ORGANIC CHEMISTRY-III

UNIT 5 NOTES

REACTION OF SYNTHETIC IMPORTANCE

- METAL HYDRIDE REDUCTION
- CLEMMENSEN REDUCTION
- BIRCH REDUCTION
- WOLFF KISHNER REDUCTION
- OPPENAEUR OXIDATION
- DAKIN REACTION
- BACKMANNS REARRANGEMENT
- SCHMIDT REARRANGEMENT
- CLAISEN-SCHMIDT CONDENSATION

IMPERFECT PHARMACY

Reactions Of Synthetic Importance

- Reactions of synthetic importance are chemical reactions that are widely used in the synthesis of complex molecules, especially in organic chemistry & drug development.
- Examples includes :

① Metal Hydride Reduction
② Cleemensen Reduction
③ Birch Reduction
④ Wolf - kishner Reduction
⑤ Oppenaur Oxidation Reaction
⑥ Dakin Reaction
⑦ Backmann Rearrangement reaction
⑧ Schmidt Rearrangement reaction
⑨ Clairsen Schmidt Condensation Reaction

METAL HYDRIDE REDUCTION

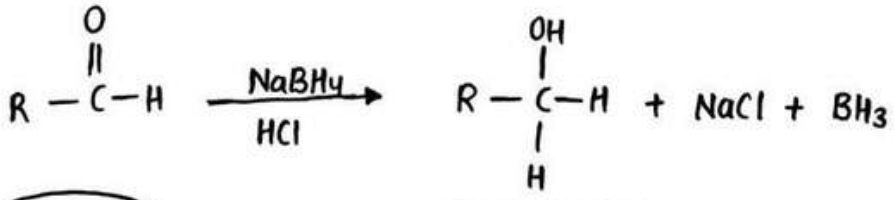
Metal Hydride reduction refers to the use of metal hydride compounds, particularly, sodium borohydride ($NaBH_4$), Lithium aluminium hydride ($LiAlH_4$) to reduce various organic compounds - mainly carbonyl - containing functional groups like aldehyde & ketones to alcohol.

Sodium Borohydride < Lithium Aluminium hydride

@ **Sodium Borohydride**

- It is milder reducing agent.
- Selectively reduces:
  - Aldehydes ⟶ Primary Alcohols
  - Ketones ⟶ Secondary Alcohols

Metal Hydride Reduction by $NaBH_4$

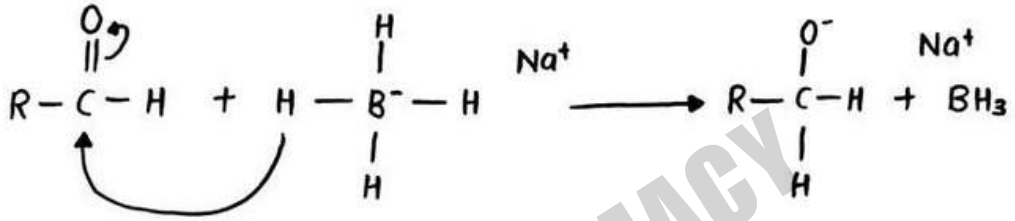


Aldehyde → Primary Alcohol

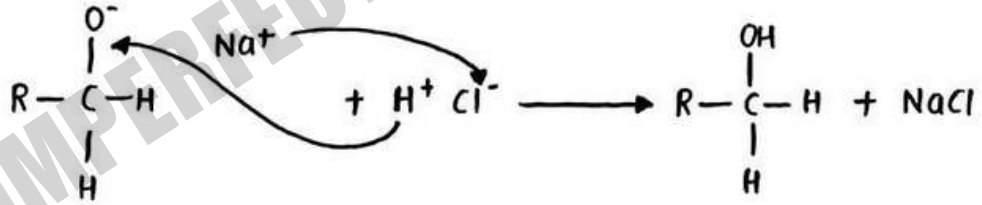
MECHANISM

It involves two step mechanisms:

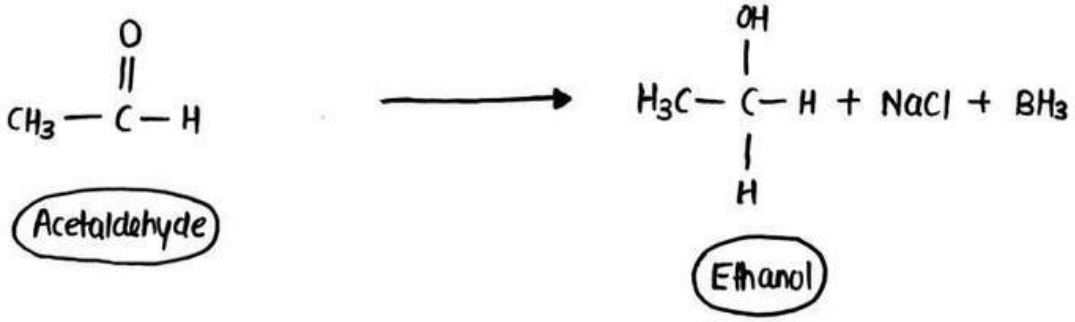
ⓘ **Step-I** : Nucleophillic attack by hydride.



ⓘⓘ **Step-II** : Protonation of Alkoxide ion.



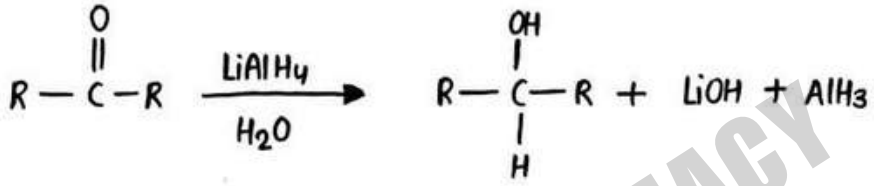
Example



ⓑ Lithium Alluminium Hydride

- It is a very strong reducing agent.
- It reduces : Aldehydes, ketones, esters, carboxylic acids, amides etc.

Metal Hydride Reduction by $LiAlH_4$

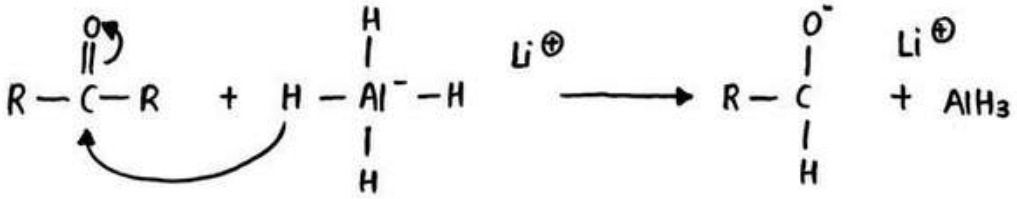


Ketone → Secondary Alcohol

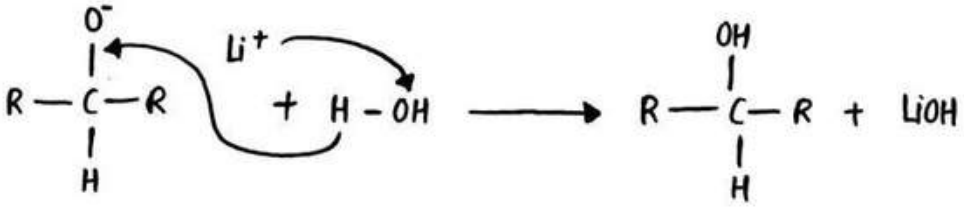
MECHANISM

It involves two step mechanism

- **STEP I :** Nucleophillic attack by hydride.



