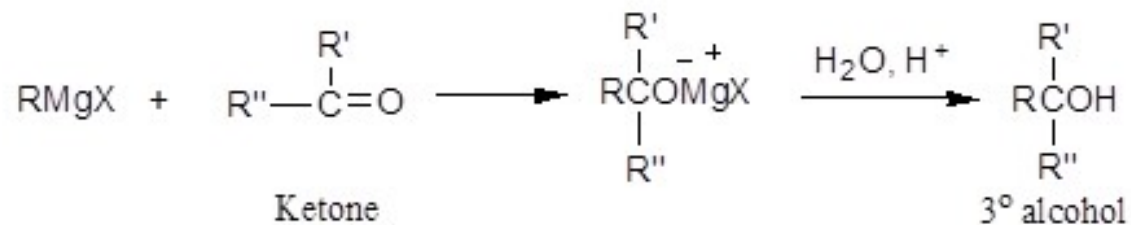
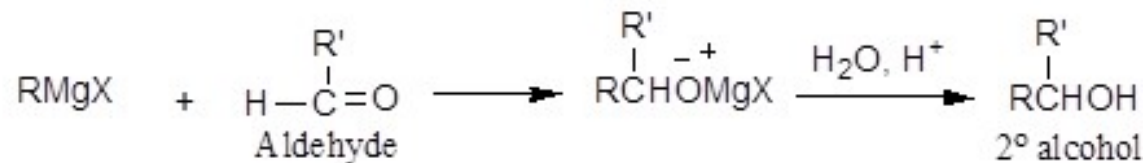
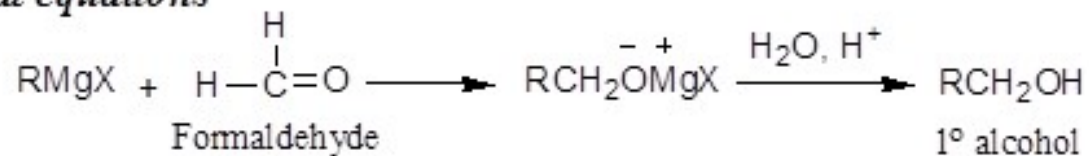
Chemical Reactions of Aldehydes and Ketones

1. Nucleophilic Addition Reactions: **Examples**

(b) Addition of Grignard Reagents:



General equations

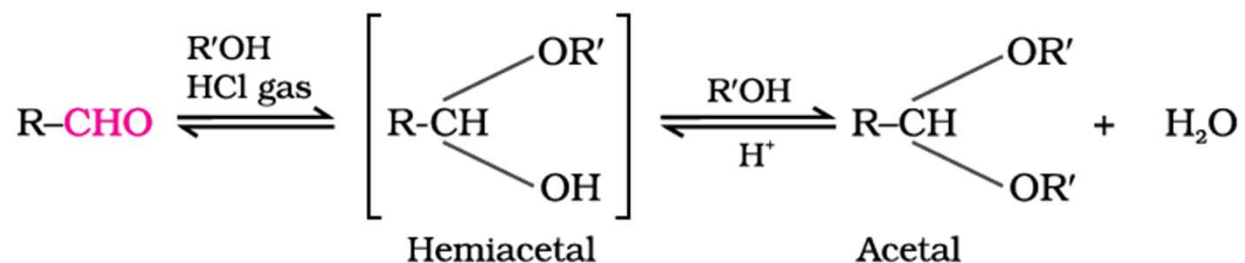


Chemical Reactions of Aldehydes and Ketones

1. Nucleophilic Addition Reactions: **Examples**

(c) Addition of Alcohols:

- Aldehydes react with one equivalent of monohydric alcohol in the presence of dry hydrogen chloride to yield **alkoxyalcohol intermediate**, known as **hemiacetals**, which further react with one more molecule of alcohol to give a **gem-dialkoxy compound** known as **acetal**.
- Acetals are hydrolyzed with aqueous mineral acids to yield corresponding aldehydes and ketones respectively.

