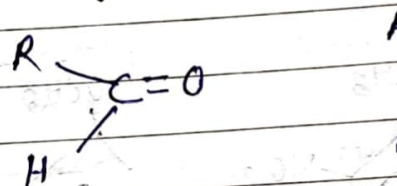
— 16th December, Thursday

DATE

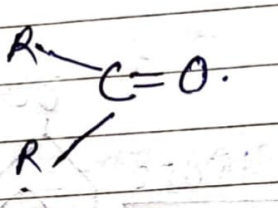
Ch→5 §Aldehydes and Ketones §

Introduction:-

Aldehydes and ketones both contain carboxyl group. Hence, they are collectively known as carboxyl compound. In aliphatic aldehydes the carboxyl carbon is linked to an alkyl group and a hydrogen atom while in ketones it is linked to two alkyl group.



Aldehydes



Ketones

Aldehydes contains functional group -CHO known as aldehyde and ketone contain the functional group $\rangle C=O$ known as ketonic group.

Due to presence of carboxyl group aldehydes and ketones have similar properties. However aldehydes are more reactive then ketones due to presence of free H-atoms.

Structure of carboxyl group:-

In carboxyl group the carbon atom is sp^2 hybridized. The three-sp^2 hybrid orbitals lies in a plane with an angle of 120° between them. The hybrid orbitals form 3-sigma bond, one with O-atom and the two with other atoms attached to the carbon. The remaining unhybridized p-orbitals of carbon atom undergoes lateral overlapping with p-orbitals of O-atom to form π-bond.

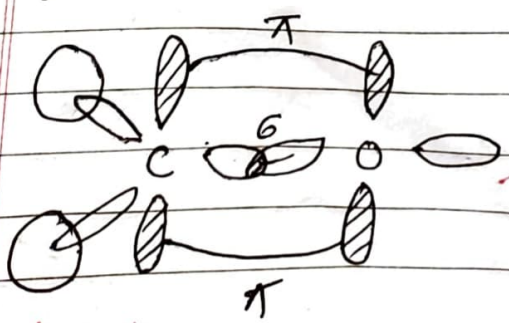


fig:- Structure of carboxyl group

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due to higher electronegativity of oxygen it pulls the shared pair of π-electron move forward it self as a result the carbon bears partial +ve charges and oxygen bears partial -ve charged. Hence, aldehydes and ketones are polar compound

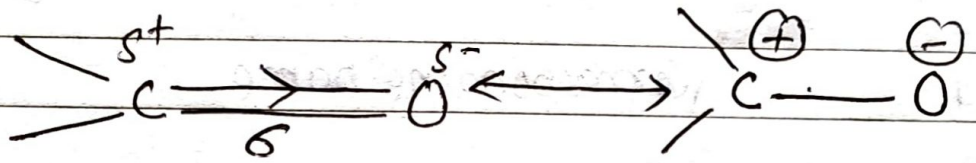

fig:- showing polar nature of carboxyl.

Nomenclature of ketone

Common system ⇒

In this system ketones are named by writing the names of alkyl group in alphabetical order. followed by the word keto ne. In this case of simple ketones the di- is added to the name of alkyl group.

Formula	Common name
$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$	Dimethyl ketones (Acetone)
$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$	Diethyl ketone.
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3$	Ethyl methyl ketone.
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$	Methyl n-propyl ketone.
$CH_3-\overset{O}{\overset{\|}{C}}-CH_3-CH-CH_3$	Methyl iso-propyl ketone.

IUPAC system ⇒

In this system ketones are named as alkanones. The name is obtained by replacing the terminal 'e' of the corresponding alkane by the suffix 'one'.

Formula	Corresponding name	IUPAC.
$CH_3-\overset{O}{\overset{\|\|}{C}}-CH_3$	$CH_3-CH_2-CH_3$ (propane)	propanone.
$CH_3-\overset{O}{\overset{\|\|}{C}}-CH_2-CH_3$	$CH_3-CH_2-CH_2-CH_3$ (Butane)	2 Butanone
$CH_3-CH_2-\overset{O}{\overset{\|\|}{C}}-CH_2-CH_3$	$CH_3-CH_2-CH_2-CH_2$ (pentane)	3-pentanone.
$CH_3-\overset{O}{\overset{\|\|}{C}}-CH_2CH_3CH_3$	$CH_3CH_2-CH_2-CH_2-CH_3$	pentanone
$CH_3-\overset{O}{\overset{\|\|}{C}}-\underset{\underset{CH_3}{\|}}{CH}-CH_3$	$CH_3-CH_2-\underset{\underset{CH_3}{\|}}{CH}-CH_3$	2-methy'buta none

~~# Nomenclature of aldehyde ⇒~~

A) Nomenclature of aldehyde ⇒

1) common system :- → the common name of aldehyde are derived from the common name of carboxylic acids which they give up on oxidation.

→ the -ic acid of the name of acids is replaced by the word aldehyde

Formula	corresponding acid	common names
HCHO	HCOOH (formic acid)	formaldehyde
CH_3CHO	CH_3COOH (Acetic acid)	Acetaldehyde.
CH_3CH_2CHO	CH_3CH_2COOH (propanoic acid)	propionaldehyde

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$CH_3CH_2CH_2CHO$ $CH_3-CH_2-CH_2-COOH$ (n-butanoic acid) — n-butyraldehyde.

$CH_3-\underset{CH_3}{CH}-CHO$ $CH_3-\underset{CH_3}{CH}-COOH$ (iso-butyric acid) — Isobutyraldehyde

The position of substituent is denoted by Greek letter $\alpha, \beta, \gamma, \delta$ etc.

$\overset{\gamma}{CH_2}(OH)-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-CHO$ — γ-hydroxy butyraldehyde.

II) IUPAC System ⇒

In this system aldehydes are named as alkanal. The name is obtained by replacing the terminal(e) of the corresponding alkane by suffixal.

Formula	Corresponding alkane	IUPAC name.
$HCHO$	CH_4 (Methane)	Methanol
CH_3CH_2	CH_3-CH_3 (ethane)	Ethanol.
CH_3CH_2CHO	$CH_3-CH_2-CH_3$ (propanel)	propanal.
$CH_3-CH_2-CH_2-CHO$	$CH_3CH_2CH_2CH_2$ (Butanel)	Butanol.
$CH_3-\underset{CH_3}{CH}-CHO$	$CH_3-\underset{CH_3}{CH}-CH_3$ (2-methyl propanel)	2-methyl propanol.

Structural isomerism in aldehydes and ketones.

1. Chain isomerism :-

(≥4) Aldehydes having four or more & ketones having 5 or more C-atoms show this type of isomerism.

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$CH_3-CH_2-CH_2-CHO$ Butanol $CH_3-CH(CH_3)-CHO$ 2-methyl propanol → are isomer of chain.

$CH_3-C(=O)-CH_2-CH_2-CH_3$ 2-pentanone $CH_3-C(=O)-CH(CH_3)-CH_3$ 3-methy butanone → chain isomer.

2. position isomerism:- aldehydes do not show this type of isomer because -CHO group is always present at the end of chain but keton having 5 or more carbon atoms show this type of isomerism.

$CH_3-C(=O)-CH_2-CH_2-CH_3$ 2-pentanone and $CH_3-CH_2-C(=O)-CH_2-CH_3$ 3-pentanone

Position isomers.

3. Functional isomerism →

Aldehydes and ketones having same number of carbon atom show functional isomerism with eachother.

CH_3-CH_2-CHO propanal $CH_3-C(=O)-CH_3$ propan-2-one (Acetone) → functional isomerism.

General Methods of preparation of Aldehydes & Ketones.

(1) a) Dehydrogenation and b) Oxidation of alcohol.

<a) Dehydrogenation:-

Catalytic dehydrogenation is carried out by passing the vapours of alcohols over heated copper guaze at 300°C.

1) Aldehydes are obtained by catalytic dehydrogenation of primary

alcohol.

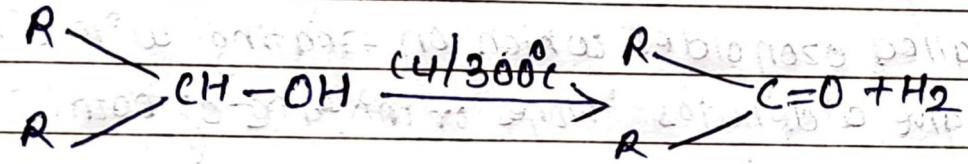
Gy.R

$$R-CH_2OH \xrightarrow{Cu/300^\circ C} R-CHO + H_2.$$

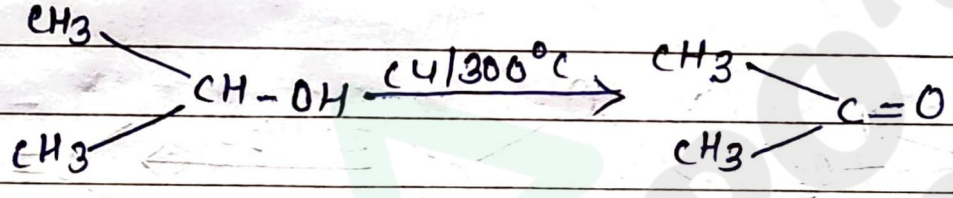
Example:-

$$CH_3CH_2-OH \xrightarrow{Cu/300^\circ C} CH_3CHO + H_2$$

4) Ketones are obtained by catalytic dehydrogenation of secondary alcohol.



e.g



b) Oxidation of alcohol ⇒ Oxidation of alcohol can be carried out with acidified $K_2Cr_2O_7$ & $KMnO_4$.

I. Aldehydes are obtained by controlled oxidation of primary alcohol

G.R:-

$$R-CH_2-OH + [O] \xrightarrow{K_2Cr_2O_7} R-CHO + H_2O.$$

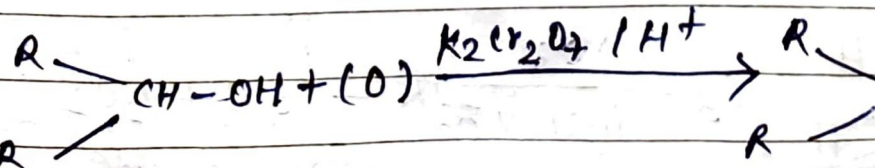
e.g:-

$$CH_3-CH_2-OH + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3CHO + H_2O.$$

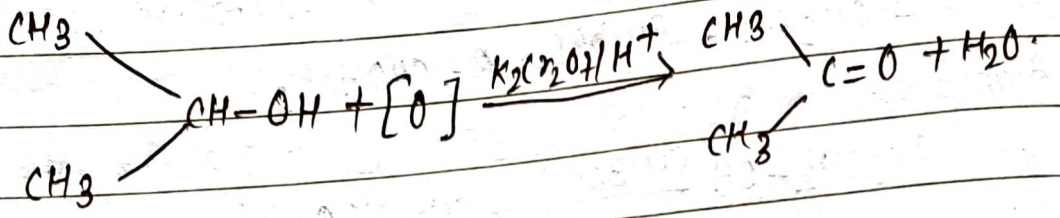
To prevent further oxidation of aldehydes to the carboxylic acid the aldehydes is removed as soon as it is formed by distillation.

