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Aldehydes, Ketons and Carboxylic Acids

Carbonyl group - $\left(-\overset{\overset{O}{\|}}{C}-\right)$

In aldehyde, the carbonyl group is bonded to a carbon and hydrogen. $\left(-\overset{\overset{O}{\|}}{C}-H\right)$

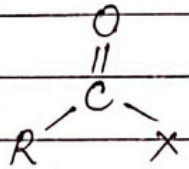
while in ketone it is bonded to two carbon atom. $\left(-\overset{\overset{O}{\|}}{C}-\right)$

And the carbonyl compound in which the carbonyl group carbon is bonded to carbon or hydrogen and oxygen group of of hydroxyl moiety are known as carboxylic acid.

$\left(-\overset{\overset{O}{\|}}{C}-OH\right)$

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

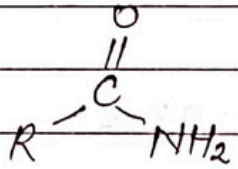
Aldehyde



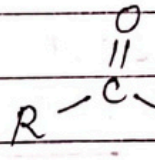
Acyl halide

$R-\overset{\overset{O}{\|}}{C}-R'$

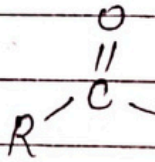
Ketone



Amide



carboxylic acid



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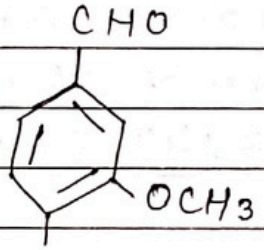
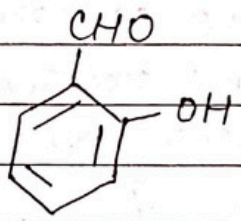
Acid anhydride.

Impartance

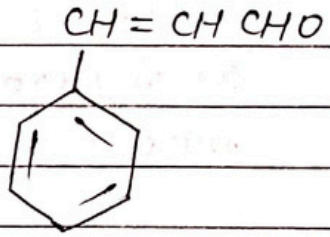
↳ Important role in biochemical process.
↳ Fragnance and flavour in nature.
↳ Used in food product and
↳ pharmaceuticals for flavour.
↳ used as solvent (i.e. Acetone).
↳ prepare materials like adhesive, paints resins, perfumes, plastic, fabrics etc.



Vanillin



Salicylaldehyde



Cinnamaldehyde

Nomenclature :

(I) Aldehyde and Ketones

@ Common name.

↳ The common name of most aldehydes are derived from common names of carboxylic acid by replacing the ending -ic of acid with aldehyde.

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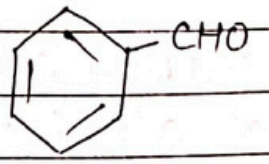
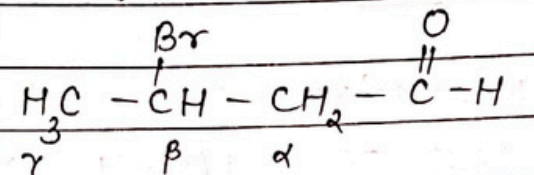
↳ α , β , γ , δ , etc are use to indicate location of substituent in carbon chain.

CH_3CHO Acetaldehyde



Benzaldehyde.



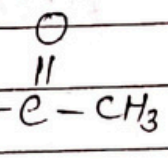
β- bromobutyraldehyde

↓

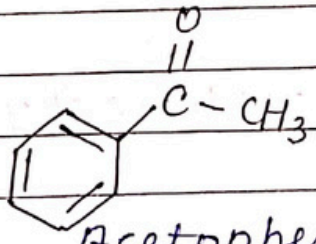
derived from butyric acid

↳ simplest dimethyl ketone is called acetone.

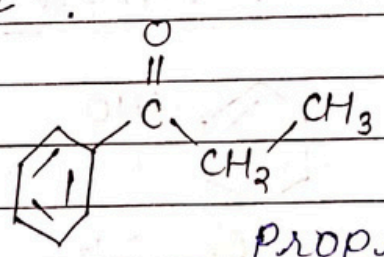
↓



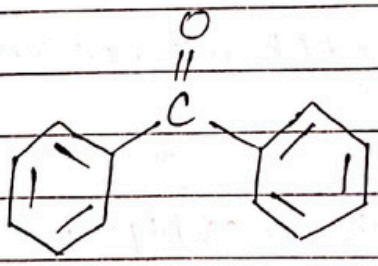
↳ Alkyl phenyl ketones are named by adding the name of acyl group as prefix to the word 'Phenone'.



Acetophenone



Propiophenone



Benzophenone.

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(b) IUPAC names :

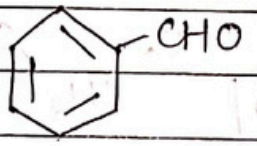
↳ Open chain aliphatic aldehyde and ketones are derived from the alkane by replacing the ending -e with -al and -one resp.

↳ In aldehyde the longest carbon chain is numbered starting from C of aldehyde group.

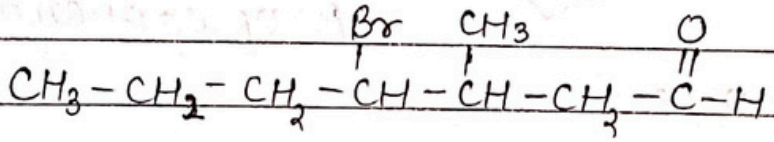
↳ In case of ketone substituent numbering begins from nearer end of carbonyl group.

↳ When -CHO group attached to a ring, suffix carbaldehyde is added after full name of cycloalkane.

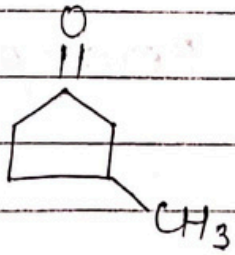
↳ The name of simplest aromatic aldehyde -



Benzenecarbaldehyde.



4 - Bromo - 3 - methylheptanal.



3 - methylcyclopentanone

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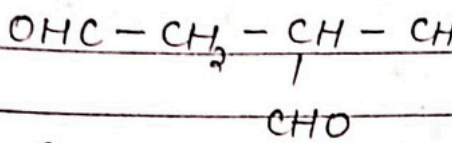
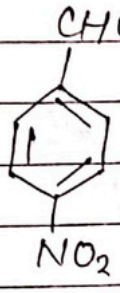
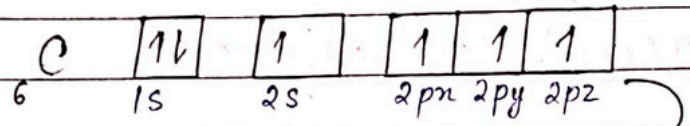


Propane-1, 2, 3-tricabaldehyde

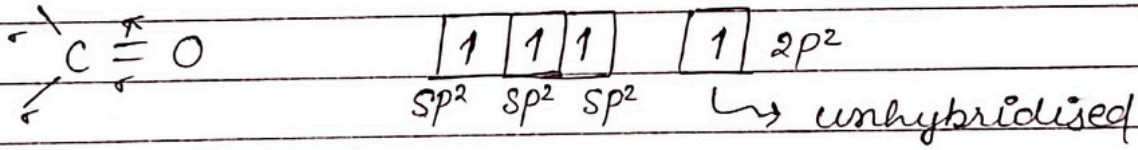


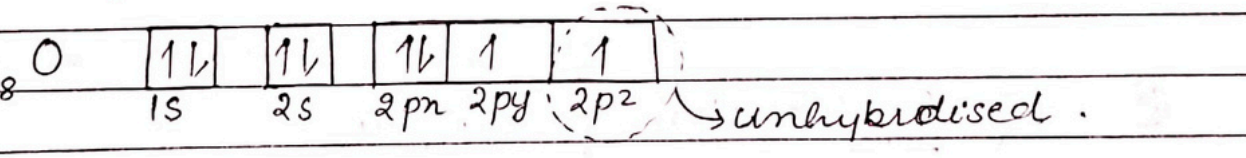
4-Nitro benzaldehyde
or
4-Nitrobenzene carbaldehyde

