

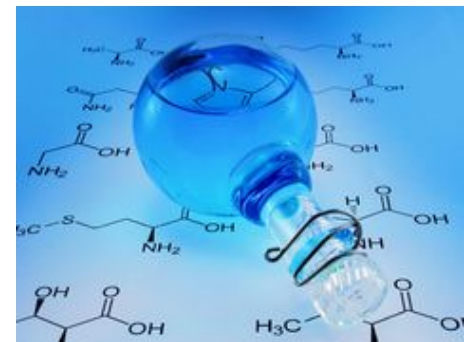
# NAMED REACTIONS

By

Dr Afzal basha shaik

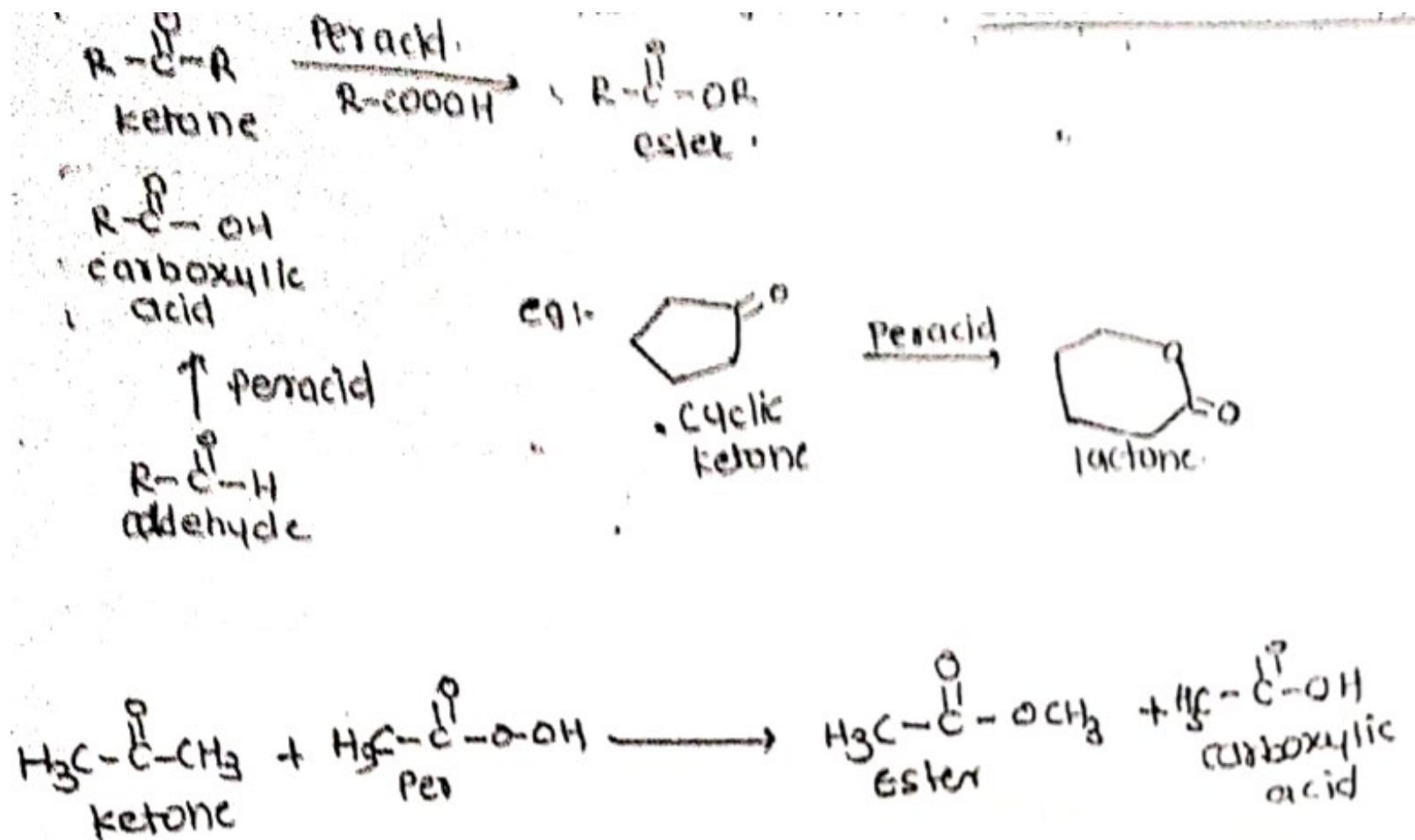
Associate Professor

Vignan Pharmacy college



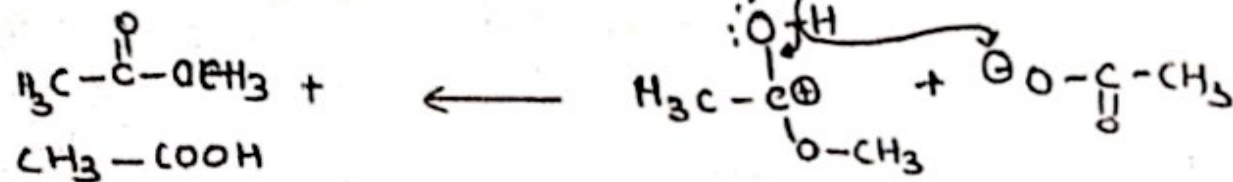
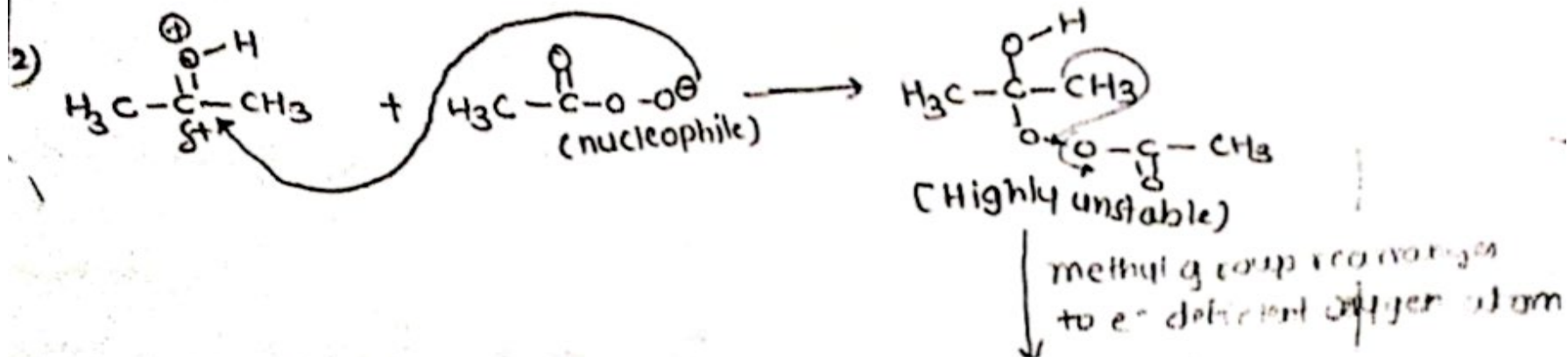
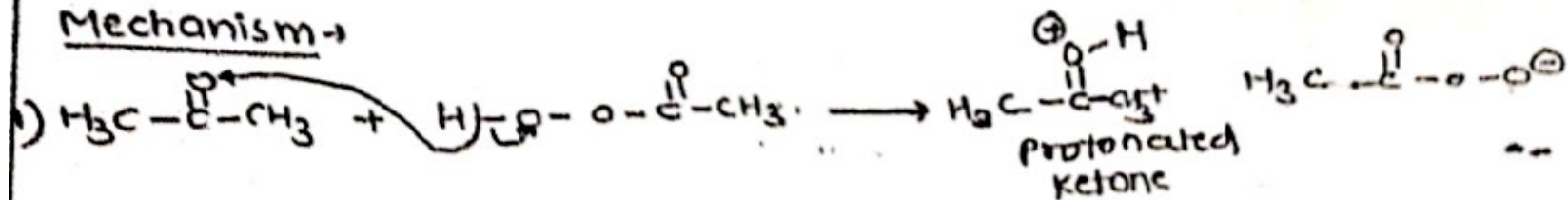
# BAYER – VILLIGER OXIDATION / REARRANGEMENT

- Rearrangement of electron deficient oxygen.



# MECHANISM:

## Mechanism-

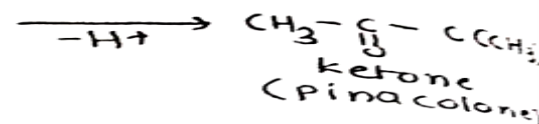
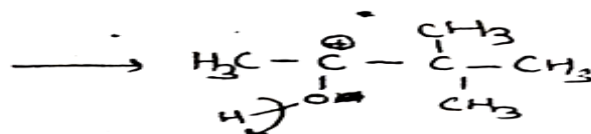
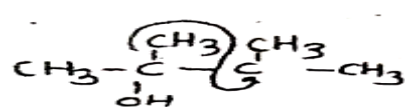
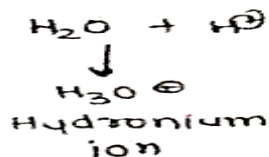
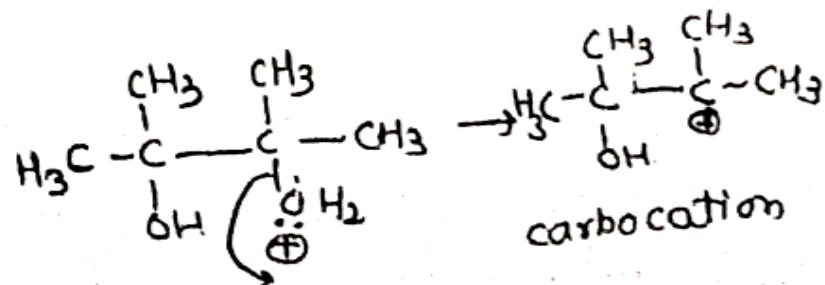
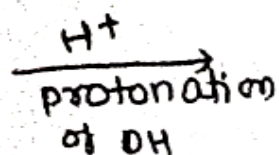
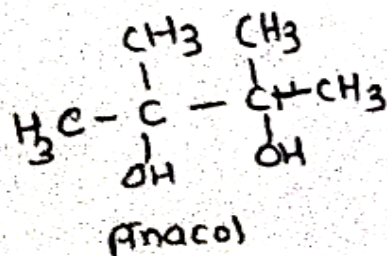


# PINACOL – PINACOLONE REARRANGEMENT

Pinacol-Pinacolone rearrangement →

↓  
Rearrangement onto electron deficient carbon atom.

