Sadiq Public School

Do the right, fear no man

Subject: Chemistry **Class: I2** **Day: Saturday, 16th Nov, 2024**

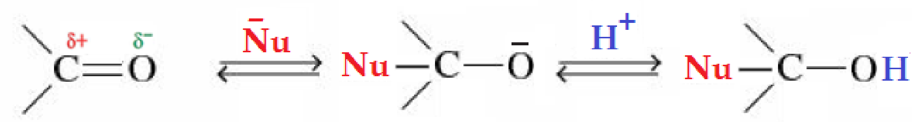
Lesson: Acid catalysed reactions, Reduction and Oxidation of Aldehydes and ketones

A) Inquiry

The nucleophilic addition reactions of aldehydes and ketones are catalyzed by bases or acids. Remember that whether the addition is base-catalyzed or acid-catalyzed, the adduct (addition product) is always same. Do you know the difference between the mechanism of acid catalyzed and base catalyzed reaction?

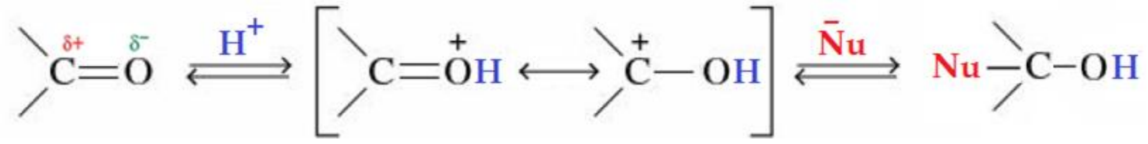
B) Information

Base Catalysed Addition reaction: We learnt in previous lesson that a basic catalyst increases the nucleophilic character of the reagent. The strong nucleophiles (anionic) then add directly to the electrophilic carbon of $>\mathbf{C}=\mathbf{O}$ group to form the intermediate alkoxide that is protonated with dilute acid to get the addition product as shown by following mechanism.



Acid-Catalyzed Addition reaction: The acid catalyzed nucleophilic addition reaction will take place with a weak nucleophilic reagent. An acid-catalyst promotes the nucleophilic attack by increasing the electrophilic character of the carbonyl carbon atom.

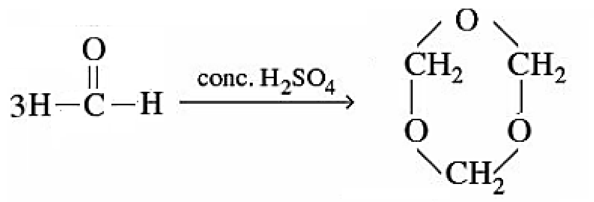
The proton liberated by the acid catalyst combines with the oxygen atom of carbonyl group, thus the electrophilic character of the carbonyl carbon increases. As a result, the attack of the weaker nucleophile on the electrophilic carbon becomes easier as shown by following mechanism.



The acid- catalyzed nucleophilic addition reactions of aldehydes and ketones are the following.

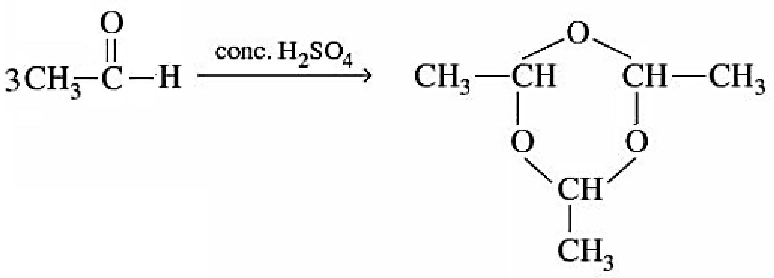
1. **Polymerization**

   In the presence of sulfuric acid, formaldehyde yields a cyclic trimer called metaformaldehyde which is also known as symmetrical trioxane.