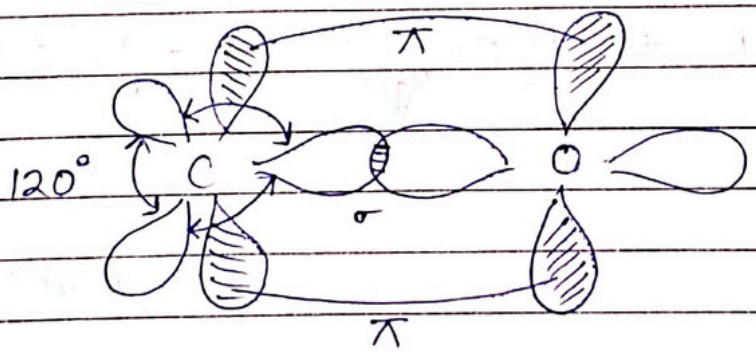
Structure of the Carbonyl Group :-



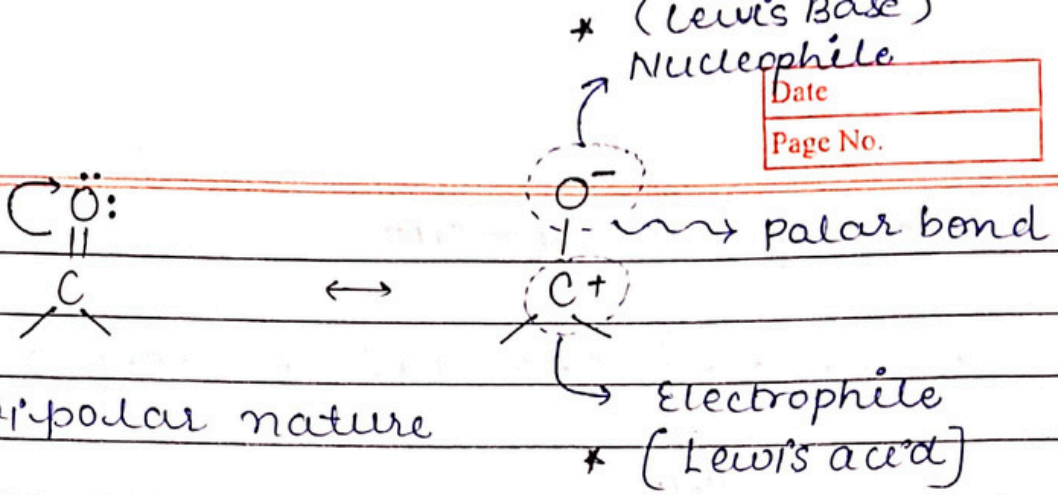
- π bond can never be formed by hybrid orbitals







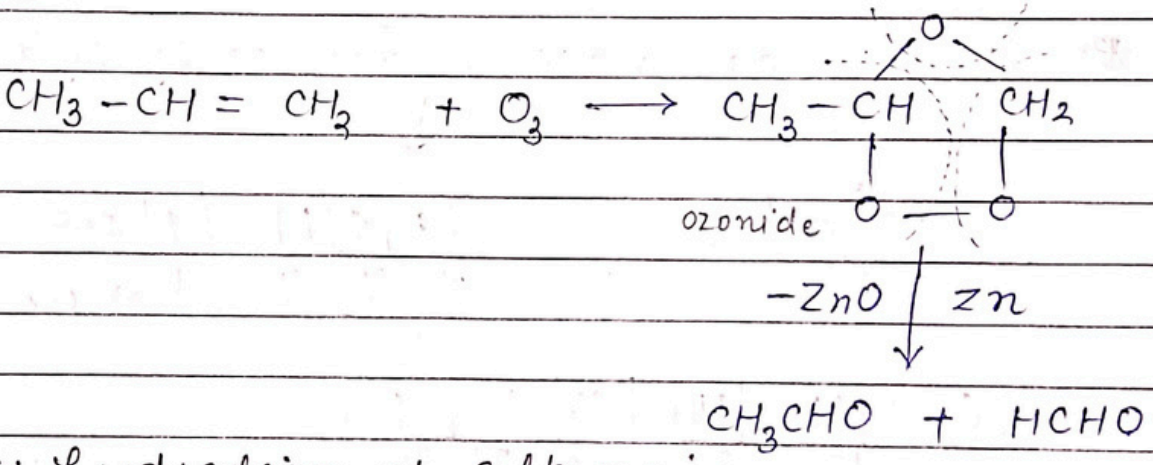
↳ sp^2 hybridised
↳ 120°
↳ Trigonal planar



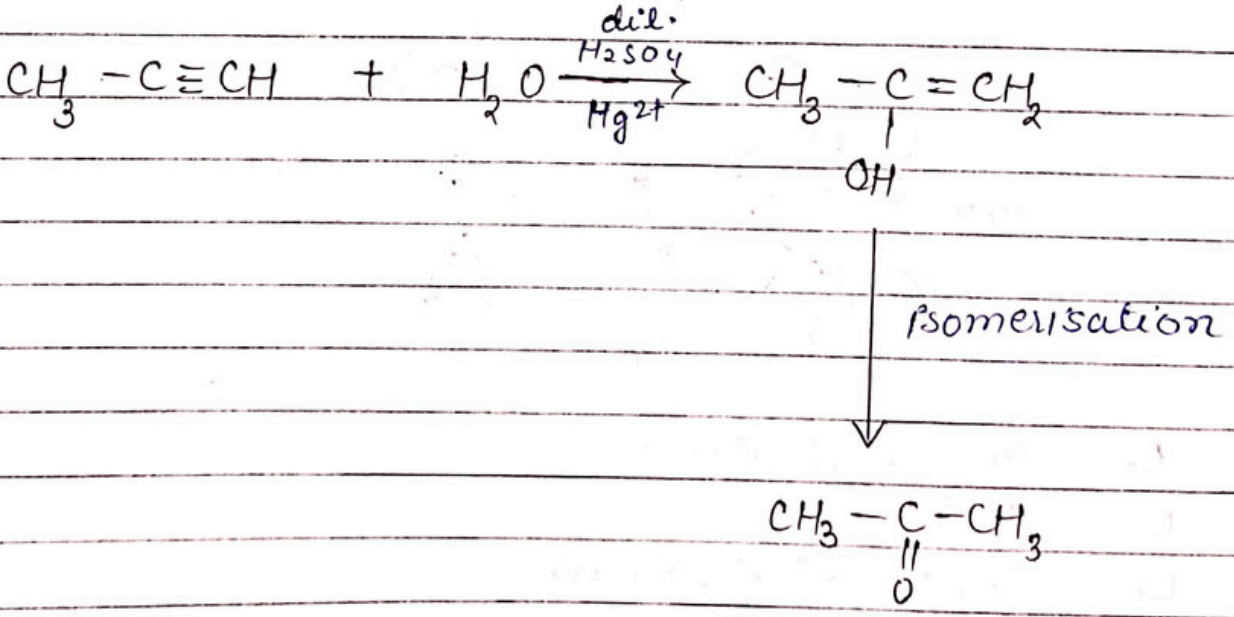
Method of Preparation of Aldehyde and Ketones :-

1. By oxidation of alcohols :
2. By dehydrogenation of alcohols :
3. From hydrocarbon :

(a) From ozonolysis of alkene :



(b) By hydration of alkyne :



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$$CH \equiv CH + H_2O \xrightarrow[dil.\ H_2SO_4]{Hg^{2+}} \underset{OH}{CH} = CH_2$$

isomerisation ↓

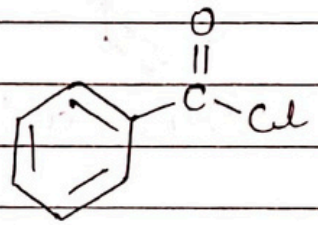
$$HC(=O)-CH_3$$

aldehyde (ethanal)

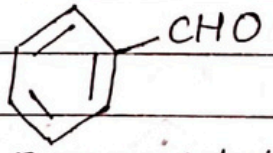
Preparation of Aldehyde :

1. From acyl chloride :

↳ also known as * **ROSENMUND** Reduction.



$$\xrightarrow[Pd - BaSO_4]{H_2}$$



Benzoyl chloride → Benzaldehyde.

2. From nitrile and esters :

$$RCN + \underset{\text{reducing agent}}{SnCl_2} + HCl \longrightarrow \underset{\text{(imine)}}{RCH=NH}$$

↓ H_2O

$$RCHO + NH_3$$

* **Stephen Reaction**

DIBAL → Diisobutylaluminium-hydride.

* ↳ only attack C≡N position

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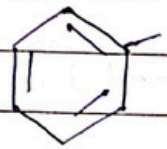
$$RCN \xrightarrow{DIBAL\text{-}H} RCH=NH \xrightarrow[H_2O]{H^+} RCHO + NH_3$$

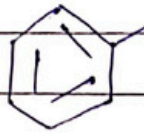
3. From hydrocarbon

(1) By oxidation of methyl benzene (Toluene) :

(a)



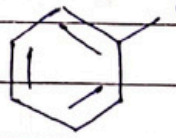
+ $2CrO_2Cl_2$ (chromyl chloride) $\xrightarrow{CS_2}$



[Toluene]

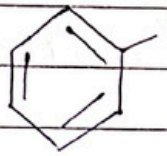
* Etard Reaction

$\xrightarrow{H_3O^+}$

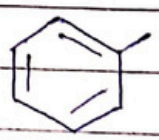


Benzaldehyde.

