17-10-24.

aldehydes

- $R-\overset{\overset{O}{\|}}{C}-H$
- alkanal

* When carbonyl group $-\overset{\overset{O}{\|}}{C}-$ is directly bonded with atleast one H-atom, the compound formed is called Aldehyde/alkanals.

Nomenclature names are derived by carboxylic acid.

1- $H-\overset{\overset{O}{\|}}{C}-H$

Methanal (IUPAC)

formaldehyde (C.N)

2- $CH_3-\overset{\overset{O}{\|}}{C}-H$

Ethanal (IUPAC)

acetaldehyde (C.N).

3- $H-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

Propanal (IUPAC)

propionaldehyde (C.N)

4- $H-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$

Butanal (IUPAC)

Butyraldehyde (C.N)

5- $CH_2(OH)-\overset{\beta}{}-CH(Cl)-\overset{\alpha}{}-\overset{\overset{O}{\|}}{C}-H$

2-Chloro-3-Hydroxypropanal

α-Chloro-β-Hydroxypropionaldehyd

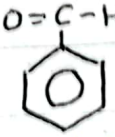
6- $H-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-H$

Ethane-1,2-dial (IUPAC).

Glyoxal (C.N)

7- $H-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H$

Butane-1,4-dial (IUPAC)

8- 

Benzaldehyde (IUPAC) or (C.N)

9- $H-\overset{O}{\overset{\|}{C}}-CH_2-CH=CH_2$

3-Butene-1-al

Butanal-3-ene.

Important

→ When 2 functional groups come together, we don't replace the end-suffix of alkane, rather we write parent name with their respective suffix & then number the functional group.

→ The α & β positions is different in alkyl halide & other than aldehyde & carboxylic acid.

Ketone

"When carbonyl group is directly bonded with 2 alkyl group compound formed are called Ketone"

* $C_nH_{2n}O$

Nomenclature

1- $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

2-Propanone (IUPAC)

acetone & Dimethyl Ketone (C.N).

2- $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

2-Butanone (IUPAC)

Ethylmethyl Ketone (C.N).

3- $C_2H_5-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$

3-Hexanone (IUPAC)

Ethylpropyl Ketone (C.N).

4- $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

2-Methyl-3-pentanone (IUPAC)

Ethyl iso-Propyl ketone (C.N)

5- $\overset{\beta}{CH_2}(Cl)-\overset{\alpha}{CH_2}-\overset{\overset{O}{\|}}{C}-CH_3$

4-Chloro-2-Butanone (IUPAC).

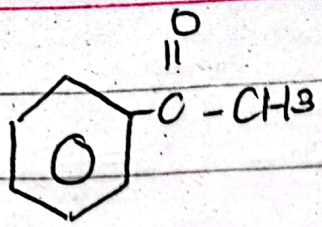
β-Chloroethylmethyl Ketone (C.N)

7- $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

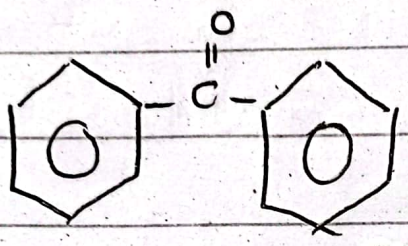
2,5-Hexane dione (IUPAC)

Hexane-2,5-dione (IUPAC)

(No C.N.)

7- 

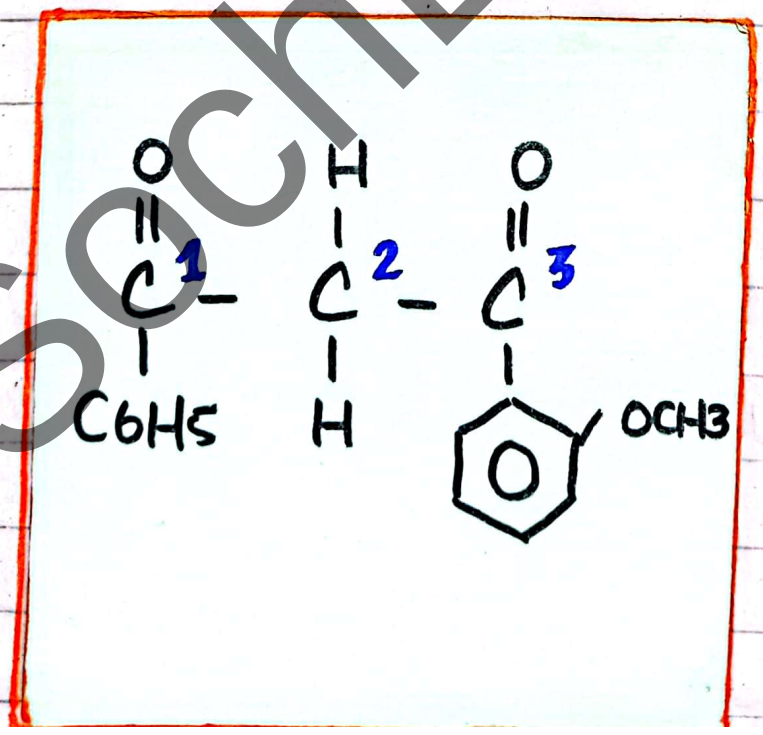
Acetaphenone (IUPAC)
Methylphenylketone (~~IUPAC~~ C.N)

8- 

Diphenylketone (...) -
benzophenone (C.N)

* Aromatic & Ketone which are aromatic don't have IUPAC names.

9- 1-phenyl-3-(2-Methoxyphenyl) 1,3-propane dione



physical properties

1. They have high melting & boiling point than analogous alkane.
The carbonyl group (C=O) is present. This group is polar which cause strong dipole-dipole interactions as compared to alkane which have Van der Waals forces.
2. They have low boiling point than analogous alcohols. Alcohols have (OH grp) which have strong strong bonds between molecules. There requires alot of energy to break. However, aldehyde & Ketone due to presence of carbonyl group have dipole-dipole interactions. That are not much strong to be broken with extensive heat.
3- They are more soluble than alkane but less soluble than alcohols in water.
Due to their interactions.

preparation

1. Ozonolysis

* Test that is used to locate the position of double bond.
* If alkene have branching it forms Ketone.
* If alkene have no branching it forms aldehyde.

examples

- $CH_3-CH=CH-CH_2-CH_3 + O_3 \longrightarrow CH_3-CHO + OHC-CH_2-CH_3$

  2-Pentene. ethanal propanal

- in order to find = bond position.
  - ↳ face the O atom of 2 compounds with eachother.
  - ↳ Skip it & then join!

$$CH_3-\underset{H}{C}=\boxed{O+O}=\underset{H}{C}-CH_2-CH_3$$

- $CH_3-\underset{CH_3}{C}H=CH-CH_2-CH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$

  2-Methyl-2-Pentene. propanal propanone.

general mechanism

$$\underset{R_2}{\overset{R_1}{C}}=\underset{R_4}{\overset{R_3}{C}} + O_3 \xrightarrow[100^\circ C]{H_2O/Zn} \underset{R_2}{\overset{R_1}{C}}=O + O=\underset{R_4}{\overset{R_3}{C}} + H_2O_2$$

mechanism

$$\underset{R_2}{\overset{R_1}{C}}=\underset{R_4}{\overset{R_3}{C}} + O_3 \longrightarrow \underset{R_2}{\overset{R_1}{C}}(O)-\underset{R_4}{\overset{R_3}{C}}(O)-O \xrightarrow{\sim}$$

(Moloznoide)

$$\underset{R_2}{\overset{R_1}{C}}(O)-\underset{R_4}{\overset{R_3}{C}}(O)-O \xrightarrow[100^\circ C]{H_2O/Zn} \underset{R_2}{\overset{R_1}{C}}=O \;\&\; O=\underset{R_4}{\overset{R_3}{C}} + H_2O$$

(Ozonide) ketone.

$H_2O_2 + Zn \longrightarrow ZnO + H_2O$

Hydration of alkynes

* It follows the property of tautomerism.

- $CH \equiv CH + \overset{+}{H}\text{-}OH \xrightarrow[75^\circ C]{HgSO_4 + H_2SO_4} CH_2=CH\text{-}\overset{\curvearrowleft}{O}H \longrightarrow$

ethyne

Vinyl alcohol

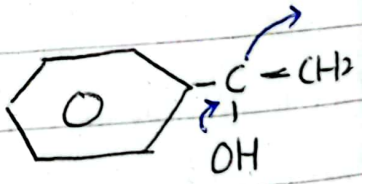
$CH_3-\overset{O}{\overset{\|}{C}}-H$

acetaldehyde.

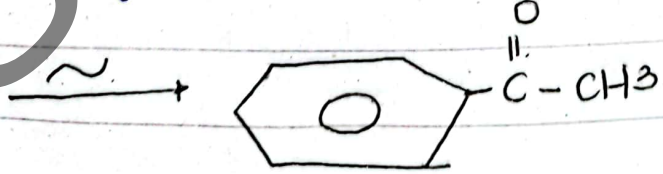
- $CH_3-C \equiv CH + \overset{+}{H}\text{-}OH \xrightarrow[75^\circ C]{HgSO_4 + H_2SO_4} CH_3-\overset{\curvearrowleft}{\underset{\curvearrowleft}{C}}=CH_2 \longrightarrow$

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

Propanone / acetone

-  $C \equiv CH + \overset{+}{H}\text{-}OH \xrightarrow[75^\circ C]{HgSO_4 + H_2SO_4}$ 

ethynebenzene.



acetophenone.

3- oxidations of 1° and 2° alcohol

- R-OH (1°) → aldehyde
- R-OH (2°) → Ketone

- $CH_3-CH_2-\underset{\underset{OH}{|}}{CH_2} + [O] \xrightarrow[\Delta]{K_2Cr_2O_7 \; H_2SO_4} CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H + H_2O$

1- Propanol — 1- Propanal

- $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 + [O] \xrightarrow[\Delta]{K_2Cr_2O_7 \; H_2SO_4} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H_2O$

2- Propanol — 2- Propanone / acetone

MDCAT

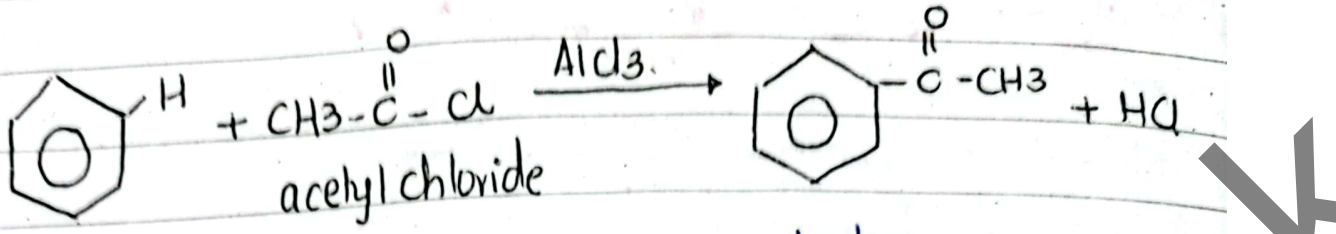
$$2CH_3OH + O_2 \xrightarrow[300^\circ C]{Pt + asbestos} 2\,H-\overset{\overset{O}{\|}}{C}-H + 2H_2O$$

methanol — formaldehyde.

* formalin is a sol of 40% formaldehyde, 8% methyl alcohol & 52% water.
* Used as Preservative.

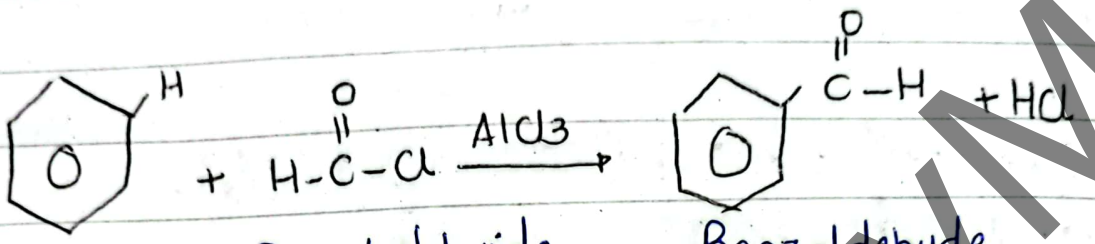
$$[CH_3OH + H-\overset{\overset{O}{\|}}{C}-H + H_2O]$$

4. Friedal-Craft acylation of benzene



acetyl chloride

acetophenone



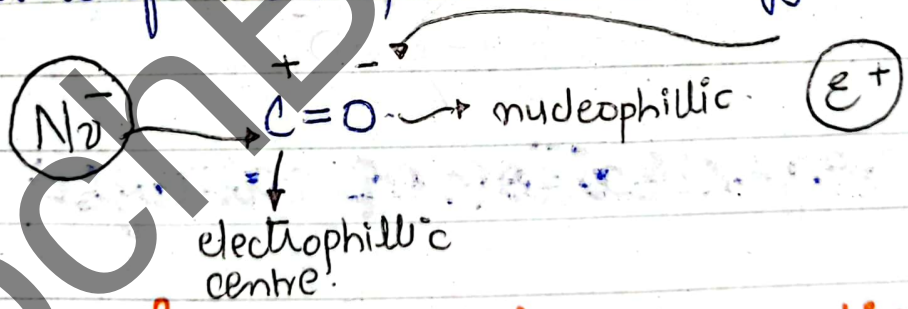
formyl chloride

Benzaldehyde

Reactivity

Carbonyl compounds are reactive due to 2 factors :-

- C=O bond is polar due to more electronegative O
- Presence of π bond b/w Carbon & Oxygen:



Aldehyde & Ketone who's more reactive?

- Aldehyde is more reactive than Ketone.

1) less steavic hinderance
2) C-O bond is more polar due to less alkyl group which are e⁻ donar. (Polarity ∝ Reactivity)

$H-\overset{O}{\overset{\|}{C}}-H > R-\overset{O}{\overset{\|}{C}}-H > R-\overset{O}{\overset{\|}{C}}-R$.

nucleophillic reaction

Carbonyl can undergo 2 types of rxn:

- Base catalysed Nucleophillic addition rxn
- Acid catalysed Nucleophillic addition rxn

General Mechanism of base catalysed rxn

Step 1: Reaction of base and reagent

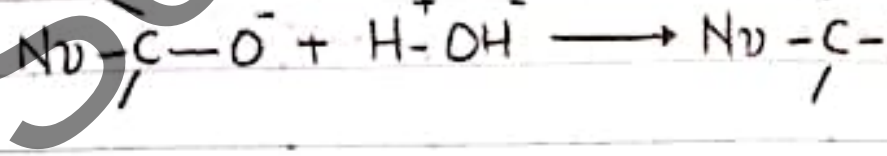
$OH^- + H\text{-}Nu \longrightarrow H_2O + Nu^-$

base catalysed

reagent

Step 2: Attack of Nu^- of carbonyl

Step 3:- regeneration of catalyst



base catalyst

Types

There are 5

Addition

Addition

Addition

Condens

Haloform

MCQs:

Nucle

Conc

The reac

compar

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a) A

- same

underg

- 2 mol

to for

Types

There are 5 based catalysed nucleophillic addition rxn:

Addition of HCN
Addition of Grignard reagent ✓✓ imp
Addition of sodium bisulphide
Condensation rxn ✓✓ very imp
Haloform rxn ✓✓ very imp

MCQs: When base is used as catalysed increases Nucleophillic character of Reagent.

base-catalyse reaction

Condlensation Reaction

The reaction in which 2 molecules of the same or different compounds combine to form a new compound with or without elimination of small molecules H_2O, NH_3.

a) Aldol condensation

- Same or different carbonyl compounds containing α Hydrogen undergo aldol condensation.
- 2 molecules of either same or different $-\overset{O}{\overset{\|}{C}}-$ combine to form Aldol or Ketol usually by losing H_2O.

- carbon next $-\overset{O}{\overset{\|}{C}}-$ is called α carbon & its H are also α H.

mild base

Reaction take in presence of Dil NaOH, $Ba(OH)_2$, $NaHCO_3$, Na_2CO_3

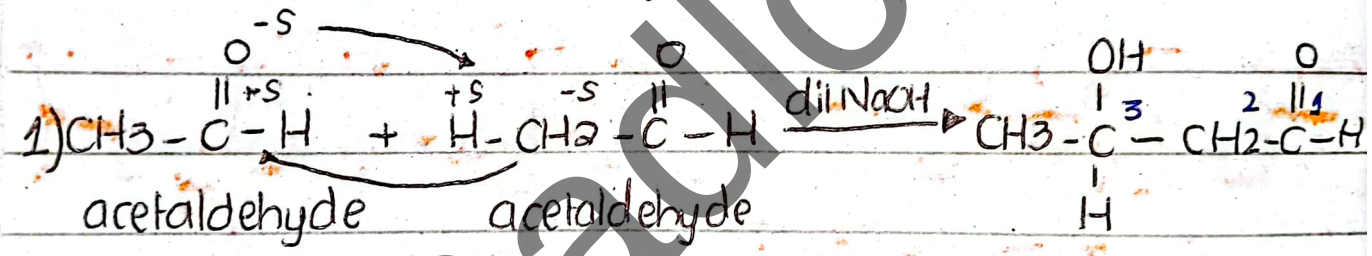
Types

1- between 2 aldehyde (same/diff) → Aldol.

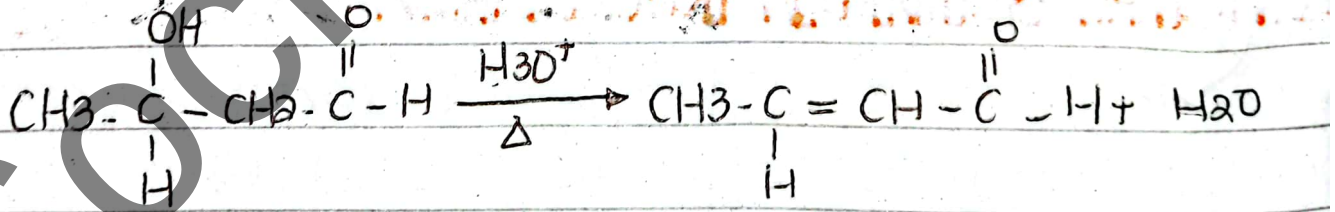
2- between 2 Ketone (same/diff) → Ketol

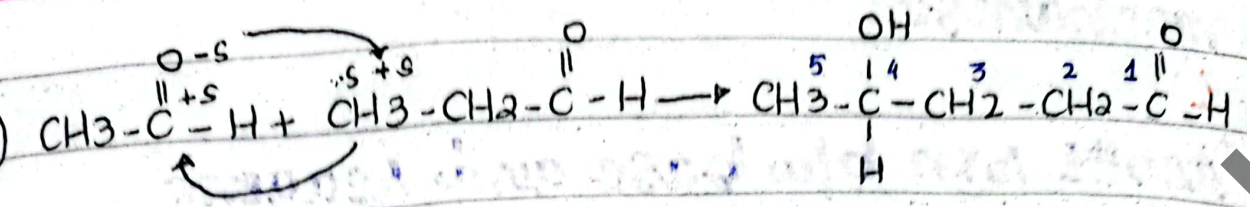
3- between aldehyde & Ketone → Ketol

→ Condensation b/w 2 $H-\overset{O}{\overset{\|}{C}}-R$



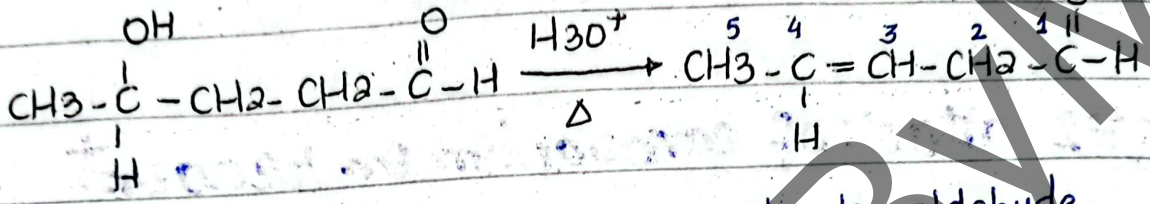
Hydrolysis



2) 

4-Hydroxypentanal

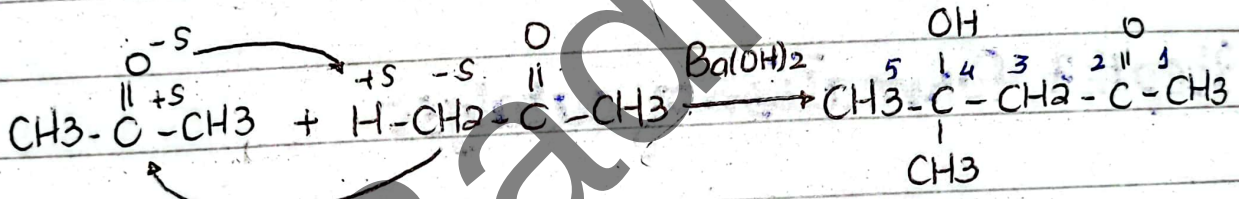
Hydrolysis



Chrotonaldehyde.

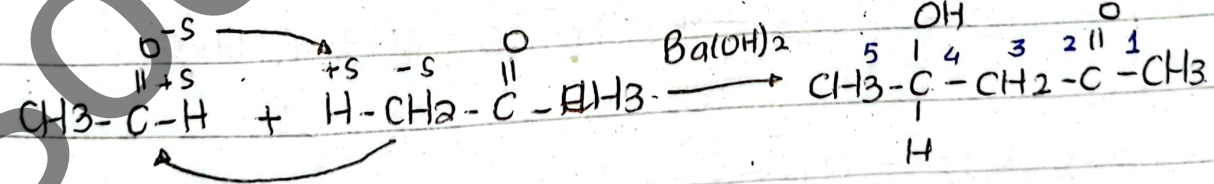
3-Pent-enal

2- Condensation with R-C(=O)-R



(Ketol) 4-Hydroxy-4-methyl-2-Pentanone.

3- Condensation with R-C(=O)-R and H-C(=O)-R



4-Hydroxy-2-Pentanone

(Ketol)

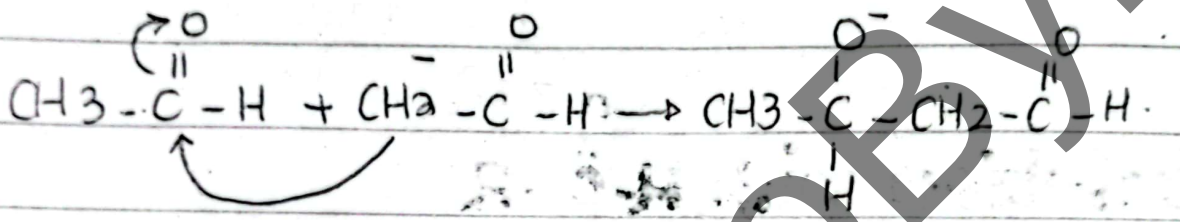
mechanism

1)

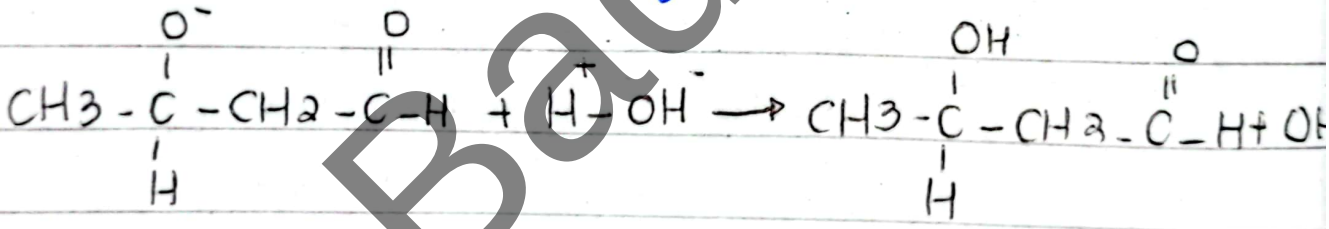
Step#1 rxn b/w base and reagent

base ethanal carbanion water

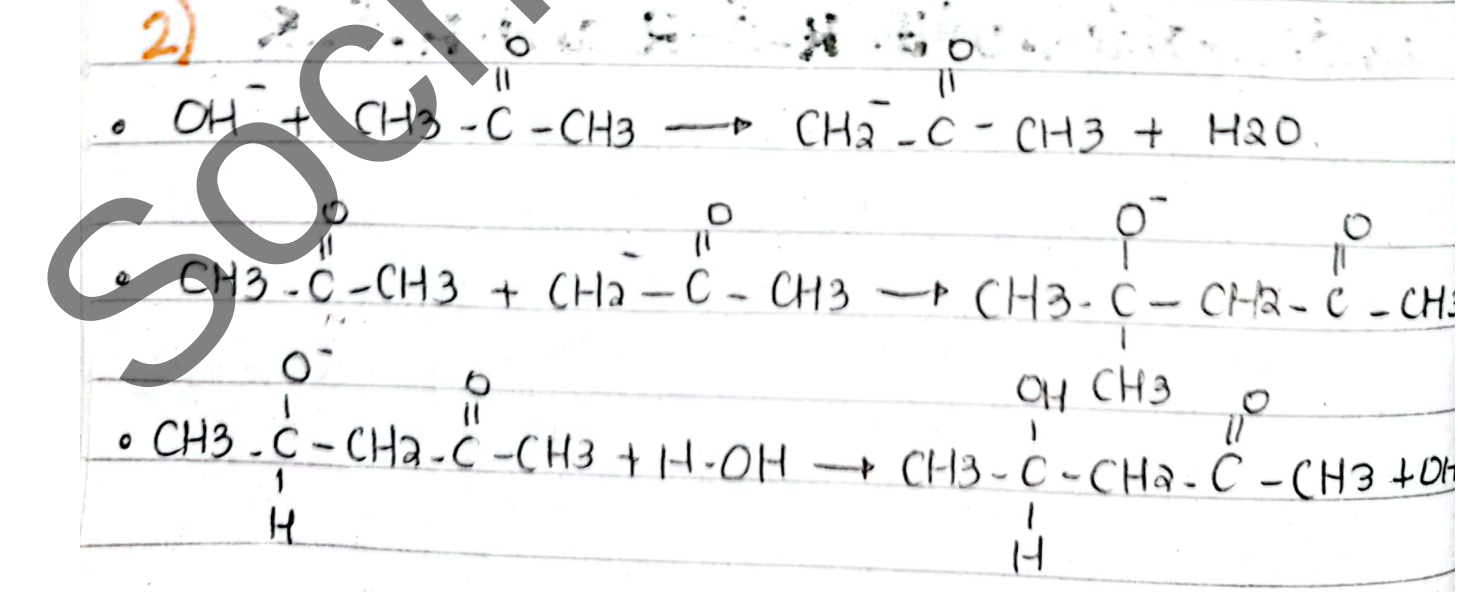
Step#2 attack of carbanion on reagent



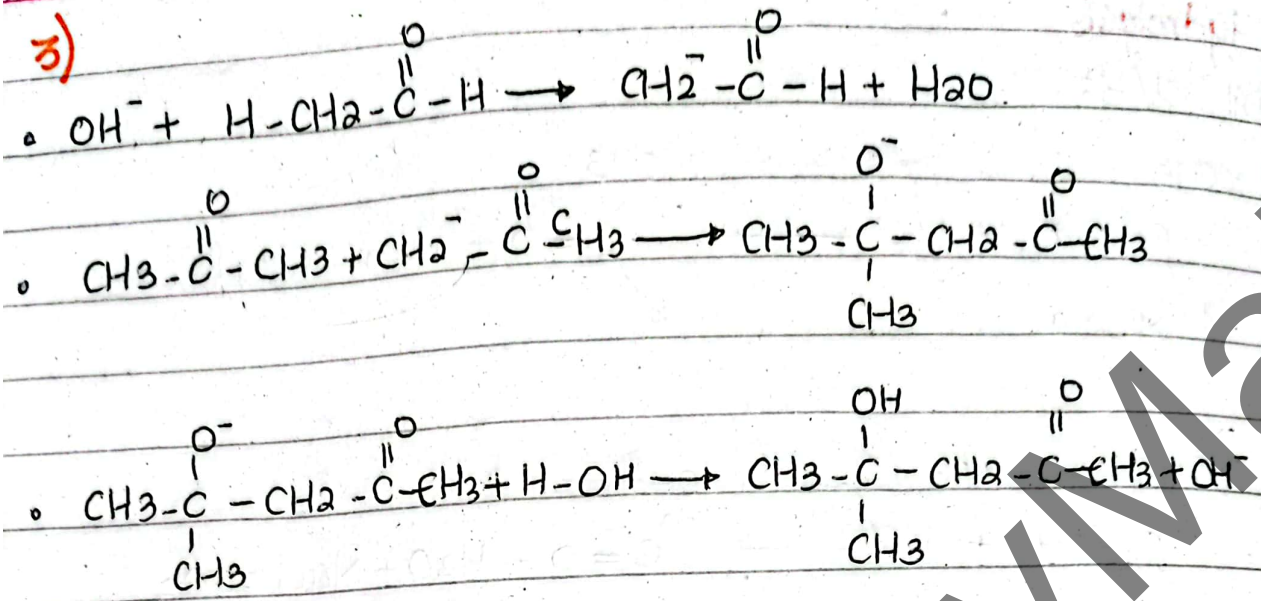
Step#3 formation of catalyst



2)

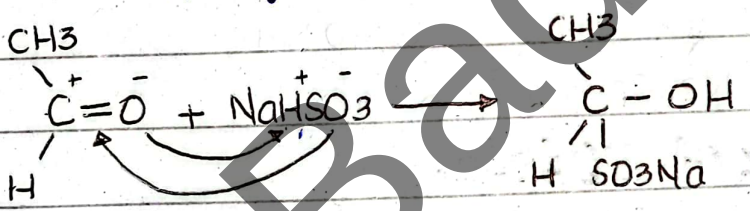


3)

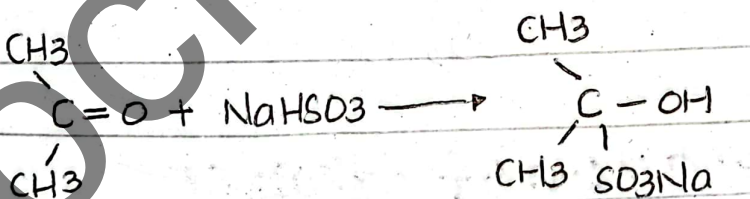


b) addition of NaHSO3 or identification test for carbonyl compound

→ Aldehyde and small methyl Ketone react with NaHSO3 give white ppt of addition product (adduct).



white ppt
acetaldehyde adduct

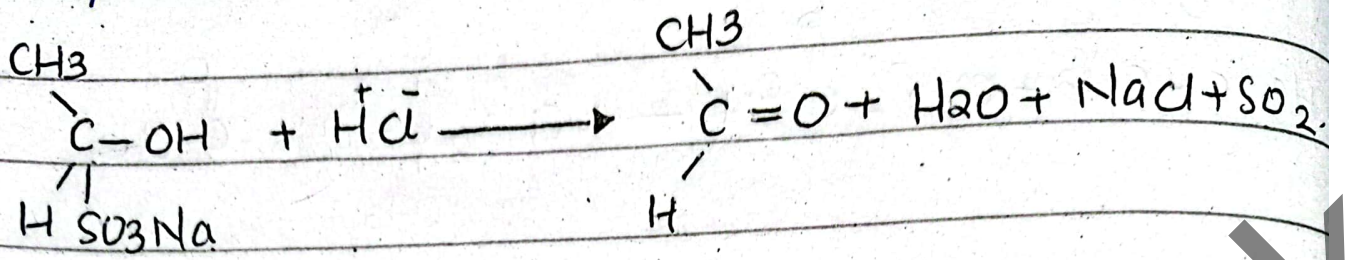


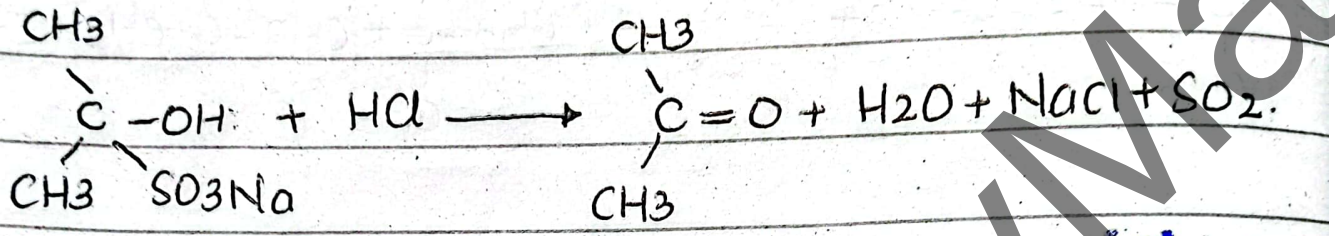
propanone adduct
white ppt

→ Test used to distinguish b/w carbonyl & non-carbonyl compounds.

Hydrolysis

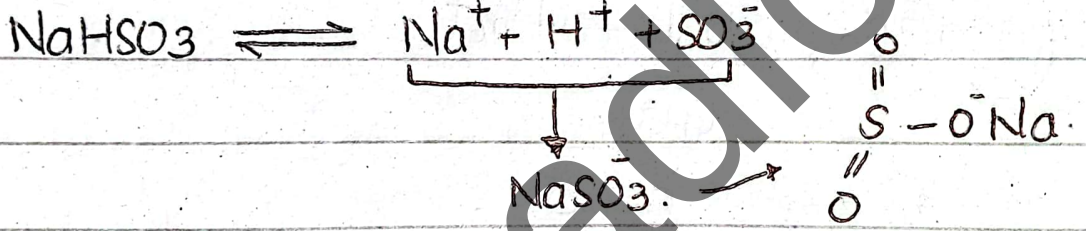
Dil HCl/H_2SO_4.



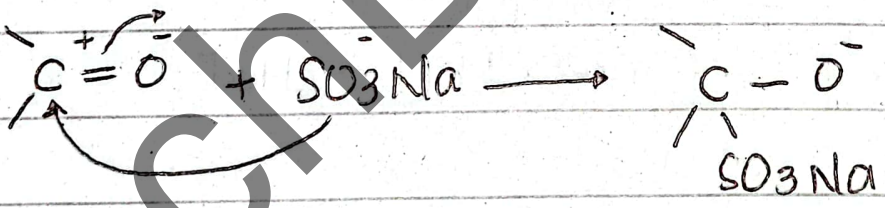


Mechanism:

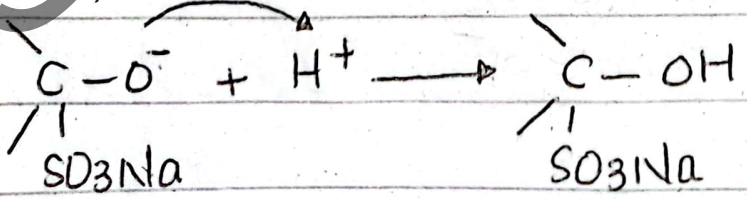
Step 1: Rxn base with reagent



Step 2: attack of SO_3^-Na



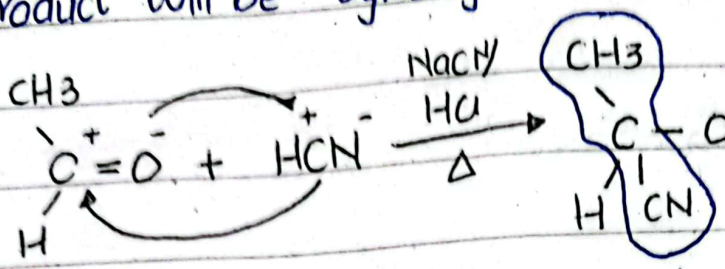
Step 3:- Regeneration of catalyst



3- addition of HCN

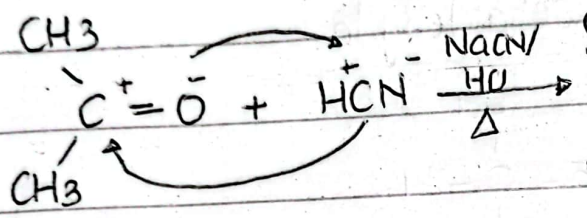
halohydrin (Cl-OH)

- Product will be cynohydrin. (CN-OH).



ethanalcynohydrin.

2-Hydroxypropanenitrile.

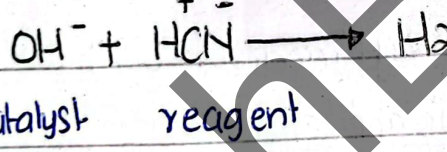
- 

propanalcynohydrin.

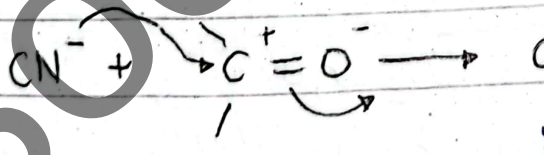
2-Hydroxy-2-methylpropanenitrile.

Mechanism:

Step 1:

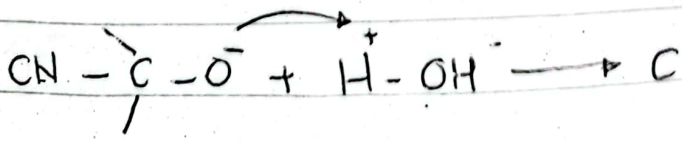


Step 2: attack of CN^- on reagent $-\overset{O}{\overset{\|}{C}}-$



intermediate.