vicinal diols  $\xrightarrow{H^+}$  carbonyl compounds

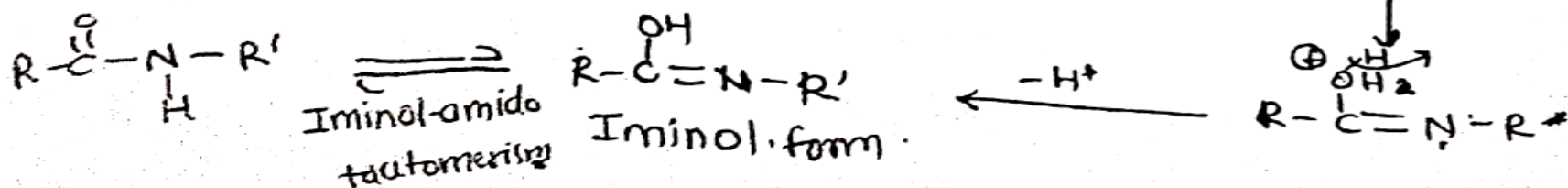
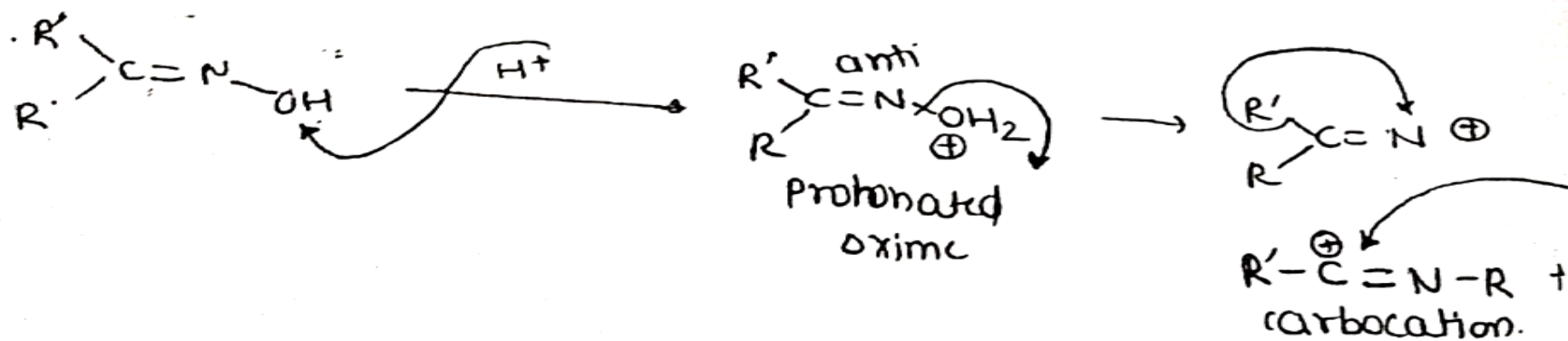
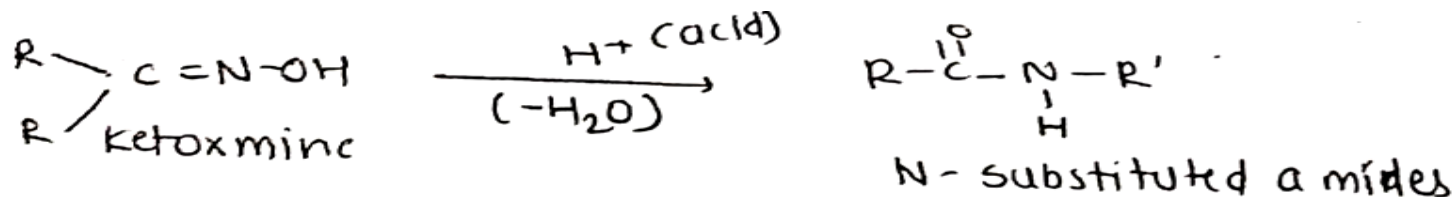


# **REARRANGEMENT ON ELECTRON DEFICIENT** **NITROGEN ATOM**

- Beckmann's rearrangement
- Curtis rearrangement
- Lossen rearrangement
- Hofmann rearrangement
- Schmidt rearrangement