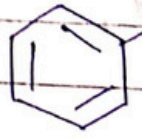
(b)



+ CrO_3 + $(CH_3CO)_2O$ (chromic oxide) $\longrightarrow$



$\xrightarrow[\Delta]{H_3O^+}$



Benzaldehyde

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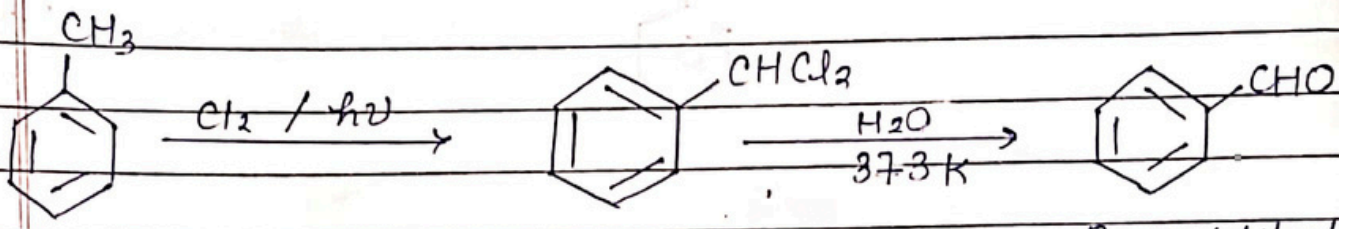
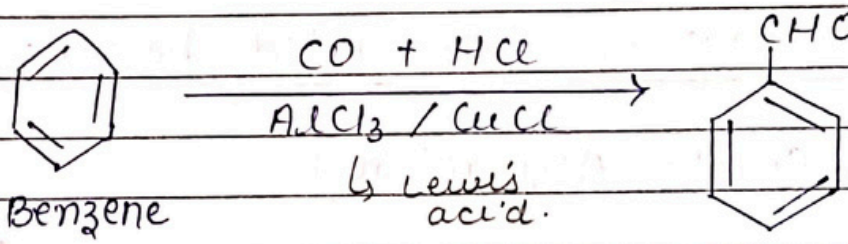
(ii) By side chain chlorination followed by hydrolysis :



↳ commercial method.

Benzaldehyde

(iii) By Gatterman - Koch reaction :



Benzene

Benzaldehyde.

Preparation of Ketone :

1). From acyl chlorides :

$$2R\text{-}Mg\text{-}X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$

$$2R'\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl + R_2Cd \longrightarrow 2R'\text{-}\underset{\underset{O}{\|}}{C}\text{-}R + CdCl_2$$

Acyl chloride

Ketone

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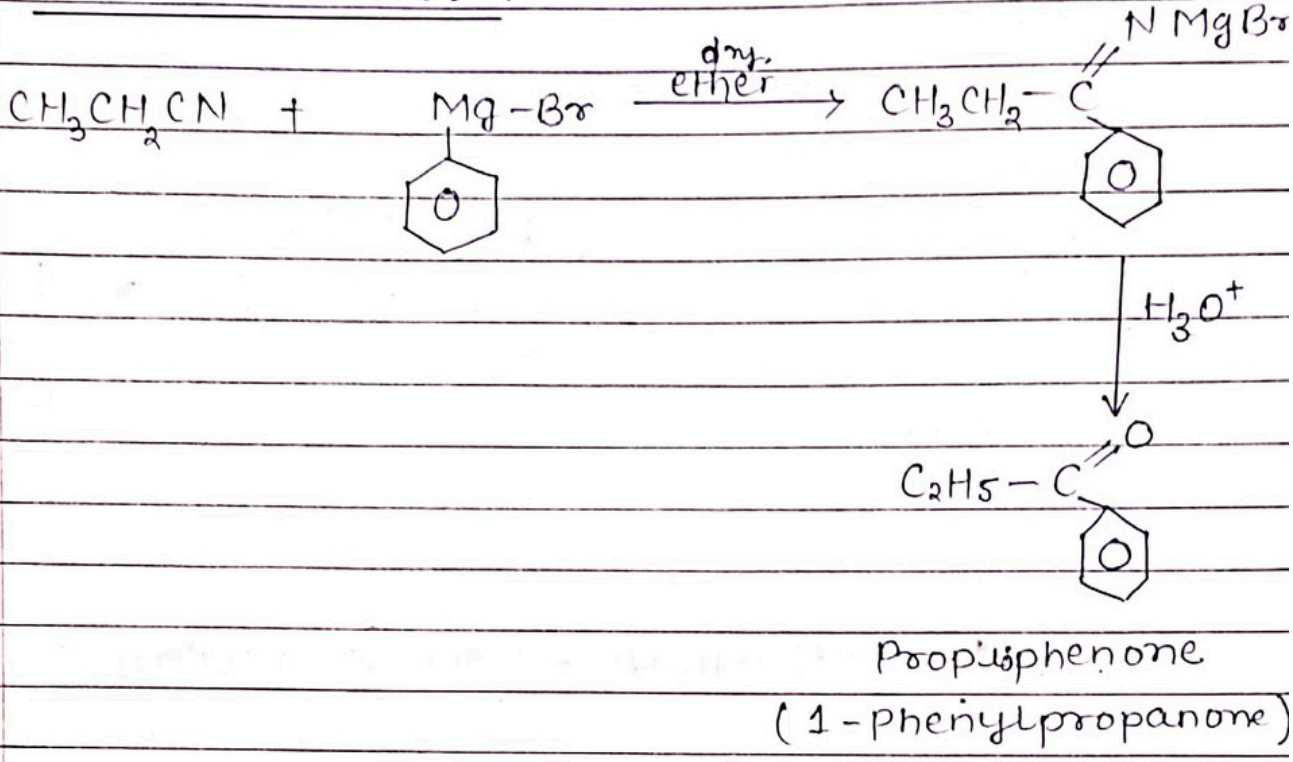
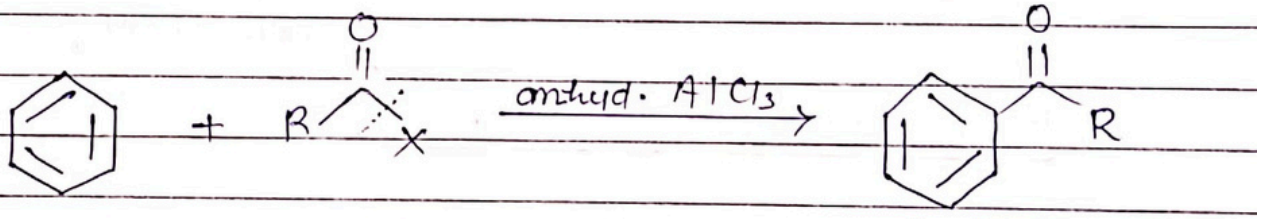
2). From nitriles :



Propiophenone
(1-Phenylpropanone)

3). From Benzene or substituted benzene:

* Friedel Crafts Acylation



Acetophenone.

Physical Properties :-

↳ HCHO is gas ; CH_3CHO is volatile liquid at room temperature, while other aldehyde and ketone are liquid or solid at room temperature.

↳ B.P of aldehyde and ketone are higher than hydrocarbon and ether of comparable molecular mass but lower than alcohol.

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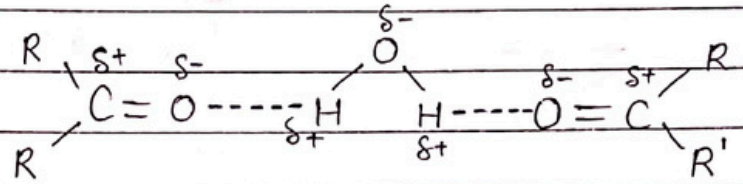
Note:
* Dipole-Dipole interaction between aldehyde and ketone is stronger than ether and hydrocarbon.

* Alcohols have hydrogen bonding which aldehyde and ketone lacks.



↳ Lower aldehyde and ketone are miscible in H_2O because of H-bond formation.

↳ but as the number of alkyl group increases hydrophobic nature increase and solubility decreases.

↳ Benzene, chloroform, CH_3OH, ether etc also dissolve in aldehyde and ketone in them.

↳ Lower aldehyde have sharp pungent odors. but as the number of C increase pungent smell decreases and more fragrant.

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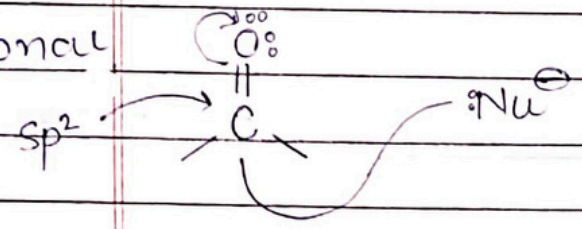
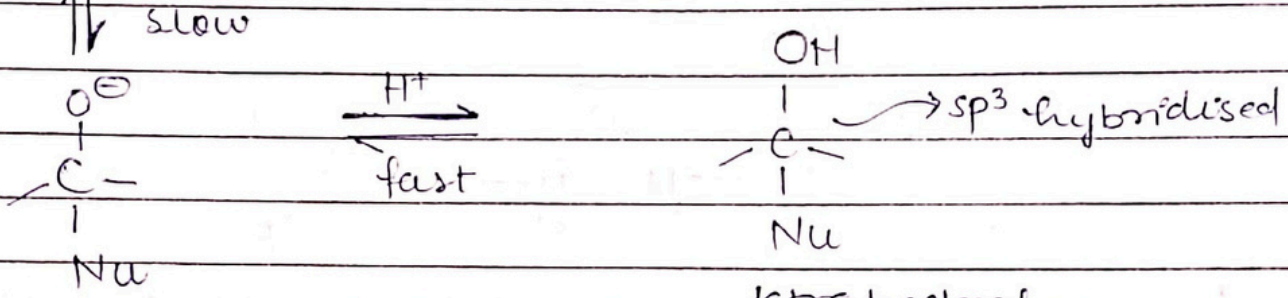
Chemical Reactions :-

Trigonal

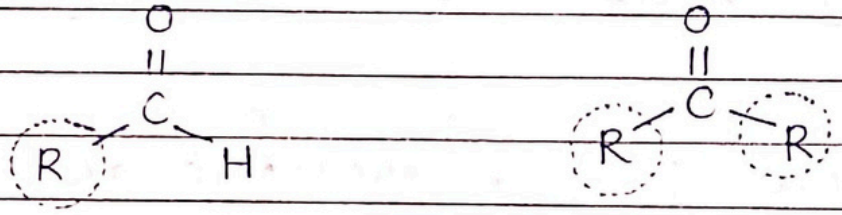


Mechanism :



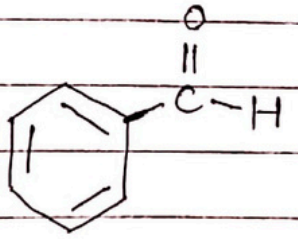
tetrahedral.

Reactivity :



As compared to ketones, aldehydes are more reactive towards nucleophilic addition reaction because of having less steric hinderance than ketone.

Note :- Benzaldehyde due to the resonance do not show not show nucleophilic Addition reaction effectively.



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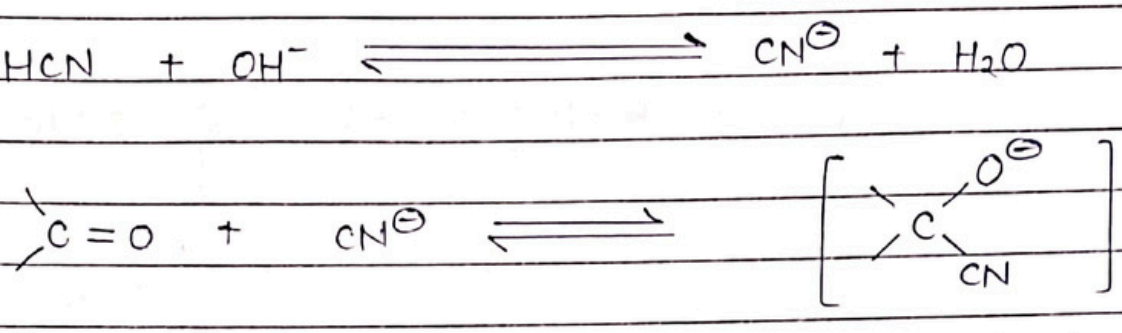
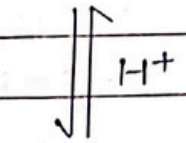
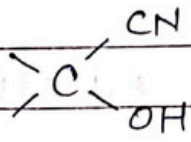
(a) Addition of hydrogen cyanide (HCN):



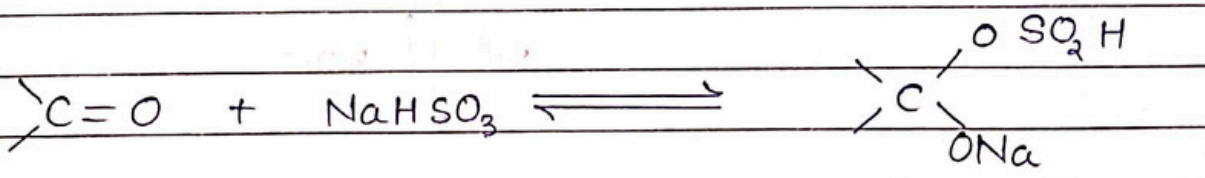
tetrahedral intermediate



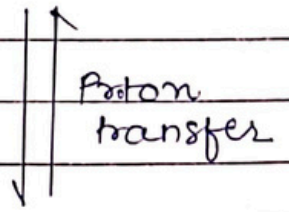


cyanohydrine

(b) Addition of sodium hydrogensulphide:-

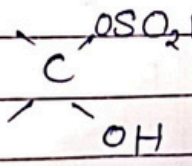


→ equilibrium is toward right in case of aldehyde but equibrium is toward left in case of ketone.



↓

due to steric hinderance.



→ treating with dilute mineral acid or alkali, it gives back Aldehyde or ketone.

↳ Used for purification and separation of aldehyde

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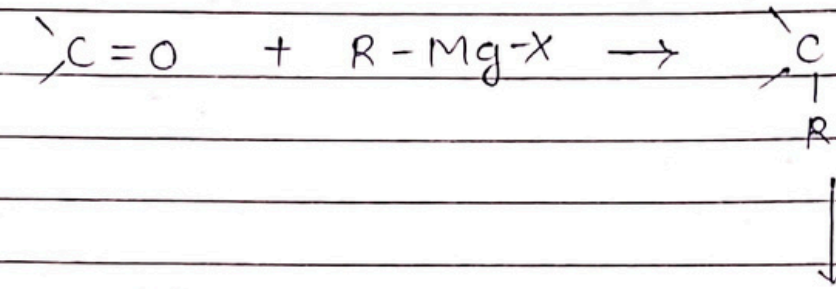
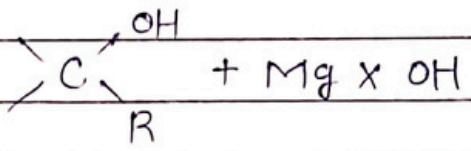
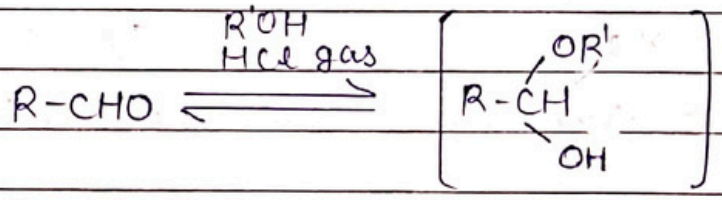
(c) Addition of Grignard reagent:



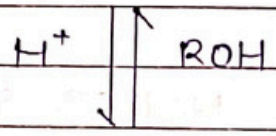
HCHO → 1° alcohol
RCHO → 2° alcohol
R-C(=O)-R → 3° alcohol.

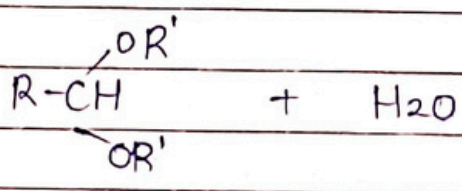


(d) Addition of alcohols:

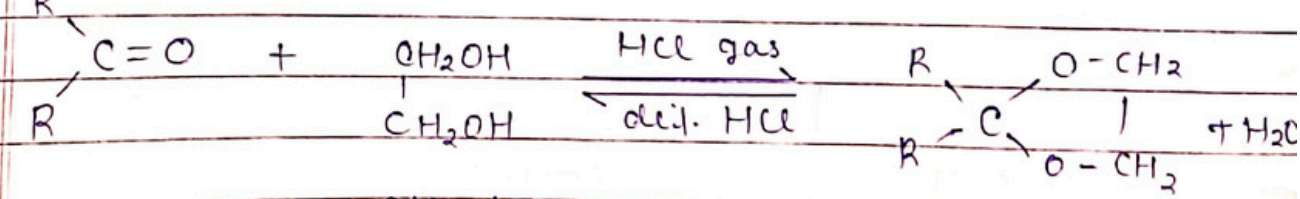


Hemiacetal





Acetal



ethylene glycol

ethylene glycol Ketal

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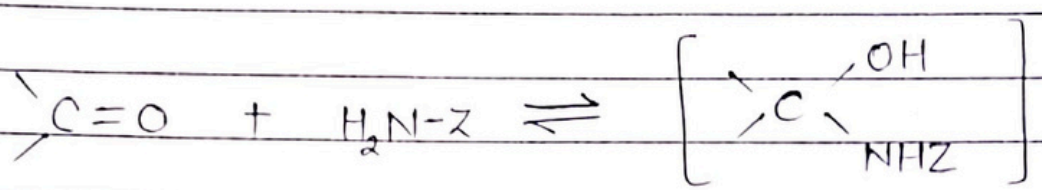
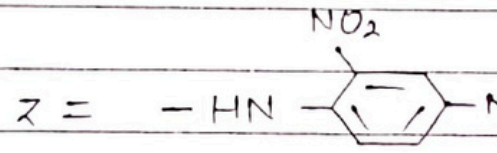
(c) Addition of ammonia and its derivatives :



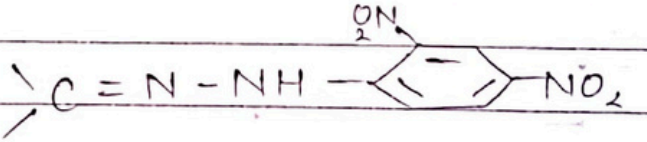
$$\text{>C=O} + H_2N\text{-}Z \rightleftharpoons \left[\text{>C}(OH)(NHZ)\right] \downarrow \text{>C=N-Z} + H_2O$$

Z = H , R , -OH , $-NH_2$ etc..

Note: * When Z = R , Product will be **Schiff's base** or Substituted Imine

When Z =  , product will be

2,4-dinitrophenyl hydrazone.



2,4-DNP-derivative are yellow, orange or red solid useful for characterisation of aldehyde and ketone.

2,4-DNP Test

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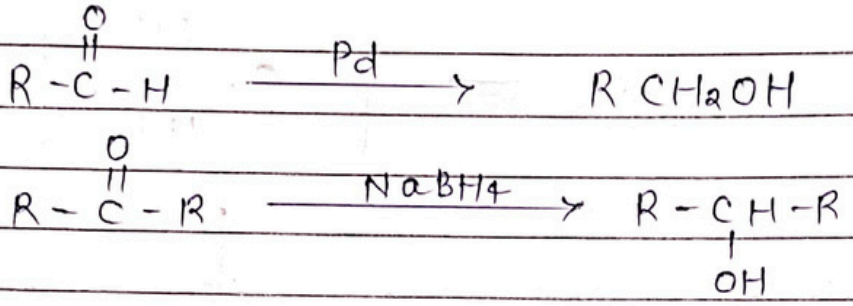
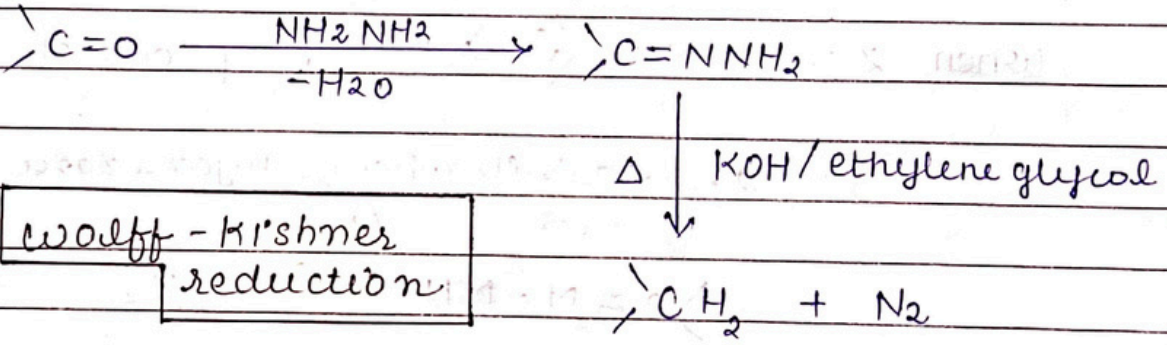
2. Reduction:

(i) Reduction to alcohol:



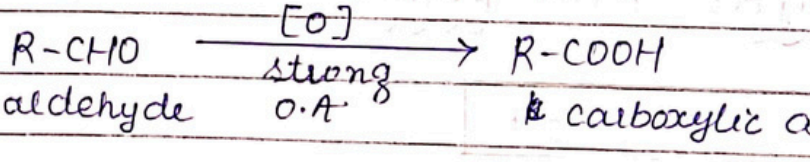
(ii) Reduction to hydrocarbon:

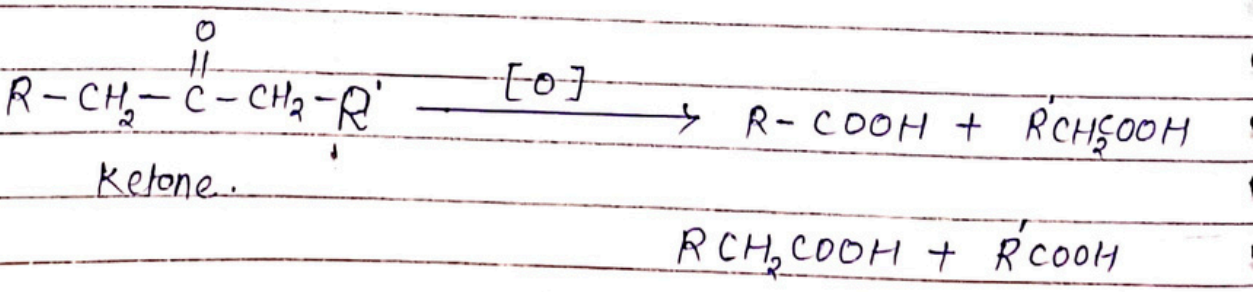
* Clemmenson reaction.



* Wolff-Kishner reduction

3. Oxidation:





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↳ aldehyde can be oxidised by use of weak oxidising Agent but ketones do not.

↳ Ketones are oxidised under vigorous condition.

(i) * Tollen's test :

↳ Ammoniacal Silver nitrate solution $[2Ag(NH_3)_2NO_3]$

↳ silver mirror test.

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow RCOO^- + 2Ag + 2H_2O + 4NH_3$$

* Note: [Tollen's reagent gives No result with ketone.]

(ii) Fehling's test :

↳ Ketones do not show any result with Fehling's test.

Aldehyde shows result but ketones do not. and aromatic alde

* Fehling's Reagent

Fehling's solution A + Fehling's solution B

A: $[CuSO_4]$ aq soln

Alkaline Roschelle salt: $NaKC_4H_4O_6 \cdot 4H_2O$

sodium potassium tartrate

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$$R\text{-}CHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + Cu_2O + 3H_2O$$

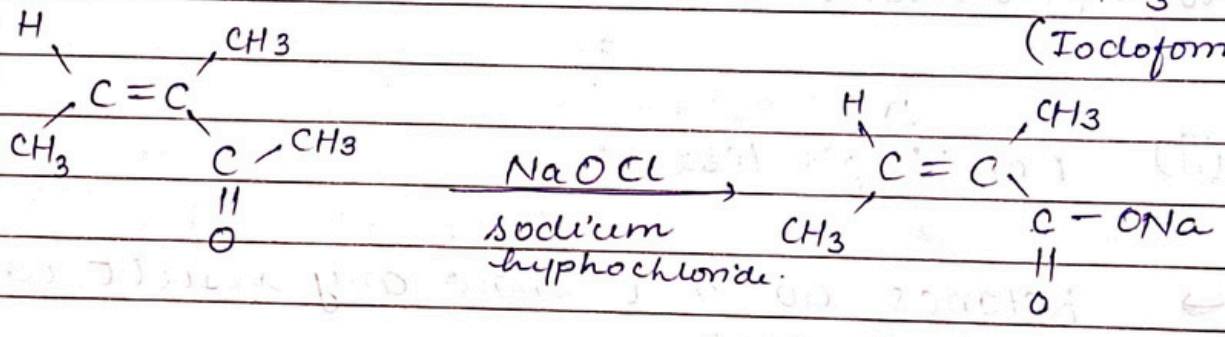
Red brown ppt.