- **STEP II :** Protonation of Alkoxide Ion.



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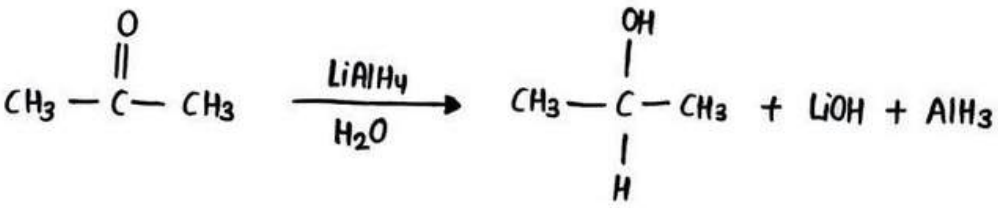
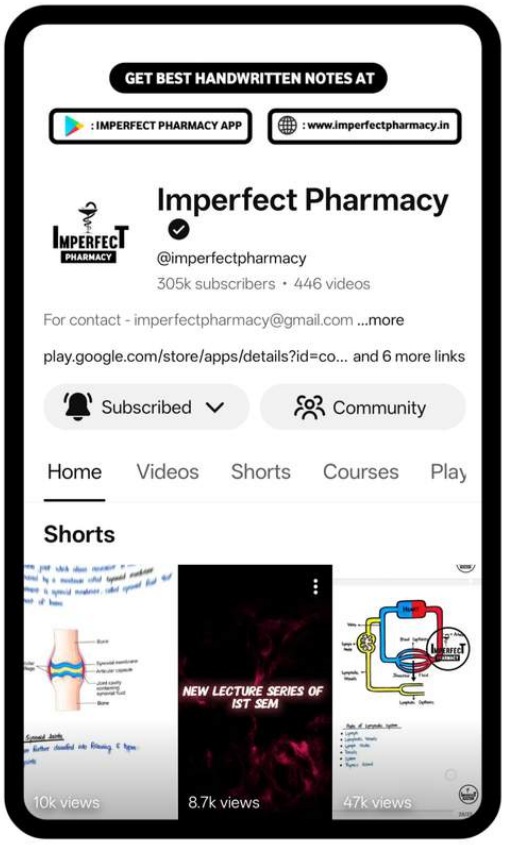
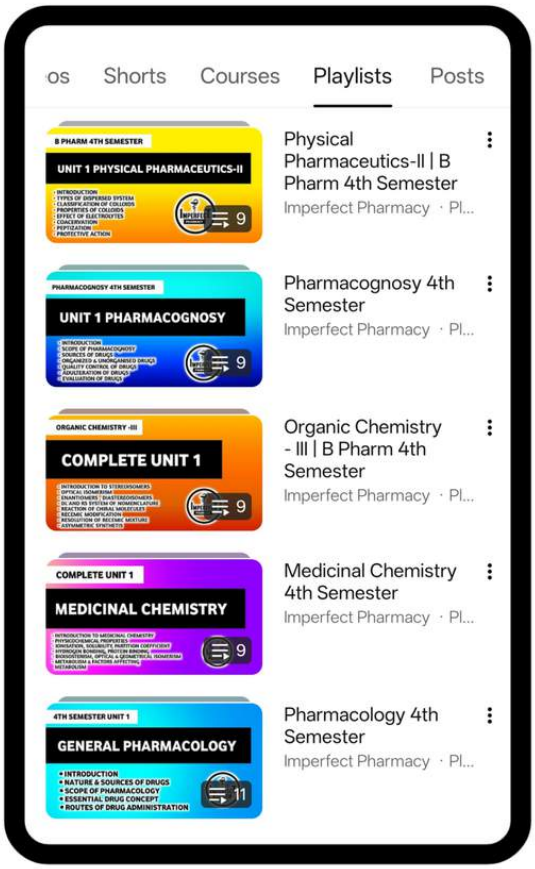