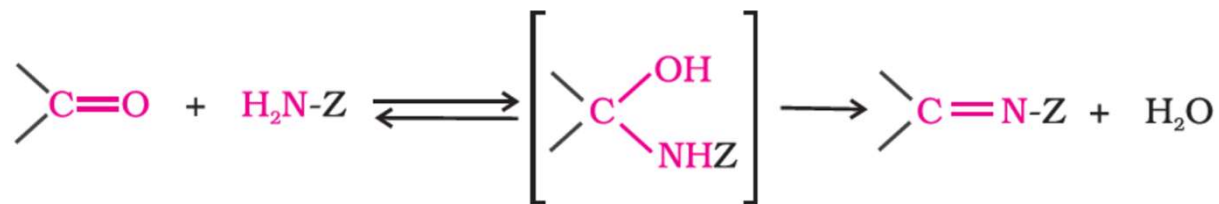


Chemical Reactions of Aldehydes and Ketones

1. Nucleophilic Addition Reactions: **Examples**

(d) Addition of Ammonia and its Derivatives:

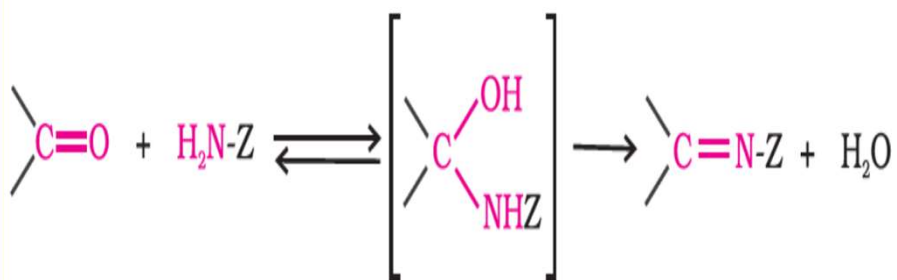
- Nucleophiles, such as ammonia and its derivatives $\text{H}_2\text{N-Z}$ add to the carbonyl group of aldehydes and ketones.
- The reaction is reversible and **catalyzed by acid**.
- The equilibrium favors the product formation due to **rapid dehydration of the intermediate to form $>\text{C}=\text{N-Z}$** .


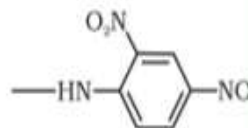
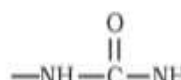


Chemical Reactions of Aldehydes and Ketones

1. Nucleophilic Addition Reactions: **Examples**

(d) Addition of Ammonia and its Derivatives:



Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	$\begin{array}{c} \diagup \\ \text{C}=\text{NH} \\ \diagdown \end{array}$	Imine
-R	Amine	$\begin{array}{c} \diagup \\ \text{C}=\text{NR} \\ \diagdown \end{array}$	Substituted imine (Schiff's base)
-OH	Hydroxylamine	$\begin{array}{c} \diagup \\ \text{C}=\text{N}-\text{OH} \\ \diagdown \end{array}$	Oxime
-NH ₂	Hydrazine	$\begin{array}{c} \diagup \\ \text{C}=\text{N}-\text{NH}_2 \\ \diagdown \end{array}$	Hydrazone
-HN- 	Phenylhydrazine	$\begin{array}{c} \diagup \\ \text{C}=\text{N}-\text{NH}-\text{C}_6\text{H}_5 \\ \diagdown \end{array}$	Phenylhydrazone
-HN- 	2,4-Dinitrophenylhydrazine	$\begin{array}{c} \diagup \\ \text{C}=\text{N}-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2 \\ \diagdown \end{array}$	2,4 Dinitrophenylhydrazone
-NH- 	Semicarbazide	$\begin{array}{c} \diagup \\ \text{C}=\text{N}-\text{NH}-\text{C}(=\text{O})-\text{NH}_2 \\ \diagdown \end{array}$	Semicarbazone

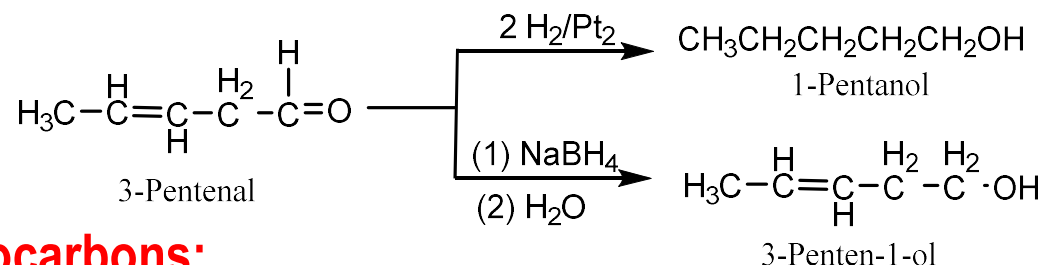
* 2,4-DNP-derivatives are yellow, orange or red solids, useful for characterisation of aldehydes and ketones.