(iii) Oxidation of methyl ketones by haloform reaction:

↝ Shown only by those aldehyde or those ketones that have atleast one $-CH_3$ group to $>C=O$ group.

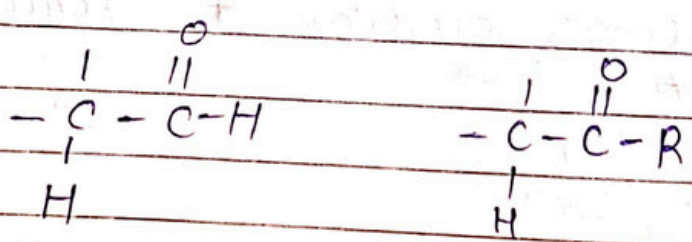
$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3I_2 + 4NaOH \longrightarrow 3NaI + R-\overset{O}{\overset{\|}{C}}-ONa + CHI_3$$

(Iodoform)



4. Reaction due to α-hydrogen:

↳ Only those aldehyde / ketone that have atleast 1 α-hydrogen will show + $CHCl_3$



α-hydrogen.

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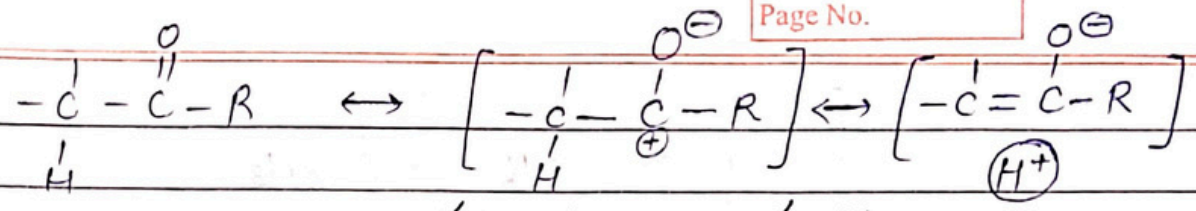
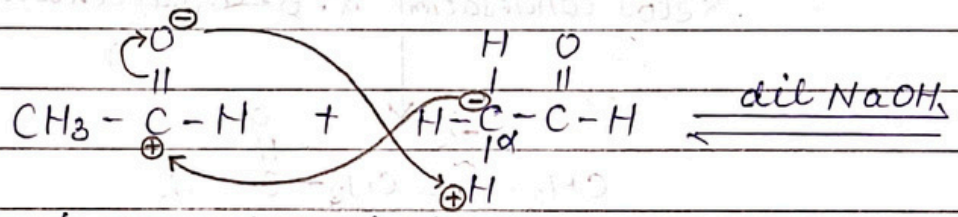


R = alkyl group / aryl group / -H

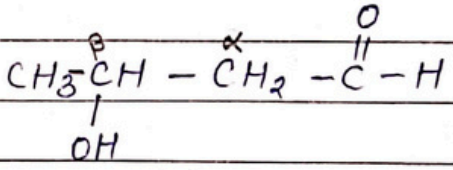
▸ more easily proton is donated more acidic is the substance

Acidity of α-hydrogen atoms of carbonyl compound is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.

(1°) aldol condensation :



(ethanal) (ethanal)

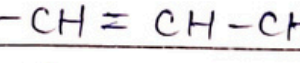


β-hydroxybutanal

[Aldol]

α,β- unsaturation | Aldol condensation

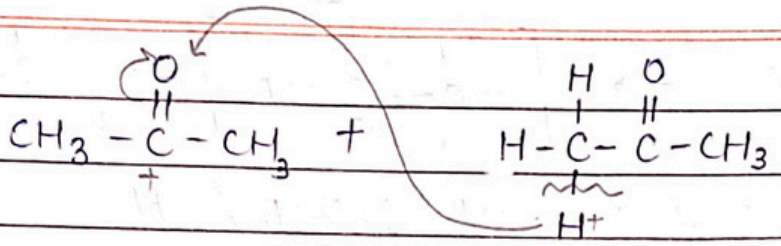
Δ ↓ -H2O

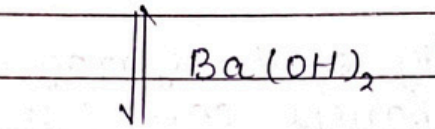


but-2-enc-1-al

[Aldol condensate]

α,β - unsaturated aldehyde

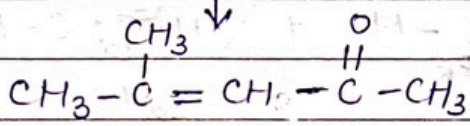




(Ketol)

β-hydroxy-β-methyl pentan-2-one

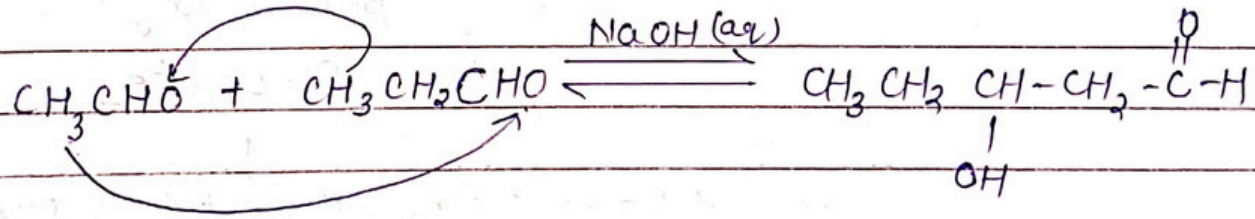
Ketol condesation | α-β-unsaturation

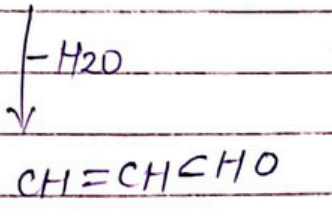


4-methylpent-3-en-2-one.

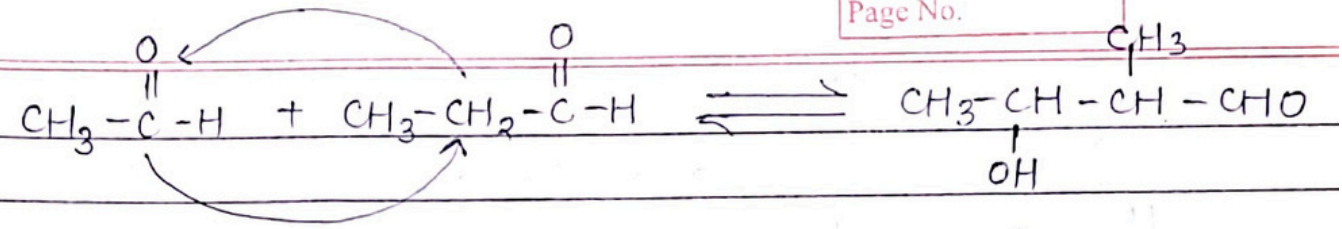
(ii) Cross aldol condensation

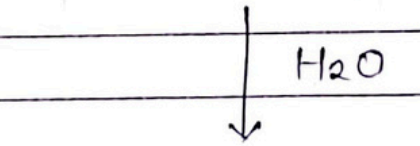
case (1)

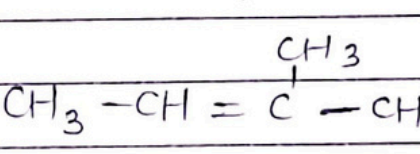


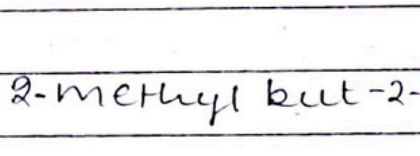


Pent-2-en-1-al.

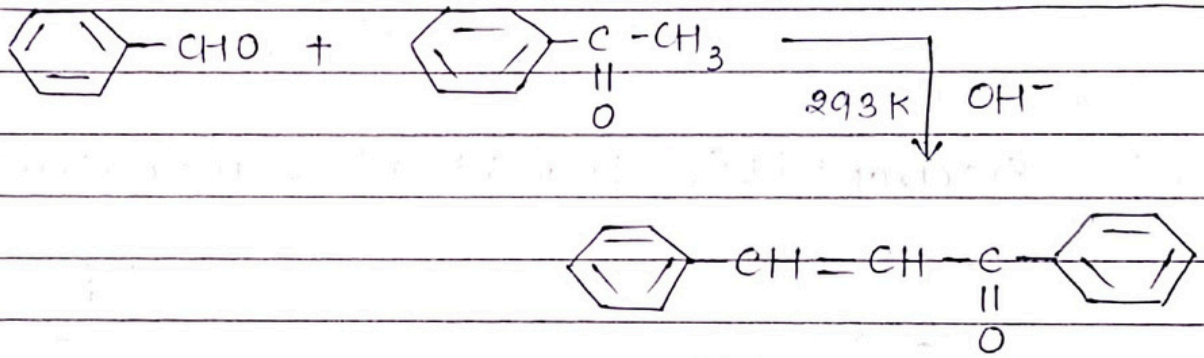








2-Methyl but-2-en al



1,3-Diphenylprop-2-en-1-one

(Benzalacetophenone)

5 (i) **Cannizzaro reaction**

↳ aldehyde which do not have α-hydrogen atom

↳ undergo self oxidation and reduction (disproportionation) reaction on heated with concentrated alkali.

do not contain α-H.