II. Ketones are obtained by the oxidation of secondary alcohol (1-alcohol)

Gy.R



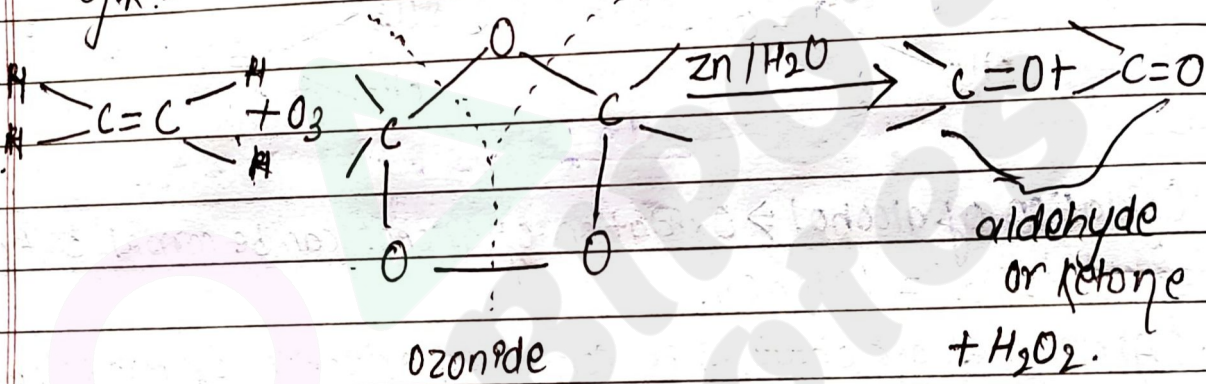
E.g:-



IMP (2) Ozonolysis of alkene ⇒

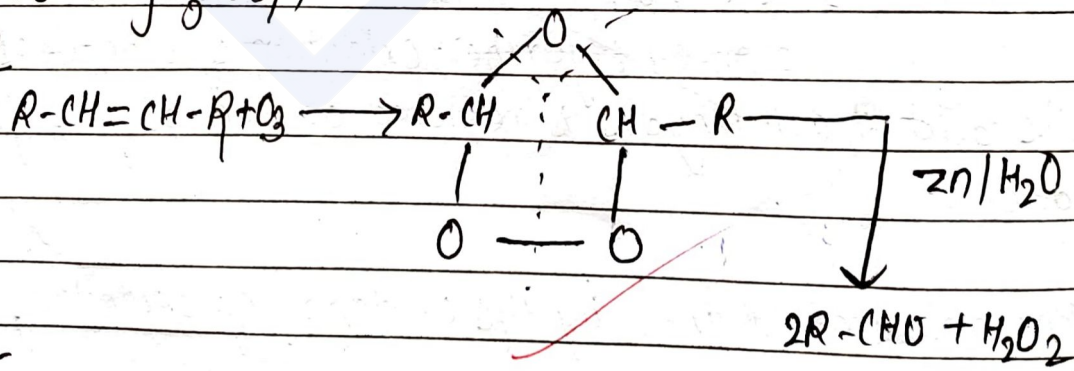
Alkenes react with ozone to form an addition compound called ozonoides which on treating with zinc dust and water give aldehydes ketones or mixture of both. The reac ps called ozonolysis.

G.R:-

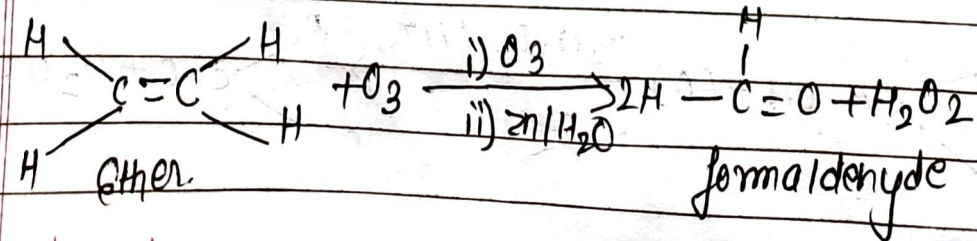


a) Alkenes of the type R-CH=CH-R gives only aldehydes (R-H or alkyl group)

G.R



E.g:-

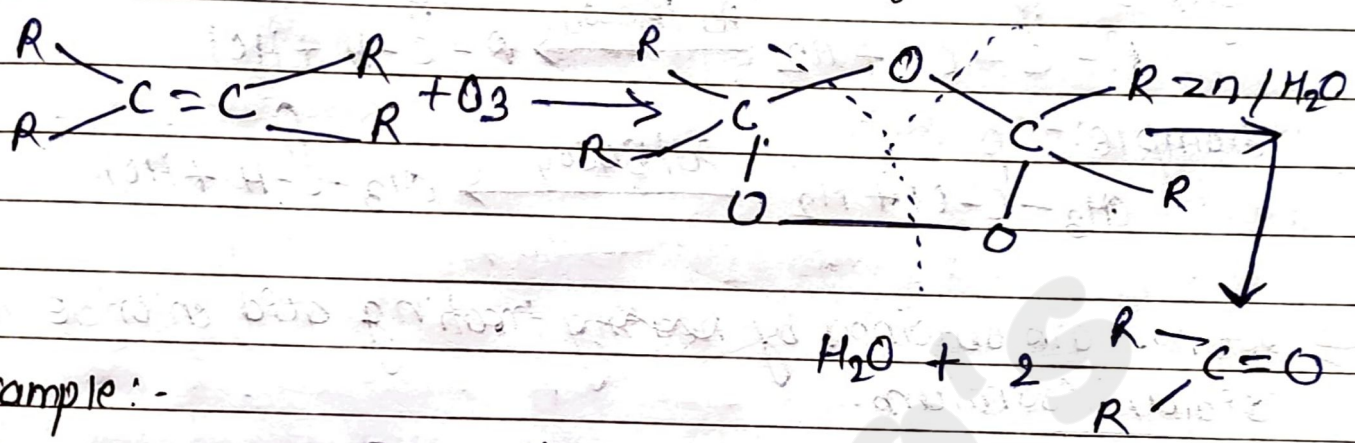


π. $CH_3-CH=CH-CH_3 \xrightarrow[ii)\ Zn/H_2O]{i)\ O_3} 2CH_3CHO + H_2O_2$

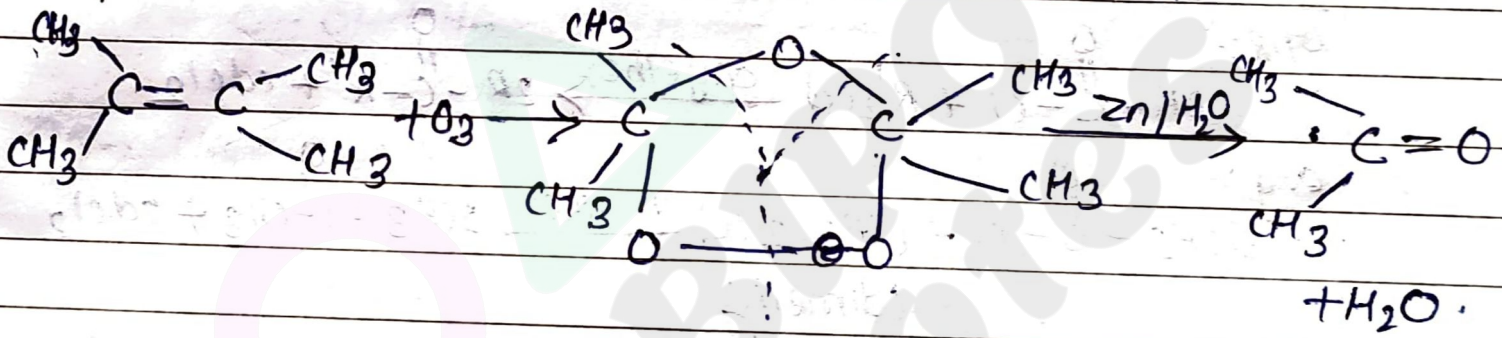
Acetaldehyde.

b) Alkenes of the type $R_2C=CR_2$ give only one ketones

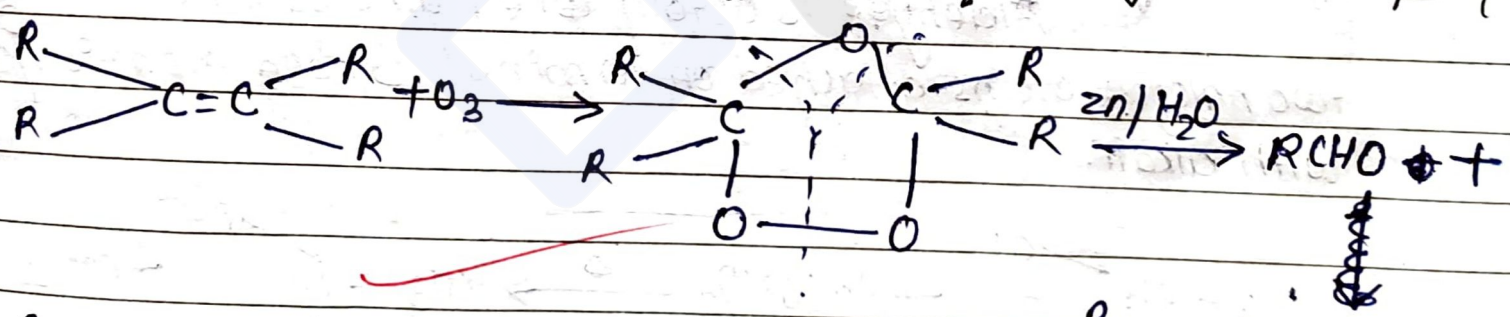
e.g.



Example:-



c) Alkenes of the type $R-CH=CR_2$ gives both aldehydes and ketones.



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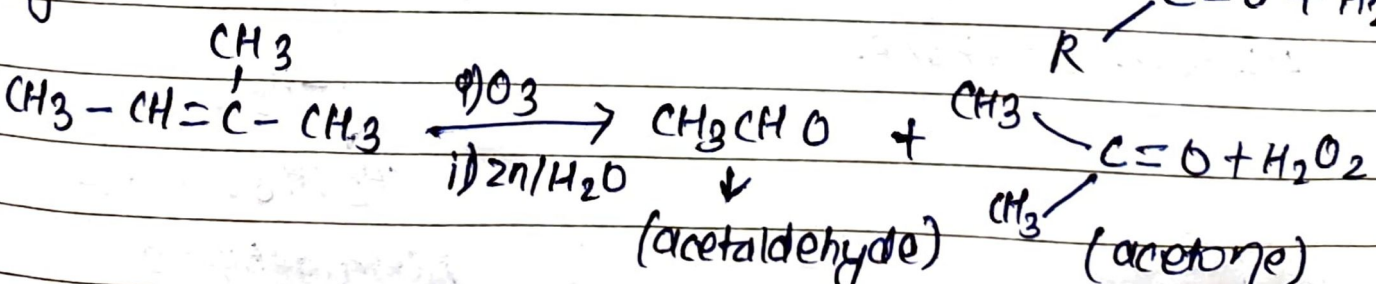


9) From acid chlorides :→ Aldehydes are obtained by the catalytic hydrogenation (reduction) of acid chloride with H_2 in the presence of pottadpum suspended over barium sulphate as catalyst. This reaction is known as Rosenmund reaction.

G.R :-

$$R-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd/BaSO_4} R-\overset{O}{\overset{\|}{C}}-H + HCl$$

Example :-

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd/BaSO_4} CH_3-\overset{O}{\overset{\|}{C}}-H + HCl$$

→ Ketones are obtained by ~~heating~~ treating acid chloride with dialkyl cadmium.

G.R :-

$$2R-\overset{O}{\overset{\|}{C}}-Cl + R'_2Cd \xrightarrow{dry\ ether} 2R-\overset{O}{\overset{\|}{C}}-R' + CdCl_2$$

E.g :-

$$2CH_3-\overset{O}{\overset{\|}{C}}-Cl + (CH_3)_2Cd \xrightarrow{dry\ ether} 2CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CdCl_2$$

(dimethy cadmium)

(4) By the hydrolysis of gem-dihalides →

Aldehyde is obtain when dihaloalkane having two halogen atoms attached on terminal carbon atom is heated with alkali.