Trioxane (Metaformaldehyde)

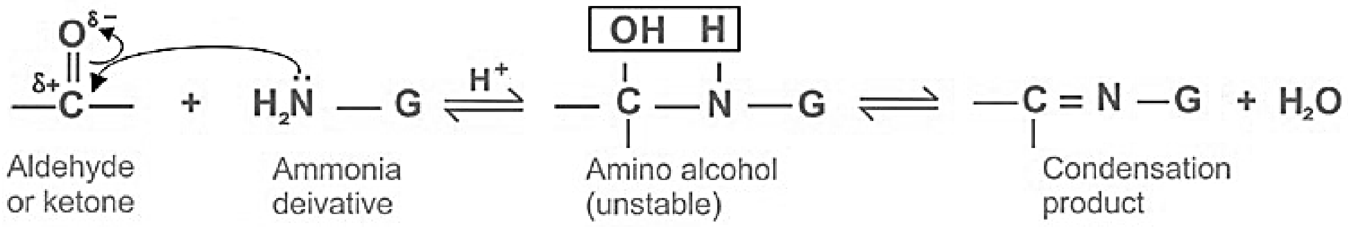
Acetaldehyde forms cyclic trimer in the presence of concentrated sulfuric acid known as paraldehyde.



Paraldehyde

2. **Reactions of Ammonia Derivatives**

   Aldehydes and ketones react with ammonia derivatives, $G-NH_2$ to form compounds containing the group, and water. The reaction is known as condensation reaction or an addition-elimination reaction because water is lost after addition occurs. The reaction is acid catalyzed. The general reaction is:



Where G = $-\ddot{O}H, -\ddot{N}H_2, -\ddot{N}HC_6H_5, -\ddot{N}HCONH_2$ etc.

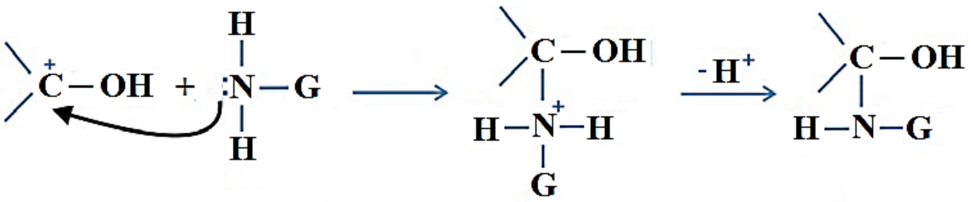
- Some commonly used ammonia derivatives are;

(i) Hydroxylamine, NH_2OH (ii) Hydrazine, NH_2-NH_2 (iii) Semicarbazide, $NH_2-NH-CO-NH_2$
(iv) Phenylhydrazine, $C_6H_5-NH-NH_2$ (v) 2,4- Dinitrophenylhydrazine, $NH_2-NH-C_6H_3-(NO_2)_2$

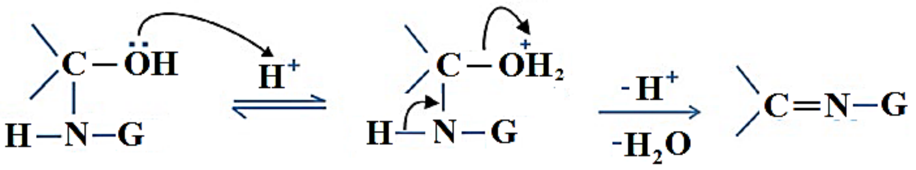
Mechanism of the Reactions of Ammonia Derivatives

Step (i) Protonation of oxygen of the carbonyl group.

Step (ii) Nucleophilic attack of nitrogen of ammonia derivative on the electrophilic positively charged carbon and deprotonation of the adduct.



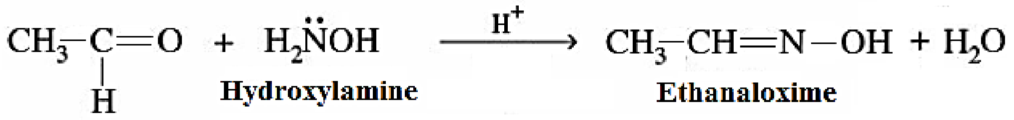
Step (iii) Protonation of oxygen of hydroxyl group followed by the removal of water.