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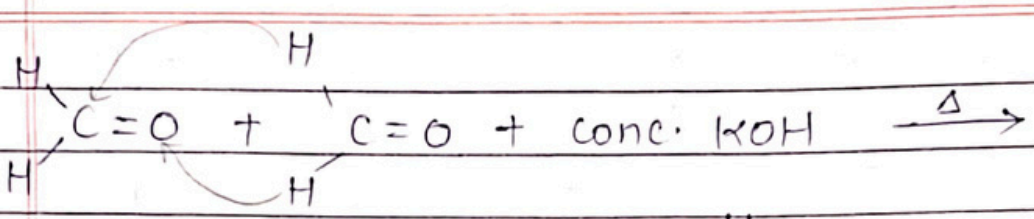
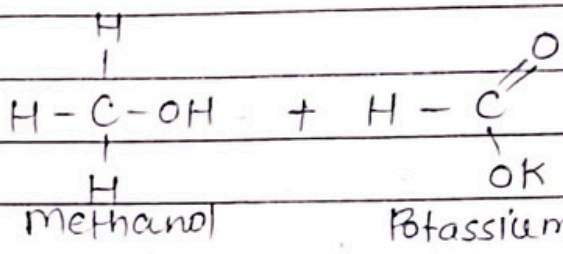
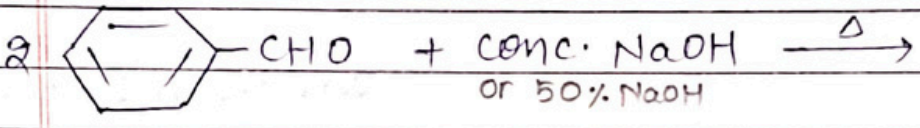


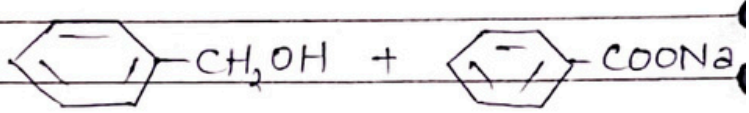
[Formaldehyde]



Methanol Potassium formate



or 50% NaOH



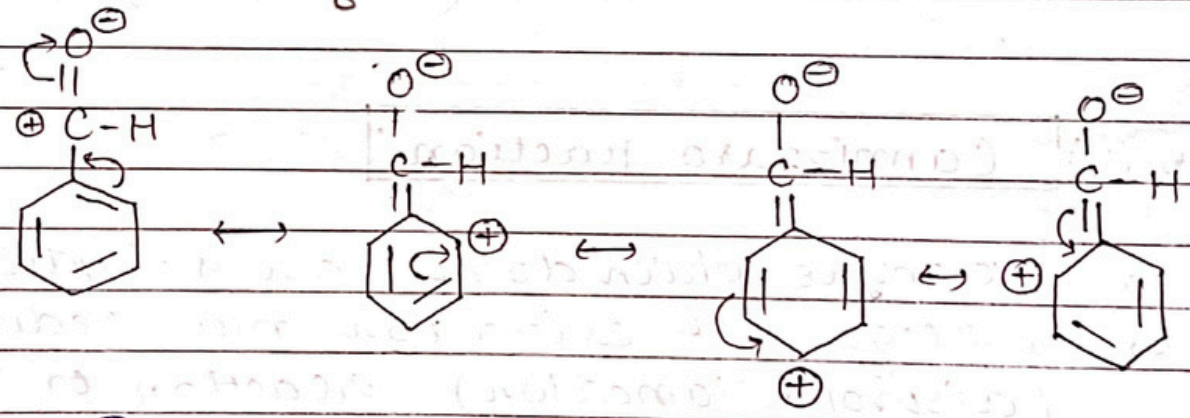
Benzyl alcohol Sodium benzoate

(ii) Electrophilic substitution reaction:

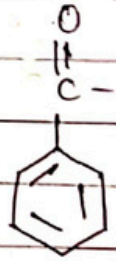
↳ deactivating
↳ m-directing

m-nitro benzaldehyde

Reason:



$NO_2^{\oplus}$ is an electrophilic and feel steric hinderance at o- & p-position.
∴ it will attack on the metaposition.



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Uses of Aldehydes and Ketones :

- Solvents
- Starting material
- formalin (formaldehyde 40%) - preserve biological specimen
- HCHO in bakelite.
- CH_3CHO (acetaldehyde) : acetic acid, ethyl acetate, vinyl acetate, drugs etc.
-  : perfumes and drugs.
- flavouring and sweetning agent.

Nucleophilic (Aldehydes and Ketones) Addition Reaction.