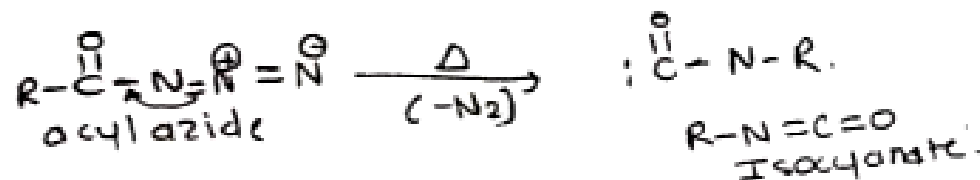
# BECKMANNS REARRANGEMENT

- It is acid catalysed conversion of

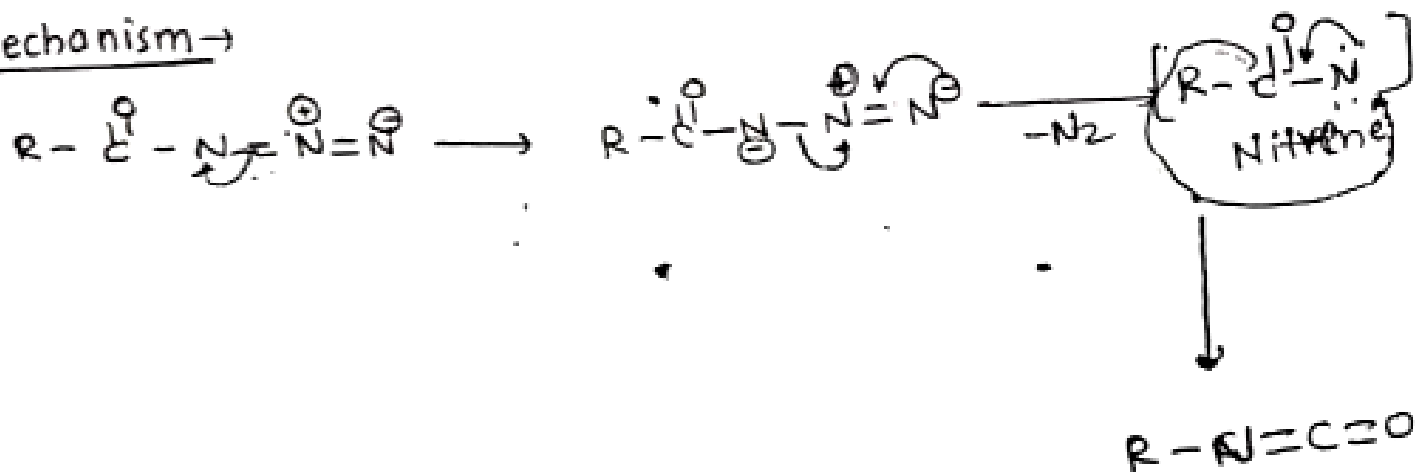


# CURTIS REARRANGEMENT

- Thermal decomposition of acyl azide to isocyanate

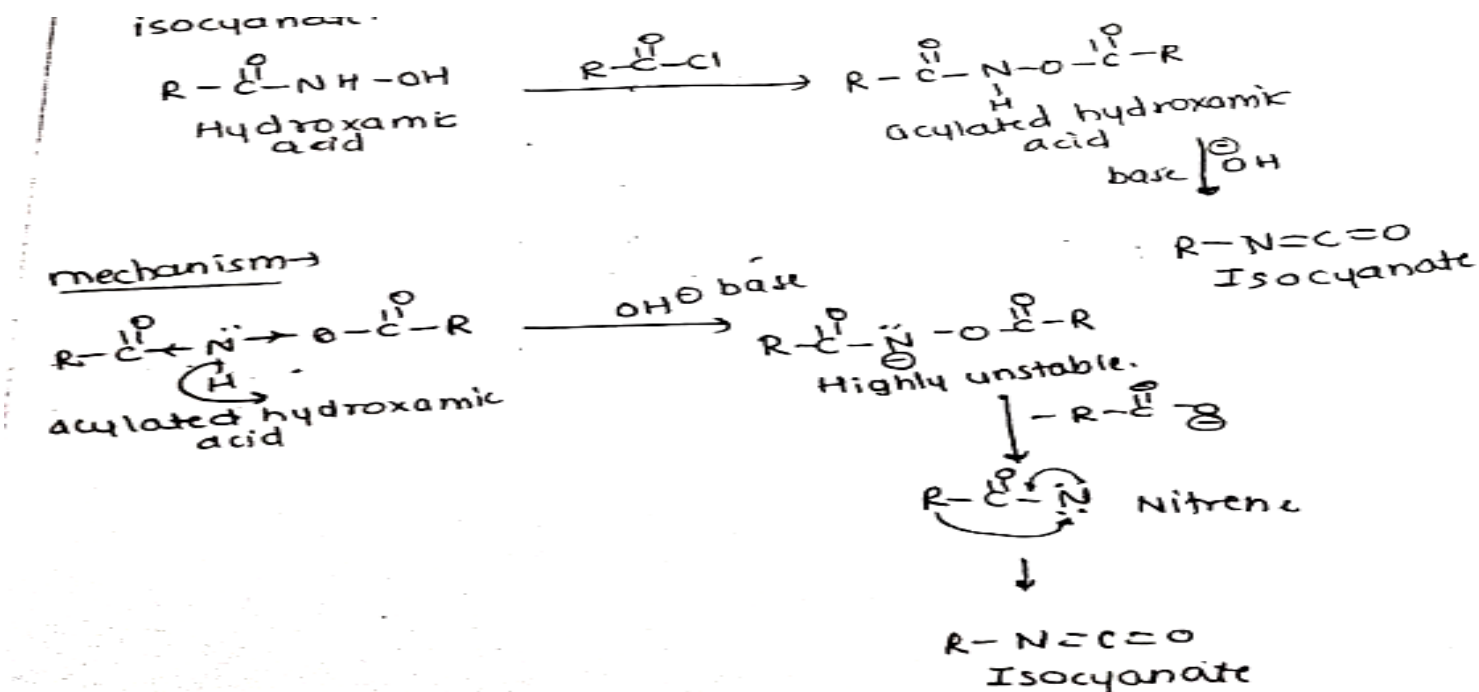


Mechanism →

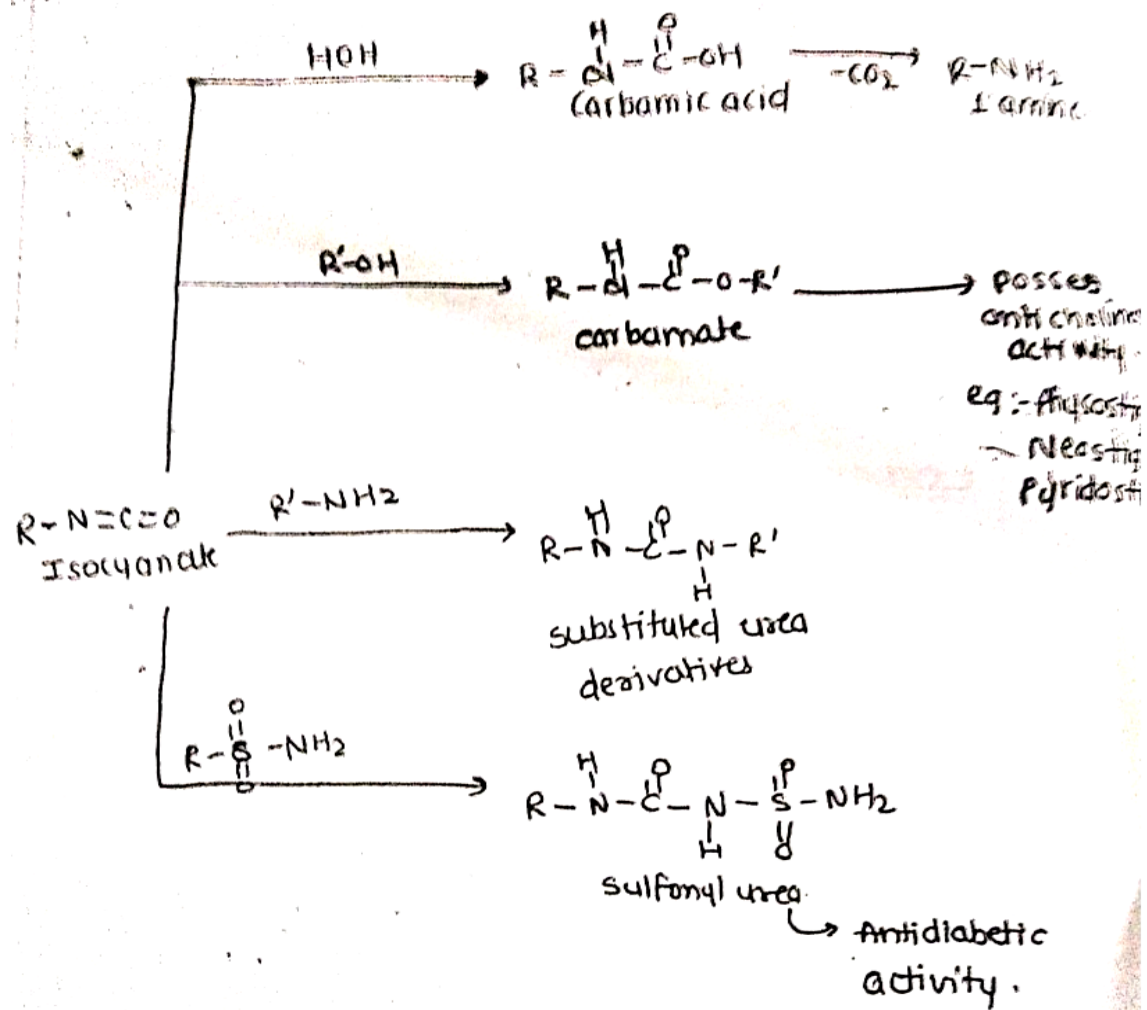


# LOSSEN ARRANGEMENT

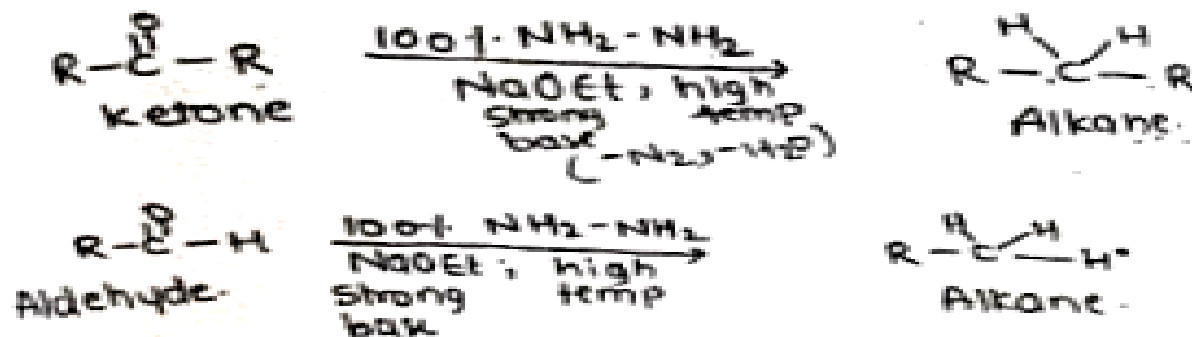
- It is the base catalysed conversion of acylated hydroxamic acid to isocyanate



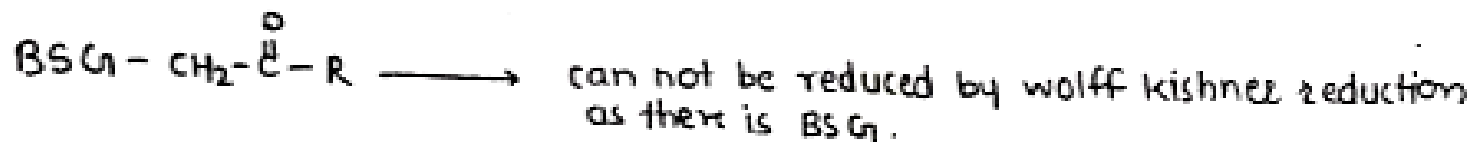




# WOLFF KISHNER REDUCTION



- Wolff - kishner reduction is used only for the reduction of the carbonyl groups of aldehydes and ketones but not other carbonyls like carboxylic acids, amides, acid chlorides, esters and anhydrides.
- Wolff kishner reduction cannot be used for reduction of carbonyl compounds containing base sensitive groups (BSG).



- Wolff kishner reduction can be used to reduce carbonyl compound with or without acid sensitive groups.

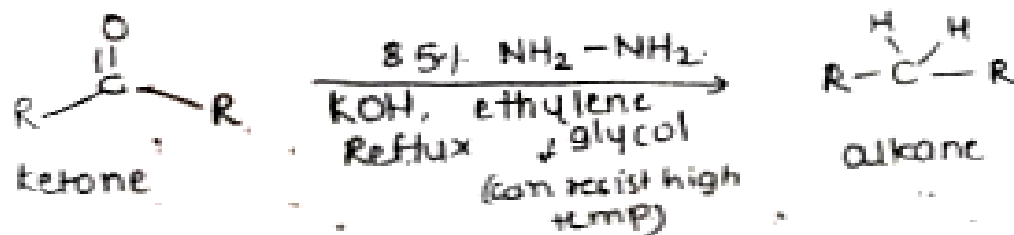
Limitation: utilisation of harsh conditions like strong base, high temperature

Clemensonns reduction :

- It is the reduction of carboxy group to  $\text{CH}_2$  group in presence of  $\text{Zn} - \text{Hg}$  and  $\text{HCl}$  (acidic condition). So cannot used for reduction of ketone containing acid sensitive groups (ASG).

# HUANG – MINLONG MODIFICATION

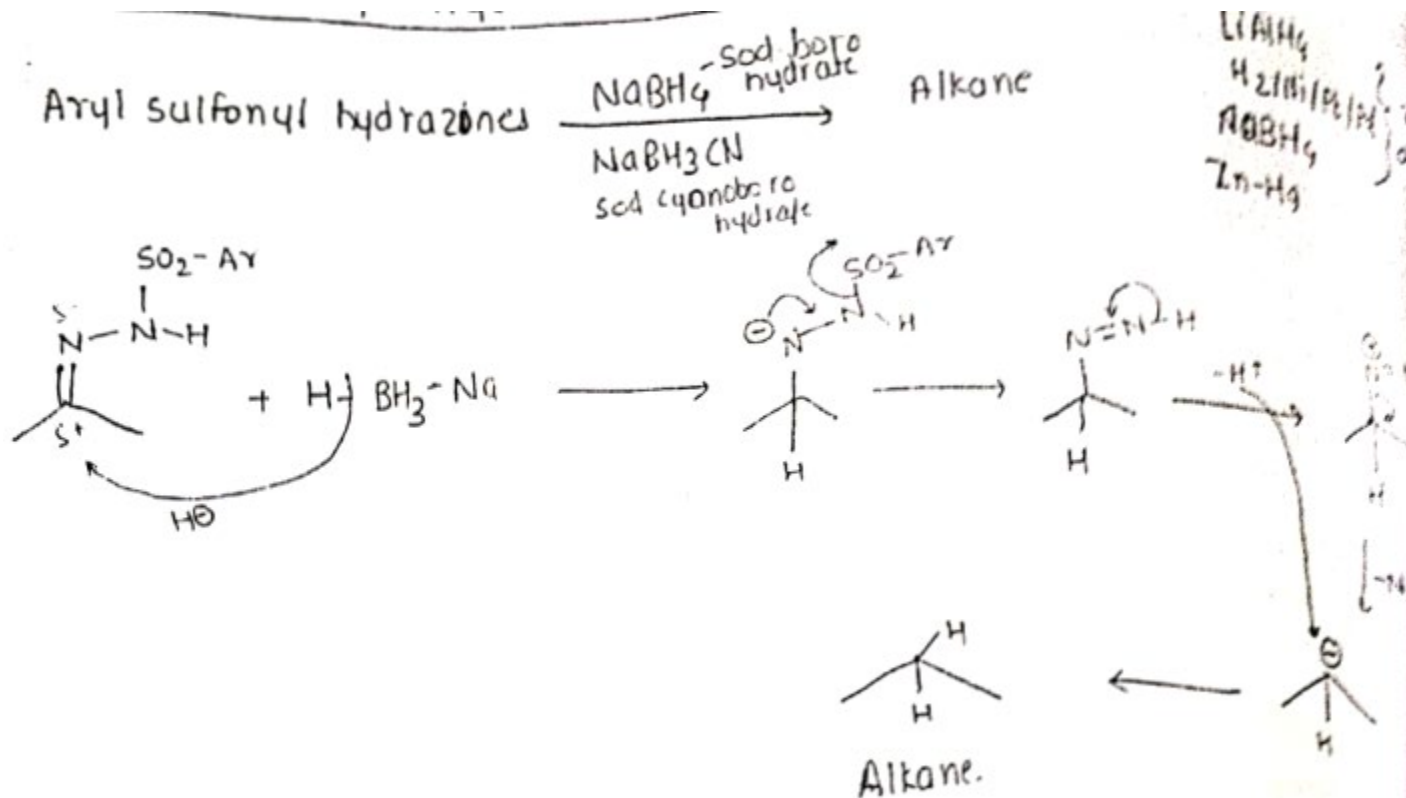
## ➤ Modification of wolff kishner reduction



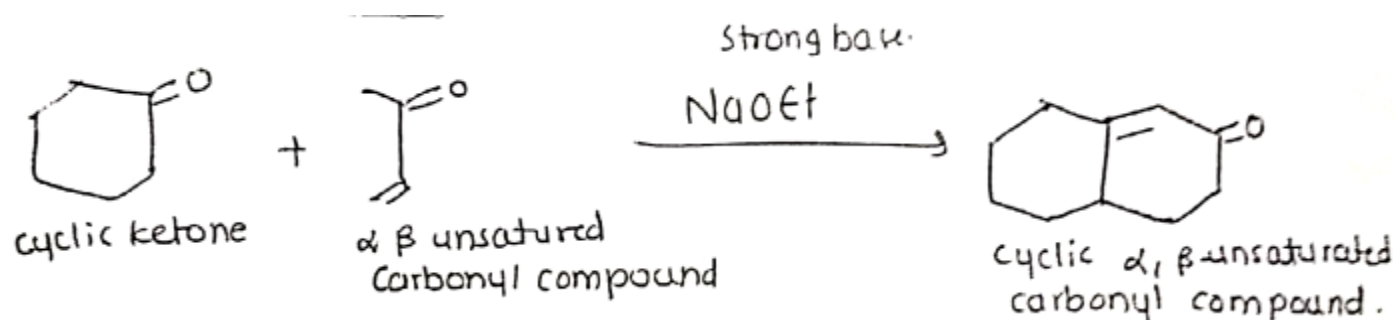
### Advantages:

- No need to use anhydrous (100%)  $\text{NH}_2 - \text{NH}_2$
- High temperature can be reached as it uses ethylene glycol
- Decreased reaction time
- Increased yield

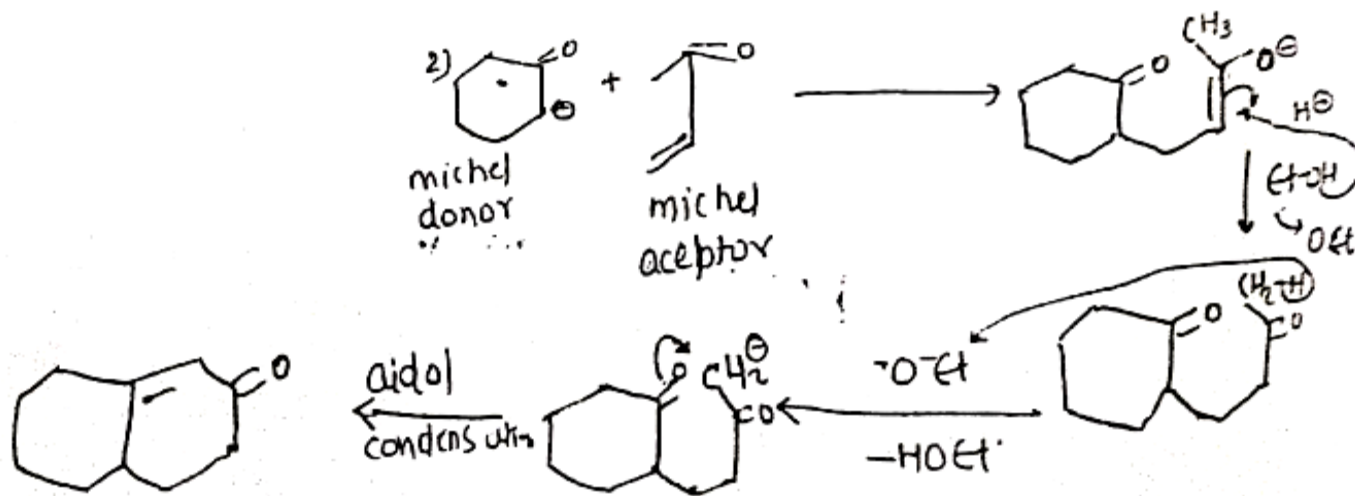
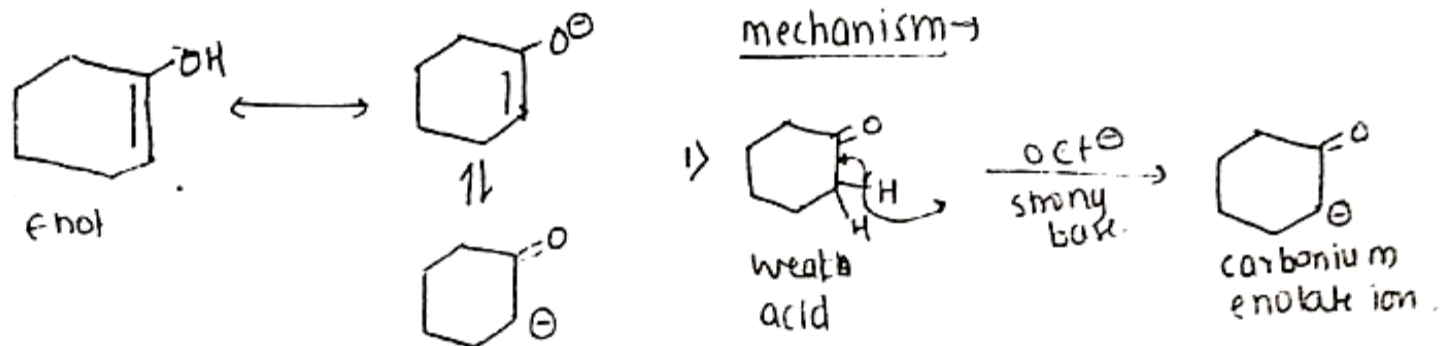
# REDUCTION OF ARYL SULFONYL HYDRAZINE/HYDRAZONES TO ALKANES



## ROBINSON ANNULATION

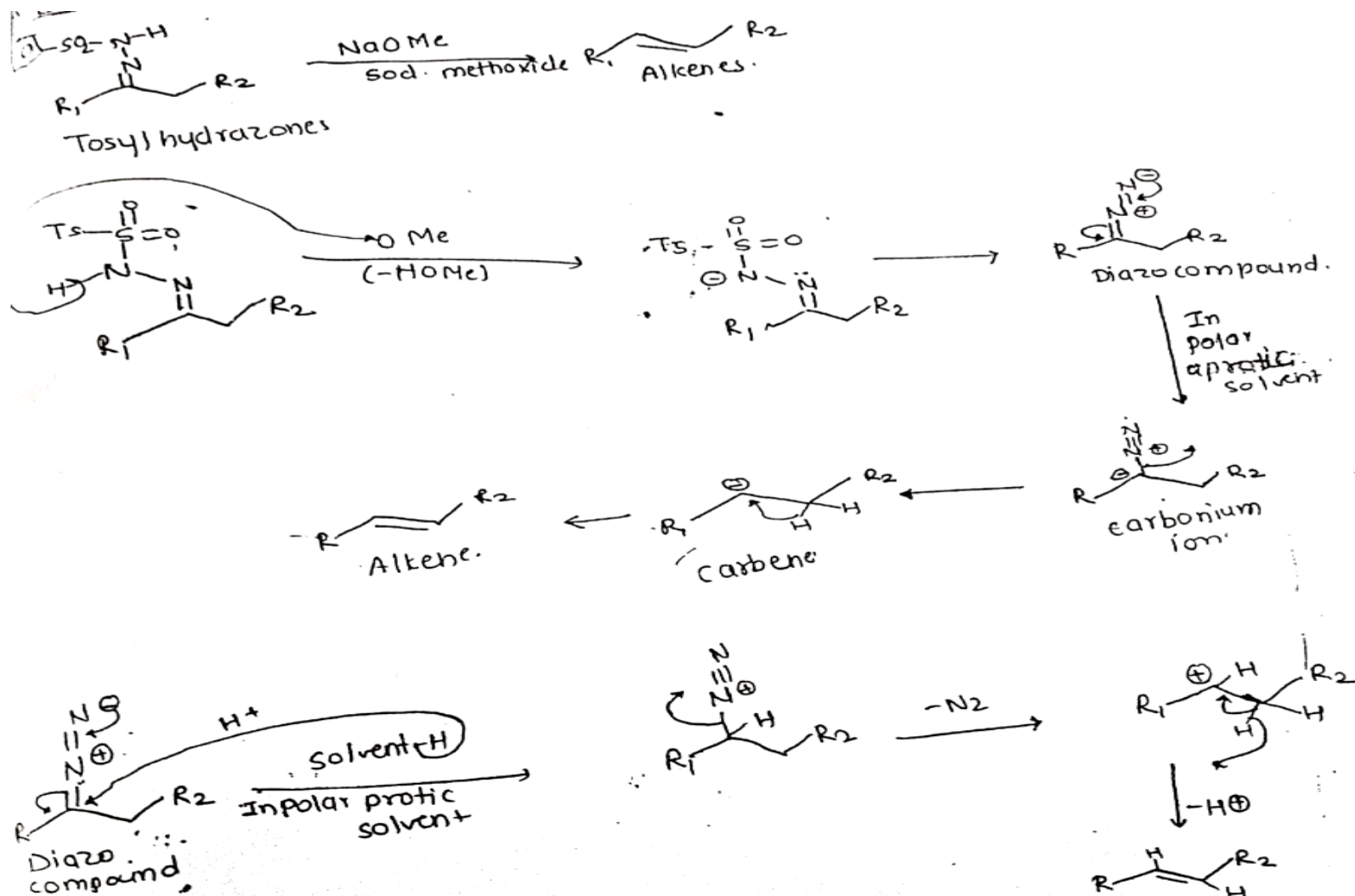


- It involves michael addition followed by intramolecular aldol condensation.

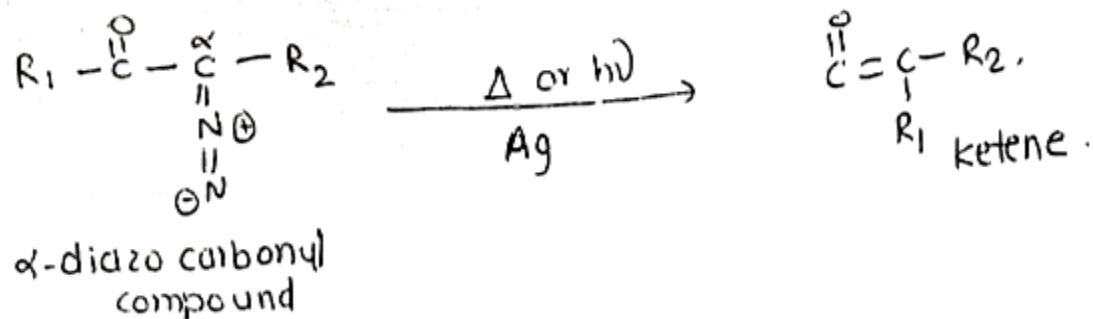


➤ The major application of Robinson annulation is synthesis of polycyclic system like steroids.