Acetone

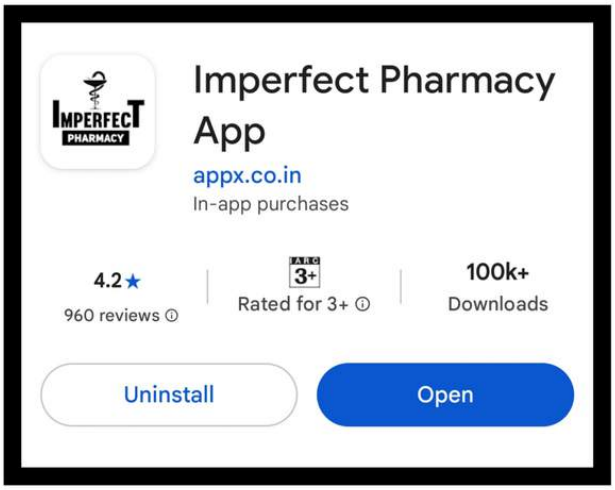
Propan-2-ol

FOR LECTURE VIDEOS VISIT OUR CHANNEL



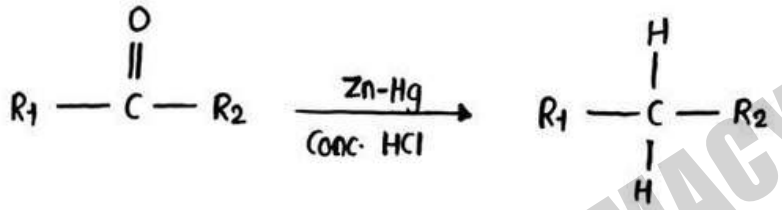


FOR MORE CONTENT : VISIT OUR APP



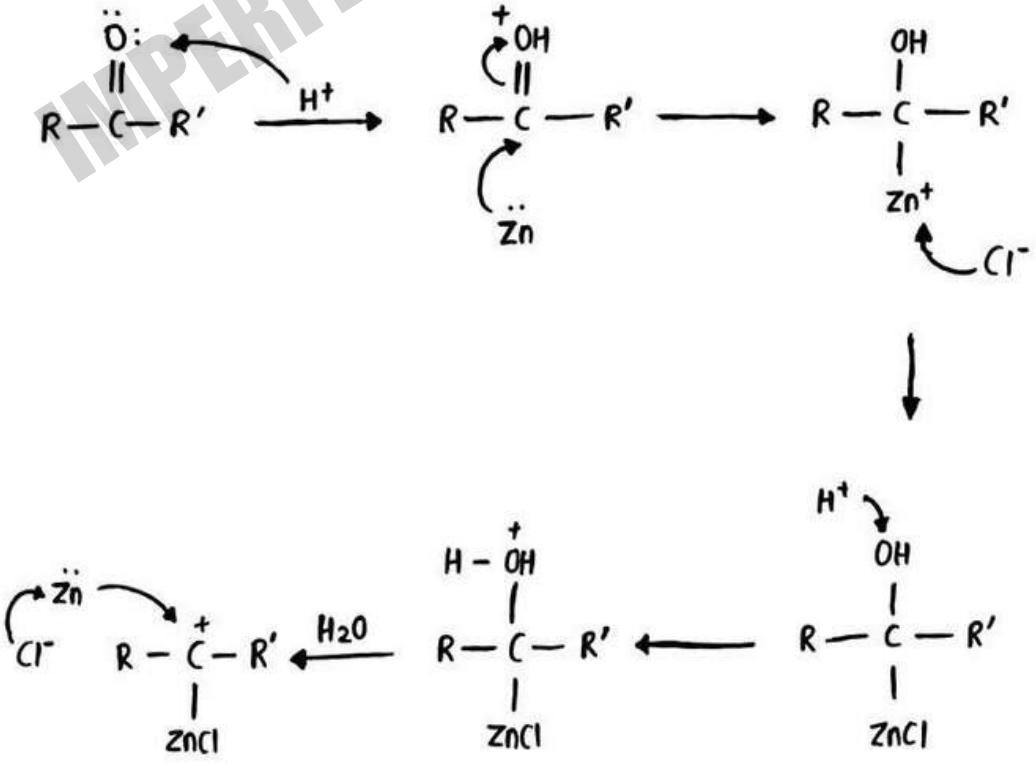
CLEMMENSEN REDUCTION

Clemmensen reduction is a chemical reaction used to reduce aldehydes or ketones to the corresponding alkanes using zinc amalgam (Zn- Hg) and, concentrated hydrochloric acid (HCl)



ketone — Alkane

MECHANISM



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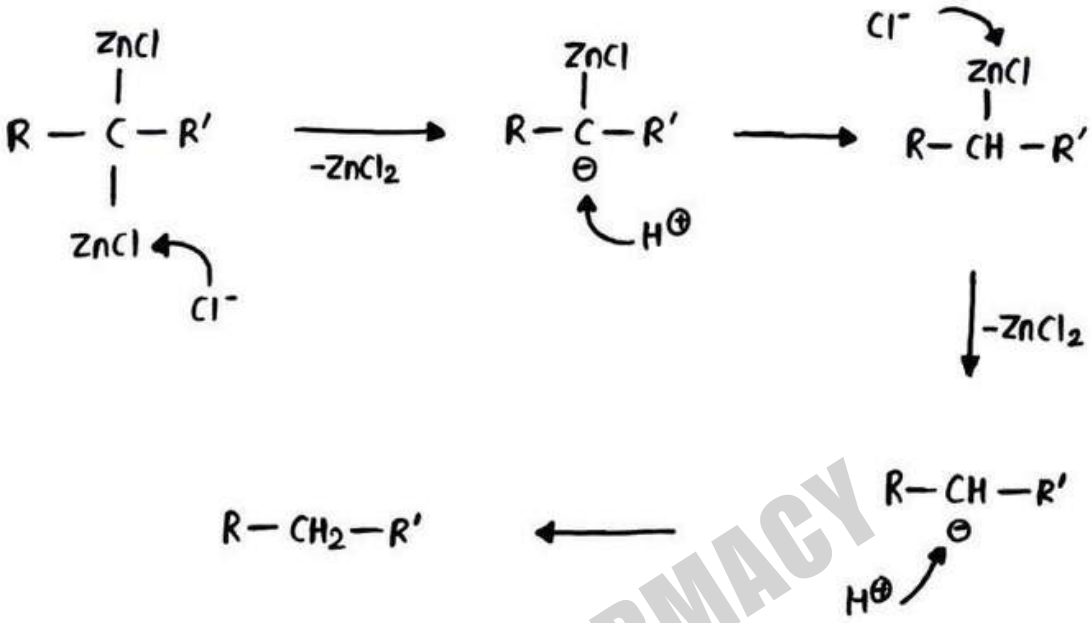
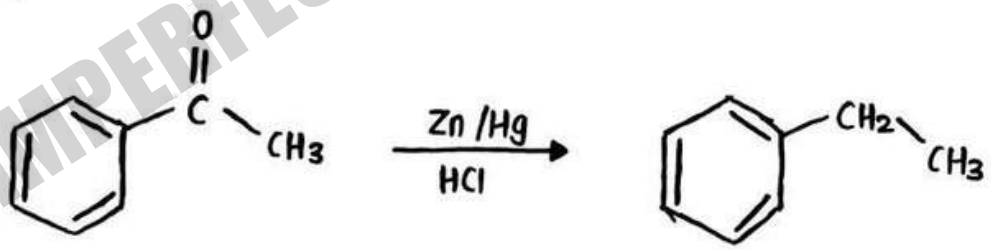