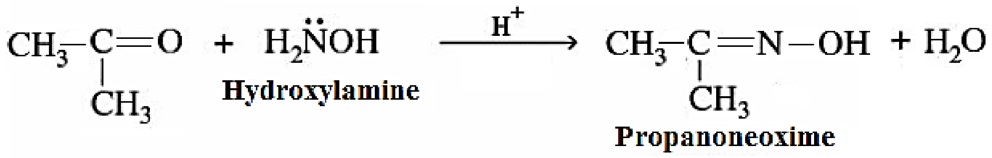
Examples of reactions of ammonia derivatives:

(i) Reaction with Hydroxylamine

Aldehydes and ketones react with hydroxylamine to form oximes in the presence of an acid.



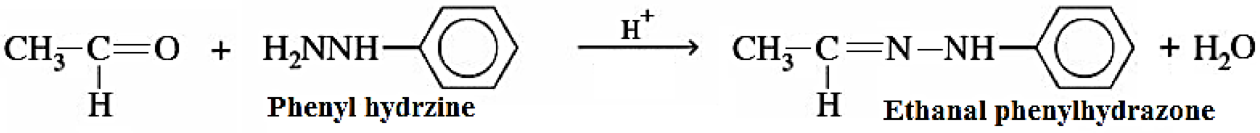
$$CH_3-\underset{H}{C}=O + \underset{\text{Hydroxylamine}}{H_2\ddot{N}OH} \xrightarrow{H^+} \underset{\text{Ethanaloxime}}{CH_3-CH=N-OH} + H_2O$$

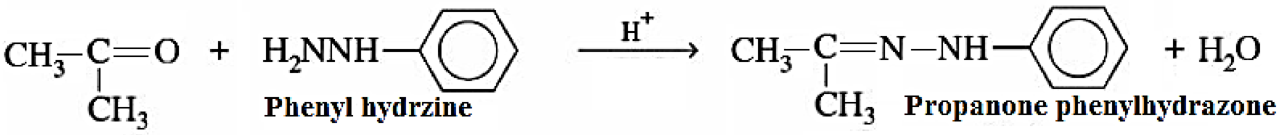


$$CH_3-\underset{CH_3}{C}=O + \underset{\text{Hydroxylamine}}{H_2\ddot{N}OH} \xrightarrow{H^+} \underset{\text{Propanoneoxime}}{CH_3-\underset{CH_3}{C}=N-OH} + H_2O$$

(ii) Reaction with Phenylhydrazine

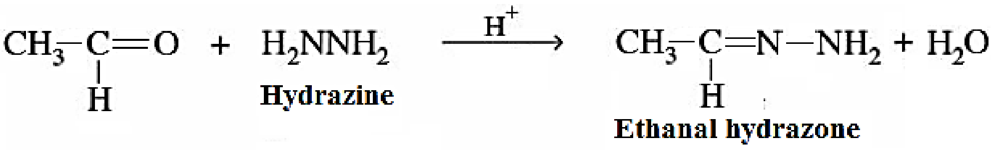
Aldehydes and ketones react with **phenylhydrazine** to form **phenylhydrazones** in the presence of an acid.



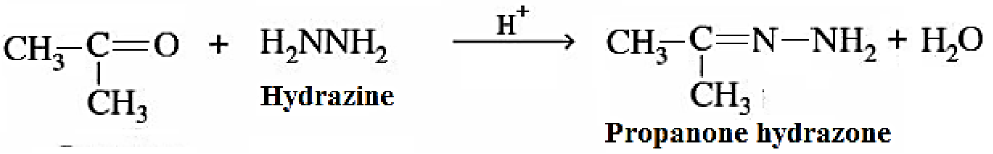


(iii) Reaction with Hydrazine

Aldehydes and ketones react with hydrazine to form hydrazones in the presence of an acid.



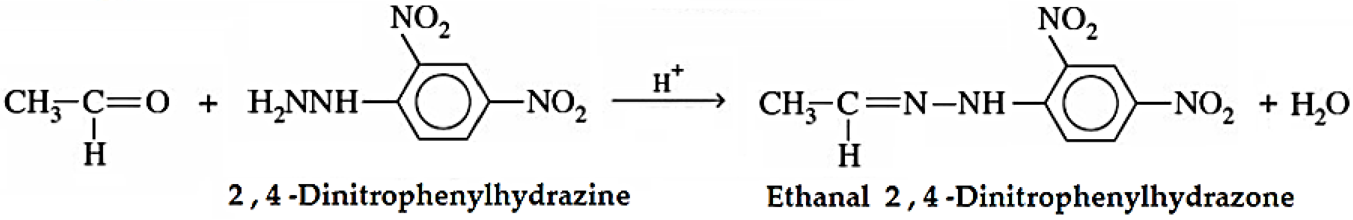
$$CH_3-\underset{H}{C}=O + \underset{\text{Hydrazine}}{H_2NNH_2} \xrightarrow{H^+} \underset{\text{Ethanal hydrazone}}{CH_3-\underset{H}{C}=N-NH_2} + H_2O$$

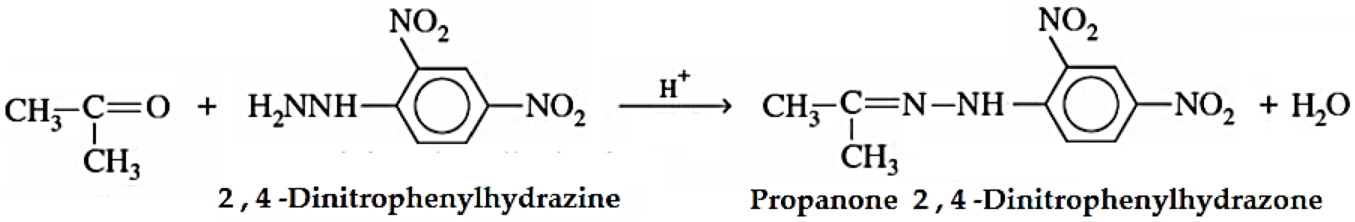


$$CH_3-\underset{CH_3}{C}=O + \underset{\text{Hydrazine}}{H_2NNH_2} \xrightarrow{H^+} \underset{\text{Propanone hydrazone}}{CH_3-\underset{CH_3}{C}=N-NH_2} + H_2O$$

(iv) Reaction with 2 , 4 -Dinitrophenylhydrazine [2 ,4-DNPH]

Aldehydes and ketones react with 2, 4-Dinitrophenyhydrazine to form 2, 4- Dinitrophenylhydrazones in the presence of an acid.

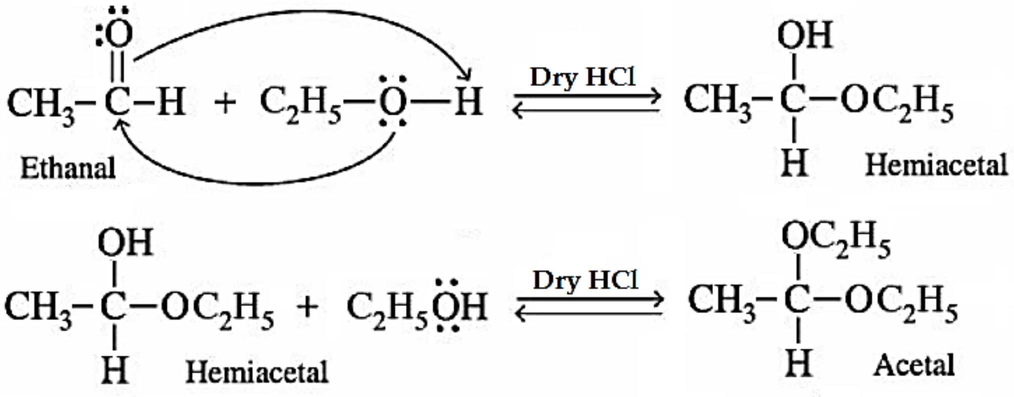




- ❖ The reaction can be used for the identification of aldehydes and ketones because 2,4-Dinitrophenylhydrazones are usually yellow or orange crystalline solids

3. **Addition of Alcohols**

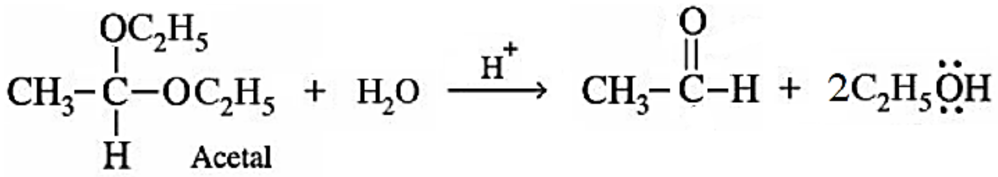
Aldehydes combine with alcohols in the presence of hydrogen chloride gas to form acetals. The hydrogen chloride gas acts as a catalyst. Both the alcohol and the hydrogen chloride gas must be dry.



$$\underset{\text{Ethanal}}{CH_3-\overset{\overset{\ddot{O}:}{\|}}{C}-H} + C_2H_5-\ddot{O}-H \xrightleftharpoons{\text{Dry HCl}} \underset{\text{Hemiacetal}}{CH_3-\underset{H}{\overset{OH}{C}}-OC_2H_5}$$

$$\underset{\text{Hemiacetal}}{CH_3-\underset{H}{\overset{OH}{C}}-OC_2H_5} + C_2H_5\ddot{O}H \xrightleftharpoons{\text{Dry HCl}} \underset{\text{Acetal}}{CH_3-\underset{H}{\overset{OC_2H_5}{C}}-OC_2H_5}$$

The reaction may be used to protect the aldehyde group against alkaline oxidizing agents. To regenerate aldehyde, the acetal is hydrolyzed in the presence of an acid.



$$\underset{\text{Acetal}}{CH_3-\underset{H}{\overset{OC_2H_5}{C}}-OC_2H_5} + H_2O \xrightarrow{H^+} CH_3-\overset{\overset{O}{\|}}{C}-H + 2C_2H_5\ddot{O}H$$

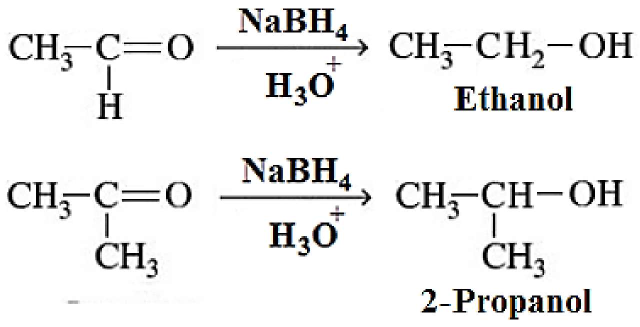
- ❖ Addition of alcohols to ketones to form hemiketals and ketals does not occur readily under these conditions because of the steric hindrance.

4. **Reduction Reactions**

Aldehydes and ketones can both be reduced. Aldehydes are reduced to primary alcohols whereas ketones to secondary alcohols. The carbonyl group is converted into an alcohol.

(i) Reduction with Sodium Borohydride

Aldehydes and ketones are reduced to alcohols with sodium borohydride, $NaBH_4$. The reaction is carried out in two steps: reaction of the carbon compound with $NaBH_4$ under anhydrous conditions and then hydrolysis.



$$CH_3-\underset{H}{C}=O \xrightarrow[H_3\overset{+}{O}]{NaBH_4} \underset{\text{Ethanol}}{CH_3-CH_2-OH}$$

$$CH_3-\underset{CH_3}{C}=O \xrightarrow[H_3\overset{+}{O}]{NaBH_4} \underset{\text{2-Propanol}}{CH_3-\underset{CH_3}{CH}-OH}$$

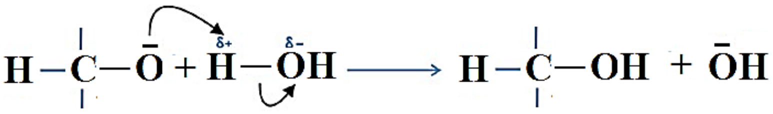
- ❖ Sodium borohydride reduces the carbon-oxygen double bond but not the carbon-carbon multiple bond.