Chemical Reactions of Aldehydes and Ketones

2. Reduction

(i) Reduction to alcohols:

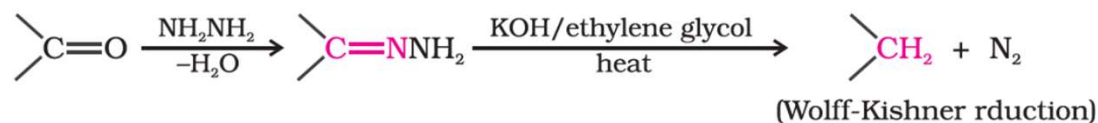
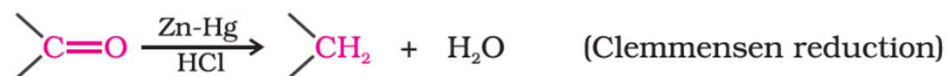
Aldehydes and ketones are **reduced to primary and secondary alcohols** respectively by sodium borohydride (NaBH_4) or lithium aluminium hydride (LiAlH_4) as well as by catalytic hydrogenation



(ii) Reduction to hydrocarbons:

The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with:

- zinc amalgam and concentrated hydrochloric acid [Clemmensen reduction].
- hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol.



Chemical Reactions of Aldehydes and Ketones

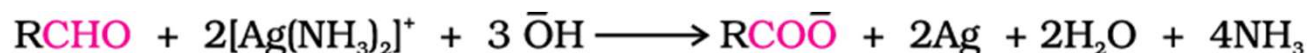
3. Oxidation

Aldehydes are easily oxidized to carboxylic acids on treatment with *common oxidizing agents* like nitric acid, potassium permanganate, potassium dichromate, etc. Even *mild oxidizing agents*, mainly Tollens' reagent and Fehlings' reagent also oxidize aldehydes.

(i) Tollens' Test:



- On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal.
- The reaction occurs in alkaline medium.



(ii) Fehling's Test:

- Fehling reagent comprises of two solutions,
Fehling solution A is aqueous copper sulphate and *Fehling solution B* is alkaline sodium potassium tartarate.
- Aldehyde are oxidized to carboxylate anion with Fehling's reagent, and a reddish brown precipitate is obtained.



Chemical Reactions of Aldehydes and Ketones

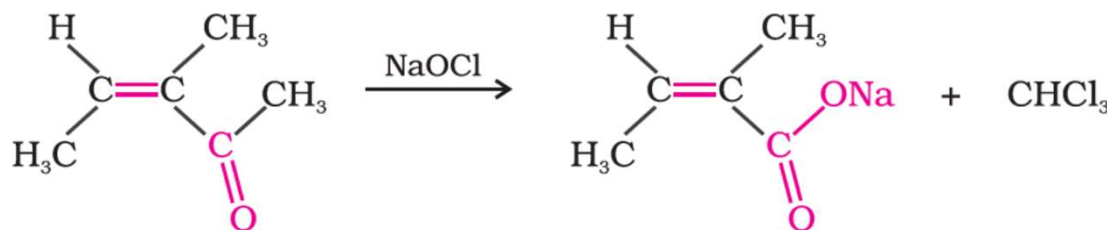
3. Oxidation

(iii) Oxidation of Methyl Ketones by Haloform Reaction:

- Aldehydes and ketones having *at least one methyl group linked to the carbonyl carbon atom* (**methyl ketones**) are *oxidized by sodium hypohalite* to
 - sodium salts of corresponding carboxylic acids* having one carbon atom less than that of carbonyl compound.
 - The methyl group is converted to haloform.



- This oxidation does not affect a carbon-carbon double bond**, if present in the molecule.



Questions

Question

An organic compound (A) with molecular formula C_8H_8O forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula $C_7H_6O_2$. Identify the compounds (A) and (B) and explain the reactions involved.

Solution

(A) forms 2,4-DNP derivative. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollens' or Fehling reagent, (A) must be a ketone. (A) responds to iodoform test. Therefore, it should be a methyl ketone. The molecular formula of (A) indicates high degree of unsaturation, yet it does not decolourise bromine water or Baeyer's reagent. This indicates the presence of unsaturation due to an aromatic ring.

Compound (B), being an oxidation product of a ketone should be a carboxylic acid. The molecular formula of (B) indicates that it should be benzoic acid and compound (A) should, therefore, be a monosubstituted aromatic methyl ketone. The molecular formula of (A) indicates that it should be phenyl methyl ketone (acetophenone). Reactions are as follows:

