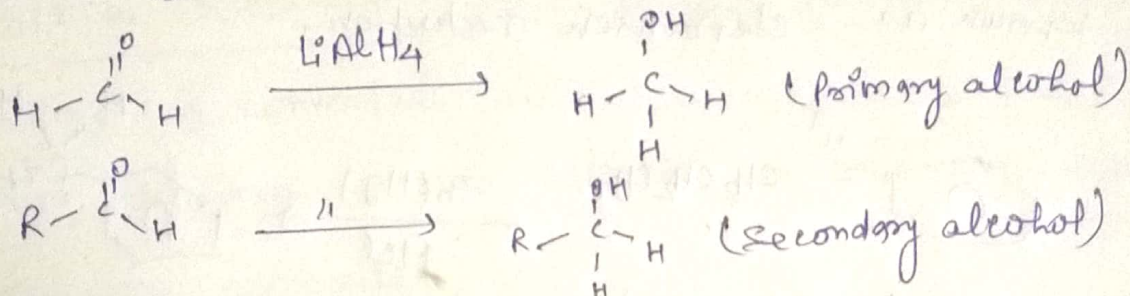


Unit - V

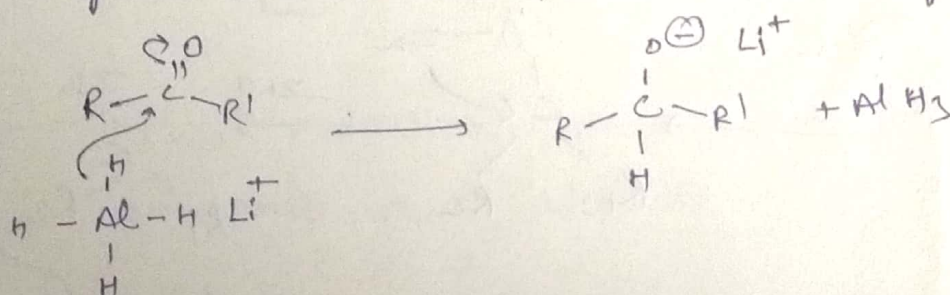
Hydride

① → Metal Hydride reduction → Reduction of various

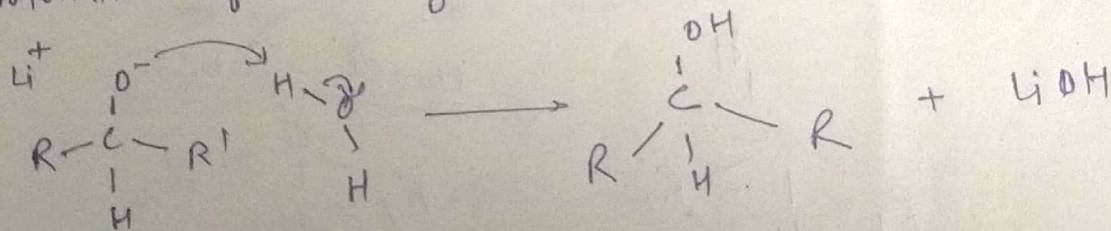
Carbonyl compounds is done by using hydride nucleophile such as lithium aluminium hydride and sodium borohydride. These hydride in the form of nucleophile attack on carbonyl compound and reduced it.



Mechanism :- Metal ~~hydride~~ ^{Hydride} react by transferring a negative hydride ion to the positive carbon of carbonyl gp.



Protonation of anion yields the corresponding alcohol.

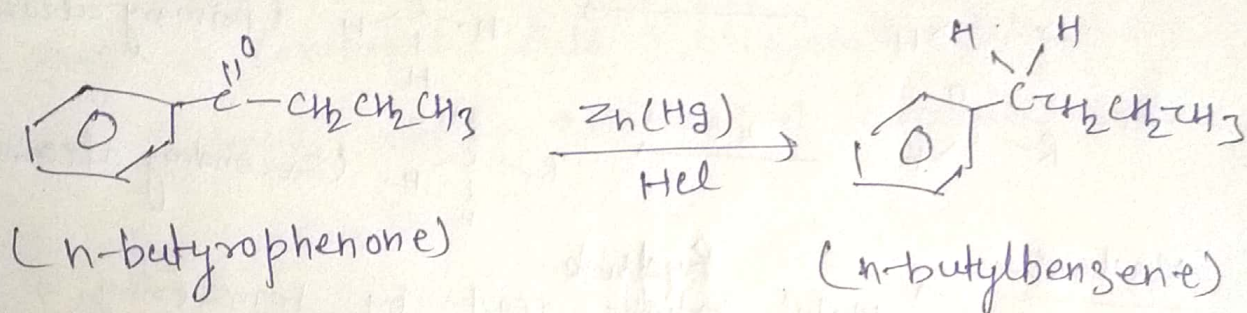


Aluminium is less electronegative than boron the Al-H bond in LiAlH₄ is more polar that's why LiAlH₄ a stronger reducing agent.

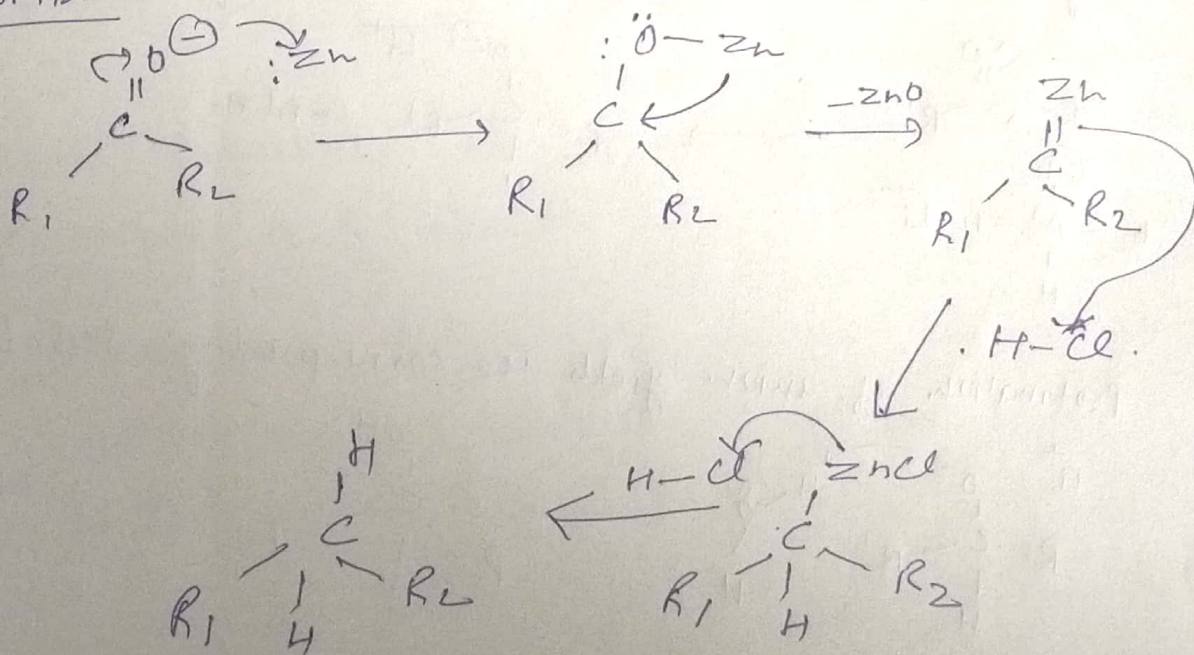
② CLEMENSEN REDUCTION :-

- It is a reduction of carbonyl gp. to methylene gp.
- This reaction done with zinc amalgam and HCl

The reduction of carbonyl gp. to methylene gp. in presence of amalgamated zinc and HCl is known as clemensen reduction.



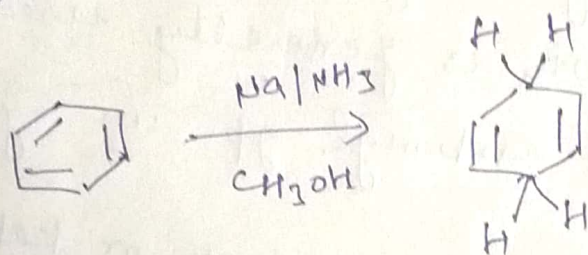
Mechanism -



Zn directly attacks to protonated carbonyl carbon.
The reduction occurs at the surface of Zn.

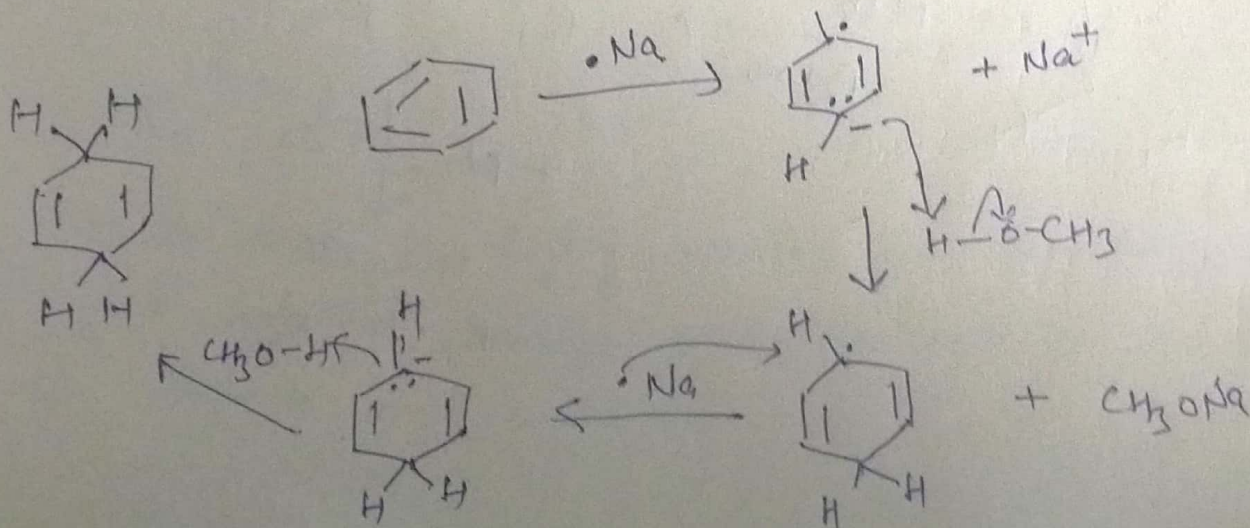
This reaction is widely used to convert a carbonyl group to methylene, such as preparation of polycyclic aromatic compound and aromatic side hydrocarbon chains.

③ Birch Reduction: In this reaction benzene ring is converted into 1,4-cyclohexadiene. Two hydrogen atoms attached at opposite sides of the molecule.



This reduction occurs in presence of sodium, ammonia and alcohol.

Mechanism: The free e^- of Na in liquid NH_3 attacks to the aromatic ring and form radical anion.



The radical anion is the protonated in presence of alcohol.

The final product is non-conjugated diene.

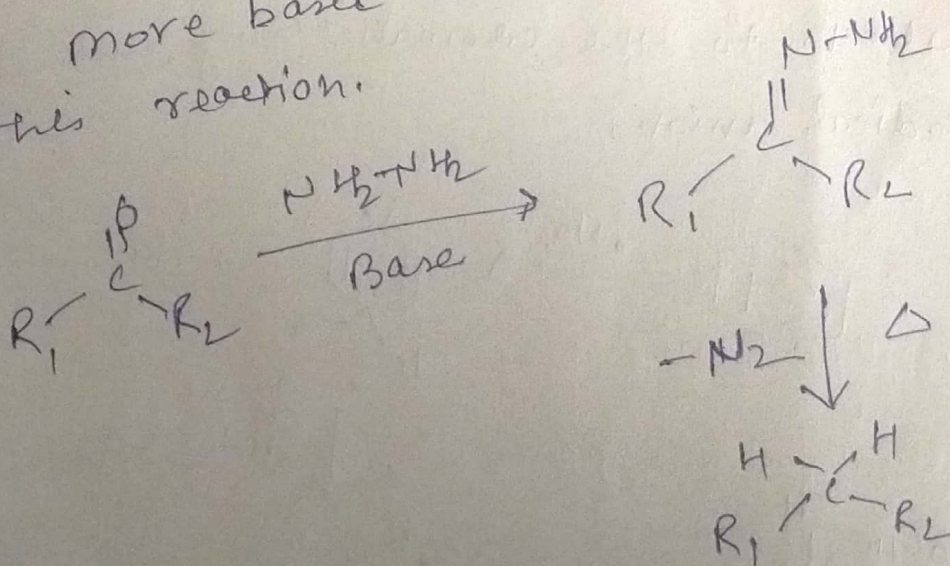
This reaction is not hydrogenation and further no reduction occurs in this reaction.

④ WOLF-KISHNER REDUCTION :->

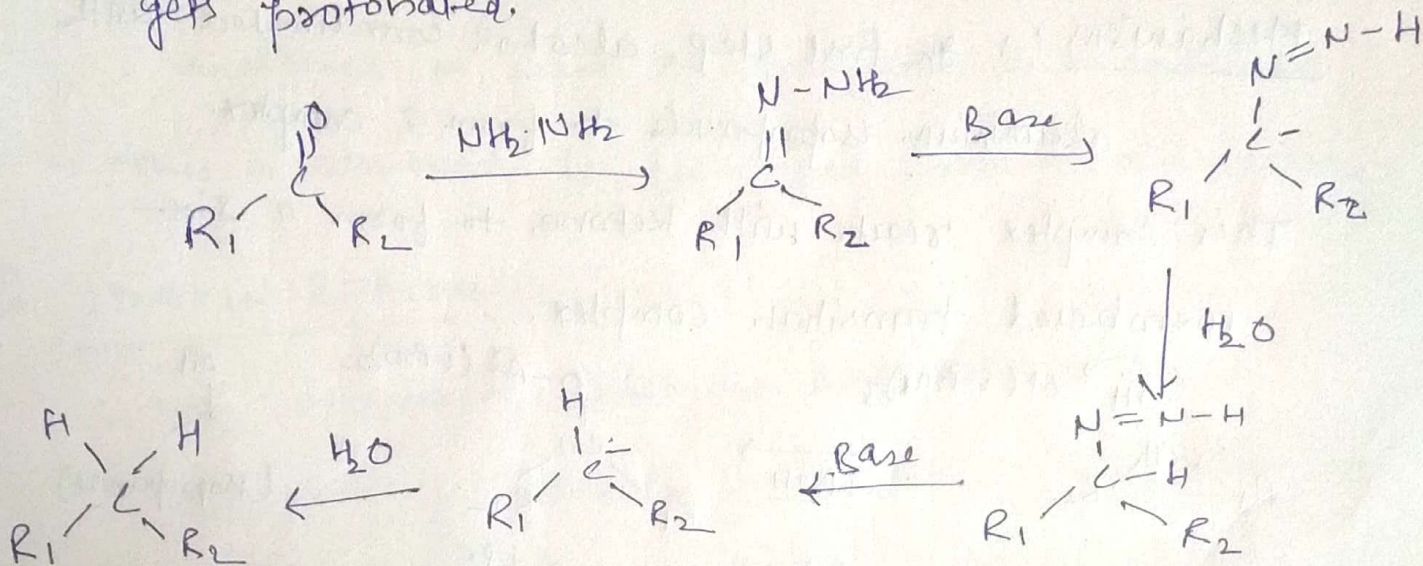
This reduction reaction is used in organic chemistry to convert carbonyl group into methylene groups.

This reduction is generally used for removing a carbonyl gp. in synthetic reaction.

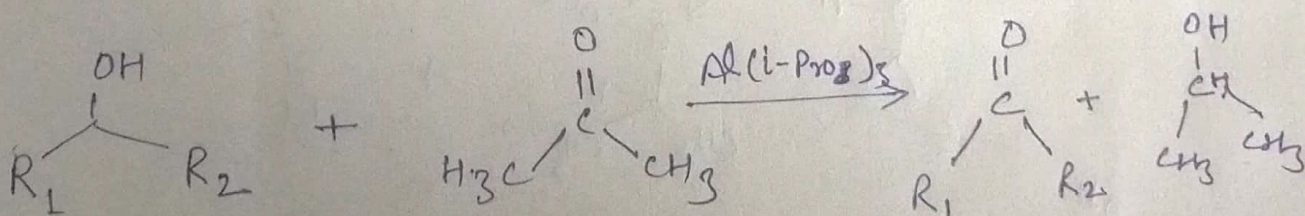
In this reaction aldehyde or ketones are converted into alkane using hydrazine, base and thermal condition. More basic condition is required for this reaction.



Mechanism: Formation of hydrazones anion by deprotonation of the terminal nitrogen in basic medium. Hydrazone anion undergoes rearrangement and the carbon atom gets protonated. Again deprotonation of nitrogen occurs and carbon gets protonated.



⑤ OPPENAUER OXIDATION: The process of conversion of secondary alcohols to ketones by oxidation in presence of aluminium isopropoxide in excess of ketones.



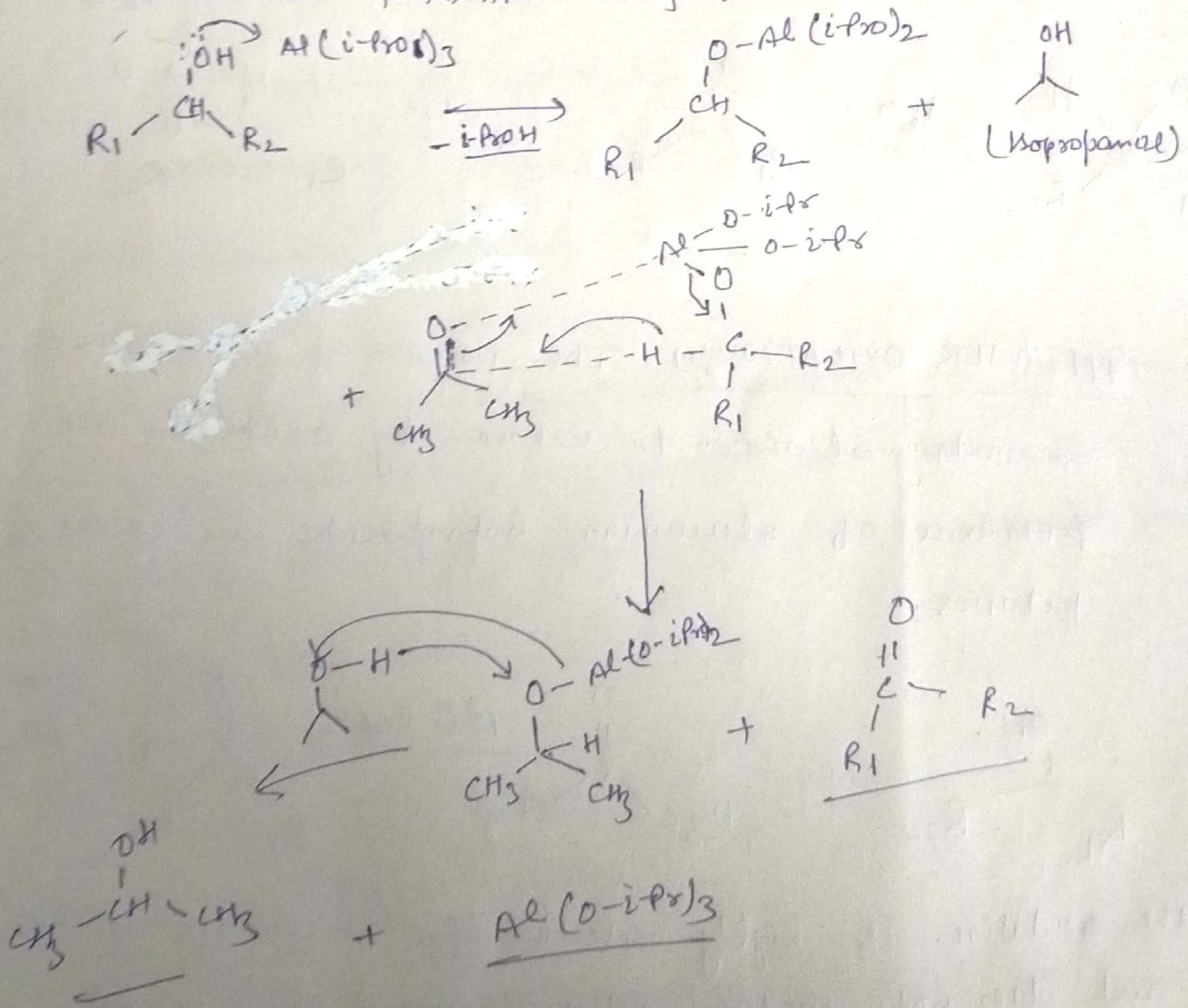
The oxidation is highly selective for secondary alcohols and does not oxidize other functional gp. such as amines and sulfides.

It is very good method to oxidise sec. alcohol to α, β -unsaturated ketones.

This is reverse of the Meerwein-Ponndorf-Verley reduction.

Mechanism: In first step, alcohol coordinated with aluminium isopropoxide to form a complex.

This complex reacts with ketone to form a six-membered transition complex.



- The alcohol is converted to the carbonyl carbon from aluminium catalyzed hydride shift.
- The ketone is formed after the hydride transfer.

* Applications: Oppenauer oxidation is used to prepare analgesics such as morphine and codeine.

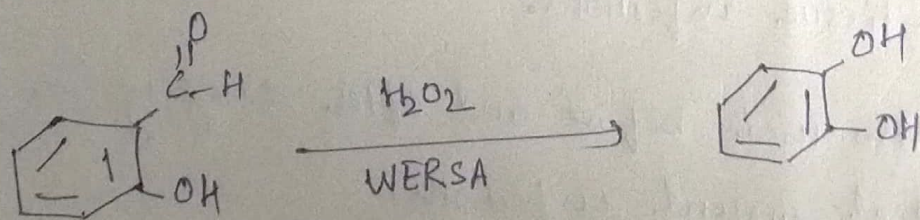
- This is also used to synthesize hormones and lactone.

⑥ DAKIN REACTION

The oxidation of aldehydes and ketones to corresponding phenols is known as Dakin Reaction.

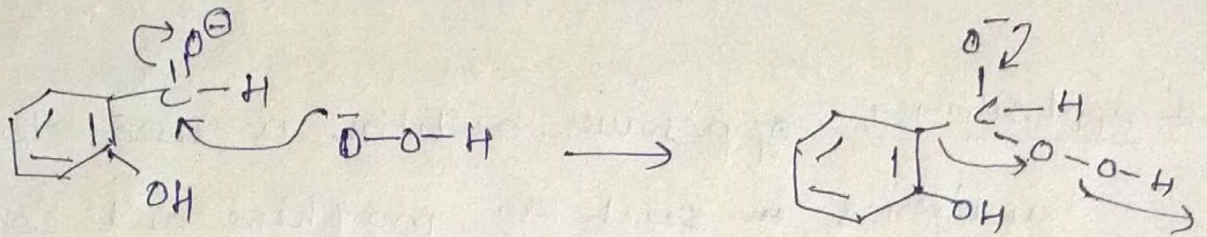
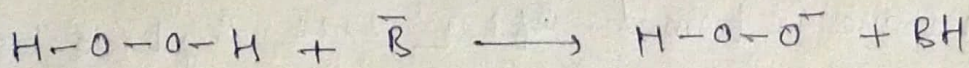
The Reaction works best if the aromatic aldehyde or ketone is electron rich.

- The reagents used in Dakin reaction are alkaline H_2O_2 , acidic H_2O_2 , Peroxybenzoic acid ($C_6H_5O_3$), 30% H_2O_2 with aryl Selenium compounds as activators and Urea- H_2O_2 adduct.

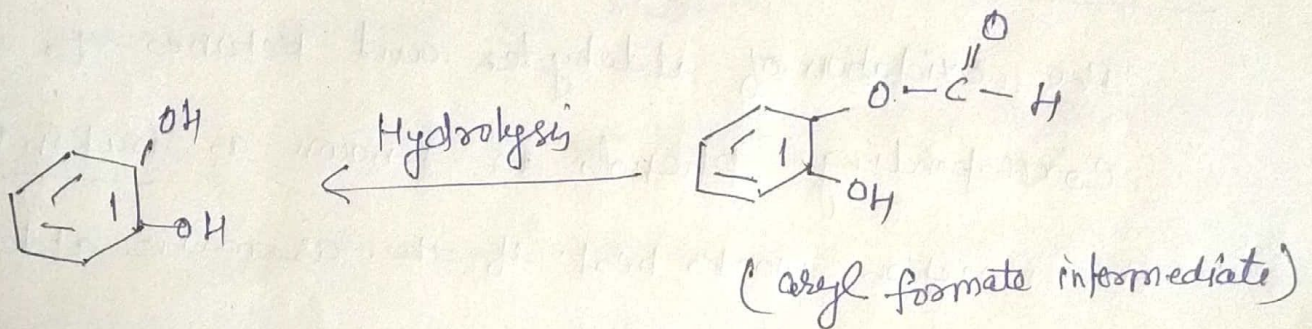


(WERSA - water extract of rice straw ashes)
AS a reaction medium

Mechanism - (Base source is WERSA) Base- \bar{B}



Ar-Migration



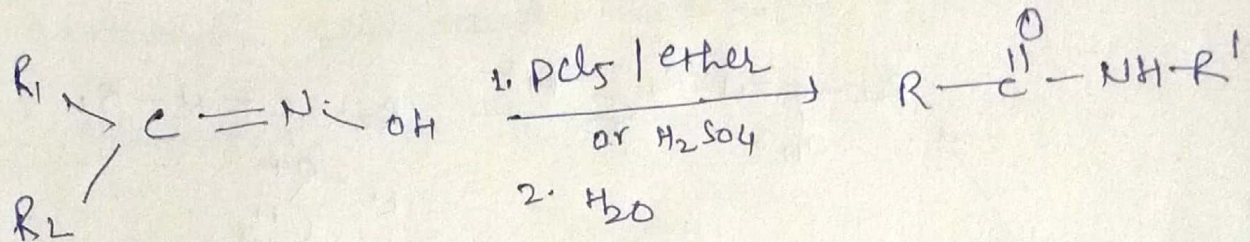
Applications Dakin reaction is most commonly used to synthesize benzene diols and alkoxyphenols.

Such as Catechol

- Dakin solution is used to prevent and treat skin and tissue infections.
- It is also used before and after surgery to prevent surgical wound infections.

⑦ BECKMANN REARRANGEMENT

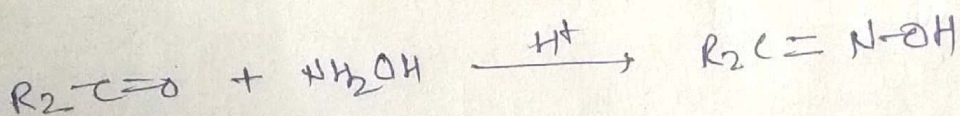
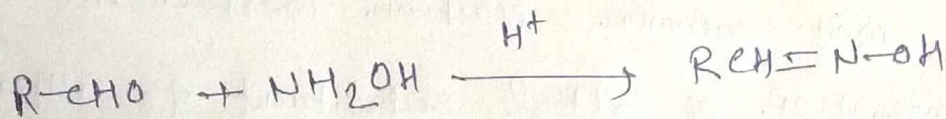
It is an acid catalysed conversion of keto oximes to N-substituted amides usually called the Beckmann rearrangement.



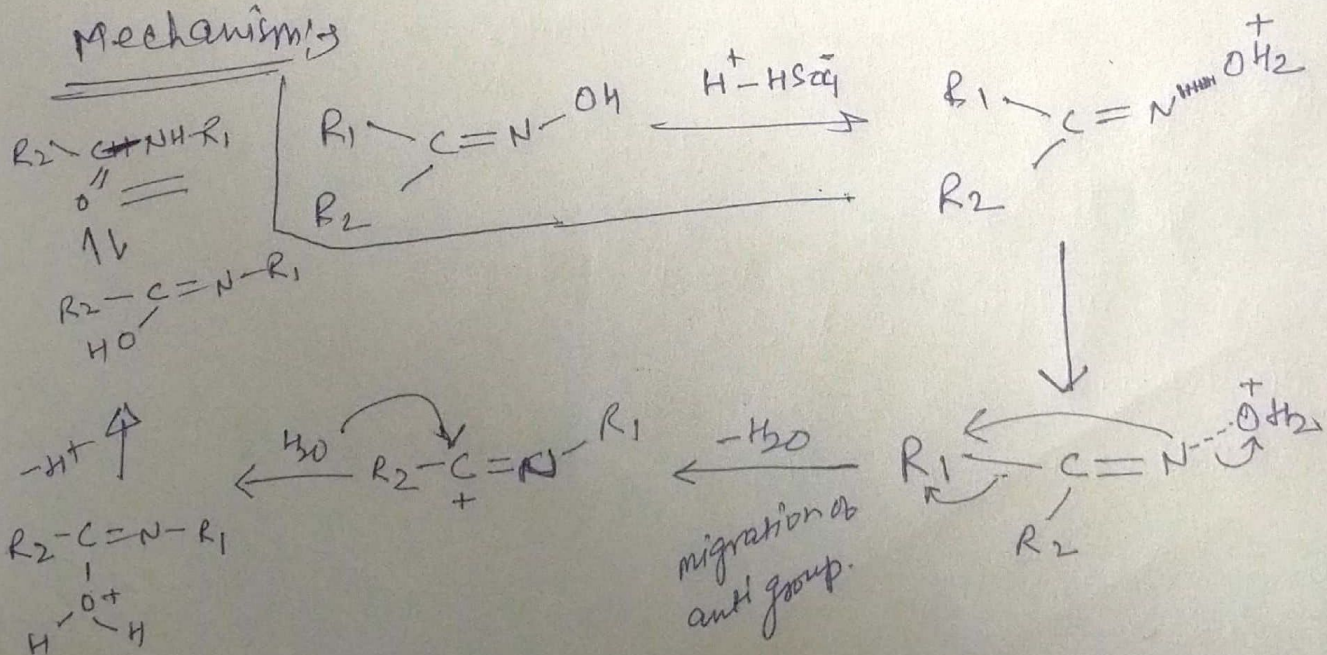
Two types of oximes are known:

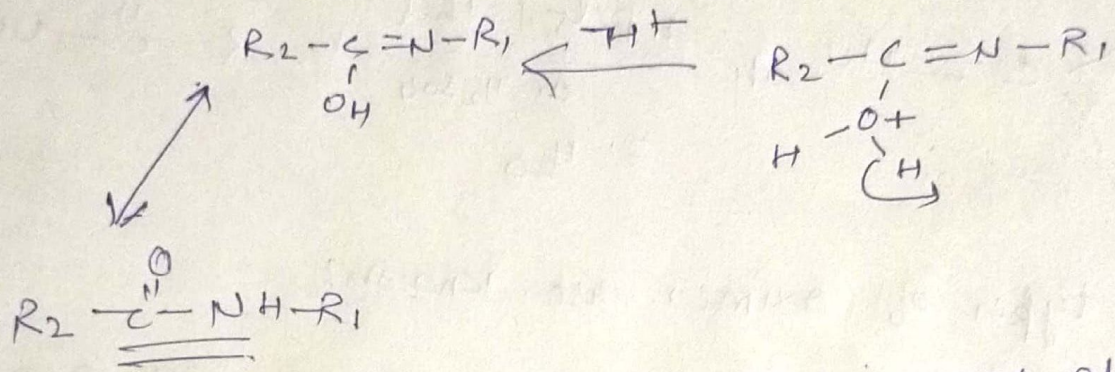
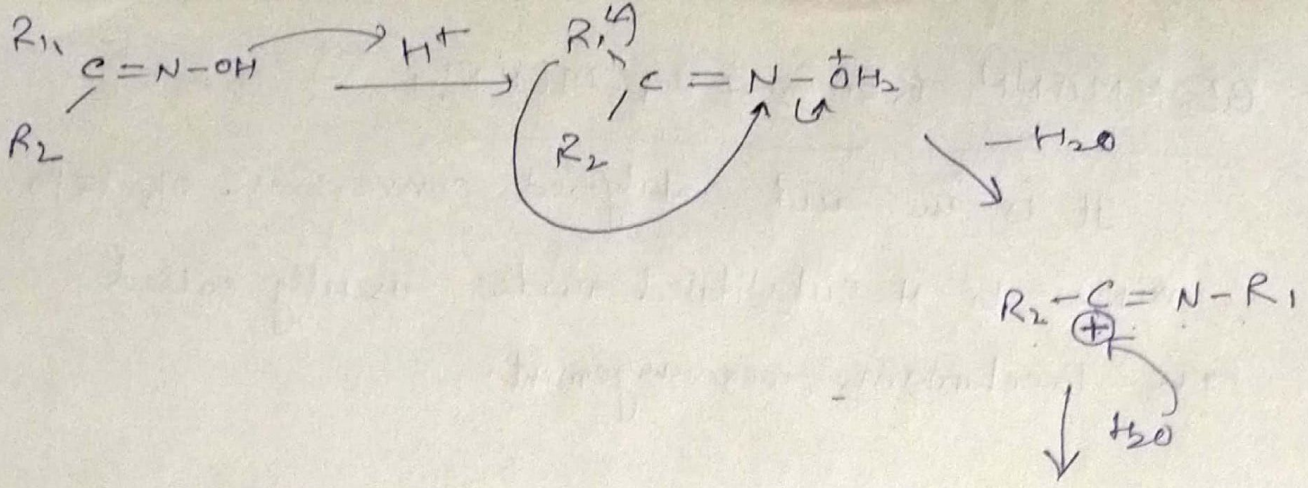
Aldoxime: combination of an aldehyde with hydroxylamine

Ketoxime: combination of ketones with hydroxylamine



Mechanism





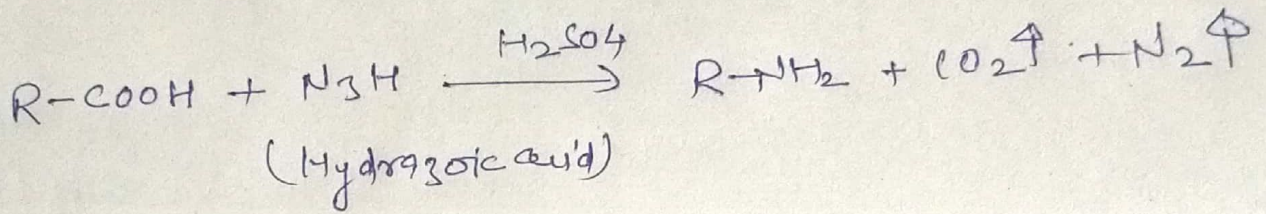
- Protonation of hydroxyl of oxime occurs after trans alkyl substituents to the nitrogen.
- The most common reaction mechanism is migration of alkyl substituent to nitrogen.

⑧ SCHMIDT REACTION :-

It is a rearrangement reaction.

- This rearrangement involves migration of an alkyl or aryl group from carbon to the adjacent nitrogen atom.

Carboxylic acids and hydrazoic acids react in presence of conc H_2SO_4 to give amines.



Schmidt reaction also occurs in ketones.