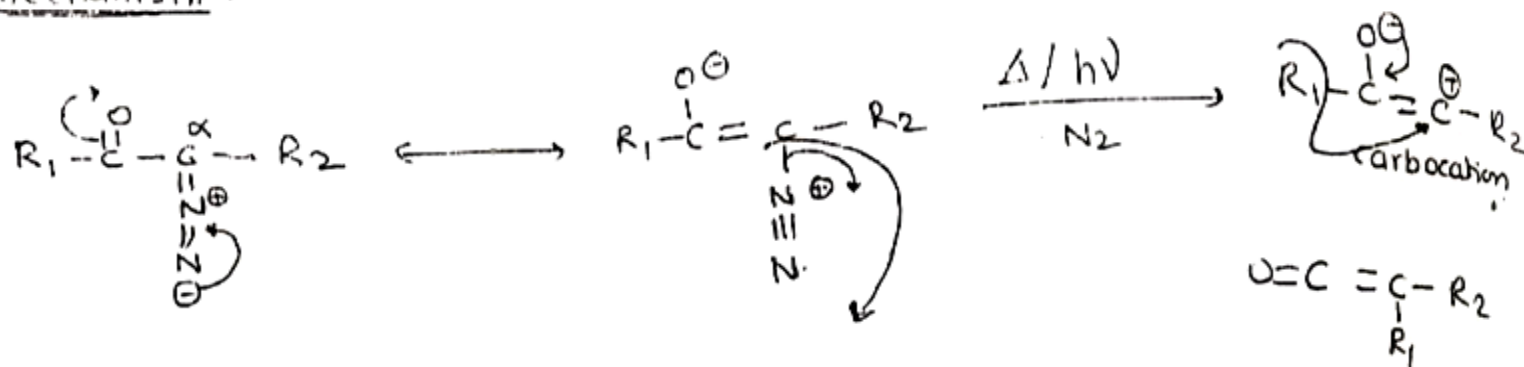
# BANFORD – STEVEN REACTION





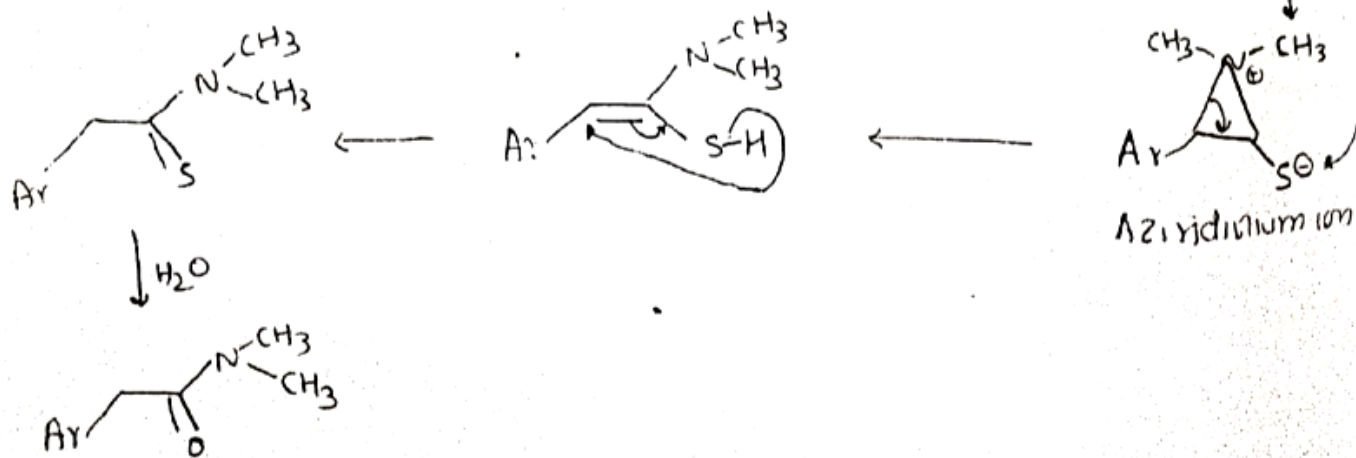
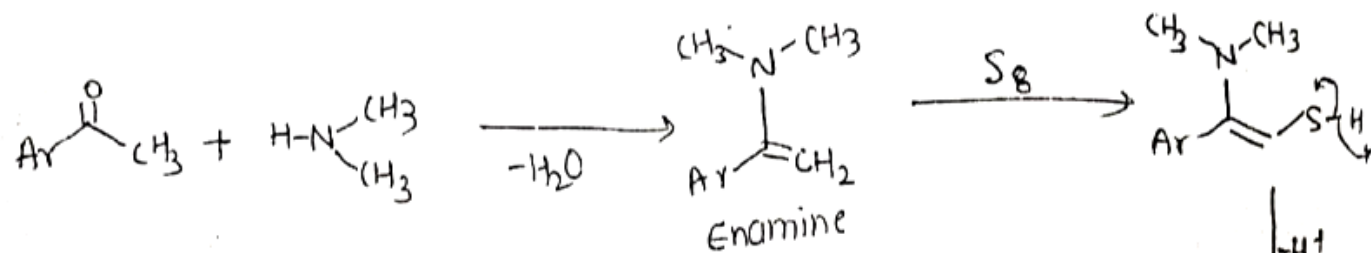
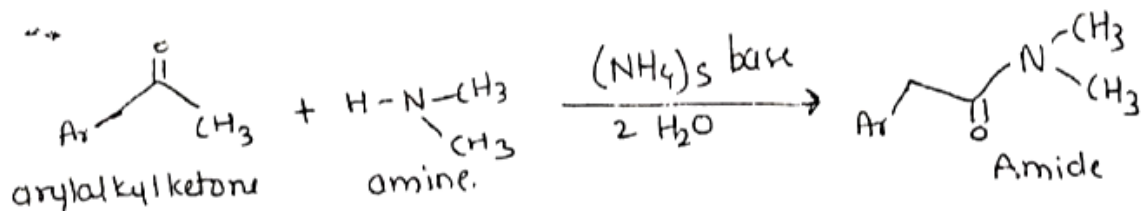


mechanism →

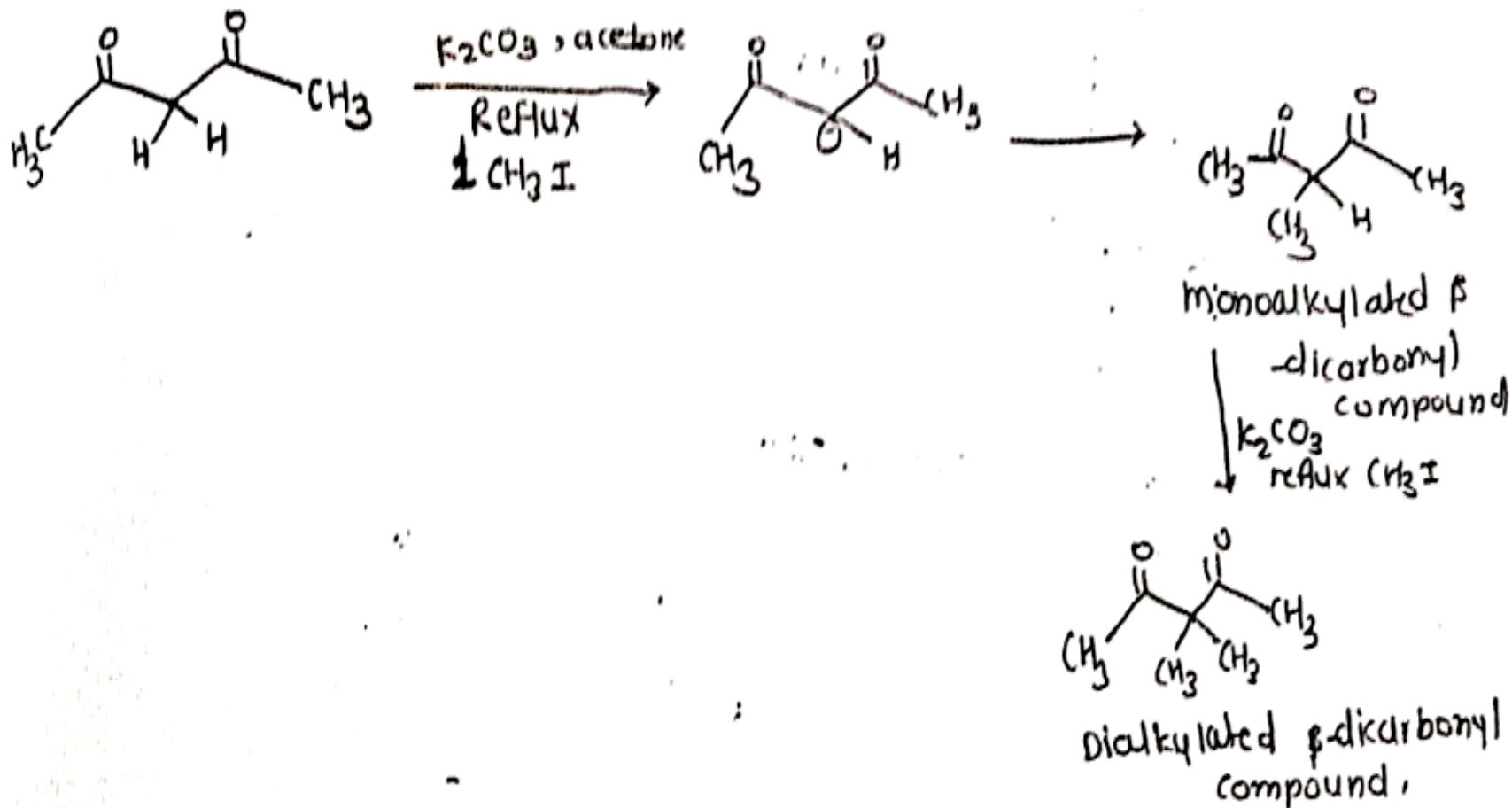


➤ Ketenes can be converted to carboxylic acid and amines.

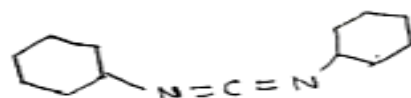
# WILLGEREDT REARRANGEMENT



# MONO AND DIALKYLATION OF 1,3 – DICARBONYL COMPOUNDS

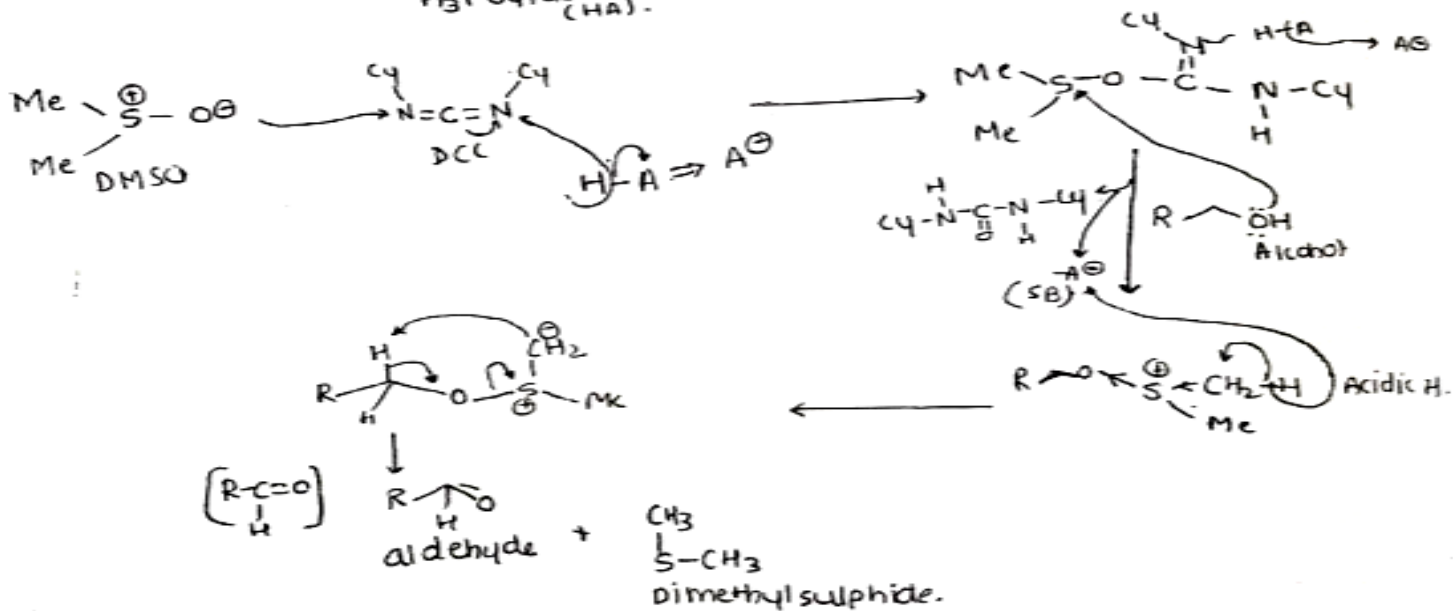


# DCC OXIDATION

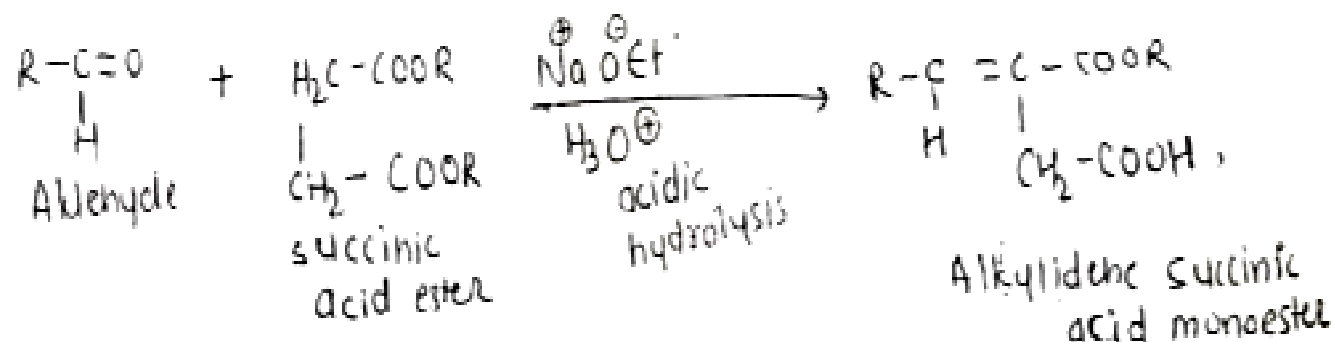


1° alcohols  $\xrightarrow[\text{acid(HA) H}_3\text{PO}_4]{\text{DCC, DMSO}}$  Aldehydes