Example

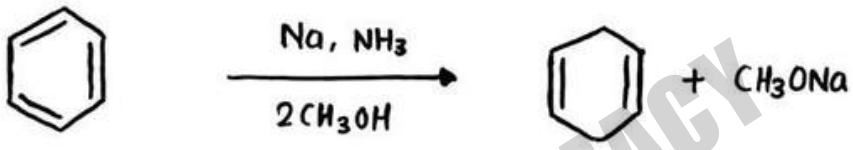


Acetophenone

Ethyl Benzene

BIRCH REDUCTION

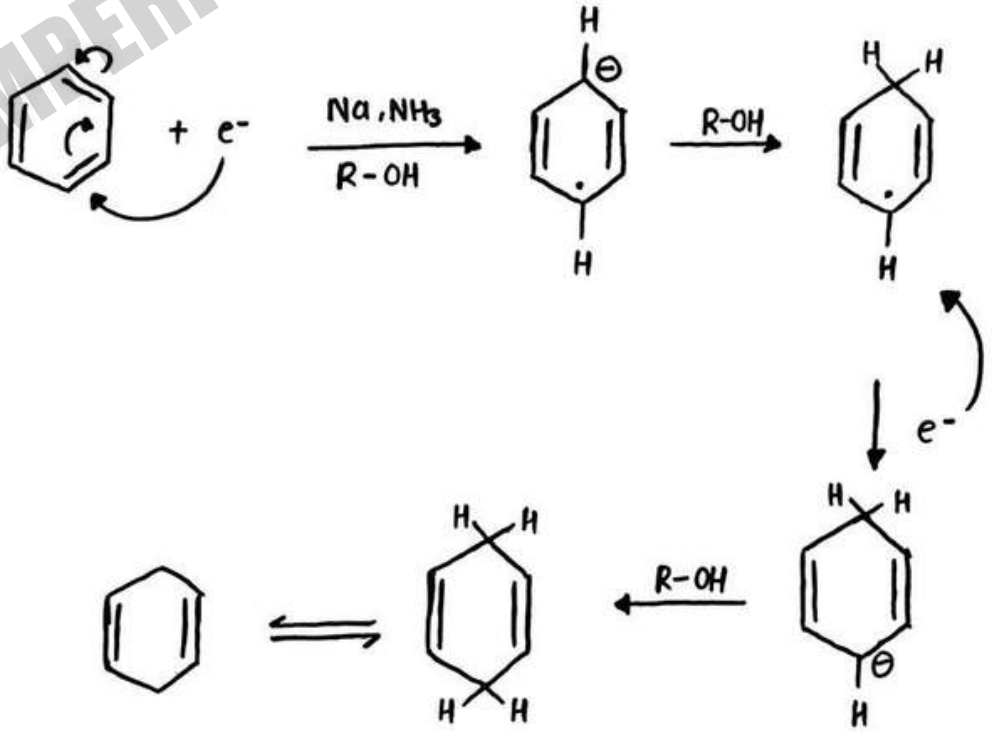
Birch reduction is a chemical reaction in which aromatic rings (like benzene) are partially reduced using alkali metals (like Na or Li) in liquid ammonia and an alcohol as a proton source.



Benzene

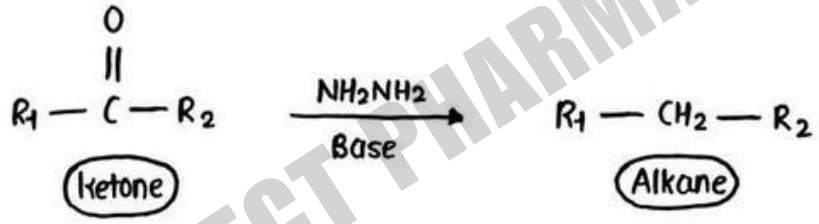
1,4 Cyclohexadiene

MECHANISM

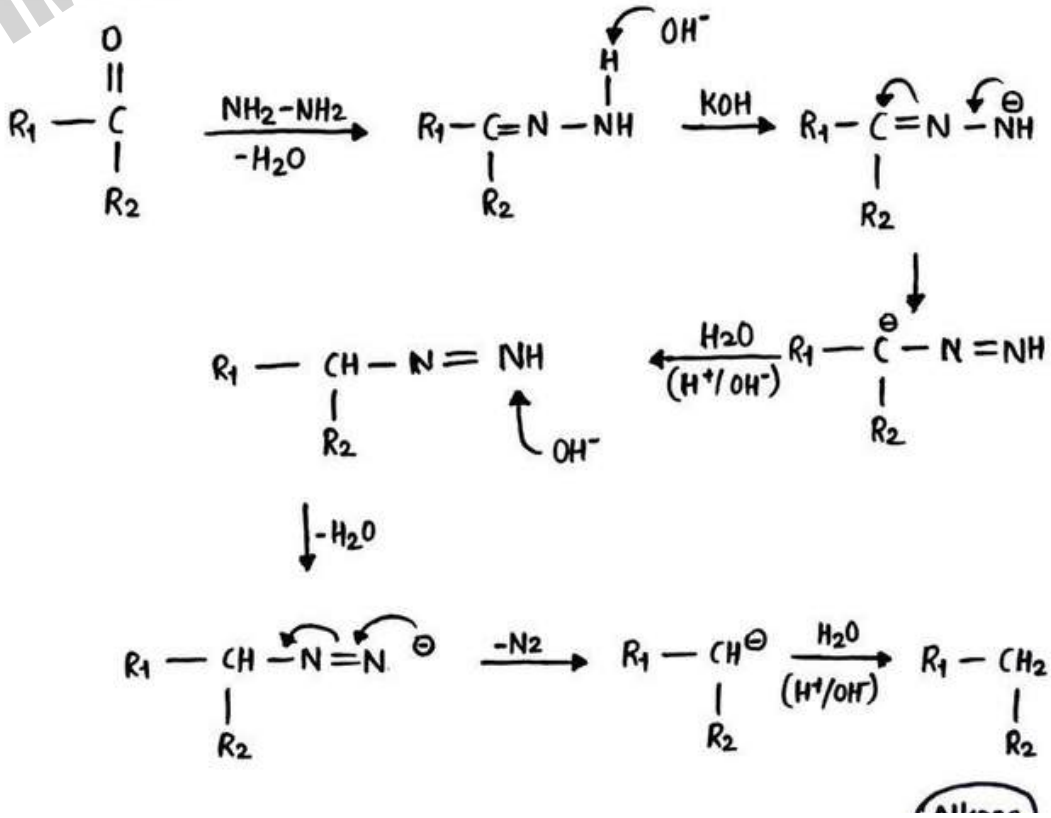


WOLFF KISHNER REDUCTION

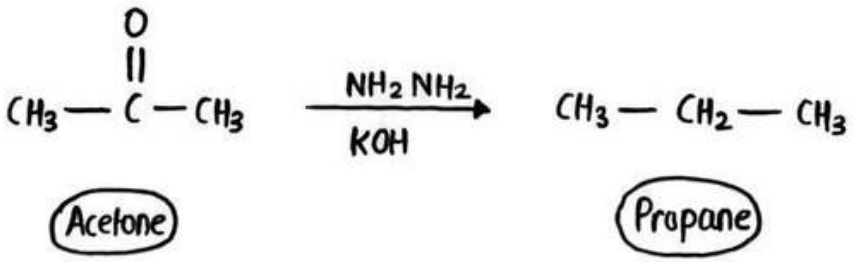
- Wolff Kishner Reduction is a chemical reaction used to reduce aldehydes or ketones to alkanes using Hydrazine (NH_2NH_2) & strong base under high heat.
- It was discovered independently by N. kishner in 1911 & L. wolff in 1912.
- It requires highly basic conditions, hence unsuitable for base sensitive substrates.