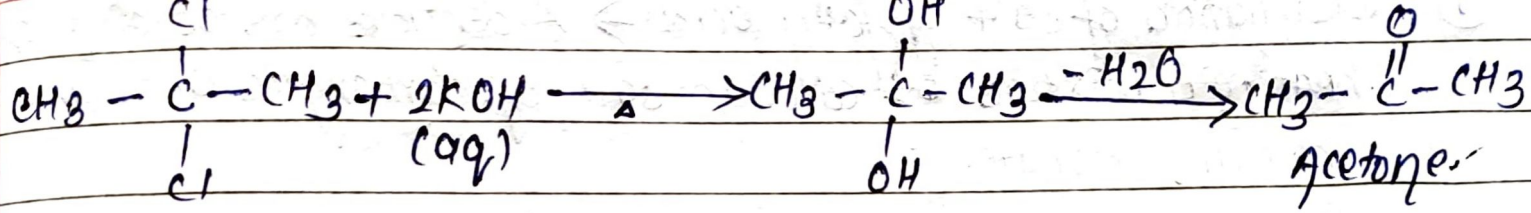
$$CH_3-\underset{Cl}{\overset{Cl}{CH}} + Ca(OH)_2 \xrightarrow{\Delta} CH_3-\underset{OH}{\overset{OH}{CH}} + CaCl_2$$

1,1-Dichloroethane.

$$CH_3-\underset{OH}{\overset{OH}{CH}} \xrightarrow{-H_2O} CH_3CHO$$

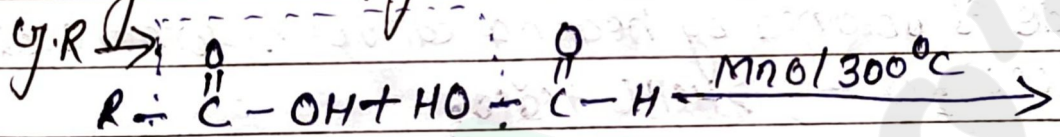
Acetaldehyde

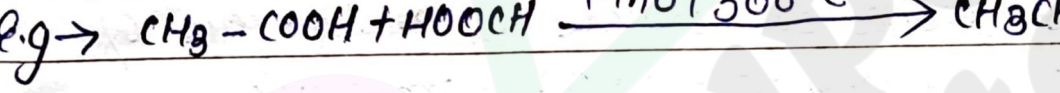
Ketone is obtained when the two highes atoms are attached to carbon atom other than terminal carbon is heated with alkali.



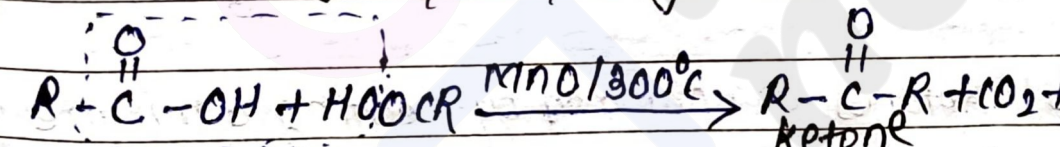
(5) catalytic distillation of fatty acids → catalytic decomposition of carboxylic acid (fatty acid) is carried out by passing the vapour of carboxylic acids over maganous oxide heated to 300°C.

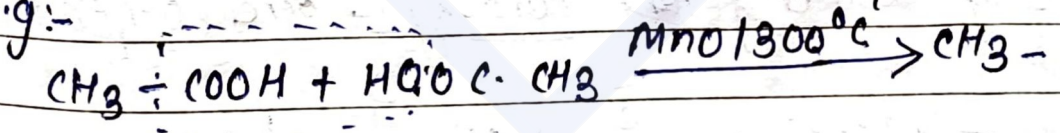
→ Aldehydes are obtained by catalytic decomposition of a mixture of carboxylic acid & formic acid.



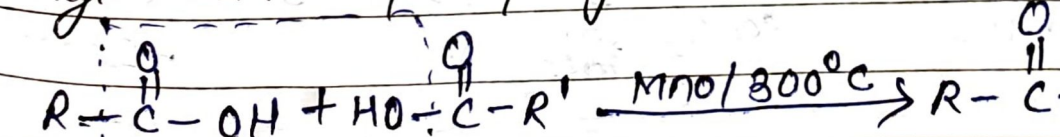


→ Symmetrical ketones are obtained by passing the vapours of a carboxylic acids only other than formic acid.

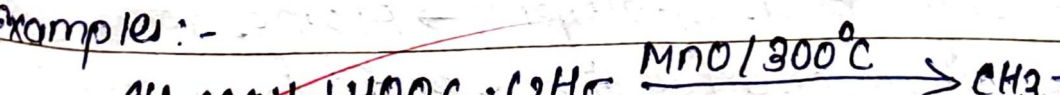




→ Unsymmetrical ketones are obtained by catalytic decomposition of 2 carboxylic acids other than formic acid



Examples:-



(6) Distillation of salt of fatty acids → Aldehydes are obtained by heating a mixture of calcium salt of carboxylic acids and calcium formate.

G.R

$(RCOO)_2Ca + (HCOO)_2Ca \xrightarrow{\Delta} 2RCHO + 2CaCO_3$

Calcium carboxylate — Ca. formate

Eg:- $(CH_3COO)_2Ca + (HCOO)_2Ca \xrightarrow{\Delta} 2CH_3CHO + 2CaCO_3$

∴ Formaldehyde is obtained by heating calcium formate alone.

$(HCOO)_2Ca \xrightarrow{\Delta} HCHO + CaCO_3$

∴ Symmetrical ketones are obtained by calcium salts of carboxylic acid alone (other than that of formic acid)

G.R $(RCOO)_2Ca \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-R + CaCO_3$

$(CH_3COO)_2Ca \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CaCO_3$

∴ Unsymmetrical ketones are obtained by heating a mixture of calcium salts of two different carboxylic acid (other than formic acid)

$(RCOO)_2Ca + (R'COO)_2Ca \xrightarrow{\Delta} 2R-\overset{O}{\overset{\|}{C}}-R' + 2CaCO_3$

e.g:-

$(CH_3CH_2COO)_2Ca + (CH_3COO)_2Ca \xrightarrow{\Delta} 2CH_3-CH-\overset{O}{\overset{\|}{C}}-CH_3 + 2CaCO_3$

Cal. propionate — Calcium acetate

(7) By catalytic hydration of alkynes → Alkynes react with water in the presence of dil sulphuric acids & mercuric sulphates to give aldehydes or ketones.

a) ethyno gives acetaldehyde →

$$H-C\equiv C-H + H_2O \xrightarrow[HgSO_4]{dil.H_2SO_4} CH_2=CH-OH \xrightarrow{Rearrangement} CH_3CHO$$

ethyne. Enol (vinyl alcohol) unstable. acetaldehyde

b) other alkyene other than ethyne give ketone

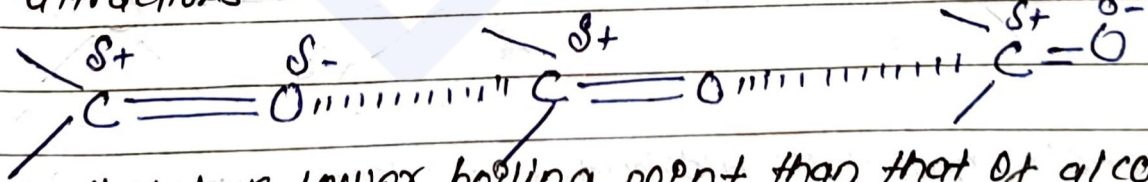
$$CH_3-C\equiv CH + H_2O \xrightarrow[HgSO_4]{dil.H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

(acetone)

Physical properties →

1) physical state :→ The lower membrane of aldehyde and ketone gene rally containing carbon number (C_1 to C_8) are found in liquid state. As molecular mass goes on ~~decreasing~~ increasing i.e above C_8 membes of aldehyde and ketone are found in solid state.

2) Boiling point :→ Aldehydes & ketones have higher boiling point than that of alkanes and ether of comparable molecular mass. It is due to polar nature of carboxyl group. They have appreciable intermole cular attractions.



they have lower boiling point than that of alcohol and carboxylic acids of comparable molecular mass. It is because aldeh ydes and ketones do not form intermolecular hydrogen bond.

3) Solubility :→ Aldehydes and ketones up to 5- carbon atoms are soluble in water due to formation of hydrogen bond between carboxyl group and H_2O molecules.

a) ethyno gives acetaldehyde →

$$H-C\equiv C-H + H_2O \xrightarrow[HgSO_4]{dil.H_2SO_4} CH_2=CH-OH \xrightarrow{\text{Rearrangement}} CH_3CHO$$

ethyne. Enol (vinyl alcohol) unstable. acetaldehyde

b) other alkyene other than ethyne give ketone

$$CH_3-C\equiv CH + H_2O \xrightarrow[HgSO_4]{dil.H_2SO_4} CH_3-\overset{\overset{O}{\uparrow}H}{C}=CH_2 \xrightarrow{\text{Rearrangement}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

(acetone)

Physical properties →

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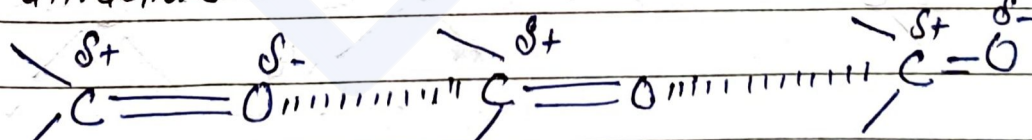

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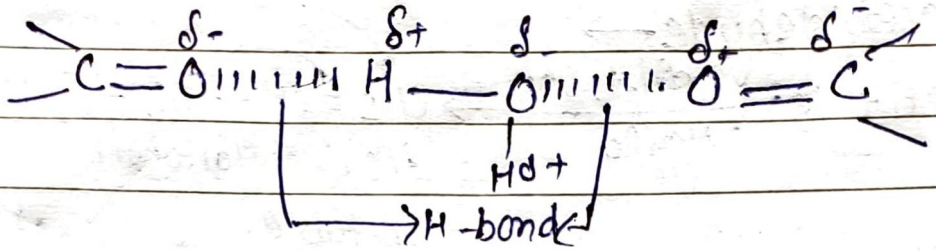


4. Smell or odour:- Lower aldehydes have pungent smell. Higher aldehydes have some pleasant smell. Ketones have always pleasant fruity smell.

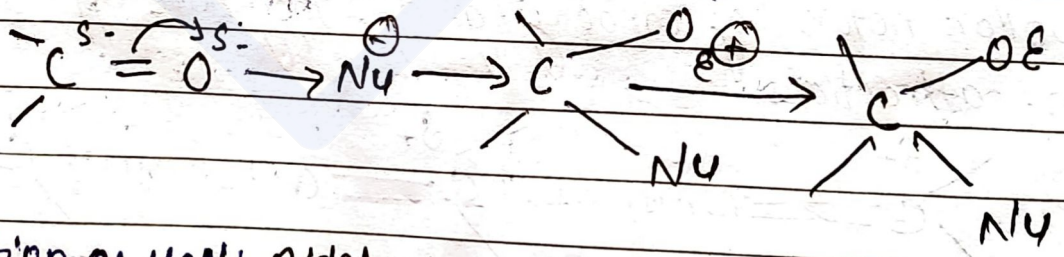
Chemical properties →

Aldehydes and ketones are highly reactive compound due to presence of carboxyl group. Aldehydes and ketones have similar properties but aldehydes are more reactive than ketone due to presence of H-atom in carboxyl group.

Nucleophilic additions reactions →

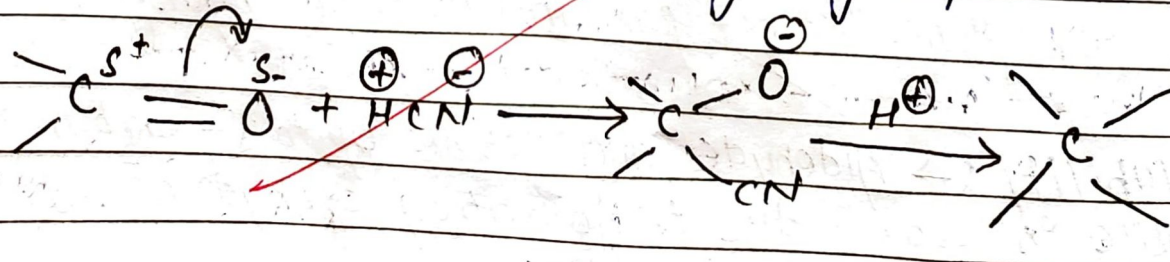
In nucleophilic addition reaction a nucleophile of the reagents attacks the tvely charged carboxyl carbon to form an intermediate anion, which then combines with electrophile of the reagents to form an addition compound.