Mechanism:

Step I: The tetrahydridoborate (III) ion, BH_4^- is source of hydride ion, H^-. The hydride ion acts as a nucleophile. It attacks on the electrophilic carbon of the carbonyl group to give an alkoxide ion.

$$\bar{H} + \overset{\delta+}{C}=\overset{\delta-}{O} \longrightarrow H-\underset{|}{\overset{|}{C}}-\bar{O}$$

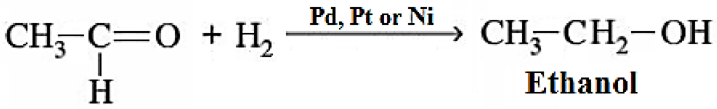
Step II: The alkoxide ion is protonated with water to give an alcohol.



$$H-\underset{|}{\overset{|}{C}}-\bar{O} + \overset{\delta+}{H}-\overset{\delta-}{O}H \longrightarrow H-\underset{|}{\overset{|}{C}}-OH + \bar{O}H$$

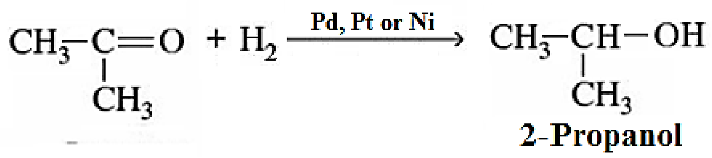
(ii) Catalytic Reduction

Aldehydes and ketones on reduction with hydrogen in the presence of a metal catalyst like Pd, Pt or Ni form primary and secondary alcohols respectively. Hydrogen is added across the carbonyl group.



$$CH_3-\underset{H}{\underset{|}{C}}=O + H_2 \xrightarrow{\text{Pd, Pt or Ni}} CH_3-CH_2-OH$$

Ethanol



$$CH_3-\underset{CH_3}{\underset{|}{C}}=O + H_2 \xrightarrow{\text{Pd, Pt or Ni}} CH_3-\underset{CH_3}{\underset{|}{CH}}-OH$$

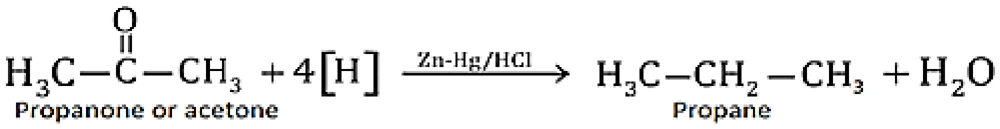
2-Propanol

(iii) Clemmensen's reduction

The reduction of carbonyl compounds (aldehydes or ketones) with zinc amalgam (Zn-Hg) in the presence of HCl to produce alkanes is called **Clemmensen's reduction**. For example;

$$H_3C-\overset{\overset{O}{||}}{C}-H + 4[H] \xrightarrow{\text{Zn-Hg/HCl}} H_3C-CH_3 + H_2O$$

Ethanal or Acetaldehyde — Ethane

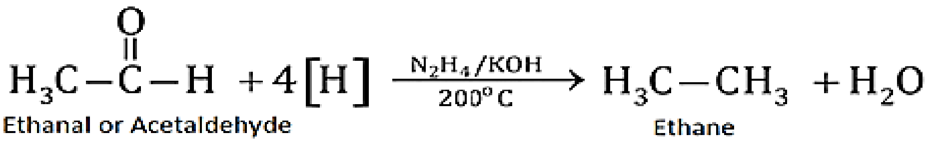


$$H_3C-\overset{\overset{O}{||}}{C}-CH_3 + 4[H] \xrightarrow{\text{Zn-Hg/HCl}} H_3C-CH_2-CH_3 + H_2O$$