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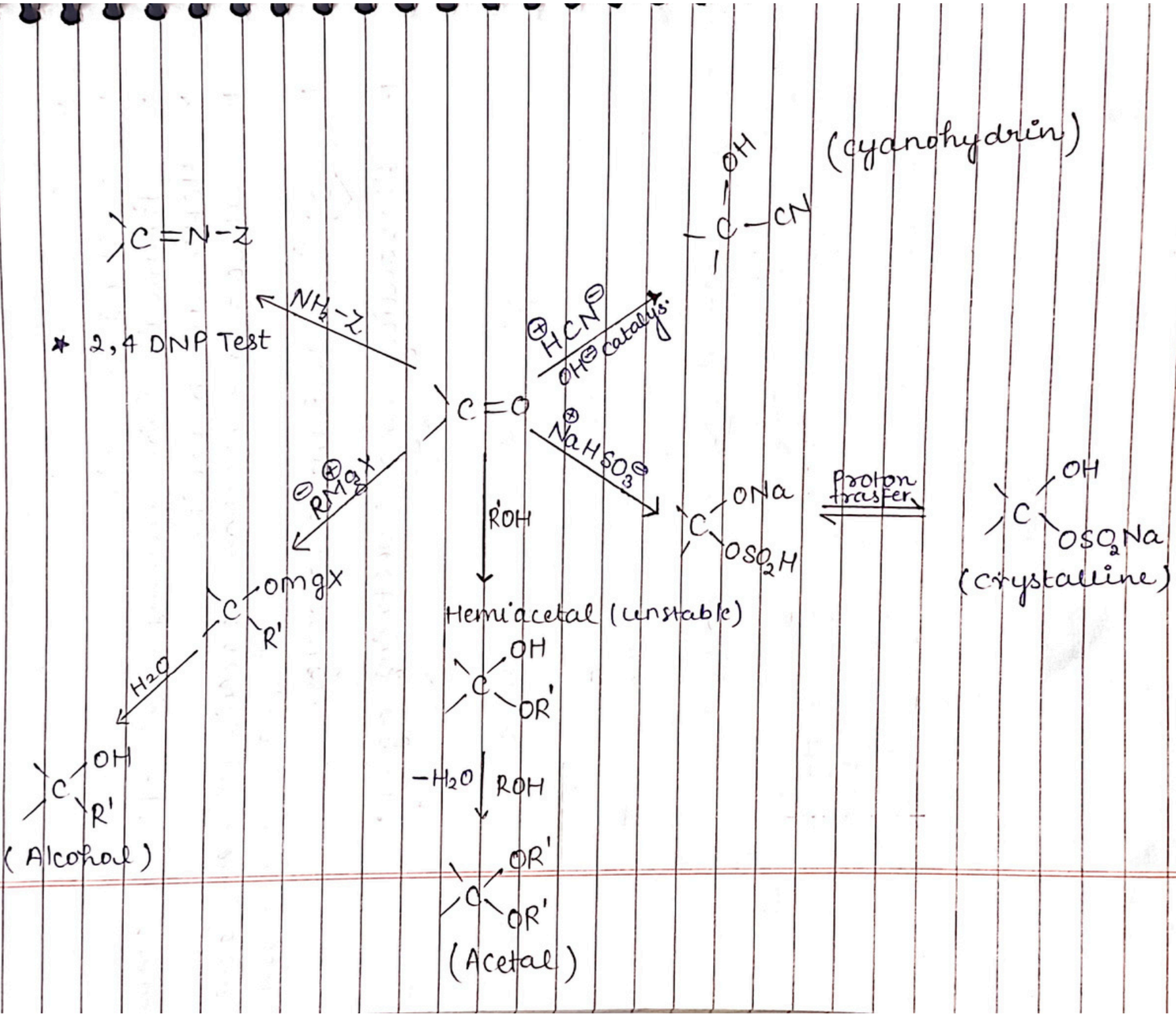
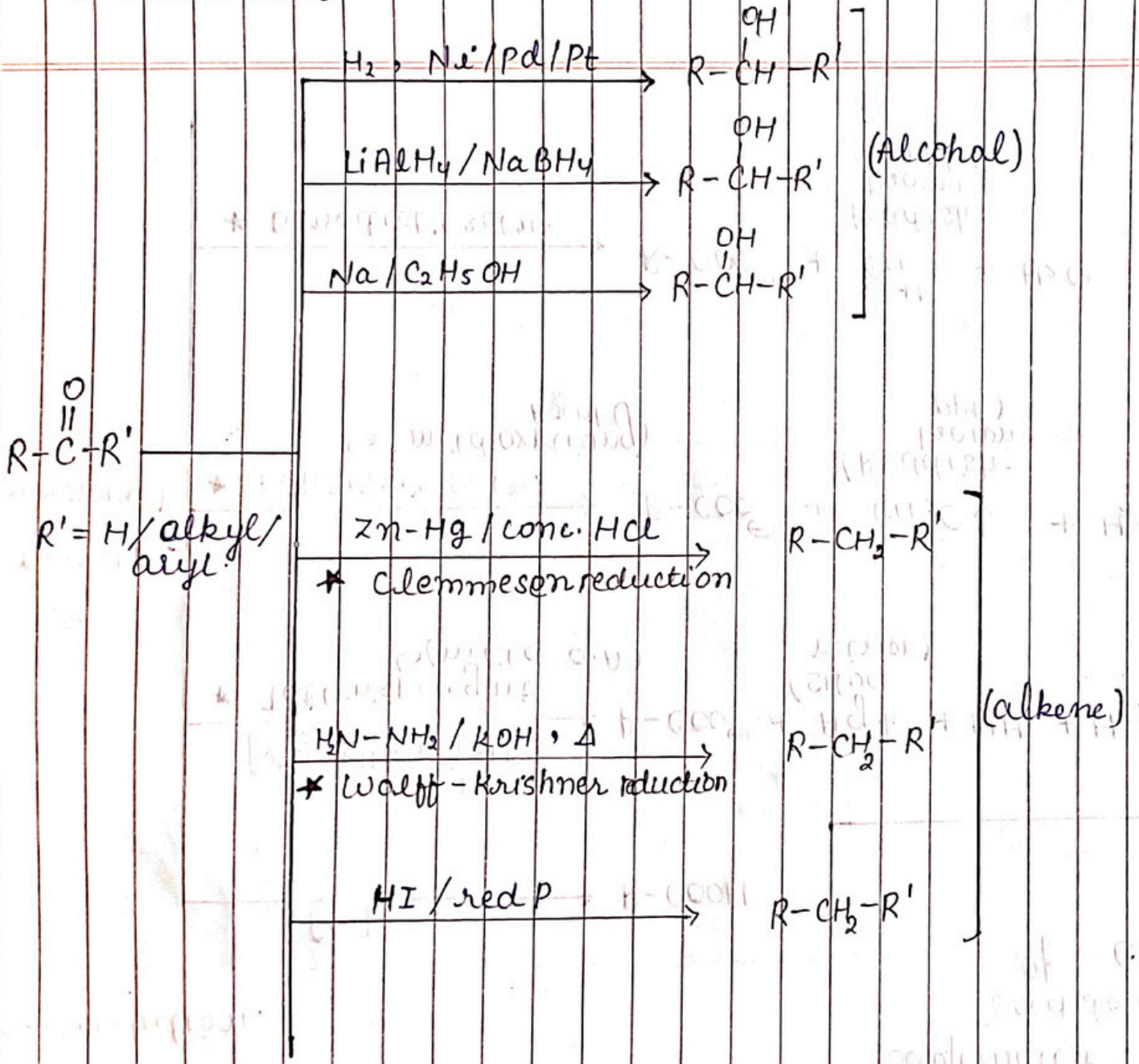


2. Reduction



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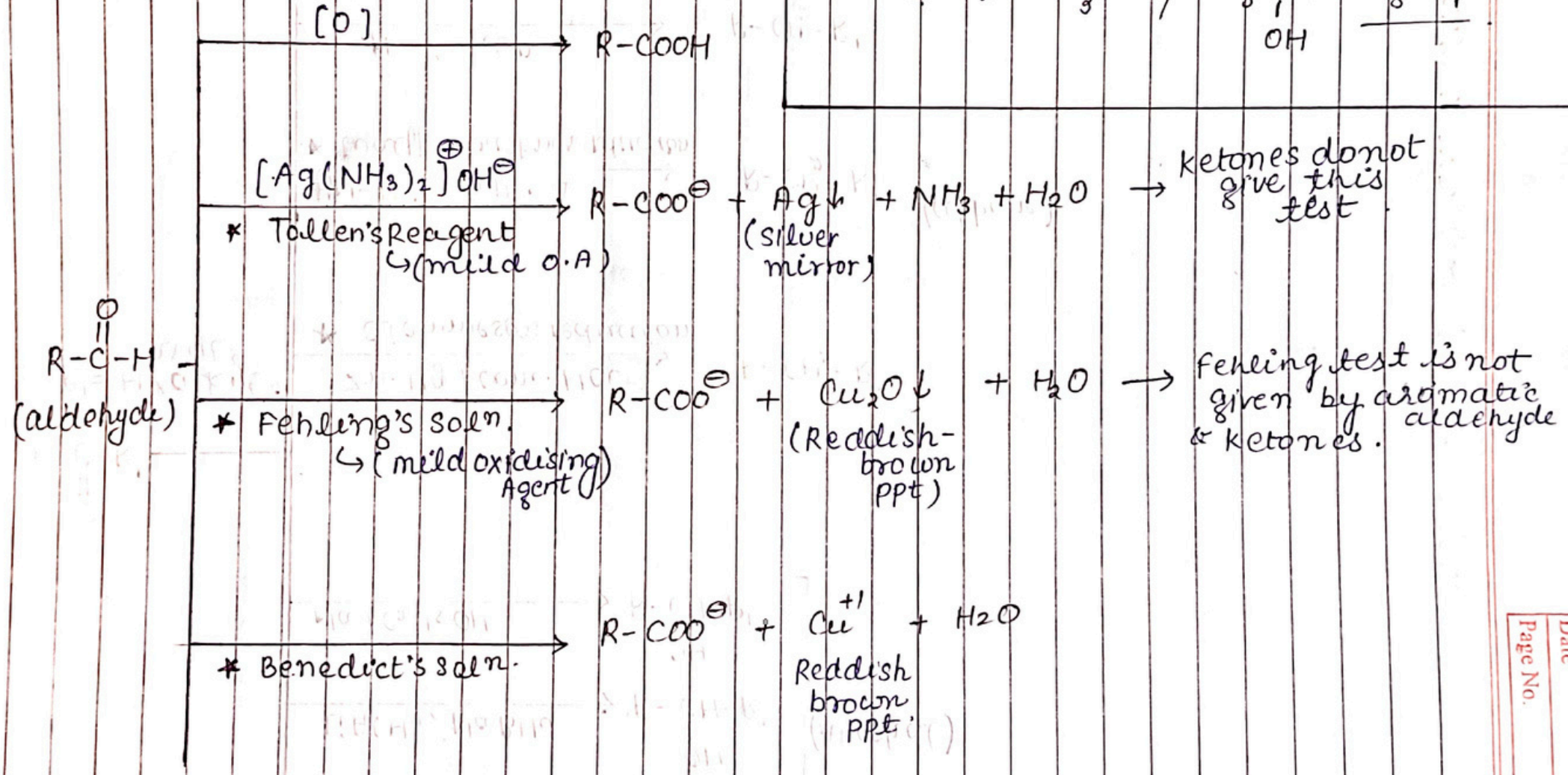
3. Oxidation:



Iodoform test:

used to distinguish the presence of $CH_3-\overset{O}{\overset{\|}{C}}-$ / $CH_3-\underset{OH}{\underset{|}{CH}}-$ group.

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Chemical Properties of carboxylic Acid :