General representation ⇒

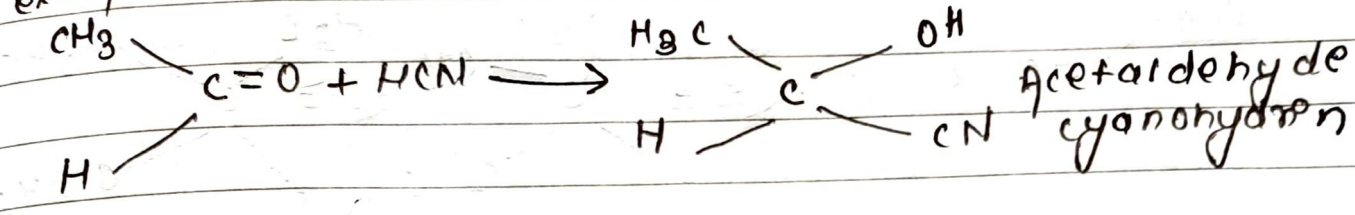


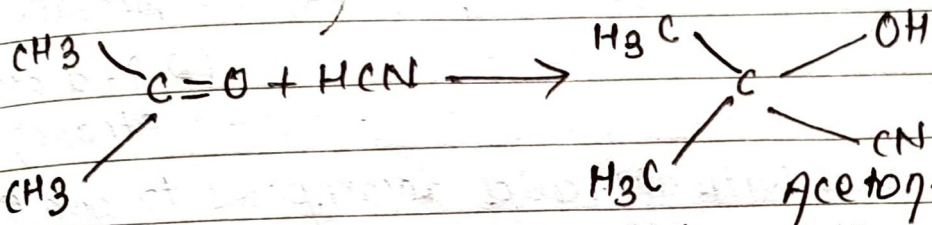
① Addition of HCN: Aldehydes and ketones react with HCN to form addition compound called cyanohydrine

eg.



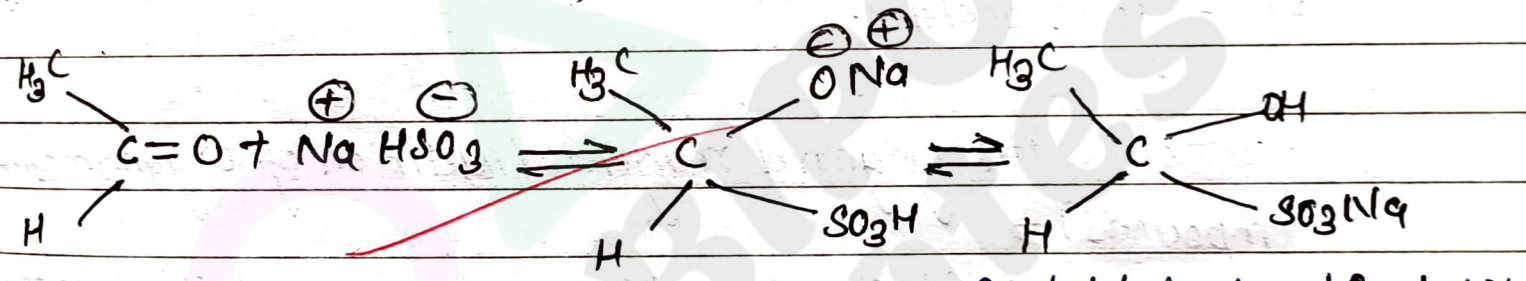
Example:



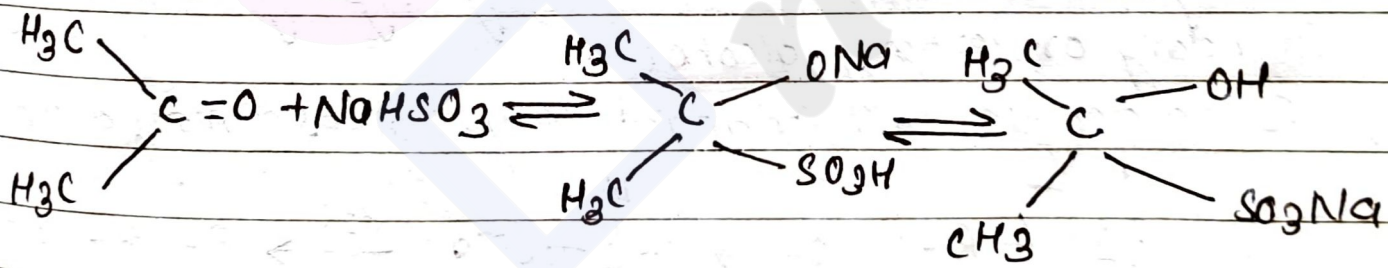


→ The reaction is carried out by adding dilute mineral acid to the mixture of carbonyl compound sodium cyanide.

(2) Addition of sodium bisulphite → Aldehydes and ketones both reacts with saturated solution of sodium bisulphite to form bisulphite addition compound.

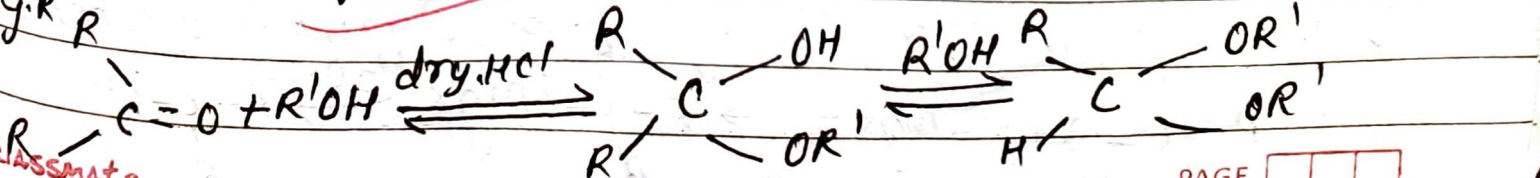


Acetaldehydes bisulphite addust

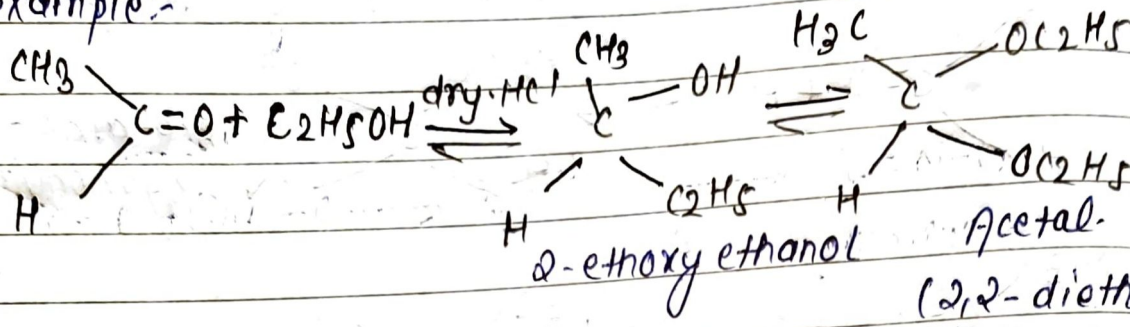


Acetone bisulphited dust

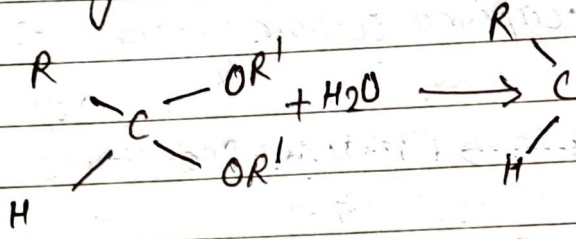
(3) Addition of alcohol → Aldehydes reacts with alcohol in the presence of dry HCl gas to form hemiacetal first which further reacts with excess alcohol to form acetals.



Example:-



→ Acetals when heated with dil. acid decomposes to give original aldehydes.

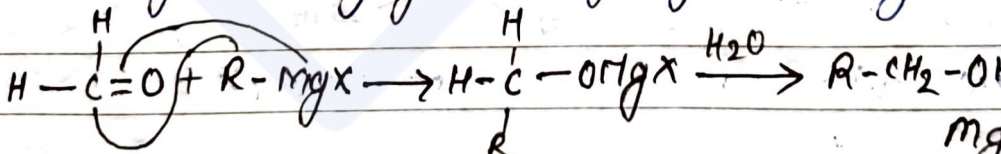


∴ Ketones do not react with alcohol in the presence of dry HCl to form acetals.

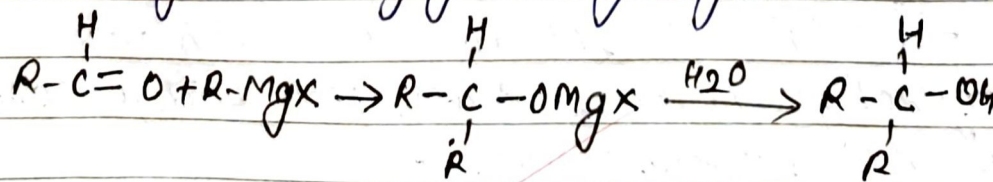
(4) Reaction with Grignard reagents (Addition of organometallic compounds) →

Aldehydes or ketones form an addition compound with Grignard reagents which on hydrolysis give primary, secondary or tertiary alcohol.

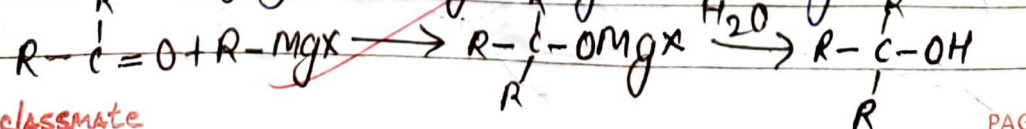
a) Formaldehyde with Grignard reagent gives primary alcohol.



b) Other aldehydes with Grignard reagent gives 2° alcohol.



c) Ketones with Grignard reagent gives tertiary alcohol.



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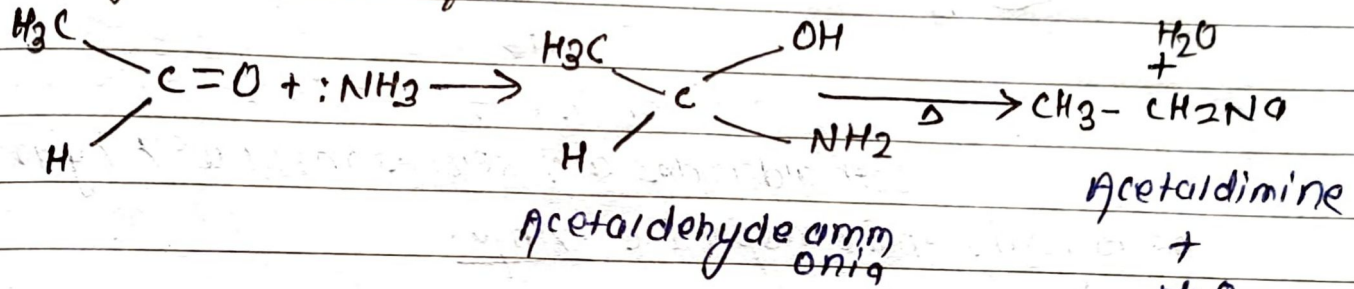
Nucleophilic Addition followed by loss of carboxyl → oxygen (condensation rxn) →

(1) Reaction with ammonia → Aldehydes (except HCHO) form addition compound called acetaldehyde ammonia with ammonia which loses water to form imine compound.



** Formaldehyde reacts with ammonia to give Hexamethylene tetramine called Urotropine. (Urinary antiseptic)

Reactions:-

$$6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O.$$

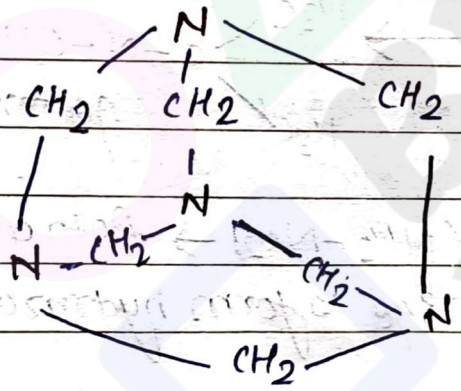
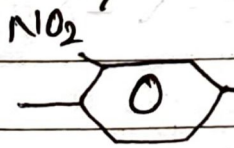


fig:- Urotropine.

(2) Reaction with ammonia derivatives → (NH_2-G)

Ammonia derivates represented by the formula:-

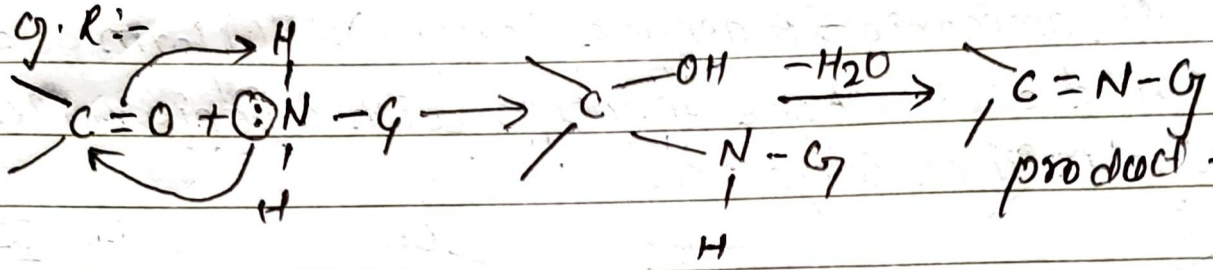
NH_2-G (where G = -OH, $-NH_2$, ~~$-NH_6$~~ NHC_6H_5



, $-NH(CONH_2)$ adds to aldehydes and ketones to form additions compounds, which then losses water to form compound having:-

$C=N-$ group

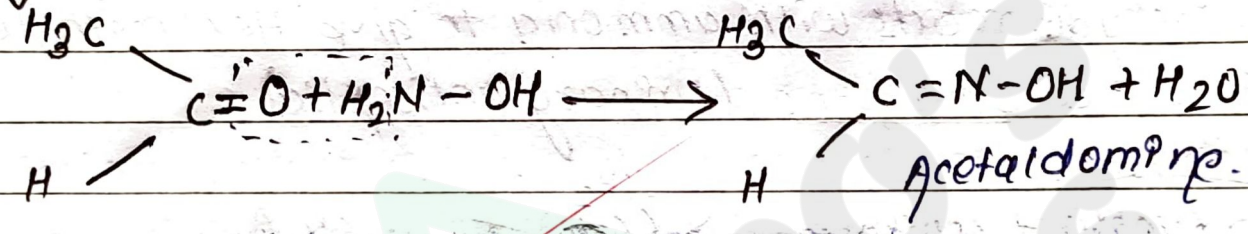
Eg. R:-



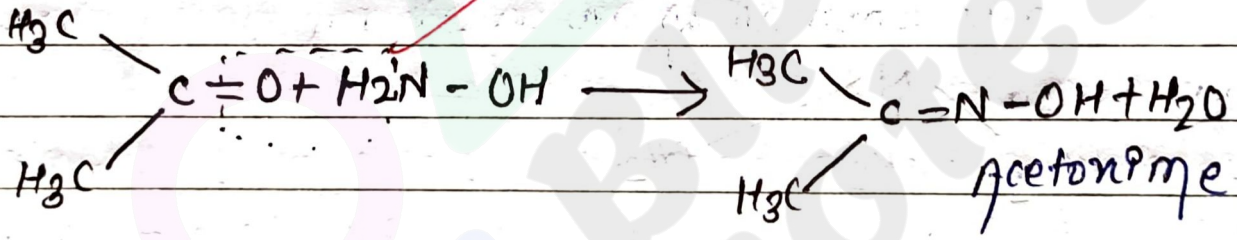
(A) Reaction with hydroxylamine → (NH_2OH):-

Both aldehydes and ketones react with hydroxylamine to form their respective oxime.

Eg:-



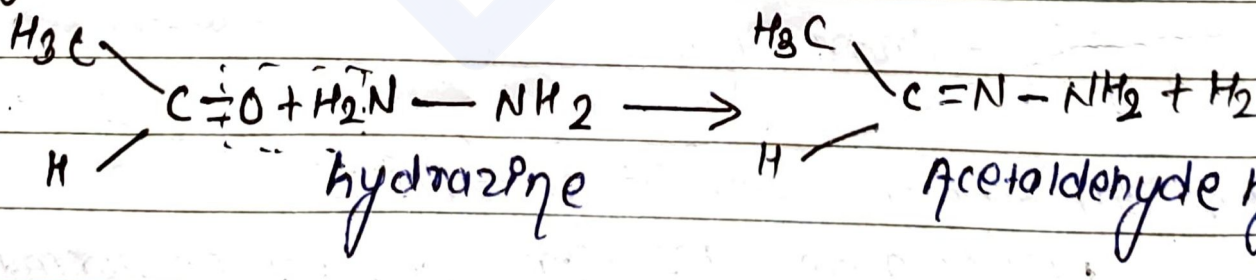
Acetaldoxime.



Acetoxime

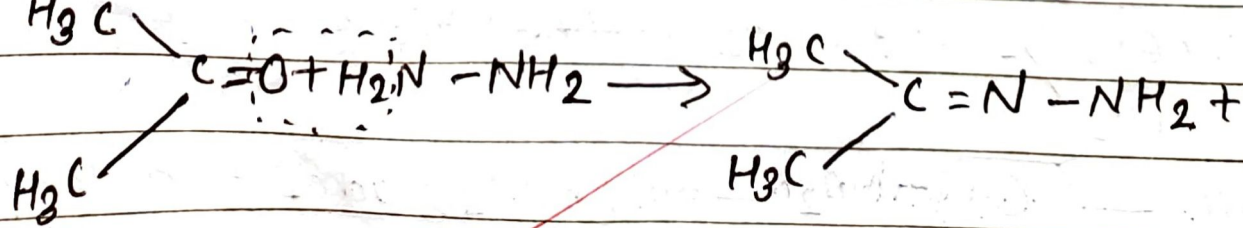
(B) Reaction with hydrazine (NH_2-NH_2) → Both aldehydes and ketones reacts with hydrazine to form hydrazones.

Eg:-



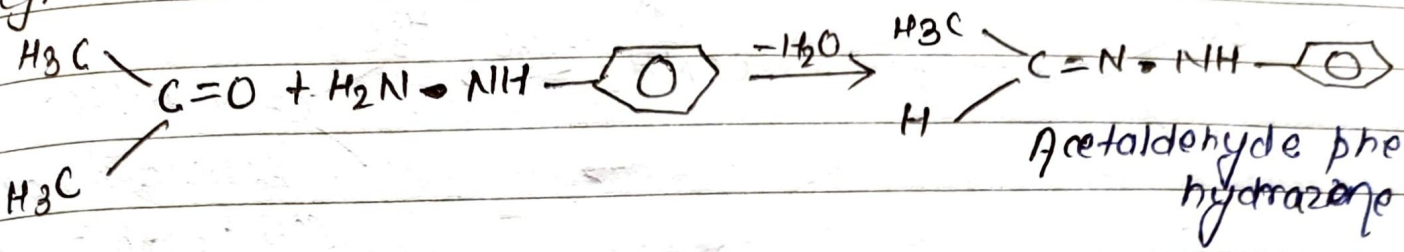
Hydrazine

Acetaldehyde hydrazone

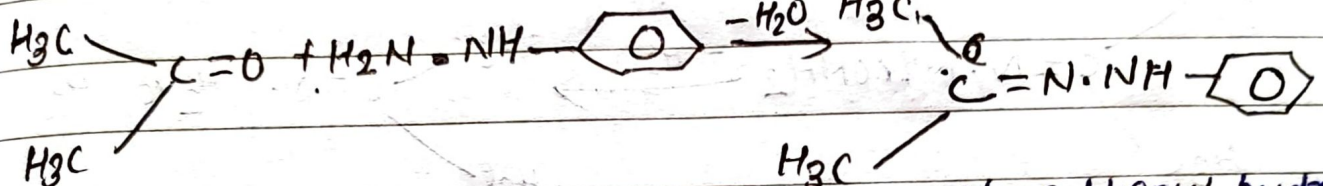


(c) Reaction with phenyl hydrazine → Both aldehydes and ketones reacts with phenyl hydrazine to form their respective phenylhydrazone.

Eg:-



Acetaldehyde phenyl hydrazone

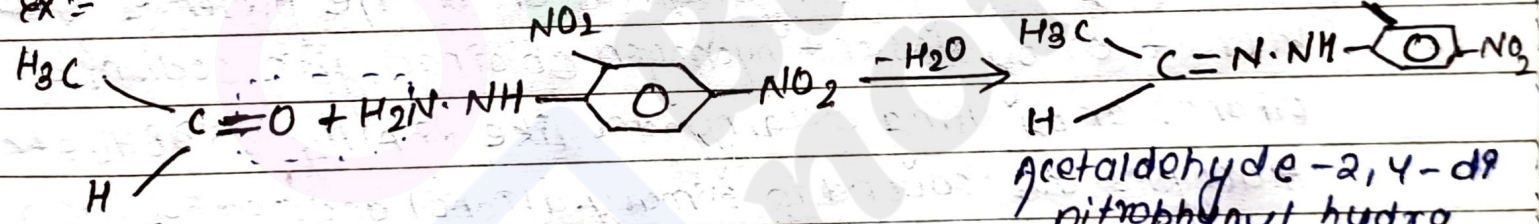


Acetone phenyl hydrazone

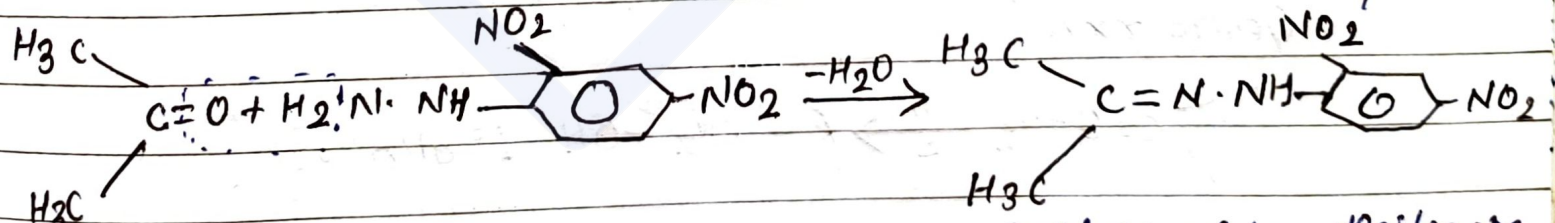
Imp

(d) Reaction with 2,4-dinitrophenyl hydrazine → Both aldehydes and ketones forms 2,4-dinitrophenyl hydrazone with 2,4-dinitrophenyl hydrazine

Ex:-



Acetaldehyde-2,4-dinitrophenyl hydrazone

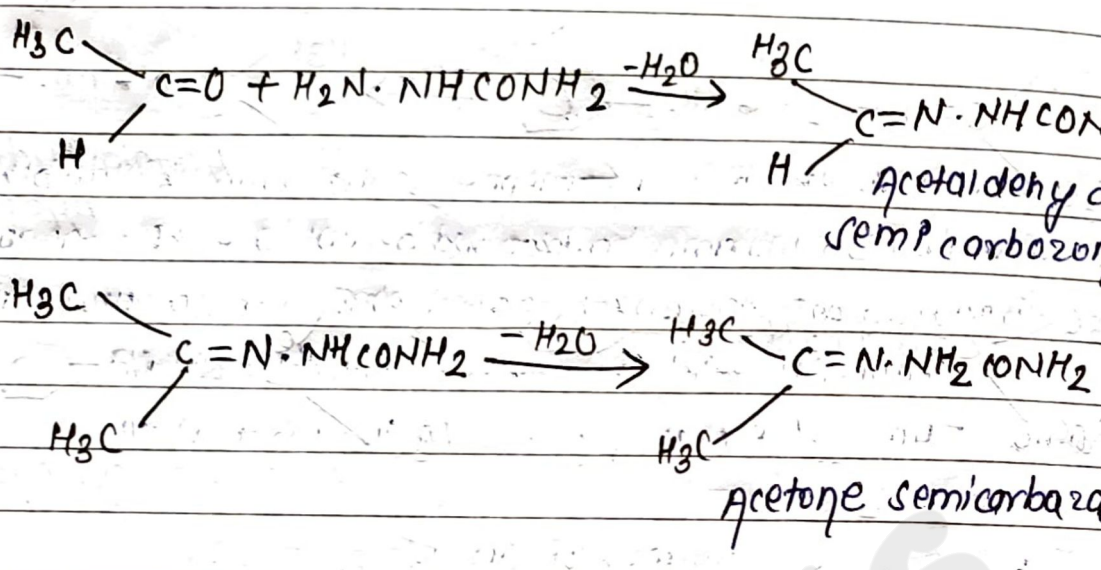


Acetone-2,4-dinitrophenyl hydrazone

Note: There are ~~ergo~~ orange red crystalline compound hence this reaction can be used as a test for aldehyde and ketones.