Propanone or acetone — Propane

(iv) Wolf-Kishner's reduction

The reduction of carbonyl compounds (aldehydes or ketones) with hydrazine (N_2H_4) by heating in the presence of base (KOH) to produce alkanes is called **Wolf-Kishner's reduction**. E.g.



$$H_3C-\overset{\overset{O}{||}}{C}-H + 4[H] \xrightarrow[200^\circ C]{N_2H_4/KOH} H_3C-CH_3 + H_2O$$

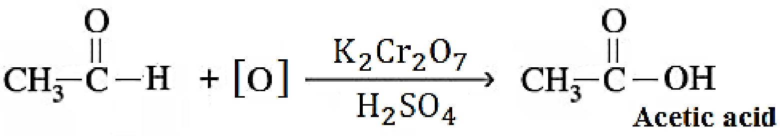
Ethanal or Acetaldehyde — Ethane

$$H_3C-\overset{\overset{O}{||}}{C}-CH_3 + 4[H] \xrightarrow[200^\circ C]{N_2H_4/KOH} H_3C-CH_2-CH_3 + H_2O$$

Propanone or acetone — Propane

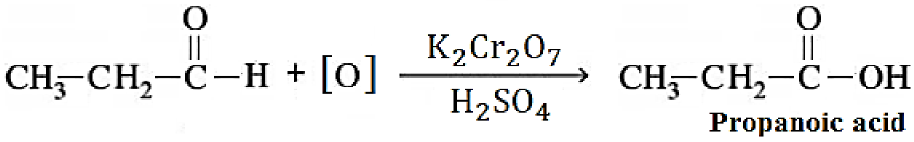
5. **Oxidation Reactions**

(i) Oxidation of Aldehydes: Aldehydes are easily oxidized by mild oxidizing agents like Tollen's reagent, Fehling's solution and Benedict's solution. They are oxidized to carboxylic acids by strong oxidizing agents such as $K_2Cr_2O_7$ / H_2SO_4 , $KMnO_4$ / H_2SO_4 and dilute nitric acid. The hydrogen atom attached to the carbonyl group in aldehydes is oxidized to $-OH$ group.



$$CH_3-\overset{\overset{O}{||}}{C}-H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{\overset{O}{||}}{C}-OH$$

Acetic acid



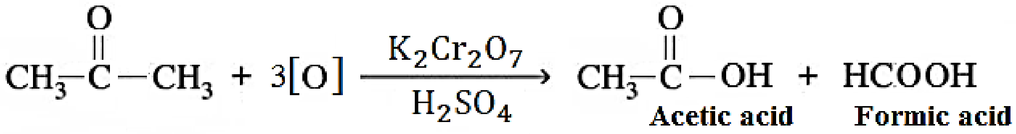
$$CH_3-CH_2-\overset{\overset{O}{||}}{C}-H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-CH_2-\overset{\overset{O}{||}}{C}-OH$$

Propanoic acid

- The carboxylic acid has the same number of carbon atoms as are present in the parent aldehyde.

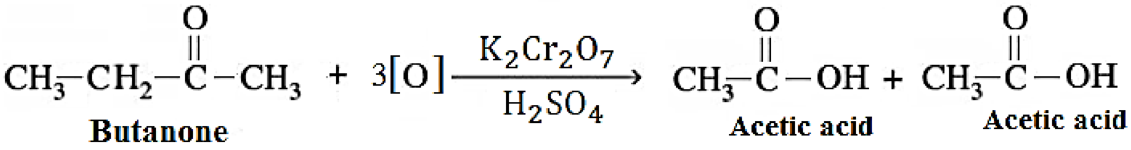
(ii) Oxidation of Ketones: Ketones do not undergo oxidation easily because they require breaking of strong carbon - carbon bond. They give no reaction with mild oxidizing agents. They are only oxidized by strong oxidizing agents such as $K_2Cr_2O_7$ / H_2SO_4 , $KMnO_4$ / H_2SO_4 and conc. HNO_3.