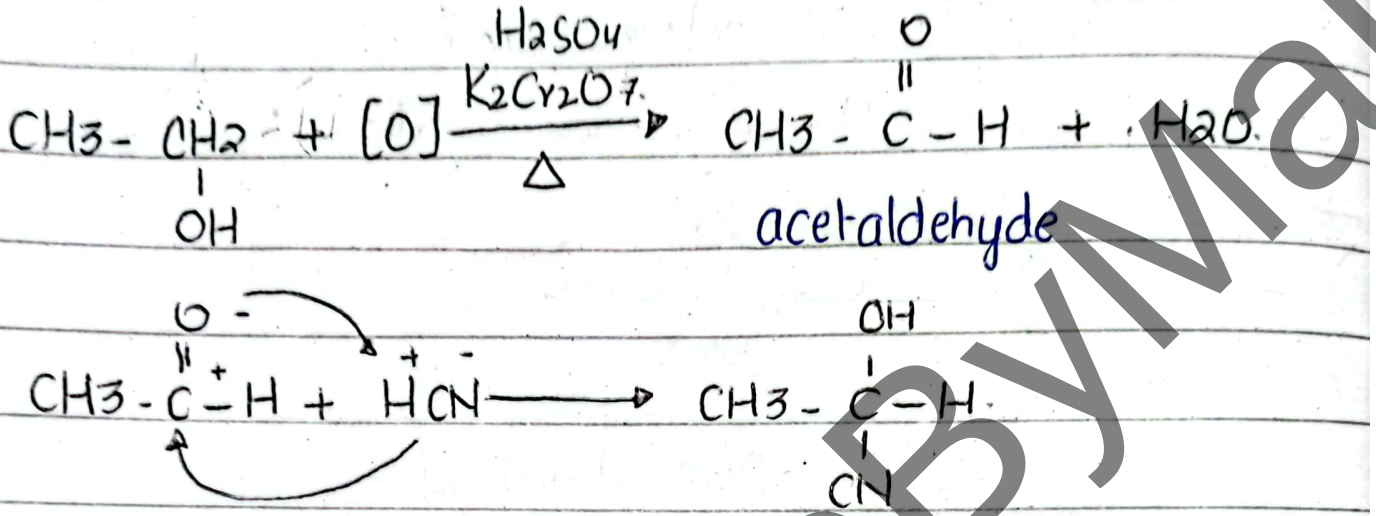
Step 3: regeneration of catalyst

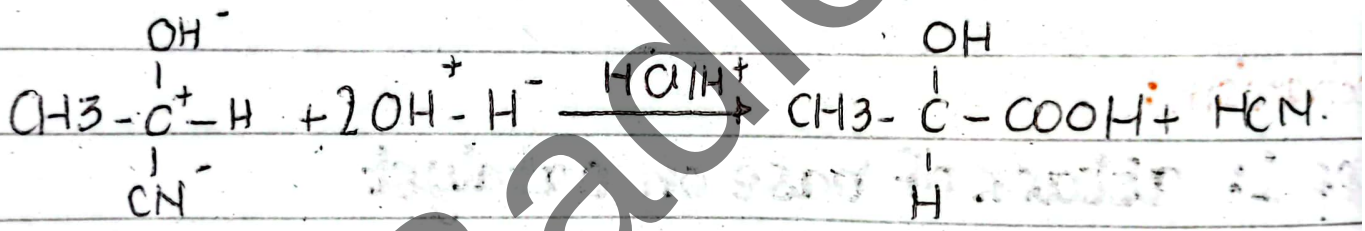


Conversion

ethanal ⟶ lactic acid

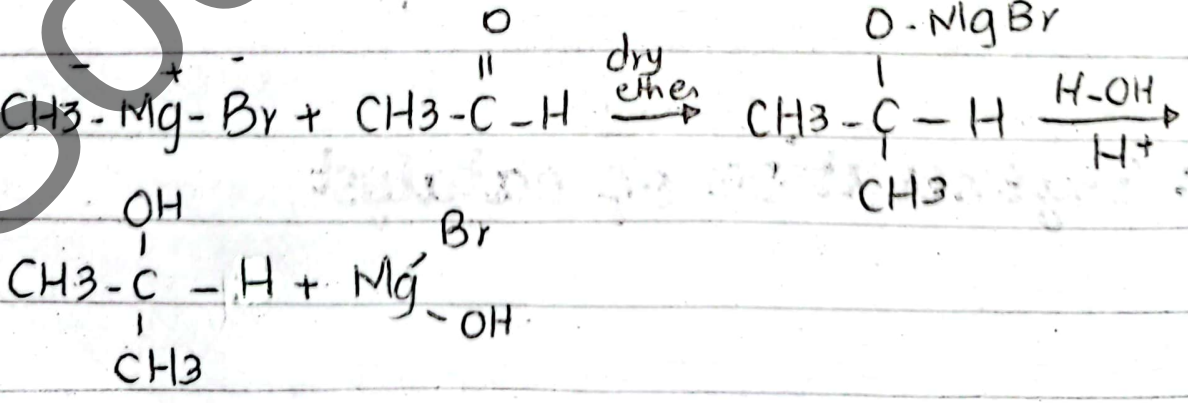
2- Hydroxypropanoic acid.



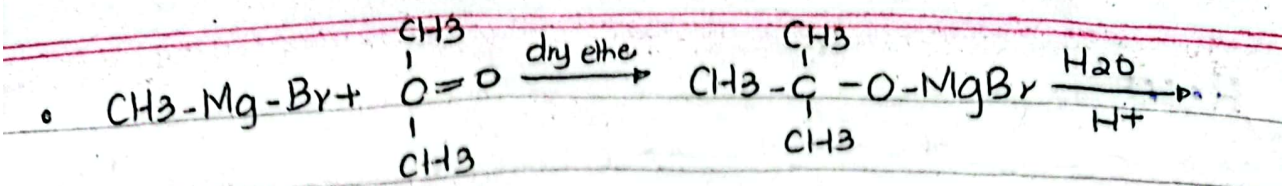


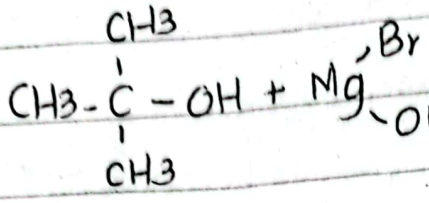
2- Hydroxy Propanoic acid.
Lactic acid.

4- Grignard reagent



isopropylalcohol.





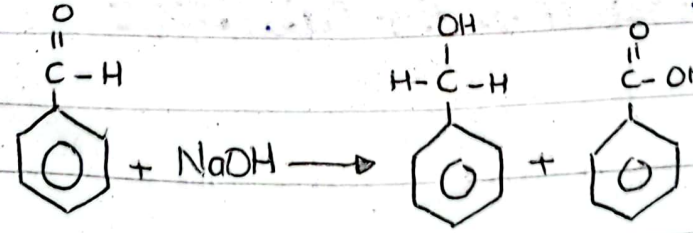
2-Methyl-~~2-Hydroxy~~ Butanol.

b) Cannizzaro's reaction

- It's also one of type of condensation reaction.
- It require no α-Hydrogen.
- Also called as disproportionation. → Same element undergo oxidation & reduction at same time.
- Only aldehyde undergo this rxn like :- formaldehyde & benzaldehyde.
- Ketone doesn't undergo this because :-
  - → they are already less reactive.
  - → Presence of ~~at~~ bulky group, decrease overall reactivity.
  - → Steoric repulsion doesn't favour attack of base.

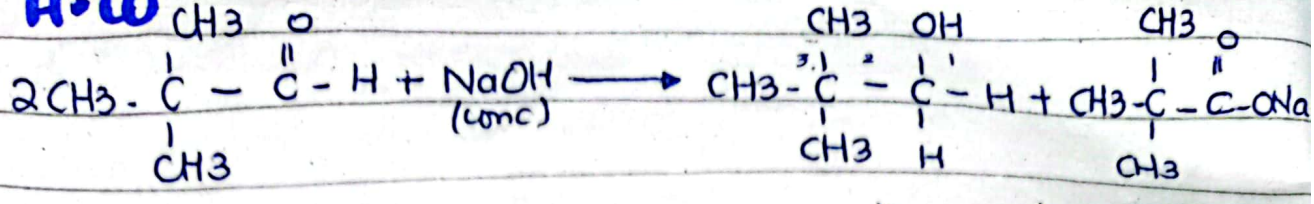
i) $2H-\overset{O}{\overset{\|}{C}}-H + NaOH \longrightarrow \underset{\text{(reduced)}}{CH_3OH} + \underset{\text{(oxidized)}}{H-\overset{O}{\overset{\|}{C}}-ONa}$

methanol — sodium formate — sodium salt of formic acid.

ii) 

Benzyl alcohol. (reduced) — Na-Benzoate. (oxidized)

H.W



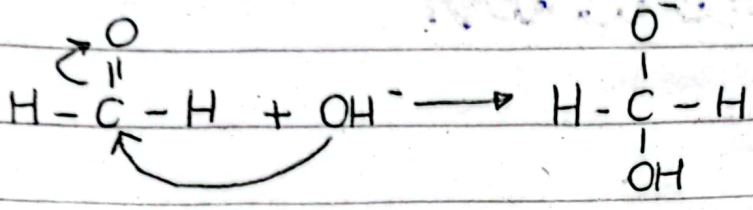
2,2-Dimethylpropanal

2,2-Dimethylpropanol

2,2-Dimelylsodiumpropanal.

Mechanism:-

Step 1: attack of base



formaldehyde

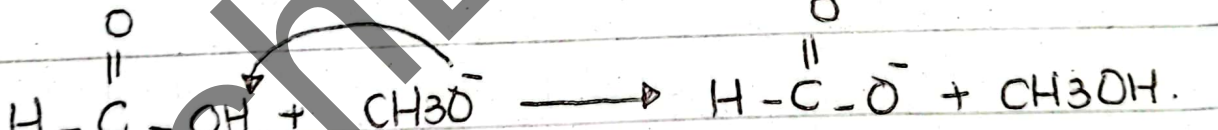
Oxonium ion

Step 2: Transfer of hydride ion

(CH_3O^-)

formaldehyde.

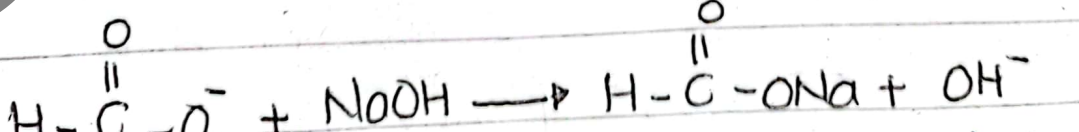
Step 3: formation of carboxylate ion



carboxylate ion methanol

formalate ion.

Step 4: Regeneration of catalyst



sodium salt of formic acid

base

5- Haloform reaction Iodoform test

The carbonyl compounds containing the $-CH_3$ group when treated with ~~benzene~~ iodine in the presence of alkali or mild/strong base like NaOH gives ppt yellowish in color called Iodoform (CHI_3).

Type of haloform:

CHX_3 = Haloform.

$CHCl_3$ = chloroform. (oily layer).

$CHBr_3$ = Bromoform (White ppt).

CHI_3 = Iodoform. (yellow ppt).

aldehyde

In aldehyde, only acetaldehyde gives haloform. $CH_3-\overset{O}{\overset{\|}{C}}-H$.

$$CH_3-\overset{O}{\overset{\|}{C}}-H + 3I_2 + 4NaOH \longrightarrow \underbrace{CHI_3}_{\text{Yellow ppt}} + H-\overset{O}{\overset{\|}{C}}-ONa + 3NaI + \underbrace{3H_2O}$$

Balancing cheat code:-

(34), (33)

Reactant product

Ketone

In Ketone, only small methyl Ketone can undergo haloform.

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3-\overset{O}{\overset{\|}{C}}-ONa + 3NaI + 3H_2O.$$

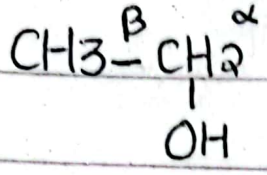
Balancing cheat code:

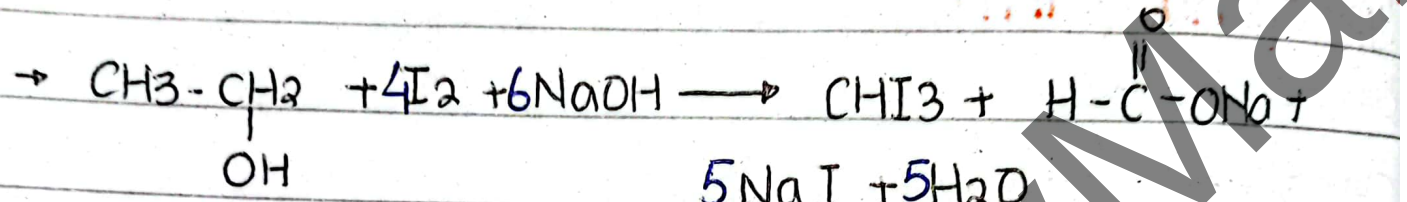
(34), (33)

Reactant product

primary alcohol

Only ethyl alcohol gives this test because α carbon has CH_3 directly bonded to it.





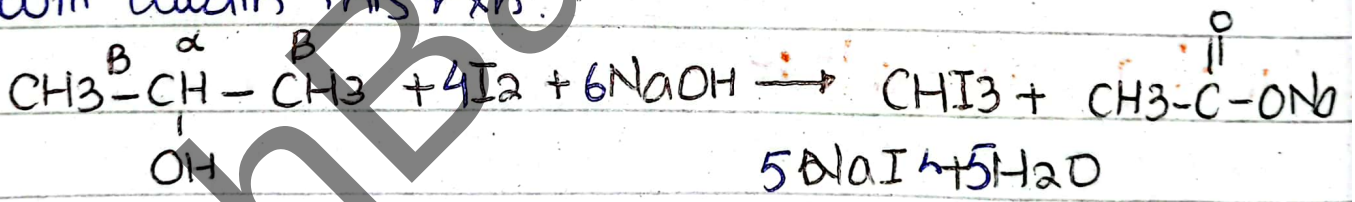
cheat code :-

(46), (55)

reactant product

Secondary alcohol

only 2° carbon containing adjacent CH_3 group will attain this rxn.



tertiary alcohol

tertiary alcohol donot undergo.

h.w

Q/ how you will distinguish b/w methanol & ethanol?

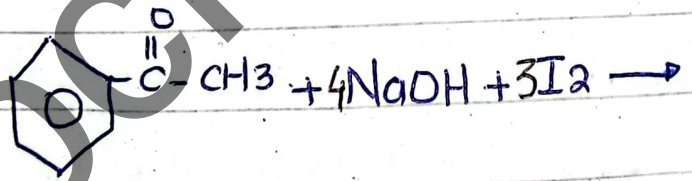
Methanol and ethanol can easily be distinguish ~~beta~~ by iodoform test. Since methanol contain only 1 C and does not have β-CH3 but ethanol has β-CH3 adjacent to α C.

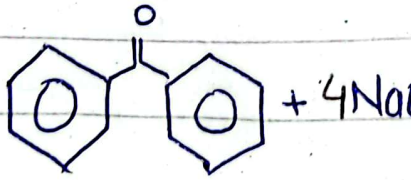
→ $CH_3-\underset{OH}{CH_2} + 6NaOH + 4I_2 \xrightarrow{\Delta} CHI_3 + 5NaI + 5H_2O + H-\overset{O}{\overset{\|}{C}}-ONa$

→ $CH_3OH + NaOH + I_2 \xrightarrow{\Delta} X$

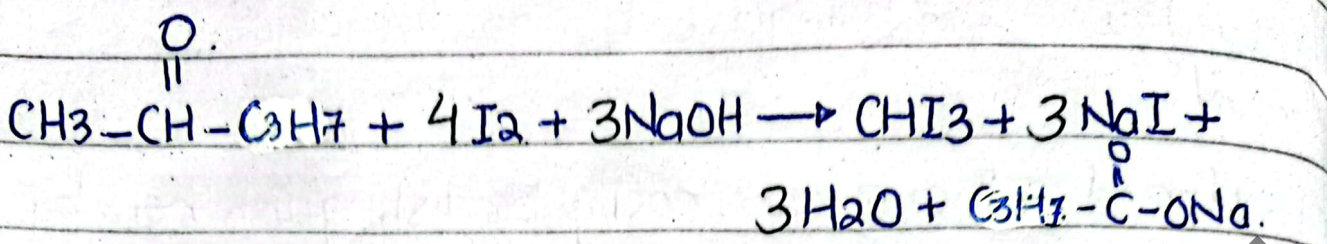
Q/ ~~=~~ between acetophenone & benzophenone.

The acetaphenone contain the methyl group attached to carbonyl but benzophenone doesn't have so.

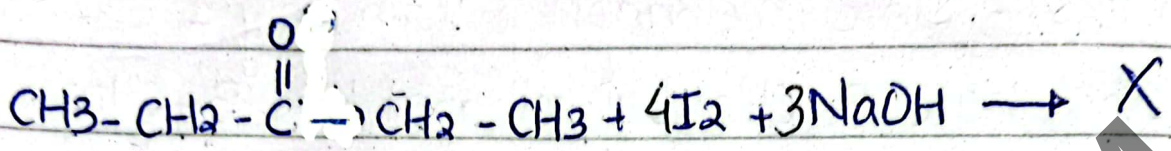




Q3. // between 2-pentanone & 3-pentanone.



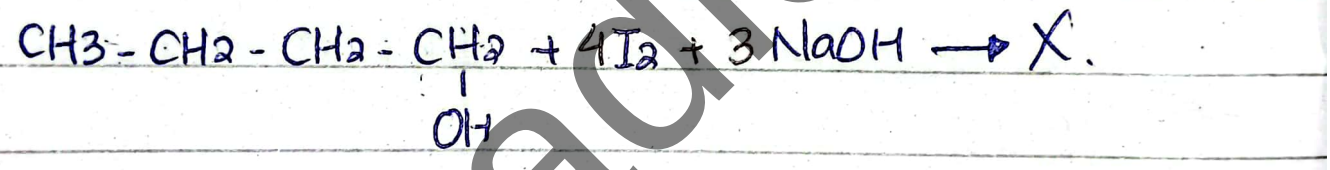
$$CH_3-\overset{\overset{O}{\|}}{C}H-C_3H_7 + 4I_2 + 3NaOH \longrightarrow CHI_3 + 3NaI + 3H_2O + C_3H_7-\overset{\overset{O}{\|}}{C}-ONa.$$



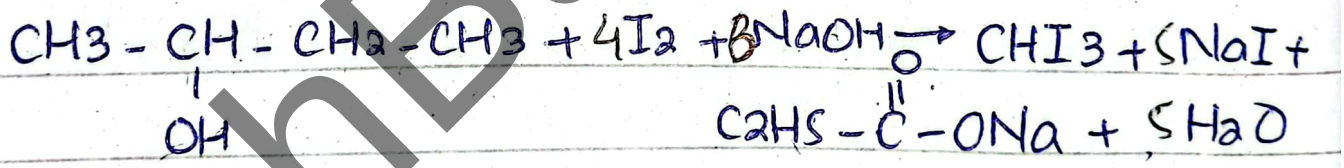
$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 + 4I_2 + 3NaOH \longrightarrow X$$

The above reactions indicate that the 2-pentanone is only eligible to perform iodoform test bcoz β-carbon is CH_3 adjocent to alpha.

Q4 // between 1-Butanol & 2-Butanol.



$$CH_3-CH_2-CH_2-\underset{\underset{OH}{|}}{CH_2} + 4I_2 + 3NaOH \longrightarrow X.$$



$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3 + 4I_2 + 6NaOH \longrightarrow CHI_3 + 5NaI + C_2H_5-\overset{\overset{O}{\|}}{C}-ONa + 5H_2O$$

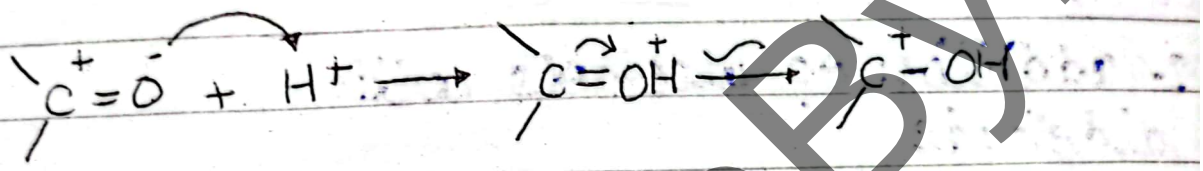
These reaction shows that the 2-Butanol have methyl group but 1-Butanol does not have so that's why it undergo iodoform reactions.

acid-catalyse reaction

* When acid is used as catalyst it increases the E^+ character of catalyst.

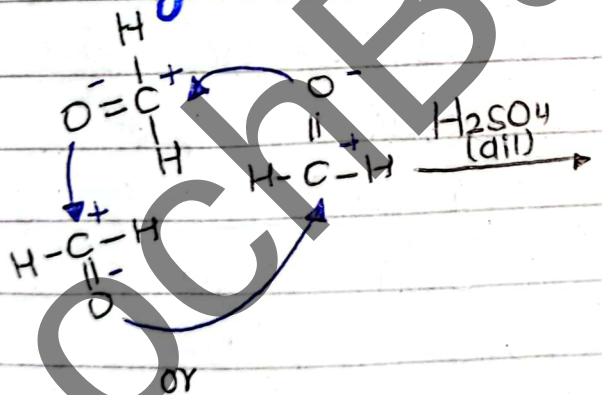
General mechanism

Step#1 protonation of carbonyl grp



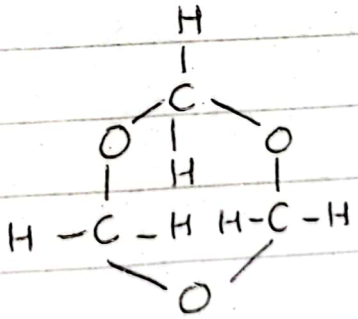
Step#2 attack of Nu

1- Polymerization of aldehyde



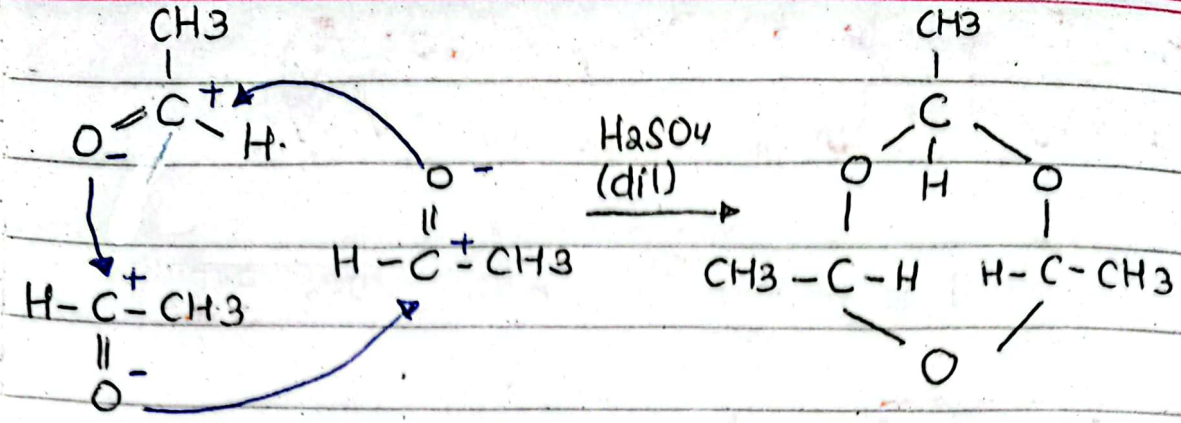
or

3 CH2O



metaformaldehyde (Trioxan)
Trimer of Methanol

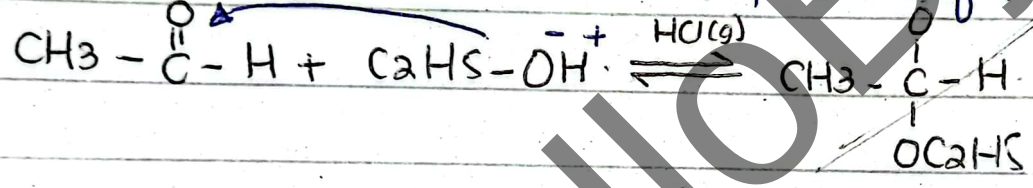
▲ Ketone donot undergo this rxn becaz of stearic Hindrance.



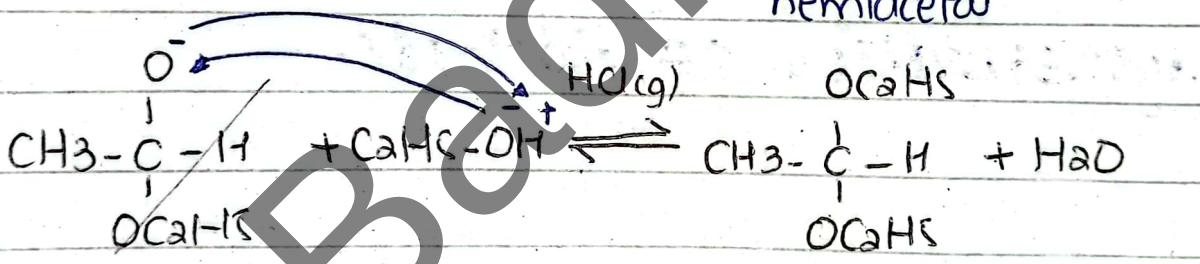
3 CH_3CHO → Paraldehyde
Trimer of ethanal

2- addition of alcohols with aldehyde

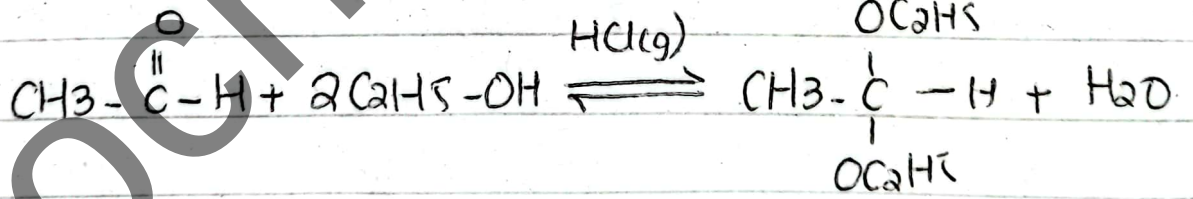
aldehyde reacts with alcohols in presence of HCl gas/fmi



hemiacetal



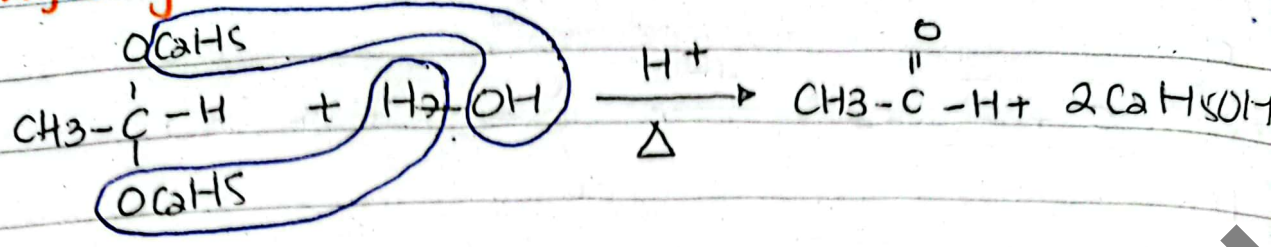
acetal



1,1- Diethoxyethane

★ These acetal are used for the purpose as to product aldehyde against oxidizing agent (alkaline) so that they can't change to carboxylic acid.

Hydrolysis



3) Nucleophillic addition reaction of carbonyl compounds with ammonia derivates

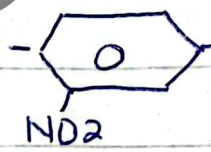
→ Aldehyde and Ketone reacts with ammonia derivates to form G-NH2 and water.

→ This reaction is also called as condensation reactions or addition-elimination reaction.
↳ water lost

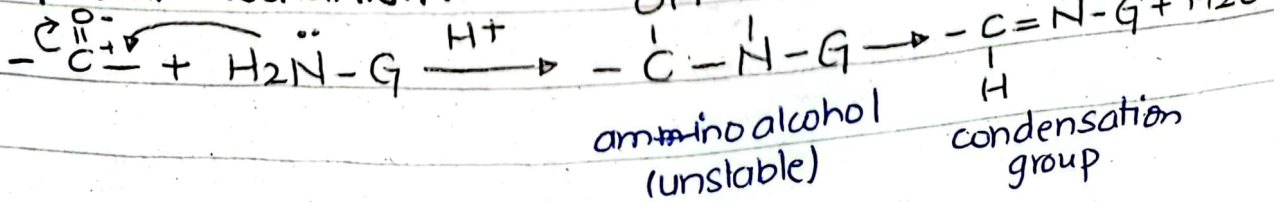
general formula

- NH2-G
- NH3 → R-NH2 → G-NH2

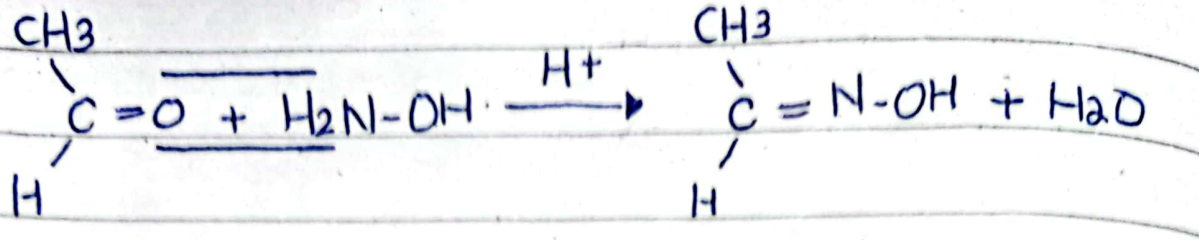
Groups :-

- NH2-OH = Hydroxylamine.
- H2N-NH2 = hydrazine.
- H2N-NH-C6H5 = phenyl hydrazine
-  = 2,4-Dinitrophenyhydrazine
- H2N-NH-CO-NH2 = semicarbazide

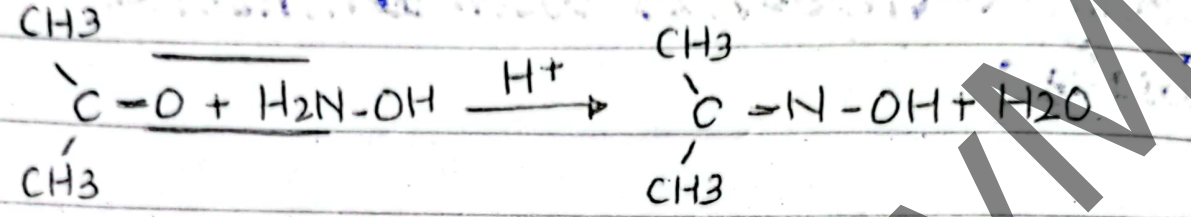
General Mechanism:



1) Reaction with Hydroxylamine :-

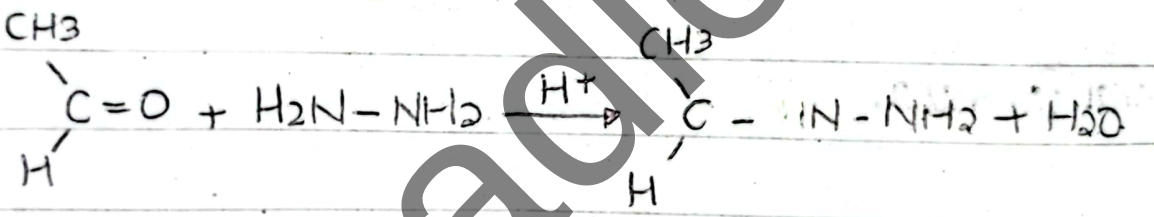


ethanal Hydroxyamine ethanal oxime (IUPAC)

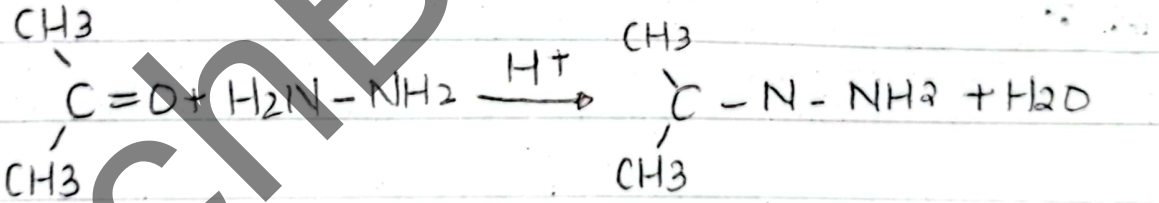


propanal propanal oxime

2) Reaction with hydrazine :-

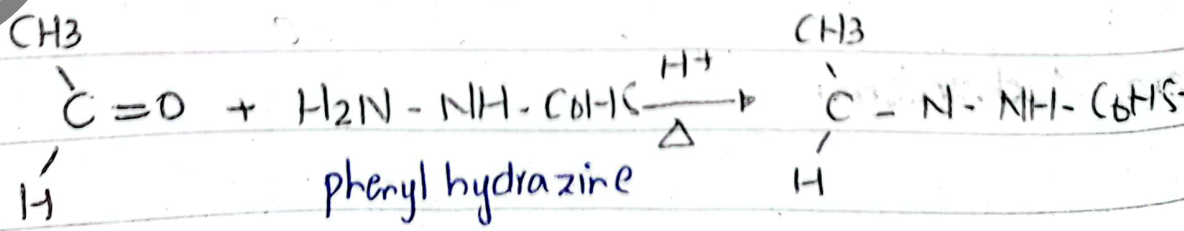


ethanal ethanal hydrazine.

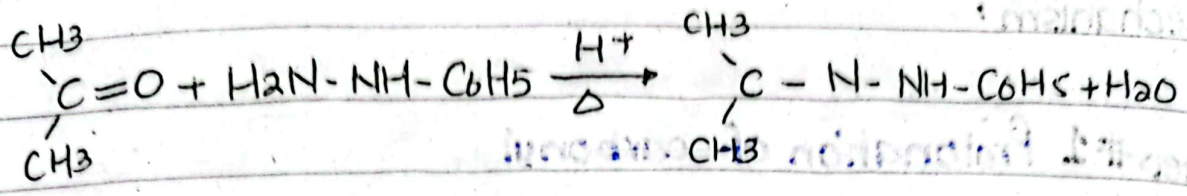


Propanone Propanone hydrazine

3) Reaction with phenyl hydrazine :-

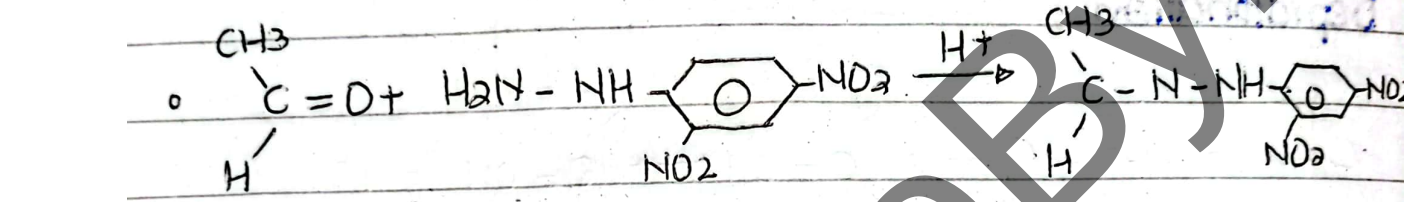


ethanal phenyl hydrazine ethanal phenyl hydrazine

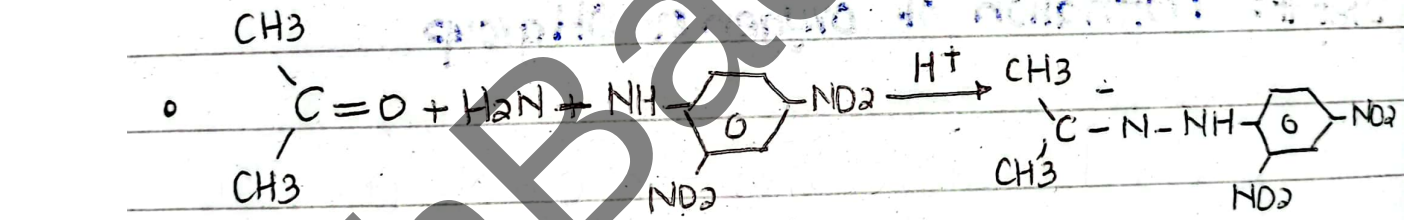


propanone — propanone phenyl hydrazone

4) Reaction with 2,4-Dinitrophenyl hydrazine
Identification test for carbonyl comp

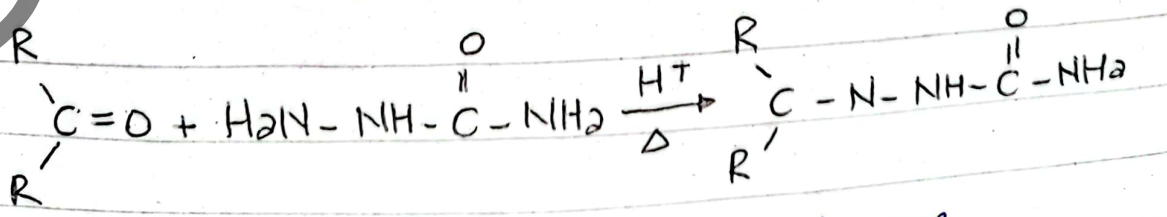


ethanal — 2,4-Dinitrophenyl hydrazone. — ethanal-2,4-Dinitro phenyl hydrazone. (yellow orange ppt)



propanone-2,4-Dinitrophenyl hydrazone (yellow orange ppt)

5) Reaction with Semi-carbazide $H_2N-NH-\overset{O}{\overset{\|}{C}}-NH_2$

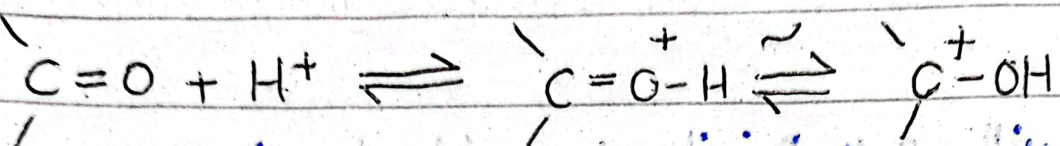


carbazone

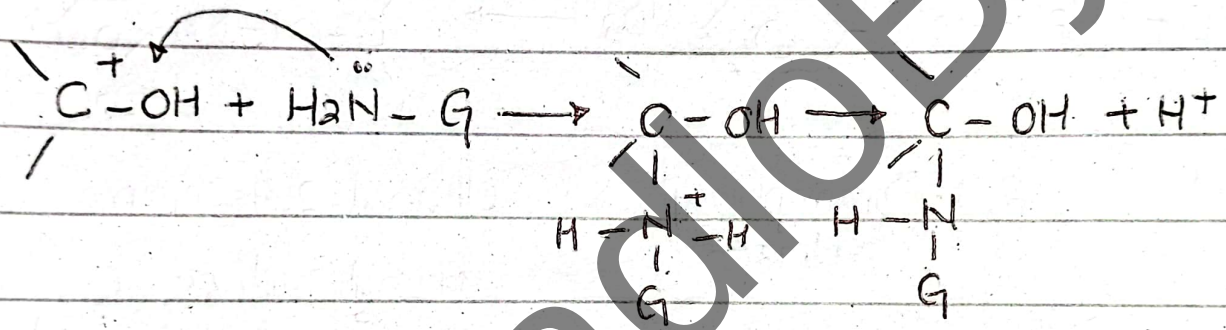
General for NH_3 derivates :-

Mechanism :

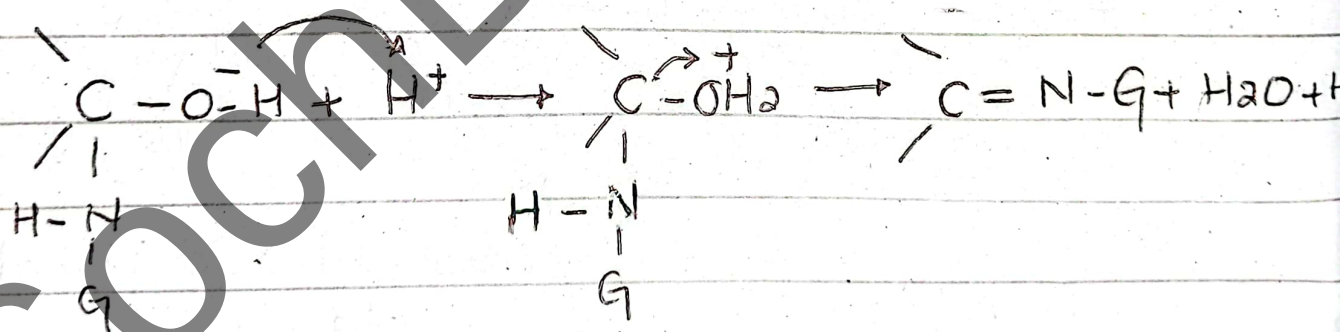
Step #1 Protonation of carbonyl



Step #2 Attack of NH_3 derivatives with Deprotonation



Step #3 Protonation of oxygen of OH group



reduction

1) reduction of hydrocarbon

a) Clemmensen's Reduction

→ Occurs in acidic medium Zn-Hg + HCl

→ Prefered for Ketone but possible for aldehyde as well

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

ethanal — ethane

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

propanone — propane.

b) Wolff's Kishnar Reduction

→ Occurs in basic medium NH_2NH_2/KOH ethylene glycol.

→ Prefered for aldehyde but Possible for Ketone as well

- $CH_3-\overset{O}{\overset{\|}{C}}-H + [H] \xrightarrow[200^\circ C]{N_2H_4/KOH} CH_3-CH_3 + H_2O + N_2$

ethanal — ethane.

- $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + [H] \xrightarrow[200^\circ C]{N_2H_4/KOH} CH_3-CH_2-CH_3 + N_2 + H_2O$

propanone — propane

5- Hydride ion reduction:-

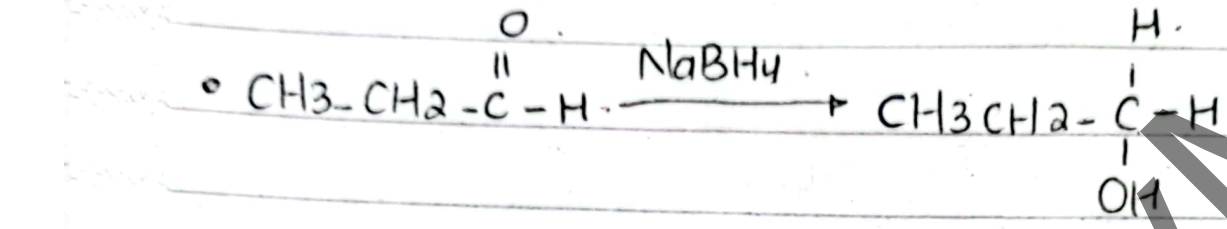
$NaBH_4$ = Sodium tetra hydrio borate III

$LiAlH_4$ = Lithium tetrahydrio aluminate III

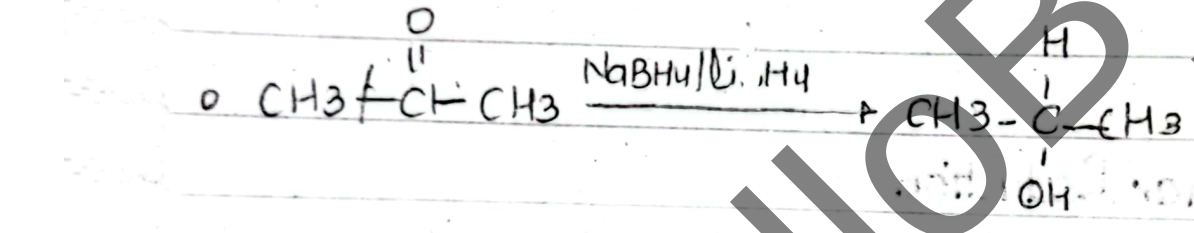
→ BH_4^- & AlH_4^- act as a source of H^- ion.

$NaBH_4$ = weak

$LiAlH_4$ = Strong



propanal — 1-propanol



propanone — 2-propanol.

Difference b/w Clemmensen and Wolff-Kishner reduction.

Clemmensen Reduction	Wolff-Kisher Reduction
Type of -C-	
It's preffered for Ketone but possible for aldehyde as well.	It's preffered for aldehyde but possible for Ketone too.
Medium	
It is done in acidic medium.	It's done in basic medium

Reducing agent

Zn-Hg + HCl is used as reducing agent.	NaH_4 + KOH is used as reducing agent.

Limitations

Sensitive to acid-sensitive functional groups.	Requires harsh basic & thermal conidition.

$NaBH_4$	$LiAlH_4$

Strength

Mild reducing agent	Strong reducing agent.

Reactivity

Less reactive, stable in air & water.	Highly reactive with water and air. & require dry cond.

Selectivity

More selective, fewer side reactions	Less selective, reduce wider range of functional groups.

Solubility

Soluble in H_2O, methanol & ethanol.	Soluble in dry. ethers.

Safety

Safe, easier to handle.	Hazardous.

Cost

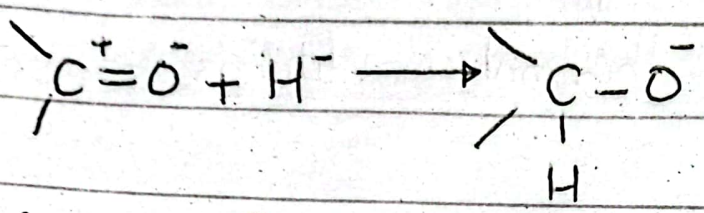
less expensive	more expensive

Mechanism of $NaBH_4$

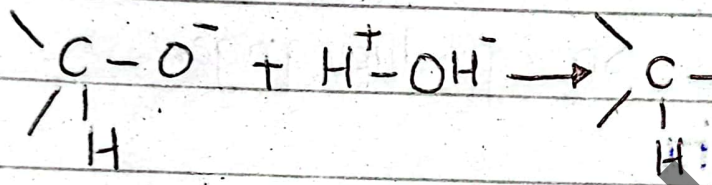
$NaBH_4 \rightleftharpoons Na^+ + BH_4^-$

BH_4^- was a source of hydride ion H^-

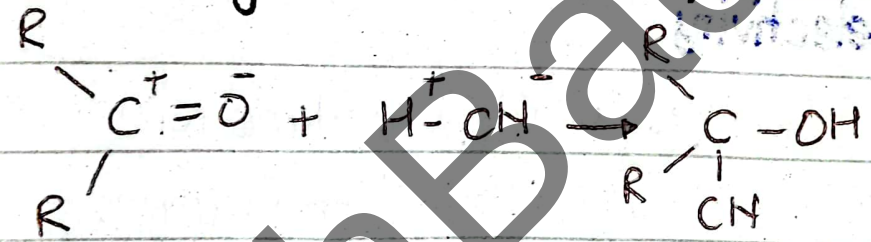
Step #1 attack of H^- ion



Step #2 Protonation

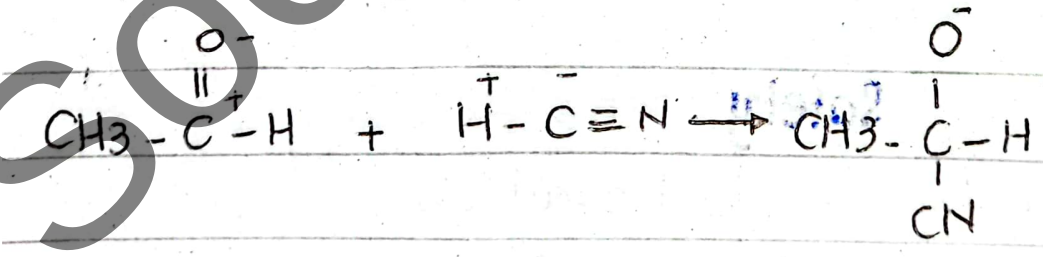


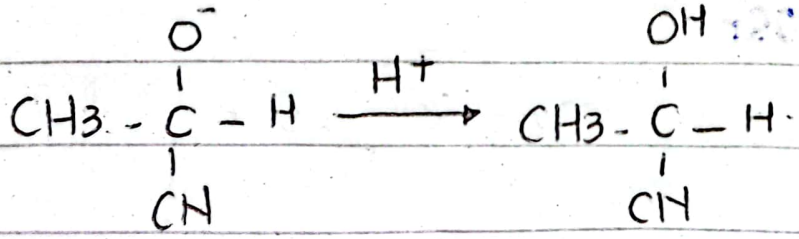
4) Using Carbon Nucleophile



aynanohydrin.

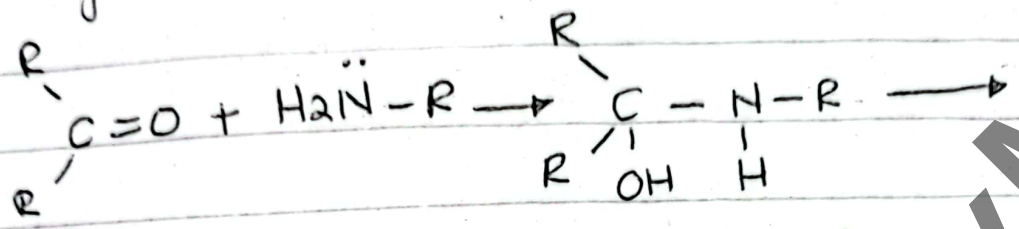
Mechanism :-



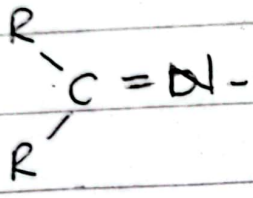


5) Using nitrogen nucleophile. (Schiff base)

- These reactions are usually carried out in a acidic buffer to activate C=O bond & faciliate dehydration but without inhibiting the nucleophile.