MECHANISM

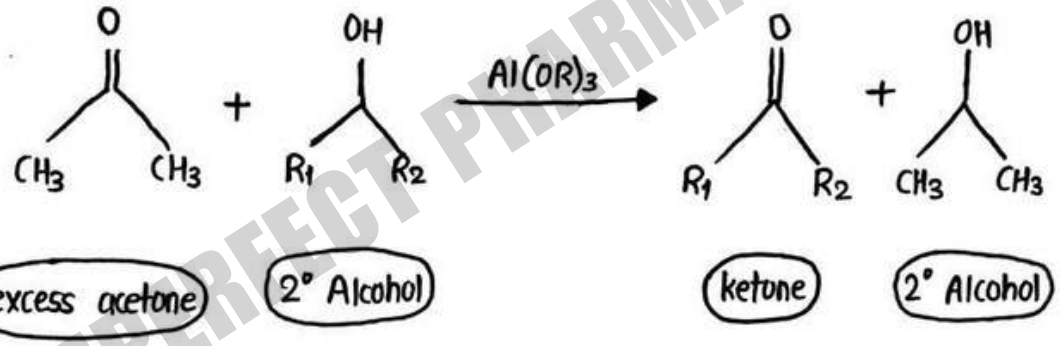


Example



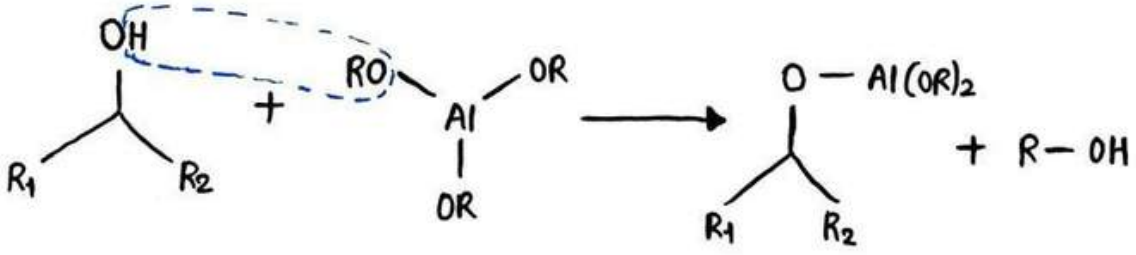
OPPENAUER - OXIDATION

- This reaction is named after Rupert Vikhor Oppenauer.
- Oppenauer oxidation is an organic chemical reaction used for selectively oxidizing secondary alcohols to ketones, using alumminium isopropoxide in excess acetone.
- It is an important reaction used in the synthesis of alkaloids, hormones, steroids & terpens.



MECHANISM

STEP I



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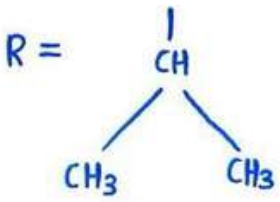
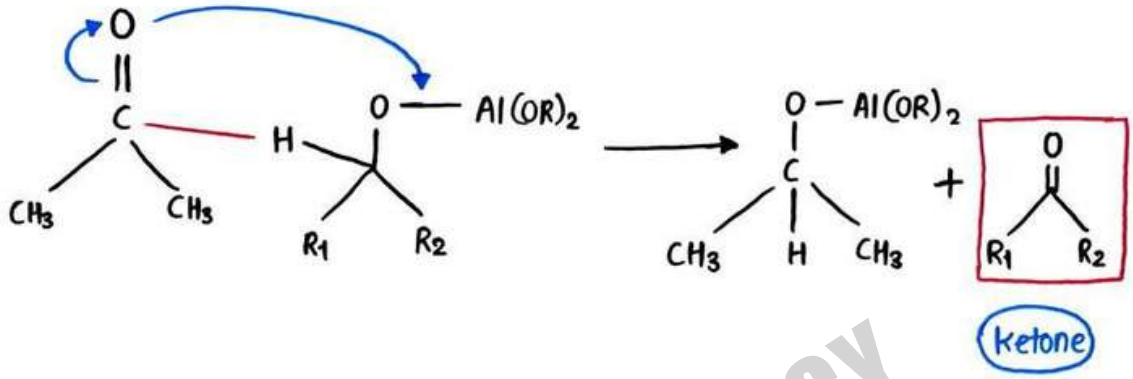
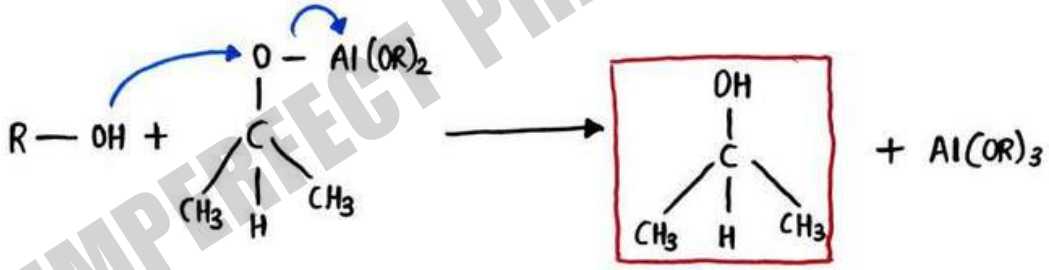


STEP II

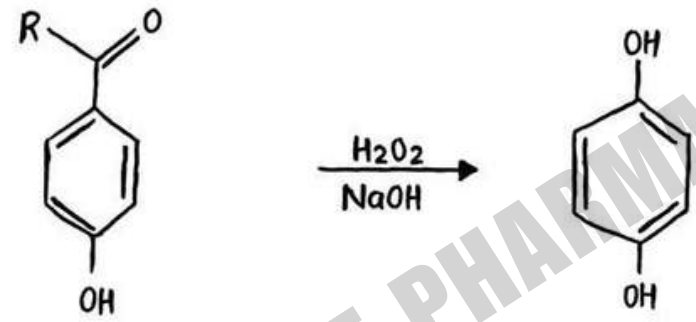


STEP III



DAKIN REACTION

The Dakin reaction is an organic reaction in which aromatic aldehydes or ketones (containing hydroxyl group at ortho or para position) are oxidized to phenols in the presence of hydrogen peroxide and a Base.

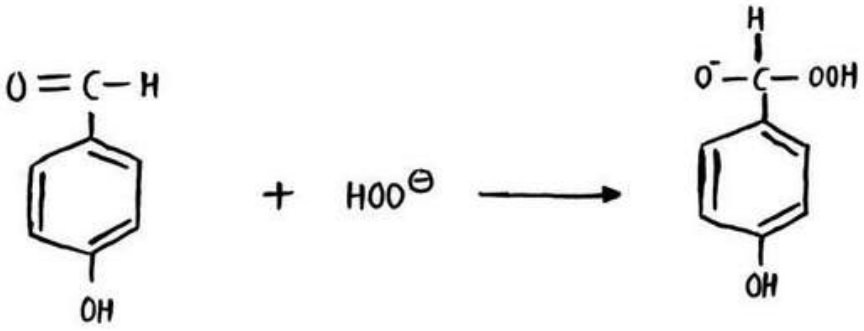


Aldehyde ketone

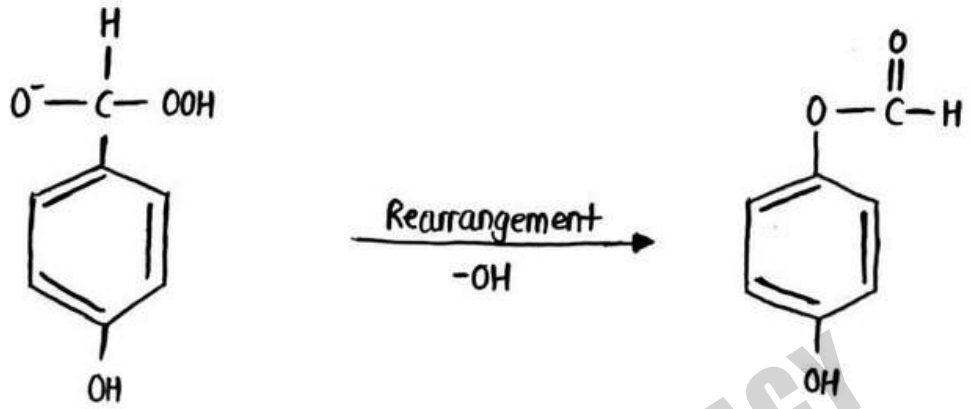
MECHANISM

STEP-I

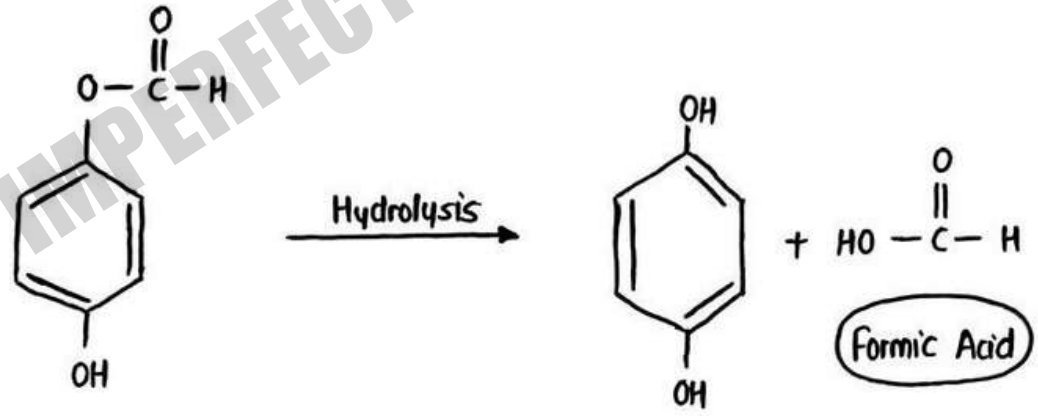
STEP-II



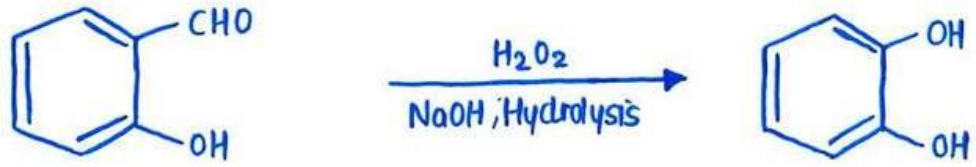
STEP-III



STEP-IV



Example

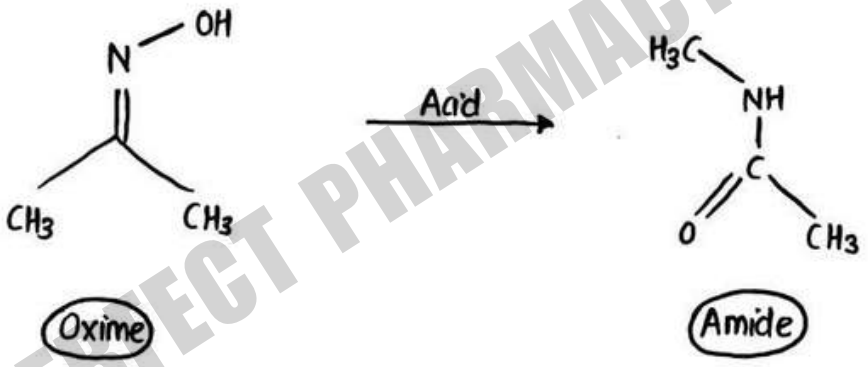


Salicylialdehyde

Catechol

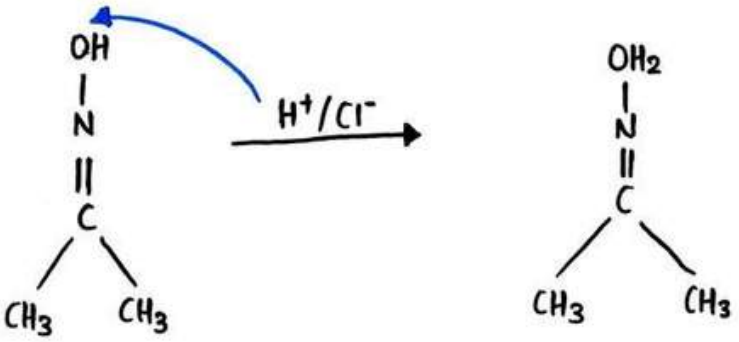
BACKMANN REARRANGEMENT

- The Backmann Rearrangement is a chemical reaction in which Oximes (derived mainly from ketones) are converted into Amides upon treatment with an acid catalyst or dehydrating agent.
- It involves a migration of an alkyl or aryl group from carbon to the nitrogen.



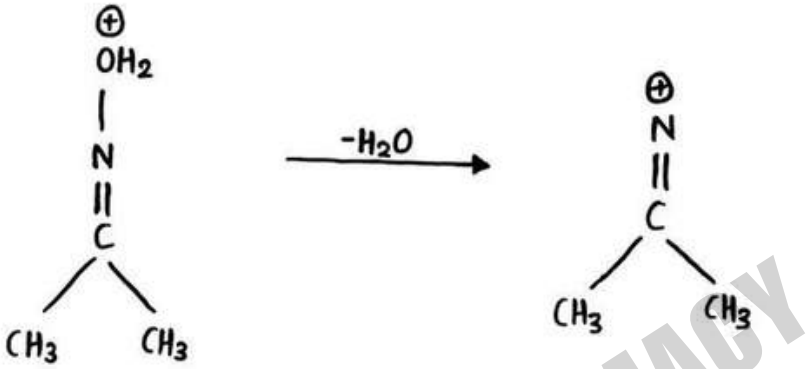
MECHANISM

- STEP-I : Protonation of oximes.



STEP -II

Loss of water.

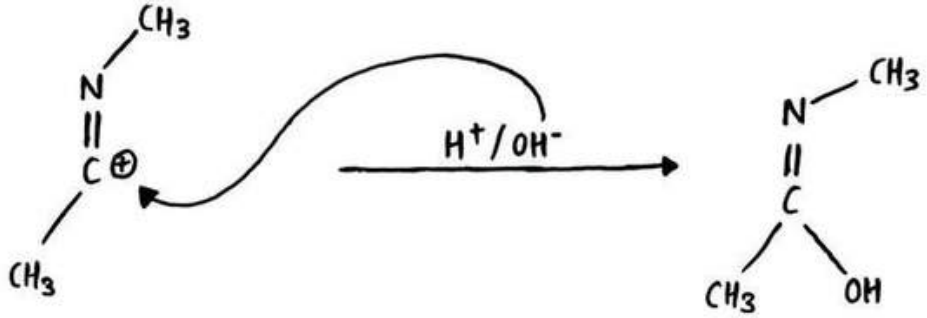


STEP -III

Rearrangement

STEP - IV

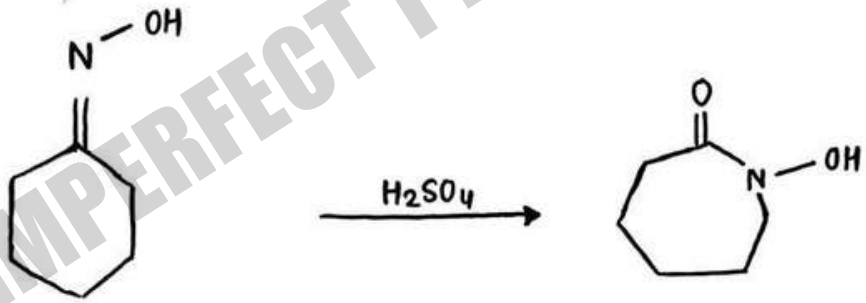
Nucleophillic Attack



STEP - V

further arrangement.

Example

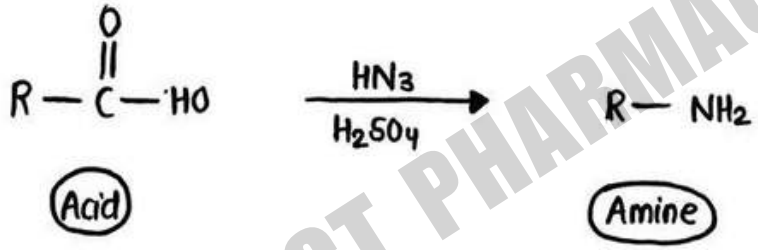


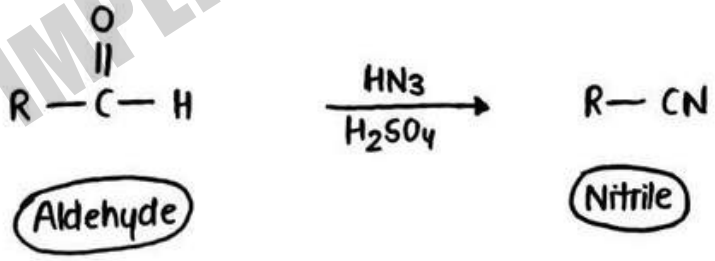
Cyclohexanoxime

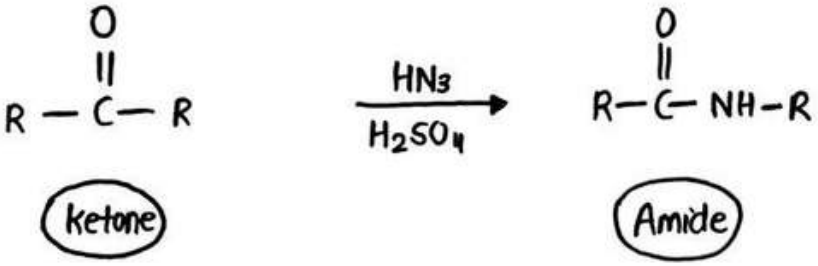
Caprolactam

SCHMIDT REARRANGEMENT

- Schmidt Rearrangement is an organic reaction in which carboxylic acids, aldehydes or ketones react with hydrazoic acid (HN_3) in the presence of strong acids to give amines, amides or nitriles, depending on starting compound.
- For example:

① 

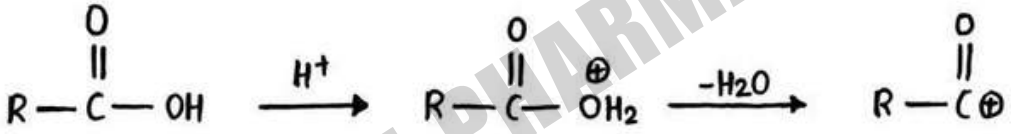
② 

③ 

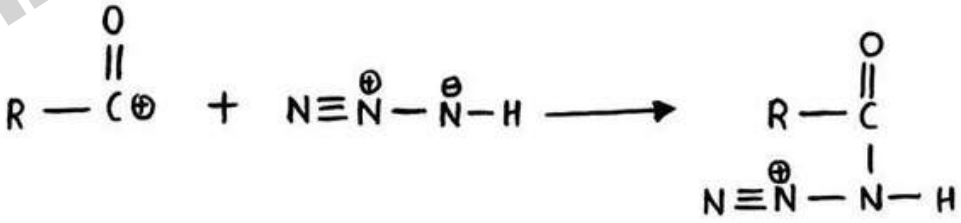
MECHANISM

- **STEP-I :** Rearrangement of HN_3

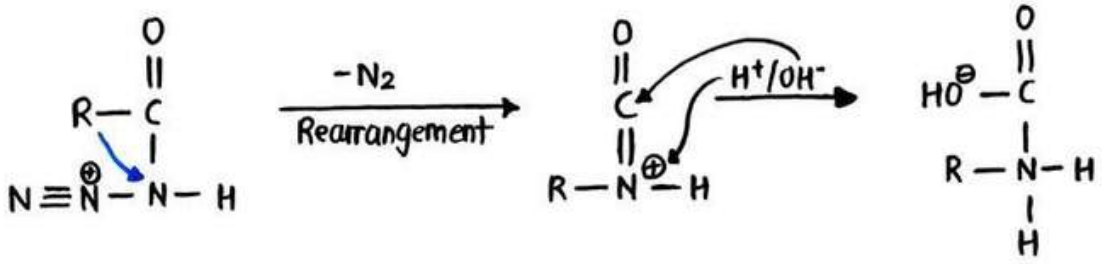
- **STEP-II :** Protonation & Removal of water from carboxylic acid.