(E) Reaction with semicarbazide → Both aldehyde and ketone react with semicarbazide to form their respective semicarbazone

Eg:-

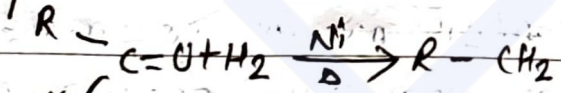


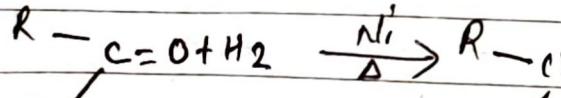
Reduction reactions of aldehydes and ketones →

Aldehydes and ketones can be reduced to different products depending upon the nature of reducing agent.

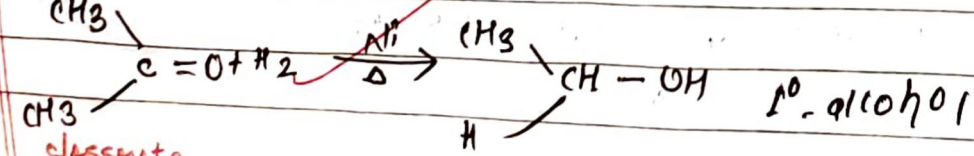
1. Reduction to alcohol → Aldehydes and ketones are reduced to alcohols by catalytic hydrogenation in the presence of Ni, Pd or Pt or by Nascent hydrogen obtained from sodium and ethanol or by using metal hydrides like $LiAlH_4$, $NaBH_4$ etc. Aldehydes are reduced to primary alcohol and ketones are reduced to secondary alcohol:-

General rxn





Example



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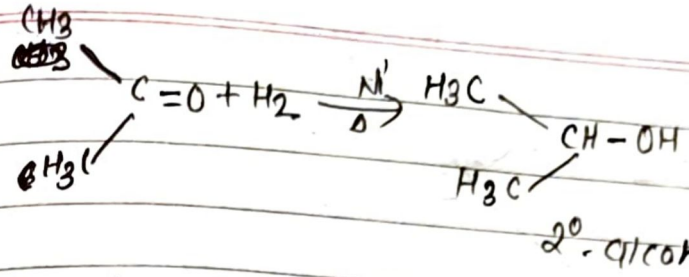
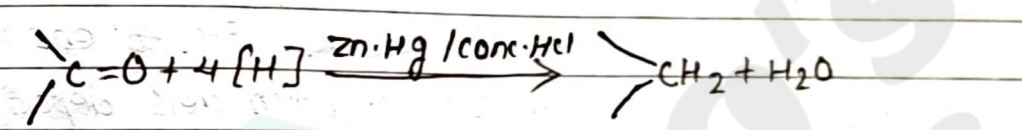


2°. alcohol.

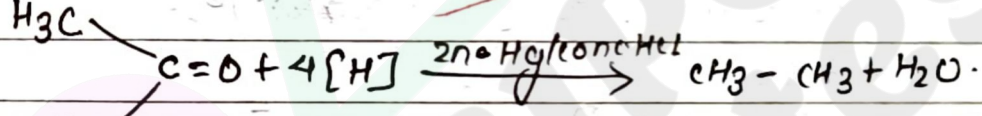
(2) Reduction to hydrocarbons → Aldehydes and ketones are reduced to their parent hydrocarbon by any one of the following method.

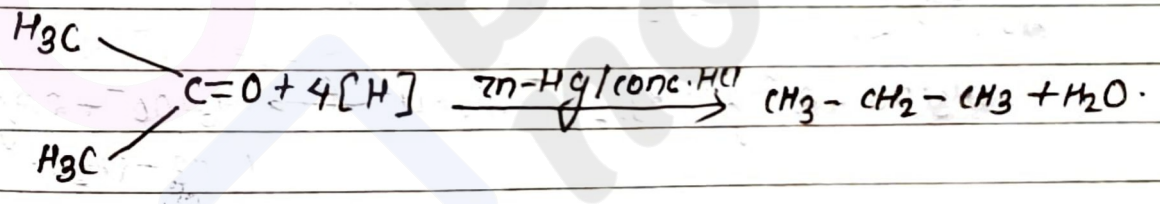
(A) Clemmensen's reduction → When aldehyde and ketones is reacted with clemmensen's reagent in zinc-amal gam in presence of concentrated hydrocarbon acid (Zn-Hg / conc. HCl) is reduced in to corresponding alkane. this's type of reduction is called clemmensen's reduction

General reaction:-

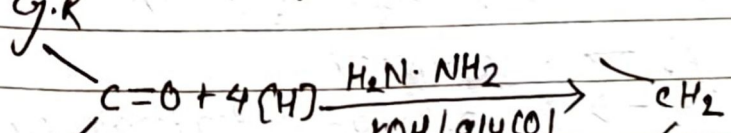


Example:-

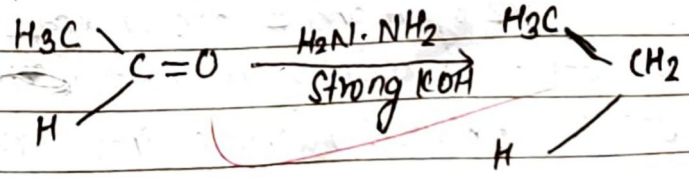


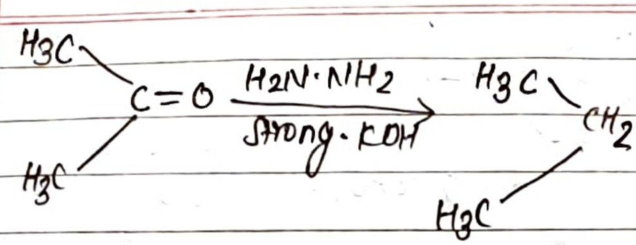


(B) Wolf-kishner reactions → Aldehydes and ketones are reduced to their corresponding alkanes with strong basic solution of hydrazine.



Example:-





(3) Oxidations with Tollens reagent → Ammonical solution is Tollens reagent - It is obtained by adding ammonia solution to the $AgNO_3$ solution till once formed precipitate gets dissolved,

$$AgNO_3 + NH_4OH \longrightarrow \underset{(grey)}{AgOH}\downarrow + NH_4NO_3$$

$$AgOH + 2NH_4OH \longrightarrow \underset{(T.R)}{[Ag(NH_3)_2]^+ OH^-} + 2H_2O$$

when an aldehyde is warmed with tollens reagent then later is reduced to metallic silver which gets deposited as shining silver mirror on the inner wall of the test tube.

This is known as 'Silver Mirror Test'.

general reaction →

$$R-CHO + 2[Ag(NH_3)_2] + 3OH^- \xrightarrow{\Delta} RC\bar{O}O + 2Ag\downarrow + 4NH_3 + 2H_2O$$

Example:-

$$CH_3CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \xrightarrow{\Delta} CH_3COO^- + 2Ag\downarrow + 4NH_3 + 2H_2O.$$

Fehlings solution test → It is an alkaline copper sulphate solution containing some sodium p. tartarate (Rochelle salts) as complexing agent ($CuSO_4$ + NaOH) rochelle salts) A.

Fehlings (A) → $CuSO_4 + NaOH$

fehlings (B) → Sodium pottasium tartarate soln (rochelle salts)

The equal volumes of A and B are mixed to form copper tartarate. This copper tartarate furnished Cu^{++} ion in the solution. This Cu^{++} ion oxidise aldehyde into corresponding

CHEMISTRY (SKY)

carboxylic acids. During this test brick red ppt is obtained which indicates the oxidation of aldehydes.

$$R-CHO + Cu^{++} + 5OH^- \longrightarrow R-COO^{\ominus} + Cu_2O\downarrow + 3H_2O$$

brick red ppt.

Benedict's solution test: Benedict solution is prepared by mixing two solution. A first solution is prepared by $CuSO_4 + Na_2CO_3$ and second solution is sodium citrate. When an aldehyde is heated with benedict is solution reddish brown precipitate of cuprous oxide is obtained.

Eg.

$$R-CHO + Cu^{++} + OH^- \xrightarrow{\Delta} RCOO^- + Cu_2O\downarrow + 3H_2O$$

(Red brown ppt) ↓

Examples:-

$$CH_3CHO + Cu^{++} + 5OH^- \xrightarrow{\Delta} CH_3COO^- + Cu_2O\downarrow + 3H_2O.$$

$$HCHO + Cu^{++} + 5OH^- \xrightarrow{\Delta} HCOO^- + Cu_2O\downarrow + 3H_2O.$$

Miscellaneous reaction → (Special type of Reaction).

1. Aldol concentration:- 2- molecule of an aldehyde or a ketone which have at least one α- hydrogen atom undergo condensation in the presence of dilute alkali to give β-hydroxyaldehyde or β-hydroxyketones known as aldol. This reaction is called aldol concentration. During this reaction the α- hydrogen of 1- molecule adds to the carboxyl group of other molecules.

Reaction:

$$CH_3-\underset{H}{\underset{|}{C}}(=O) + HCH_2CHO \xrightarrow[NaOH]{dil.\ alkali} H_3C-\underset{H}{\underset{|}{C}}(OH)-CH_2-CHO$$

3-hydroxybutanol.

(B-hydroxy butanol)

$$H_3C-\underset{CH_3}{\underset{|}{C}}(=O) + HCH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{dil.\ NaOH} H_3C-\underset{CH_3}{\underset{|}{C}}(OH)-CH_2-\overset{O}{\overset{\|}{C}}H-CH_2$$

classmate

β-hydroxy ketone or 4-hydroxy ~~2-pentane~~ 4-Methyl pentan-2-one.

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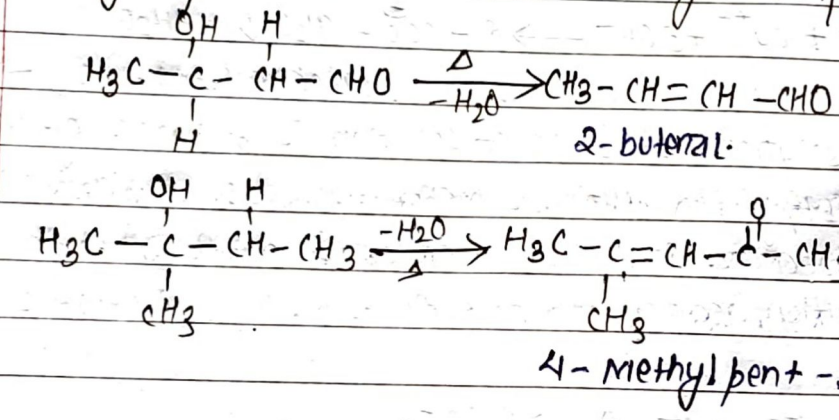
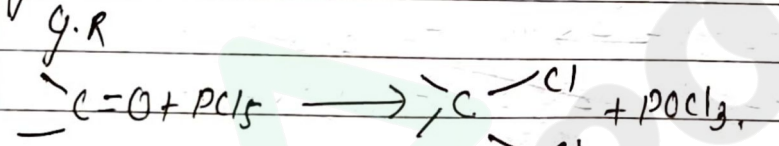
Note point:

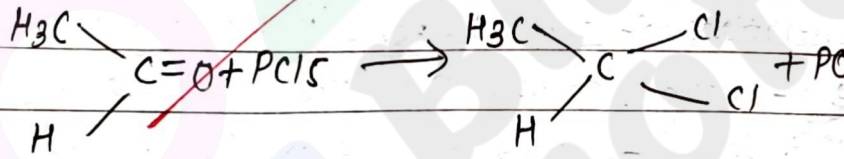
β-hydroxyaldehyde or β-hydroxyketones are dehydrated on heating to form α, β-unsaturated aldehydes or ketones.