2° alcohols  $\xrightarrow[\text{H}_3\text{PO}_4, \text{acids (HA)}]{\text{DCC, DMSO}}$  Ketone

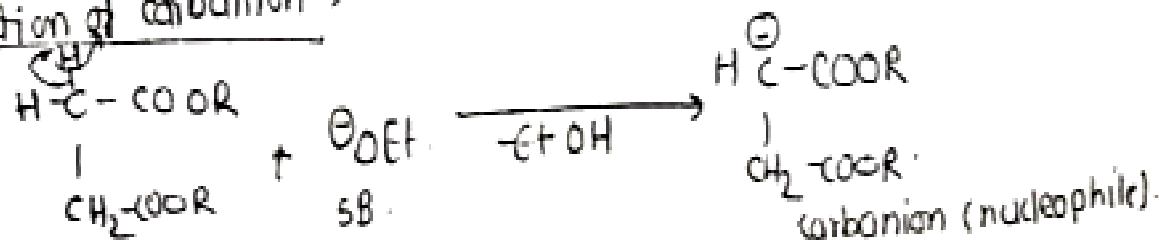


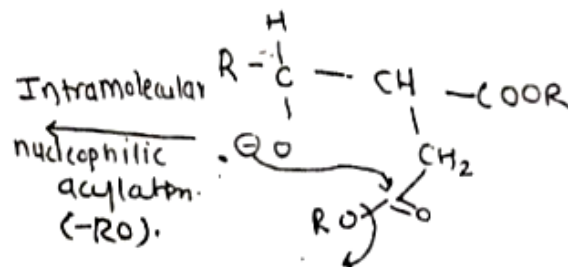
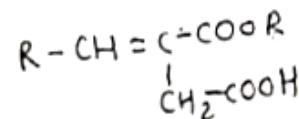
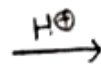
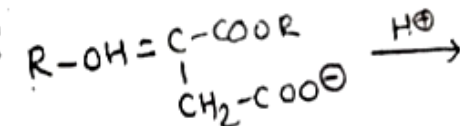
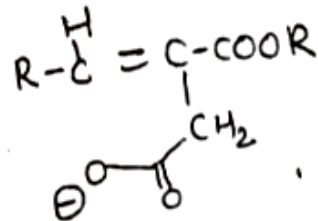
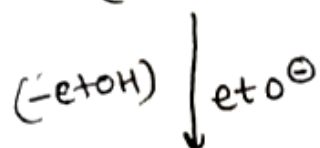
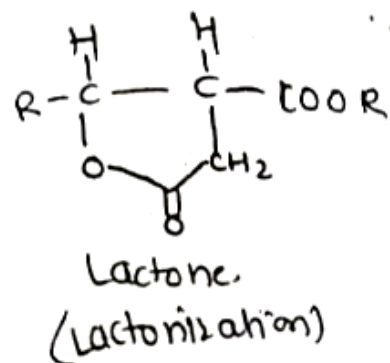
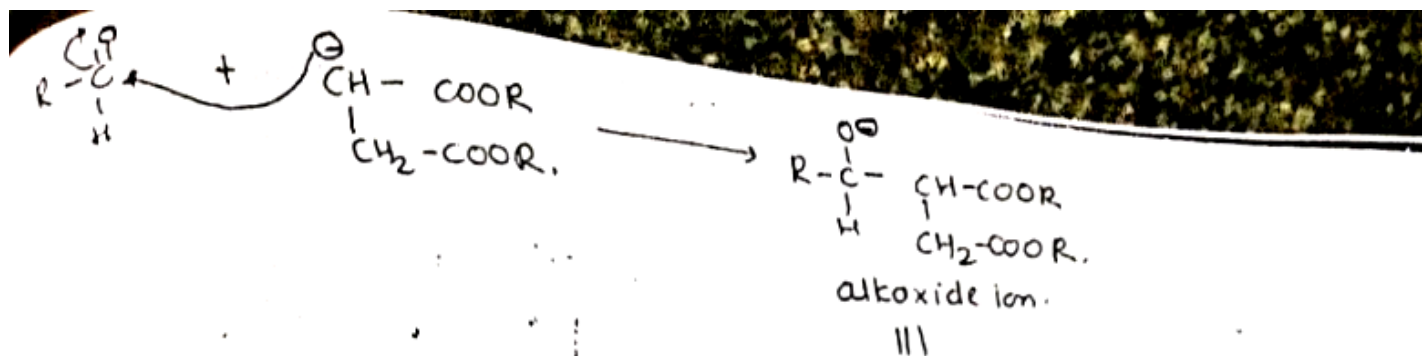
# CONDENSATION



mechanism →

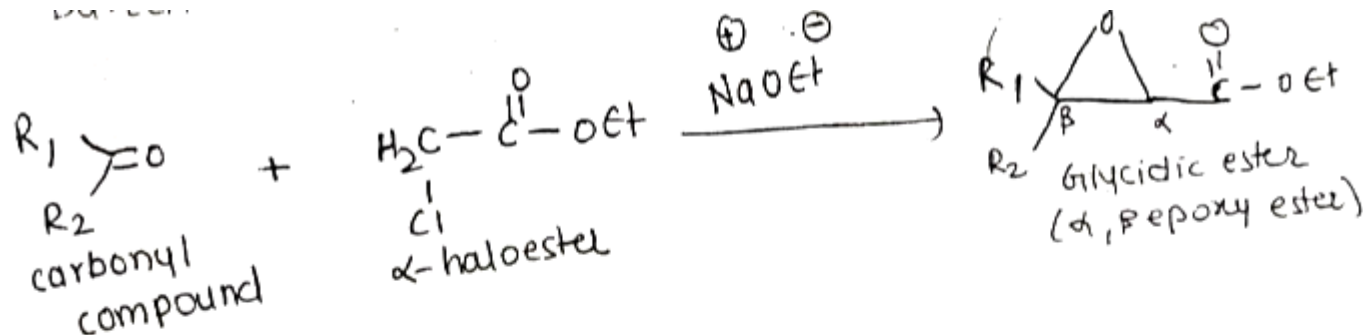
1) formation of carbanion →



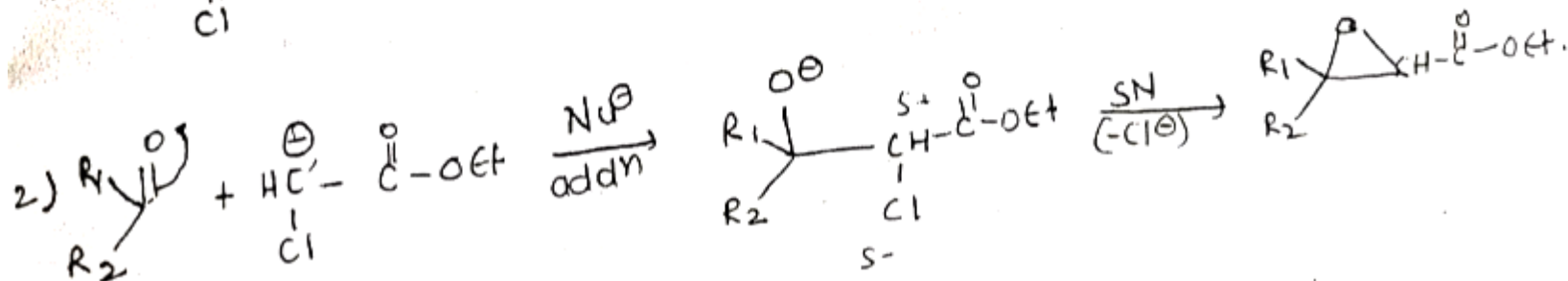
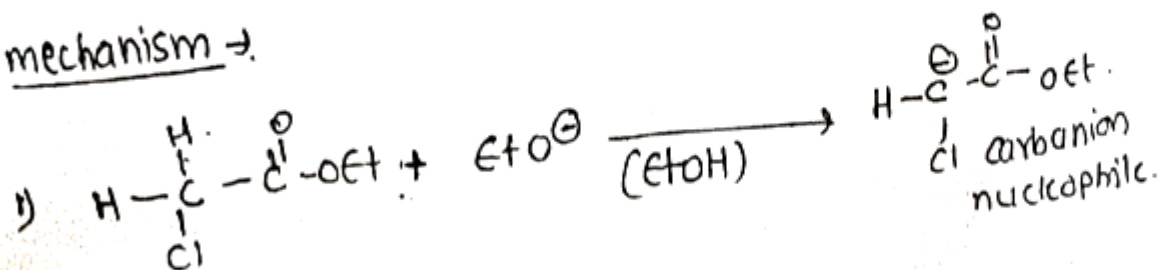


# DARZENS GLYCYDIC ESTER SYNTHESIS

- Also known as darzen condensation

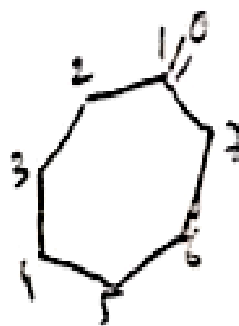
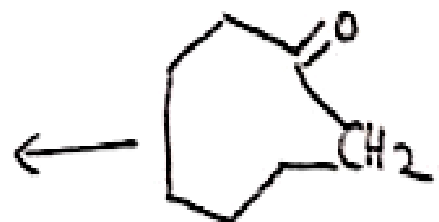
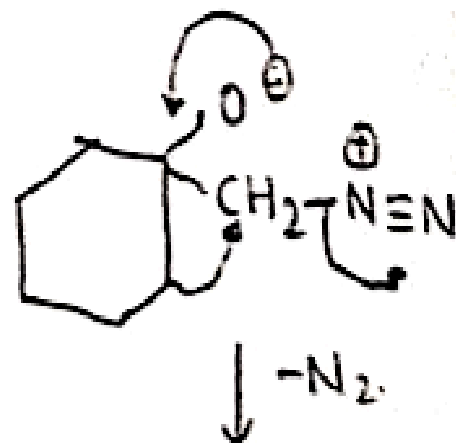
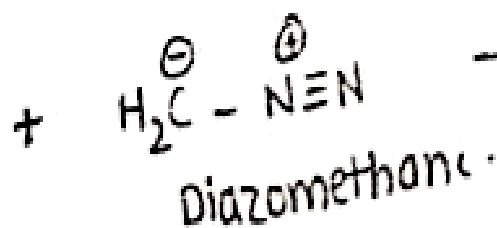
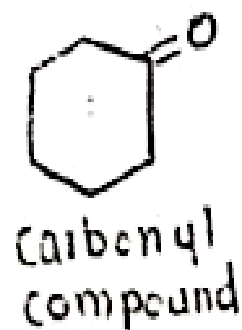