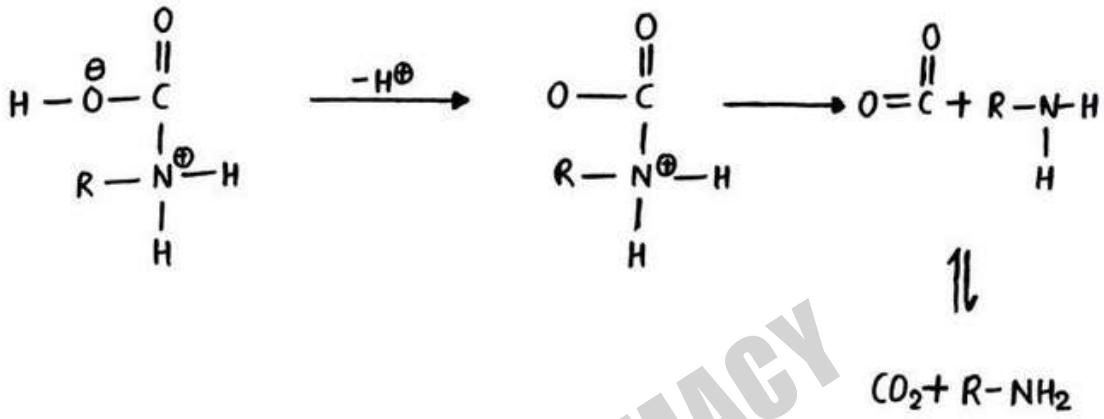
- **STEP-III :** Nucleophillic attack by HN_3



- **STEP-IV :** Removal of N_2 & Rearrangement.

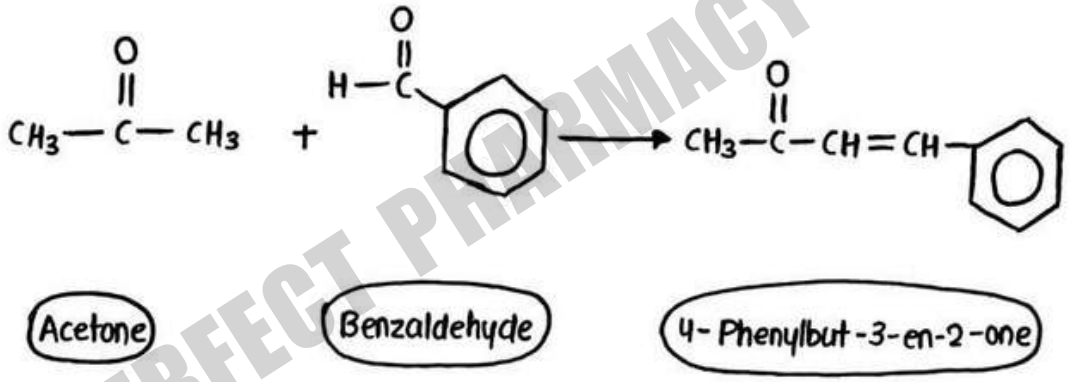


- **STEP-V:** Deprotonation of isocyanate ion.



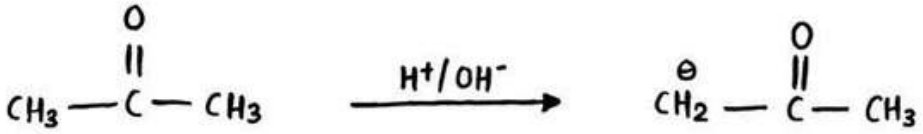
CLAISSEN-SCHMIDT CONDENSATION

It is a type of crossed aldol condensation reaction between an aromatic aldehyde (usually without α-hydrogens) and an aliphatic or aromatic ketone (with atleast one α-hydrogen) in the presence of a base to form an α-β- unsaturated carbonyl compound.

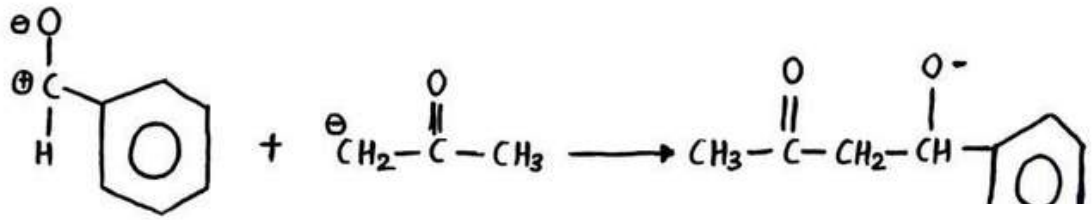


MECHANISM

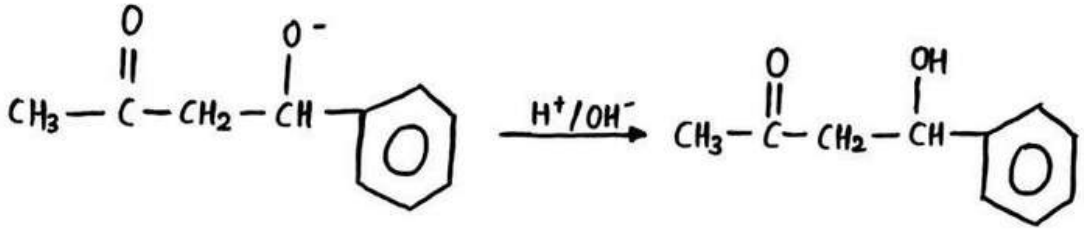
- **STEP-I:** Enolate Ion formation.



- **STEP-II:** Nucleophillic attack

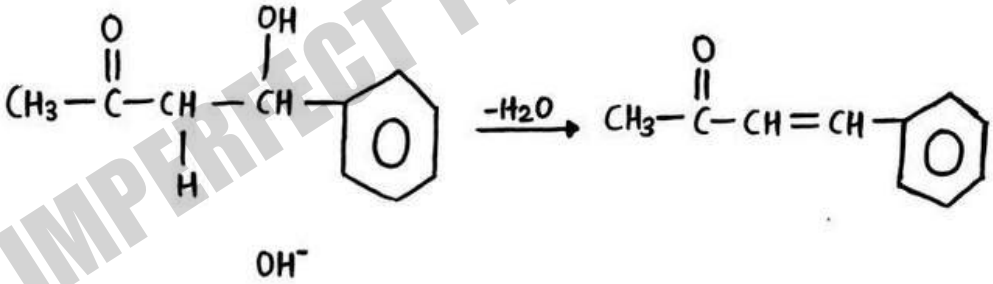


- **STEP - III :** formation of Aldol.



Aldol

- **STEP - IV :** Condensation (Removal of water)



THANK YOU

FOR CHOOSING IMPERFECT PHARMACY AS YOUR STUDY PARTNER

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