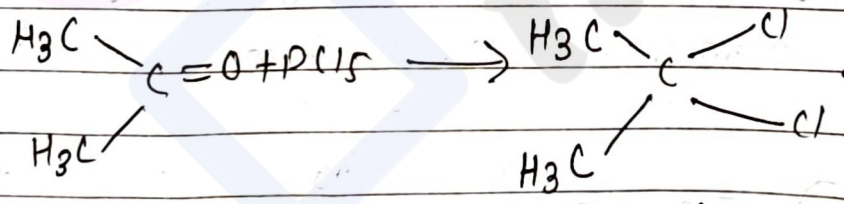


2. Action with PCl_5 :- Aldehydes and ketones react with PCl_5 to give geminal dichlorides



Example:-





Special reaction of Methanol:-

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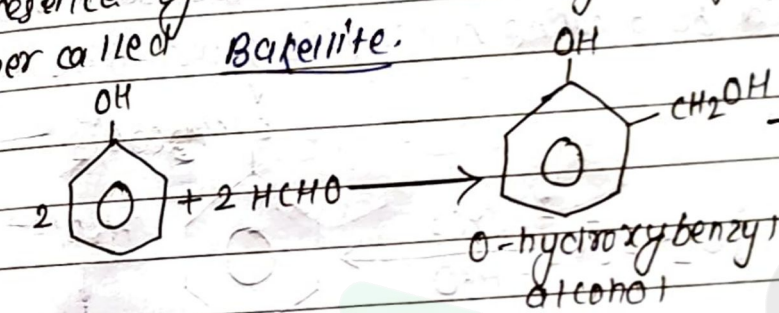
(a) Cannizaro's reaction → Methanol reacts with conc. NaOH gives methanol and formate

$$2HCHO + NaOH \longrightarrow CH_3-OH + HCOONa$$

Formaldehyde, Sodium hydroxide → Methanol (Alcohol), formate sod. methanate (Salt)

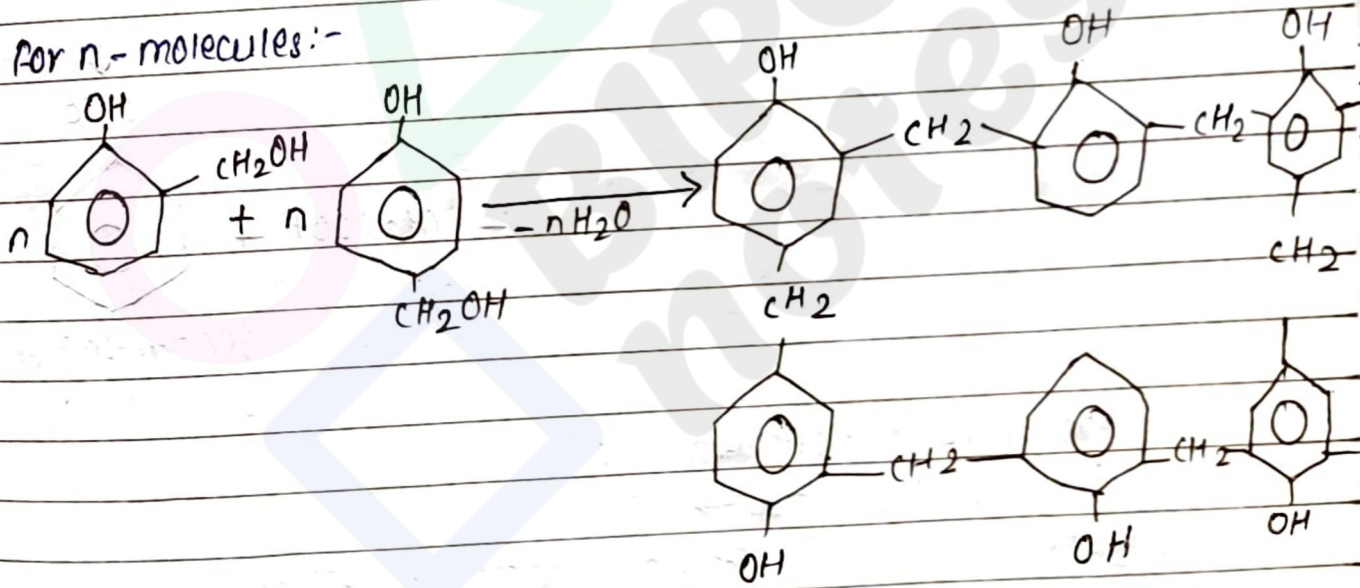
(b) Action with phenol → phenol condense with formaldehyde in the presence of acid or basic catalyst to form a highly crosslinked polymer called Bakelite.



O-hydroxybenzyl alcohol

P-hydroxy bond alcohol.

For n-molecules:-



It is small part of Bakelite.

(c) Formalin → 40% aqueous solution of formaldehyde is called formalin

Uses of Methanol.

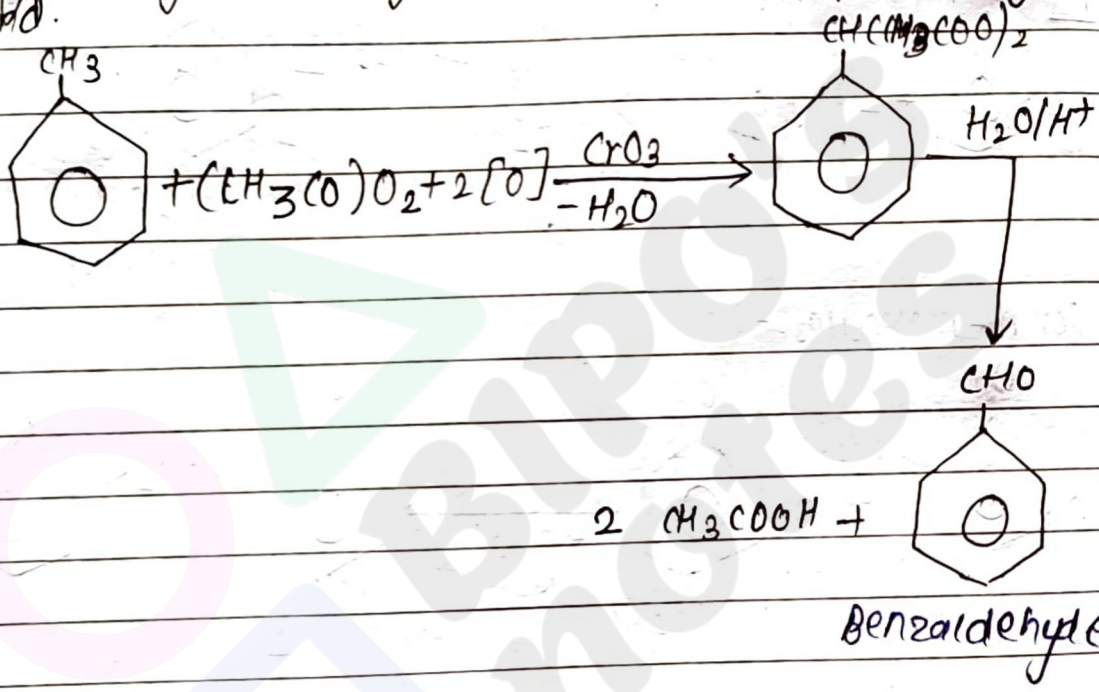
1. In the manufacture of urotropine, bakelite etc.
2. As germicides and disinfectants.

PAGE

3. As preservative for biological specimens.
4. Used in the silvering of the mirror.

Aromatic aldehydes and ketones.

1. preparation of benzaldehyde from toluene → It is obtained by the oxidation of toluene with chromium trioxide and acetic anhydride followed by alkaline hydrolysis of resulting compound.



Properties of benzaldehyde

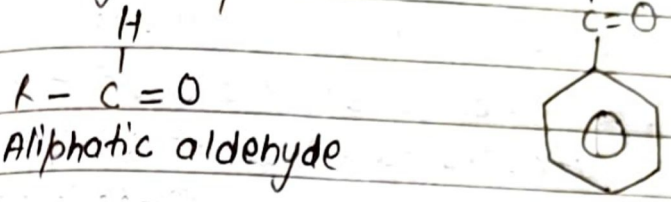
Physical properties →

1. It is colorless liquid with a smell of bitter almonds.
2. It boils at 175°C
3. It is slightly soluble in water but readily dissolves in organic solvents.

Chemical properties →

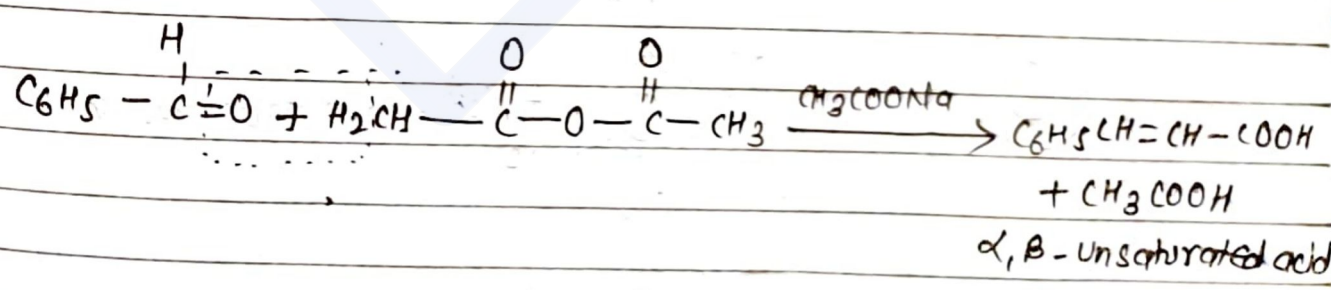
Aromatic aldehydes and ketones are less reactive than aliphatic aldehydes & ketones. It is because the aryl group

in aromatic aldehydes & ketones decreases the positive charge of the carboxyl compound.



5) Benzoin condensation → when two molecules of benzaldehyde reacts in the presence of alcoholic potassium cyanide gives α-hydroxy ketone, which is also known as benzoin. This reaction is also known as benzoin condensation.

6) Perkin condensation → when benzaldehyde reach with aliphatic acid anhydride in the presence of corresponding salt i.e sodium acetate gives α, β - unsaturated acid which is known as cinnamic acid. This reaction is known as perkin condensation reaction.