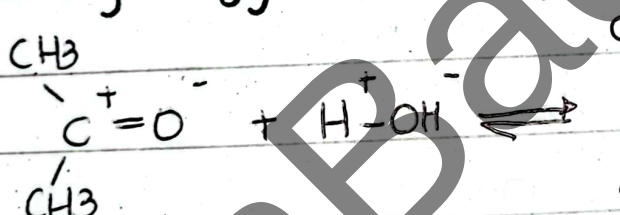


carbinol amine



imine. (Schiff base).

6) Using oxygen nucleophile



Propane-2,2diol.

- aldehyde & Ketone when react with water give gemina diols called as hydrates
- Mostly hydrates are not stable so they shift back.

Oxidation

1) Oxidation in concept of aldehyde and Ketone they convert into carboxylic acid.

Oxidation of aldehyde

Aldehyde are oxidized into carboxylic acid in the presence of mild or strong oxidizing agent & form corresponding carboxylic acid.

Reason:-

Aldehyde are reactive and don't possess stearic hindrance.

Oxidizing Agent:-

mild:-	Strong:-
Toller's reagent	$KMnO_4 + H_2SO_4$
Fehling solution	$K_2Cr_2O_7 + H_2SO_4$
Benedict solution	HNO_3

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

1 carbon aldehyde → 1 carbon carboxylic acid

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

acetaldehyde — acetic acid

ethanal — ethanoic acid

Oxidation of Ketone

Ketones are oxidized into a mixture of carboxylic acid in the presence of strong oxidizing agent.

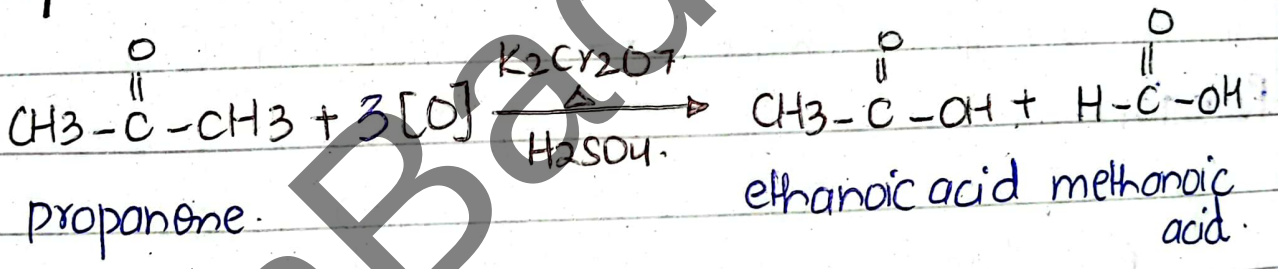
Reason:-

This is because they are not that much reactive also they possess more energy to break down because of the presence of -R group on both side creating ultimate steavic hindrance.

Tip:-

We break the C-C bond from that side which has less H in case of unsymmetrical.

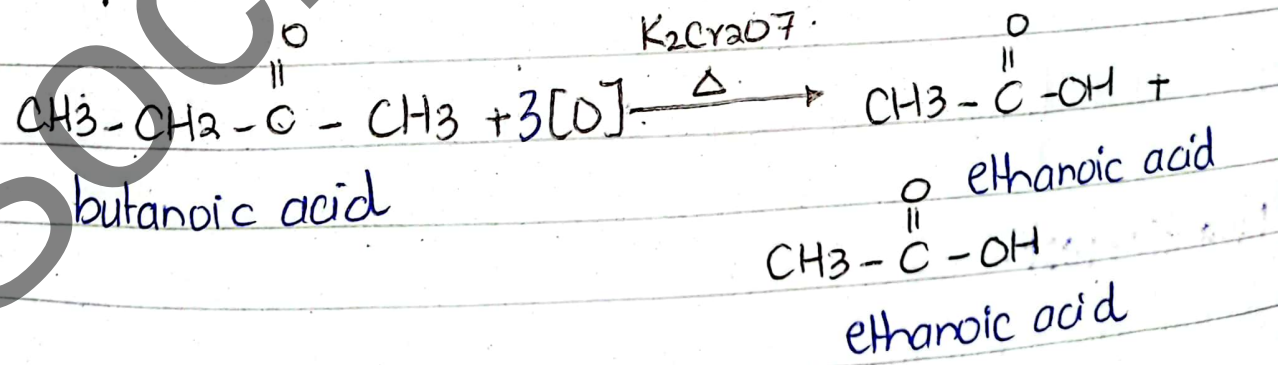
Symmetrical Case:-



propanone

ethanoic acid methanoic acid

Unsymmetrical Case:-



butanoic acid

ethanoic acid

ethanoic acid

test

Aldehyde

Fehling Solution test:-

Alkaline solution containing cupric tartarate (basic complex ion) is called fehling solution.

Fehling A: $CuSO_4$.

Fehling B: Tartaric acid

Composition: $CuSO_4 + NaOH +$ Tartaric acid.

Positive test:

Aliphatic aldehyde give this.

Use to separate Aliphatic & Aromatic aldehyde.

Results:

Aliphatic aldehyde + fehling sol ⟶ Brick red ppt

Reaction:

$$R-\overset{O}{\overset{\|}{C}}-H + 2Cu(OH)_2 + NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa + Cu_2O + 3H_2O$$

$$R-\overset{O}{\overset{\|}{C}}-R + \text{fehling sol} \longrightarrow X$$

Negative test:

Ketone don't give the test.

Benedict solution:

Alkaline solution containing Cupric citrate complex ion is called Benedict solution

Composition:

$CuSO_4$ + NaOH + citric acid

Positive test:

Aliphatic aldehyde + Benedict sol ⟶ Brick red ppt.

test to differentiate b/w aliphatic & aromatic aldehyde

Reactions:

$$R-\overset{O}{\overset{\|}{C}}-H + 2Cu(OH)_2 + NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa + Cu_2O + 3H_2O$$

Tollen's solution:

Common name: Silver mirror test.

Composition:

Ammonical silver nitrate.

($AgNO_3$ + NH_4OH)

Positive test:

$$AgNO_3 + NH_4OH \longrightarrow [Ag(NH_3)_2]OH + NH_4NO_3 + H_2O$$

Aldehyde + tollen's reagent $\xrightarrow{\Delta}$ silver mirror

Reaction

$$R-\overset{O}{\overset{\|}{C}}-H + [Ag(NH_3)_2]OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONH_4 + Ag + NH_3 + H_2O$$

Ag ↓ silver mirror

Compounds that give test:

Aliphatic & aldehyde both give this rxn but Ketone don't.

Ketone

Sodium nitroprusside test

Positive test:

Ketone.

Ketone + $Na_2[Fe(CN)_5NO]$ ⟶ wine red / orange red so

formula:

$Na_2[Fe(CN)_5NO]$

Negative results

~~Ket~~ aldehyde

Q#1 How can you identify / distinguish between carbonyl and non-carbonyl compounds.

To discern between carbonyl and non-compound compounds, there are several sophisticated techniques that can be employed.

- **$NaHSO_3$:**

A reaction with $NaHSO_3$ will ensure that carbonyl compound is present by forming white ppts or white crystals.

- **Tollen's Test:**

This will help to discern the carbonyl and non-carbonyl compounds by reducing tollen's reagent. Only aldehyde will give positive tests.

- **DNPH Test:**

Carbonyl compounds when reacted with 2,4-Dinitrophenyl hydrazine will give yellow / orange ppt of 2,4-Dinitro phenyl hydrazone.

Q# Explain which compounds will undergo Aldol condensation reactions.

Aldol condensation is a reaction in which enolate ions react with carbonyl compound to form β-Hydroxy Ketone and aldehyde. Therefore, there's a condition, only those compounds that have α-Hydrogen will undergo the reaction.

$CH_3-\overset{\alpha}{C}-\overset{\parallel}{H}$

Q#3. Why Ketones don't undergo Cannizaros reactions?

Ketones are not likely to undergo Cannizaros reactions because the main concrete reason is the steric hindromce, on the both side of carbonyl group is - R group. This make a difficult blocki for attacking as nucleophile.

Q#4. Suggest a method to distinguish between ethanal & butana

We can distinguish them very easily merely performing Iodoform test.

The Ethanal have $-CH_3$ directly to caubonyl grp. will tend to give positive results by showing yellow ppt.

Whereas, the butanal won't show positive results.

Q#5. What's the necessary condition to perform iodoform test?

All the caubonyl groups compound donot give the iodoform test because the pivotal condition is not fullfilled. The condition of the presence of $-CH_3$ directly after the

carbonyl group is essential.

Q# Why only acetaldehyde tend to give haloform test?

→ Some reason as mentioned above.

Q# How you can distinguish between methanol and ethanol.

→ Some reason as mentioned above.

Q# Difference b/w Acetaphone & benzophenone.

- The Acetaphone group having $-R-\overset{O}{\overset{\|}{C}}$ group attached on the benzene. This is more likely to give iodoform test.
- Whereas benzophenone donot have such structural pattern, so it rather does not give iodoform test.

Q# Name the intermediate that's formed in Schiff base.

Carbinolamines.

Q# Why Ketone doesn't oxidizes easily just by using a mild oxidizing agent?

They are generally resistant to oxidization by mild oxidizing agent Because, there's lack of hydrogen rather presence of more-R group creating hindrance. This way it requires more energy, to do so. strong oxidizing agents are prefered.

Q# Discuss Some test to distinguish between addehyde & Ketone.

following are some sophisticated test:

- Tollen's reagent / test
- Fehling reagent / test
- Benedict's Test
- Sodium nitroprussaide.
- DNPH Test

Q# Difference between Clemmensen reduction and Wolff-Kishner Reduction.

Already done.

Q# Differentiate between $LiAlH_4$ & $NaBH_4$.

Previously done.

Q# Why Ketones are not likely to undergo polymerization?

This is due to following reasons :-

Structural Stability :-

C=O group: The C=O group is Ketones is generally stable and does not easily form reactive intermediates necessary for polymerization.

Lack of reactive sites: Ketone lacks the highly reactive sites that are typically required for the polymerization.

Reactivity:

absence of double bonds:

Polymerization often involves the reaction of double bond or highly reactive groups.

Steric hindrance:

The presence of 2 alkyl groups can create steric hindrance, further reducing the likelihood of polymerization.

them more readily substituted than those in alkanes.

Exercise

: Select the right answer from the choices given with each question.

i. **The carbon atom of a carbonyl group is**

a. sp hybridized b. sp^2 hybridized c. sp^3 hybridized d. none of these

ii. **Ketones are prepared by the oxidation of**

a. Primary alcohol b. Secondary alcohol c. Tertiary alcohol d. none of these

iii. **Acetone reacts with HCN to forsm a cyanohydrins. It is an example of**

a. Electrophilic addition b. Electrophilic substitution
c. Nucleophilic addition d. Nucleophilic substitution

iv. **Cannizaro's reaction is not given by**

a. Formaldehyde b. Acetaldehyde
c. Benzaldehyde d. Trimethylacetaldehyde

v. **Which of the following reagents will react with both aldehydes and ketones?**

a. Grignard reagent b. Tollen's reagent
c. Fehling's reagent d. Benedict's reagent

vi. **Aldehydes are the oxidation product of**

a. p-alcohols b. s-alcohols c. ter-alcohols d. carboxylic acids

vii. **Which of the following compounds will not given iodoform test on treatment with I_2/ NaOH.**

a. Acetaldehyde b. Acetone c. Butanone d. 3-pentanone

viii. **Aldehydes and ketones are carbonyl compounds. Which of them react both with $NaBH_4$ and with Tollen's reagent.**

a. Both aldehydes and ketones b. Aldehydes only

c. Ketones only d. Neither aldehydes nor ketones

$CH_3-CH_2-\underset{\underset{O}{\|}}{CH}-CH_2-CH_3$

ix. **Which one of the following can undergo Aldol condensation reaction?**

a. Farmaldehyde b. Acetaldehyde

c. Benzeldehyde d. Trimethylacetaldehyde

$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$

x. **Aldol condensation is not successful with compounds**

a. Having no α-hydrogen b. Having α-hydrogen

c. Having α-methyl group d. None

xi. **Phenylhydrazone is formed on treatment with carbonyl compounds with**

a. Hydroxyl amines b. Phenylhydrazine c. Oximes d. None

xii. **General formula of aldehyde and ketone is?**

a. $C_nH_{2n}O$ Ketone b. $C_nH_{2n+1}O$ aldehyde. c. C_nH_nO d. $C_nH_{2n+2}O$

xiii. **The colour of Iodoform is**

a. White b. Black c. Yellow d. Blue

...the following questions briefly