- In oxidation of ketones, only the carbon atoms adjacent to the carbonyl group are attacked.
- The carbon atom joined to the smaller number of hydrogen atoms is preferentially oxidized.
- In case of symmetrical ketones only one carbon atom adjacent to the carbonyl group is oxidized and a mixture of two carboxylic acids is always obtained.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + 3[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Formic acid}}{HCOOH}$$

- However, in case of unsymmetrical ketones, the carbon atom joined to the smaller number of hydrogen atoms is preferentially oxidized and the carbonyl group remains with the smaller alkyl group.



$$\underset{\text{Butanone}}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3} + 3[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH}$$

➢ Please read page no. 239-244 of your book for more detail of reactions of carbonyl compounds.

C) Synthesizing

1. Write a note on acid catalyzed addition of ammonia derivatives to aldehydes and ketones.
2. Discuss the chemistry of oxidation of aldehydes and ketones.
3. Compare the mechanism of acid catalyzed and base catalyzed reactions.

D) Practising

1. Differentiate between Wolf-Kishner's reduction and Clemmensen's reduction.
2. How propanal is converted into propanoic acid.
3. How acetaldehyde is converted into acetal and acetal is converted back to acetaldehyde?
4. How aldehydes undergo polymerization?

E) Assessment

Choose the most suitable answer of the following MCQs. 10 Marks

1. Which compound undergoes Cannizzaro's reaction in the presence of dilute aqueous sodium hydroxide?
(a) HCHO (b) CH_3CHO (c) CH_3-CH_2-CHO (d) CH_3-$COCH_3$

2. Formaldehyde condenses with phenol in the presence of dilute base to yield:
(a) Nylon-6,6 (b) Urotropine (c) Aniline-formaldehyde (d) Bakelite

3. Calcium acetate on dry distillation yields:
(a) HCHO (b) CH_3CHO (c) CH_3COCH_3 (d) CH_3COOH

4. Air oxidation of methanol produces:
(a) Ethanol (b) Methanal (c) Methanal + Ethanal (d) Methane

5. Acetone reacts with HCN to form cyanohydrin, it is an example of:
(a) Electrophilic addition (b) Electrophilic substitution
(c) Nucleophilic addition (d) Nuclearphilic substitution

6. Iodoform test is not given by?
(a) Acetaldehyde (b) Acetone (c) Butanone (d) 3-Pentanone

7. Which one of the following compounds is used in the preparation of throat lozenges?
(a) Formaldehyde (b) Acetaldehyde (c) Menthol (d) Menthone

8. Which one of the following compounds will react with Tollen's reagent?
(a) Acetone (b) Acetic acid (c) Methyl ethyl ketone (d) Acetaldehyde

9. The reagent which reacts with Ketones only is :
(a) Sodium nitroprusside (b) Tollen's reagent (c) Fehling's reagent (d) Benedict's reagent

10. The Nucleophilic addition reactions of carbonyl compounds are catalyzed by:
(a) Acids (b) Bases (c) Both a and b (d) None of these

Feedback

- Send an email on my official address provided below to let me know that you are receiving the lessons and to show your participation.
- You are required to send the answers of assessment only via email.
- If you have any queries about this topic, please send an email to your teacher and he/she will try to reply ASAP.

Classes	Teachers' Names	Teachers' Abbreviations	Teachers' Email Addresses	Instructions
I2A	Ali Gul	AG	Aligul313@gmail.com	I2A students will send their home assignments to their subject teacher (AG) for checking and getting feedback.
I2B	Hafiz Abdur Rehman	HAR	khawajaabdulrahman12@gmail.com	I2B students will send their home assignments to their subject teacher (HAR) for checking and getting feedback.
I2C	Saqib Ibn ul Hassan	SIR	shogup54@hotmail.com	I2C students will send their home assignments to their subject teacher (SIR) for checking and getting feedback.
I2GA	Feroz Akhtar	FAK	ferozakhtar88@gmail.com	I2GA students will send their home assignments to their subject teacher (FAK) for checking and getting feedback.
I2GB	Sumiyya Sami	SS	sumiyyasami1989@gmail.com	I2GB students will send their home assignments to their subject teacher (SS) for checking and getting feedback.