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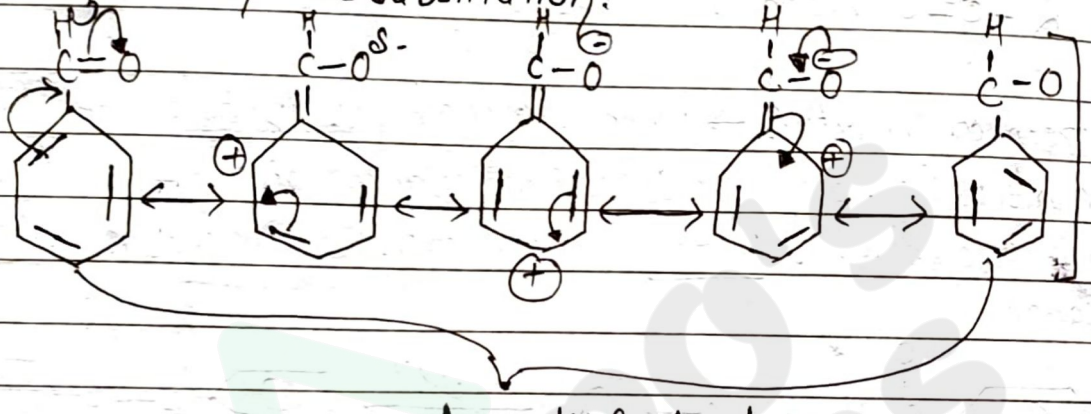
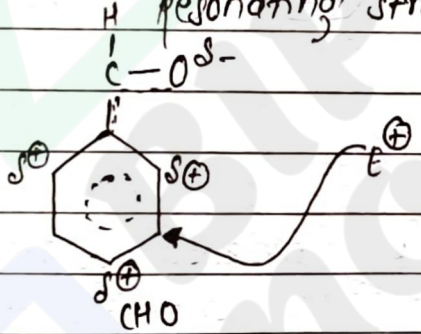
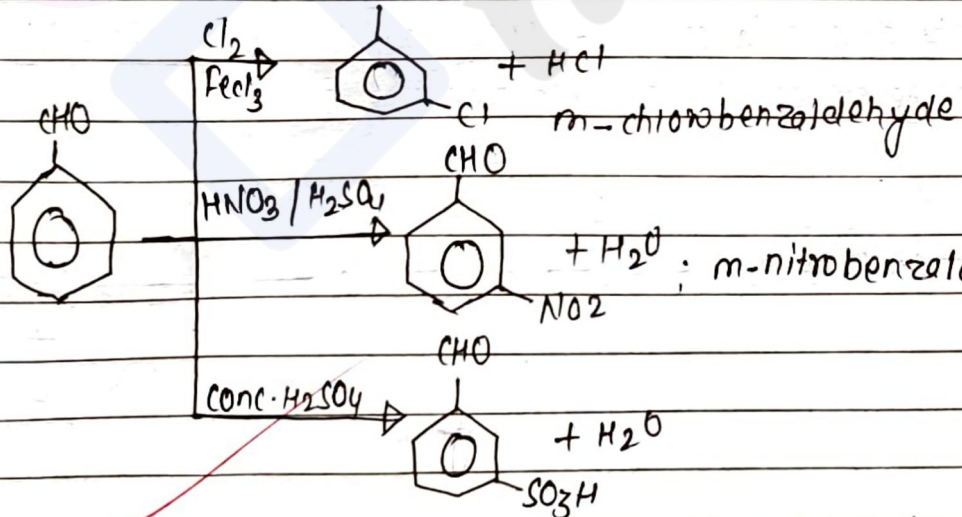
Electrophilic substitution reaction of benzaldehyde.

The -CHO group is electron withdrawing group. It decreases electron density at the benzene ring and deactivates it towards electrophilic substitution reaction. It decreases electron density at ortho and para position compared to the m-position. Hence electrophiles attacks at m-position giving meta products during electrophilic substitution.



Resonating structures



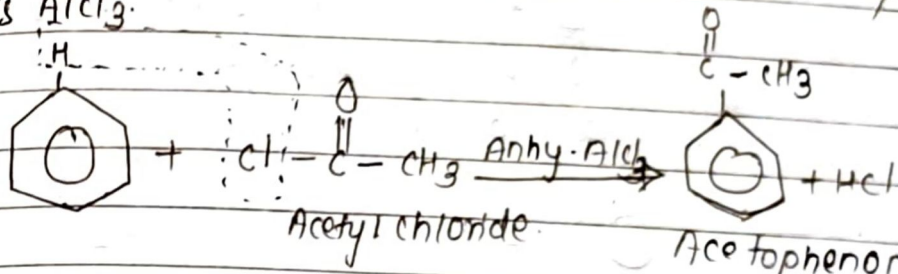


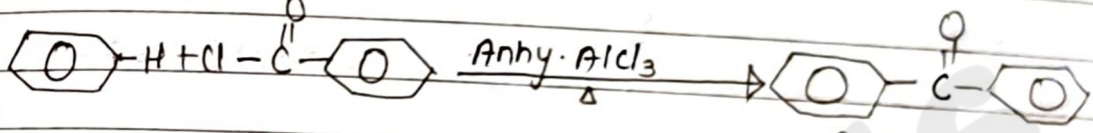
m-benzaldehyde sulphonic acid.

DATE

Preparation of Aromatic ketones →

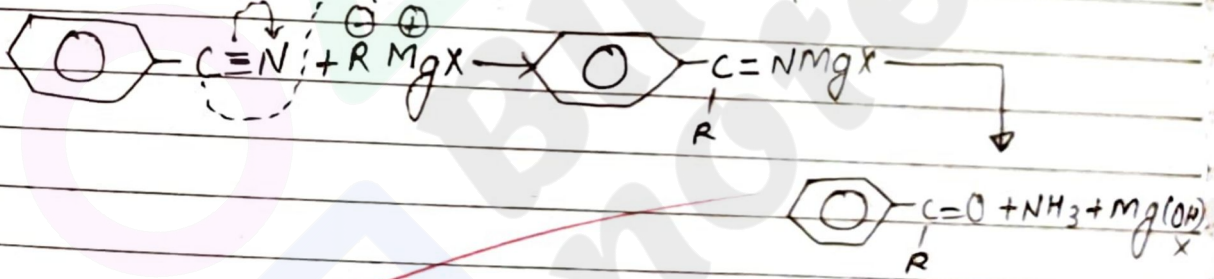
① By the Friedel craft acylation reaction → In this method aromatic hydrocarbons are heated with acid chloride in the presence of anhydrous $AlCl_3$.





Benzophenone
diphenyl ketone

② when phenyl cyanide reacts with grignard reagent form an additions compound which on hydrolysis gives aromatic ketones.



aromatic ketones where;

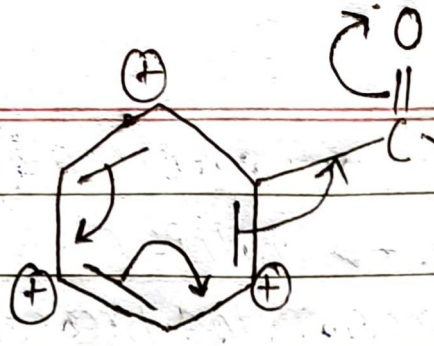
R = alkyl or aryl group.

Chemical properties:-

The chemical properties of aromatic ketones are exactly similar to that aliphatic ketones except that they do not form bisulphite addition compound with sodium bisulphite

→ Aromatic ketones gives ring substitution reaction

P.T.O

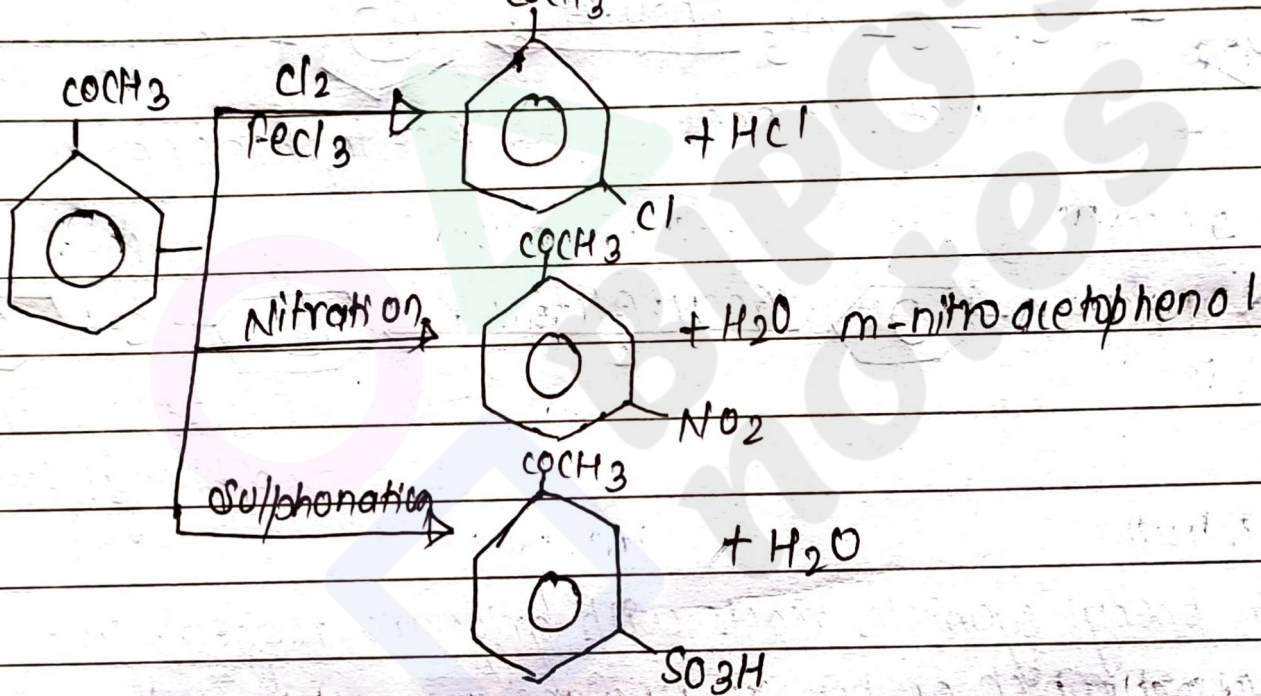


→ Keto ($-\overset{O}{\overset{\|}{C}}-$)

↳ $e^{\ominus}$ - with drawing group.

↳ deactivating group.

↳ m-director.

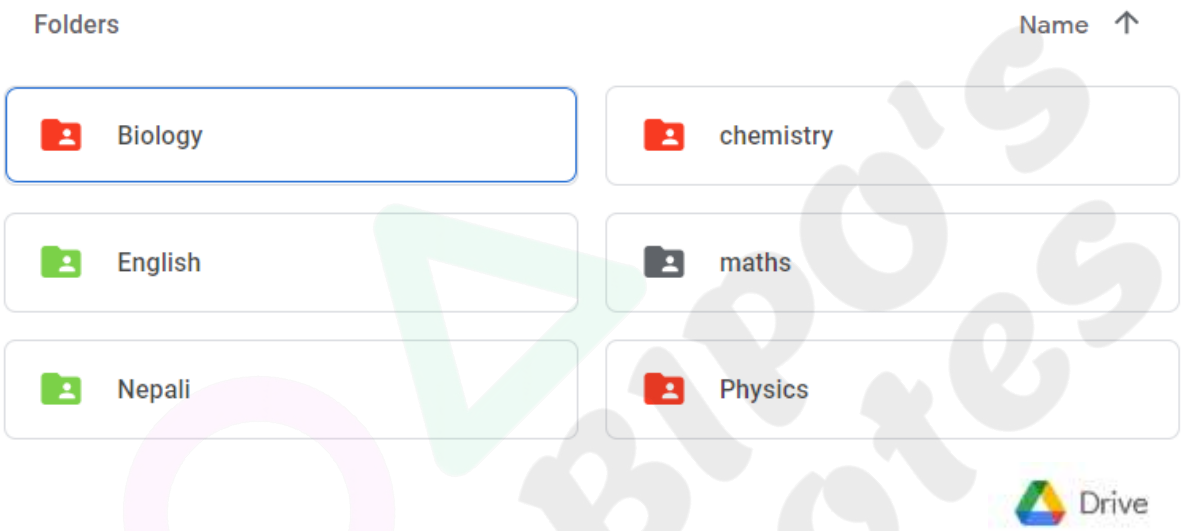


m-acetophenone sulphonic acid.

Bipin Khatri

(Bipo)

Class 12 complete notes and paper collection.



Feedbacks:

admin@bipinkhatri.com.np | bipinkhatri.ram@gmail.com

Contact:

@im.bipo www.bipinkhatri.com.np @im.bipo