mechanism →

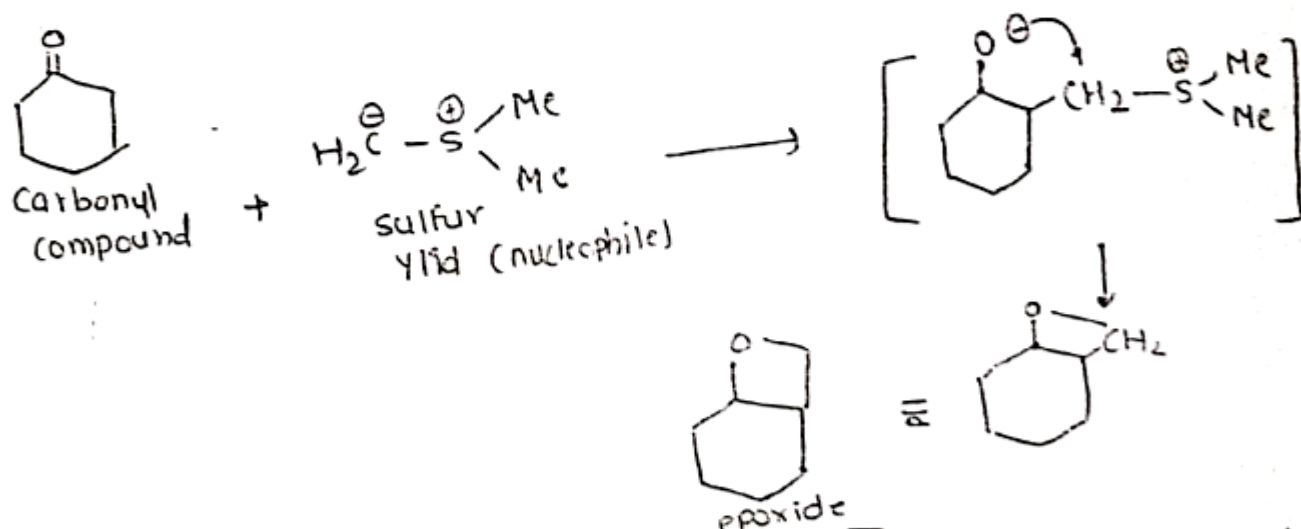


## Use of diazomethane:

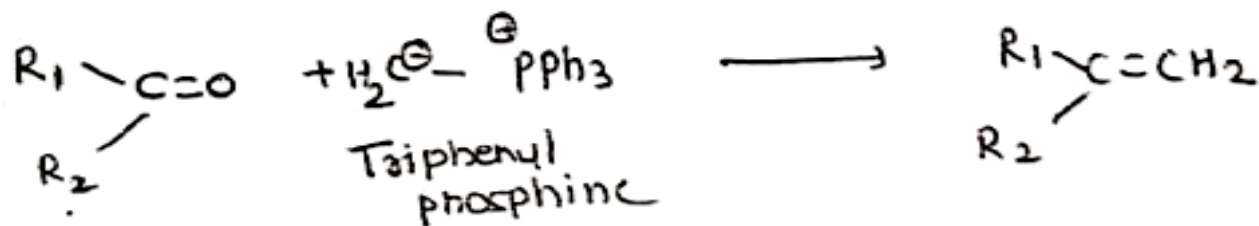
a) Use of diazomethane →





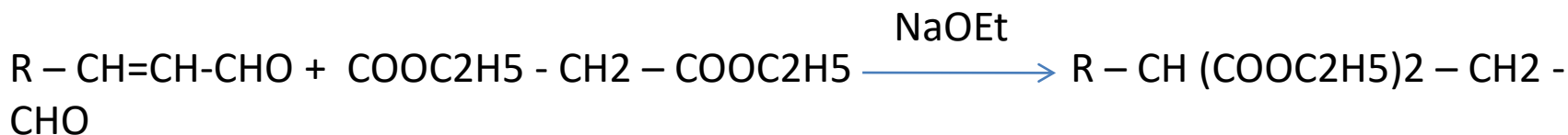
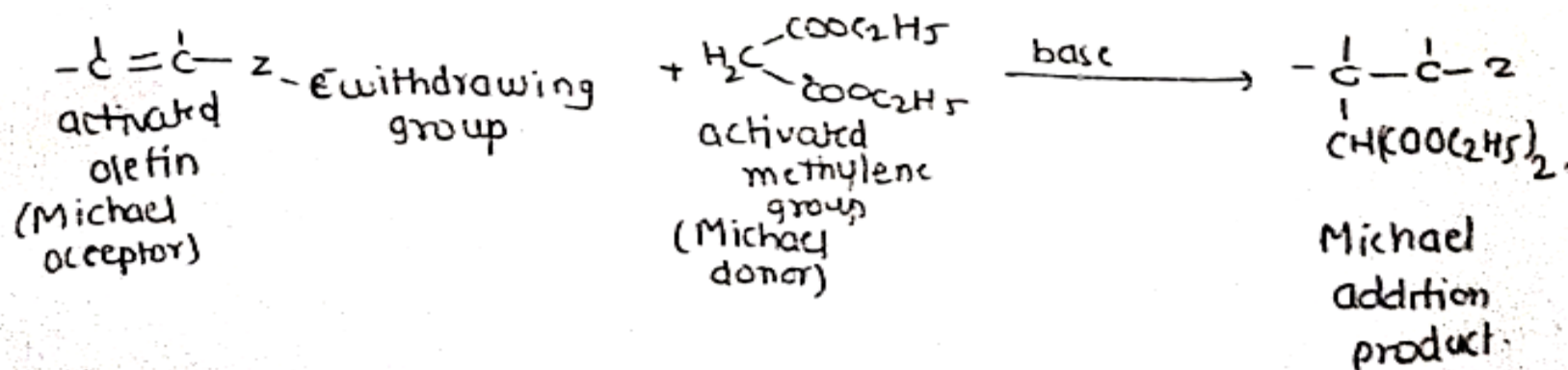


- Whenever phosphorous ylids are reacted with carbonyl compounds they form alkenes and this reaction is called as **wittig reaction**.



## MICHAEL ADDITION

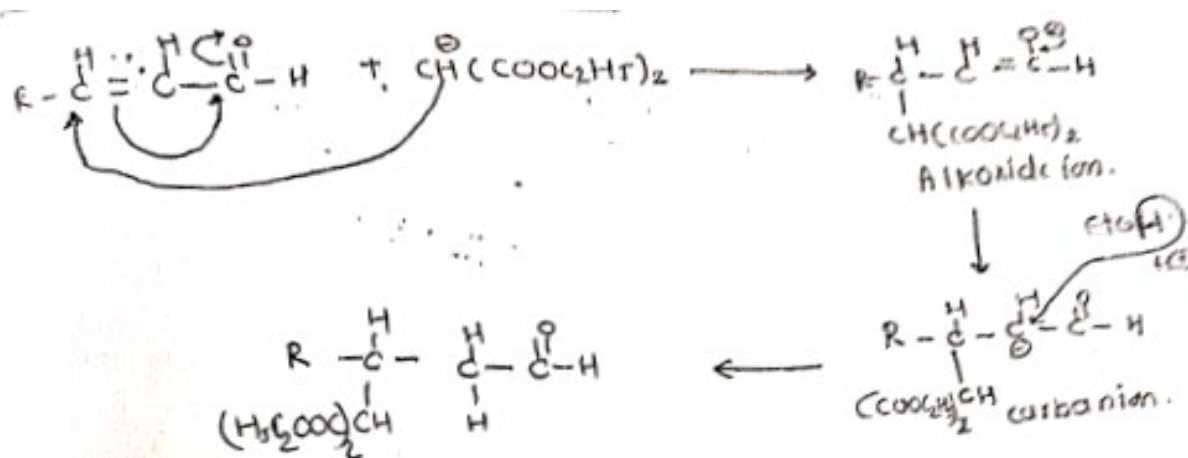
- It is the base catalysed addition of active Methylene compound to an activated olefin is called as michael addition.



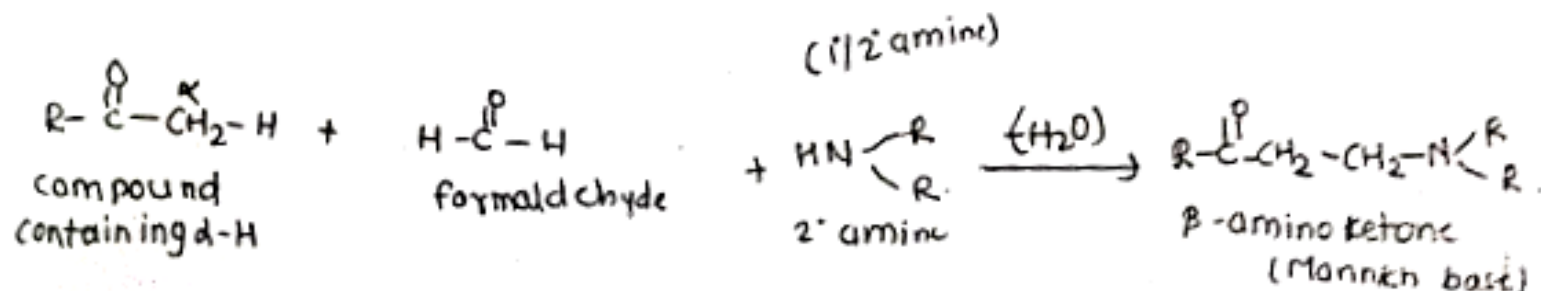
## MECHANISM:



Reaction of carbanion with acceptor:

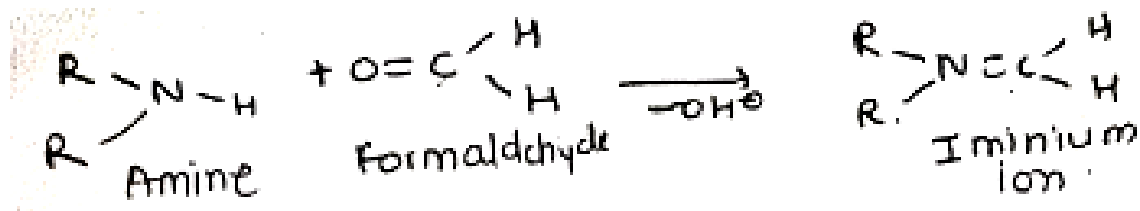


# MANNICH CONDENSATION

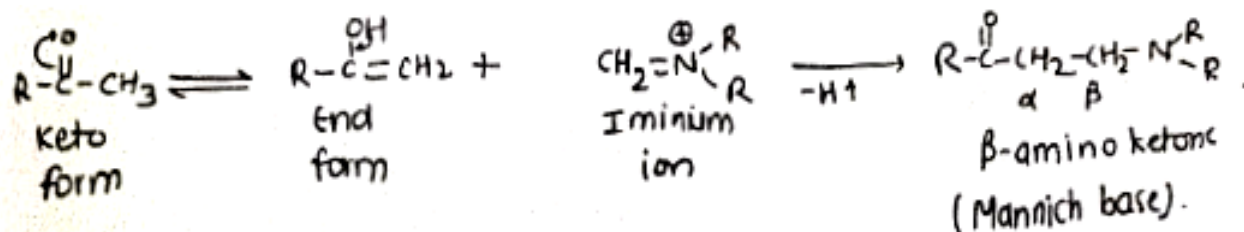


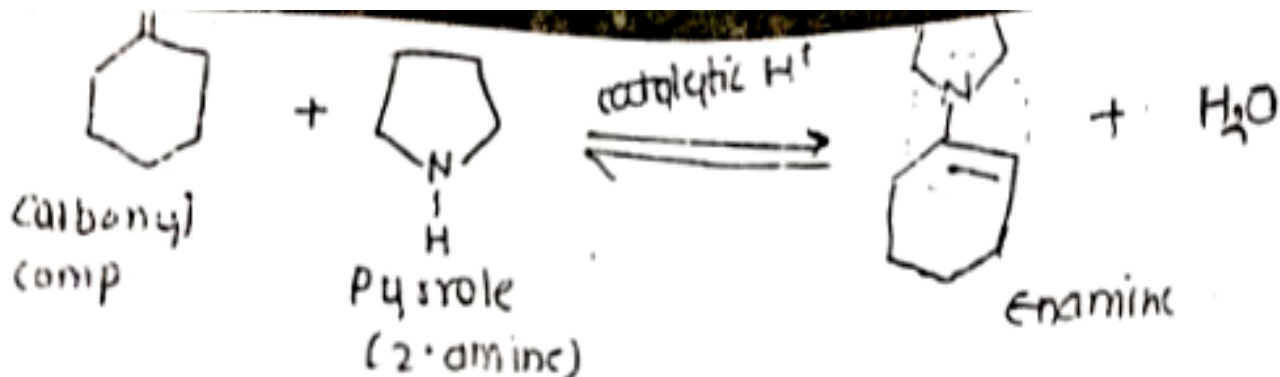
## MECHANISM:

1. Formation of iminium ion with the loss of hydroxide ion:

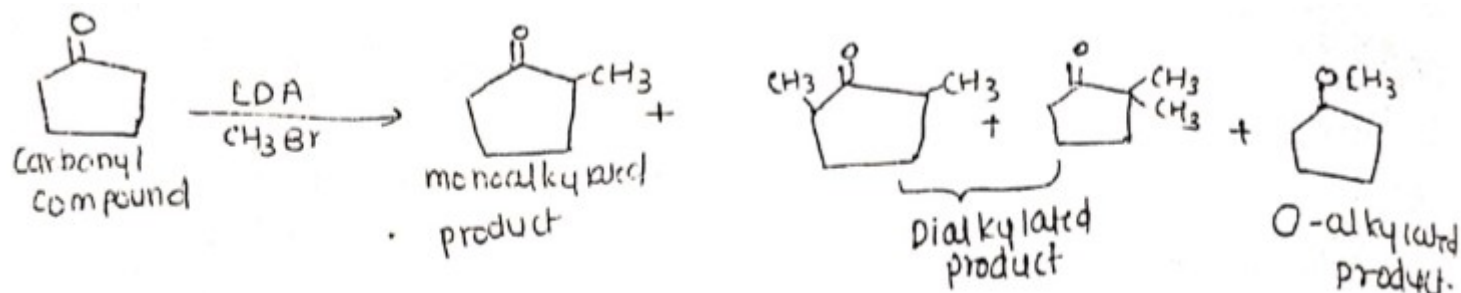


2. Reaction of iminium ion with containing alpha hydrogen:





➤ When a carbonyl group is alkylated directly, in addition to monoalkylated product, dialkylated and o-alkylated products are formed.

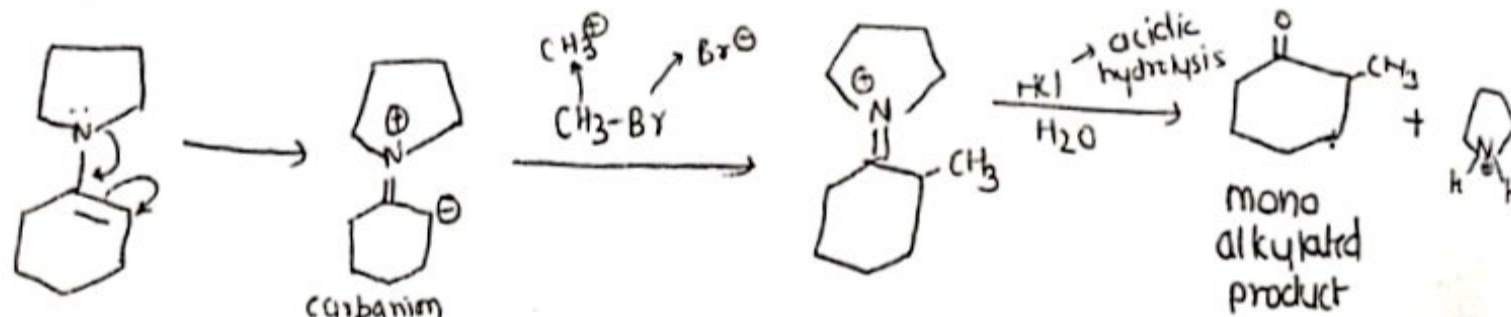


### LDA:

Lithium diisopropamide

- Strong base used as catalyst
- non-nucleophilic
- Good solubiliser in non polar solvents

## MECHANISM:

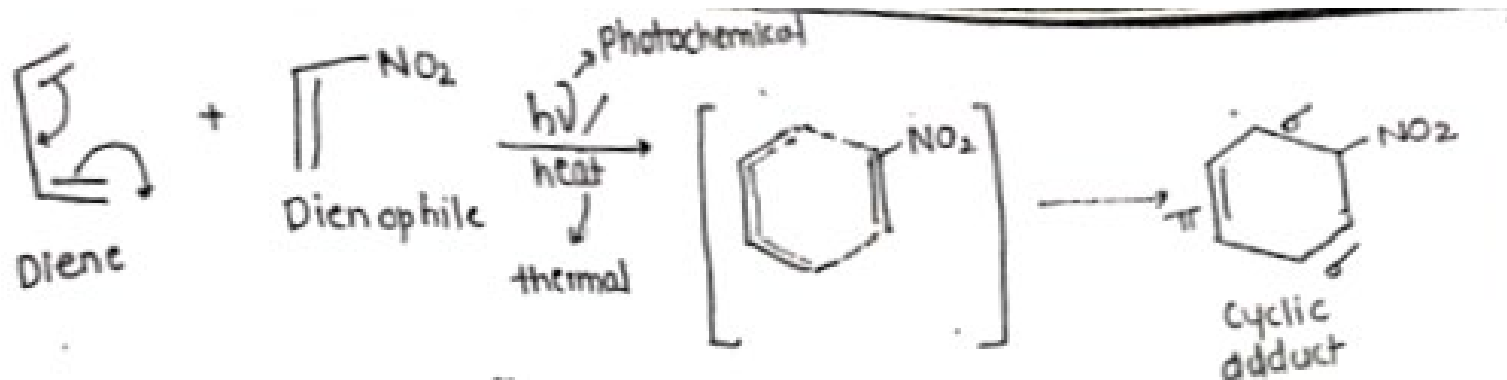


- Pericyclic reactions are concerted reactions where in there is formation of product through a cyclic transition state.

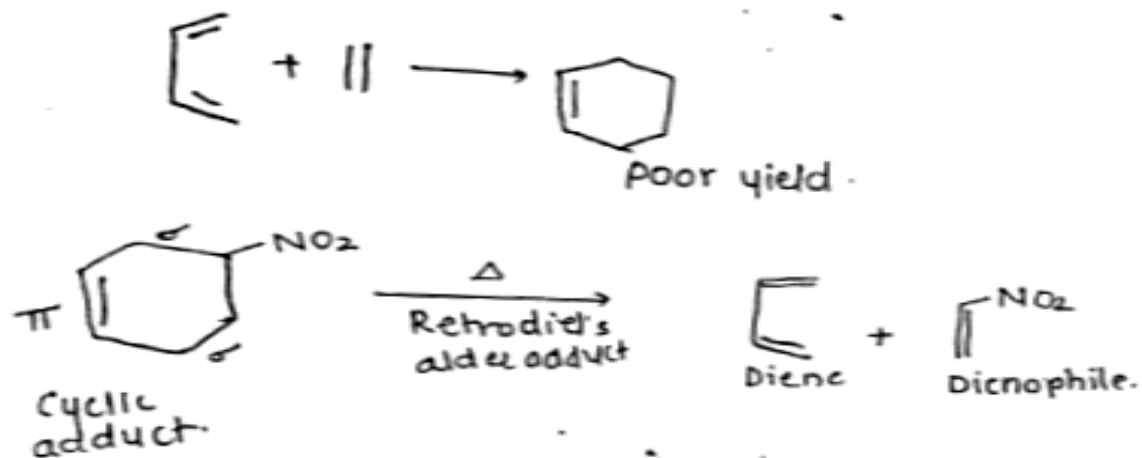
# DIEL'S – ALDER REACTION - CYCLOADDITION

3 types:

- Electrocyclic
- Sigmatropic
- Cycloaddition

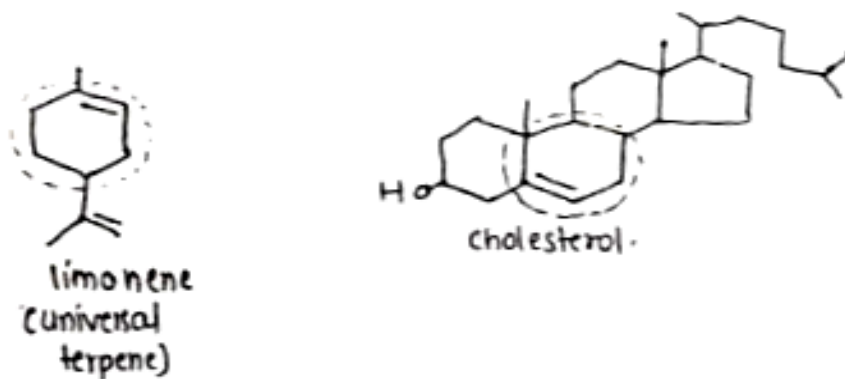


- If dienophile contains electron withdrawing group then the reaction is more effective – good yield



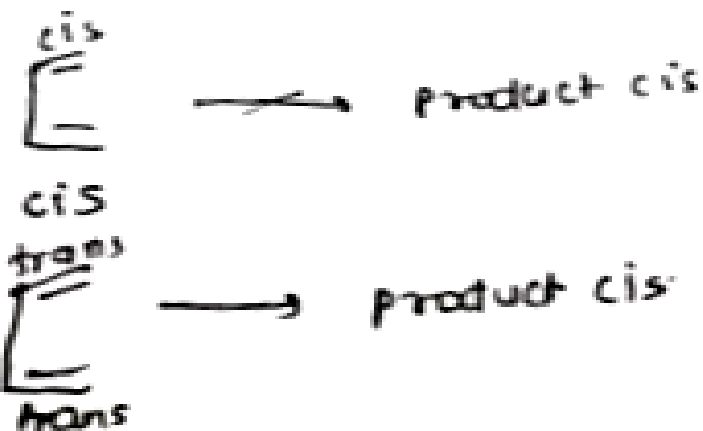
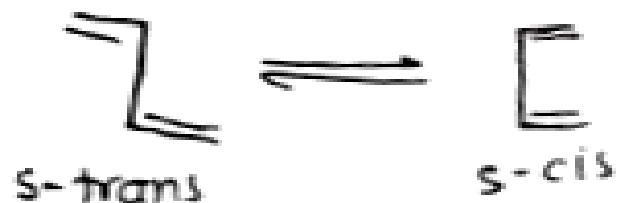
- ❖ In mass spectroscopy the compounds containing cyclohexanyl system will undergo fragmentation through retro diel's alder reaction from stable diene atom which will be detected by mass detector.

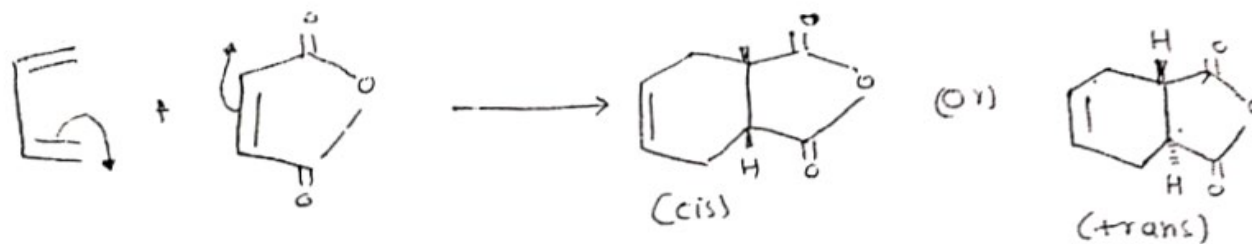
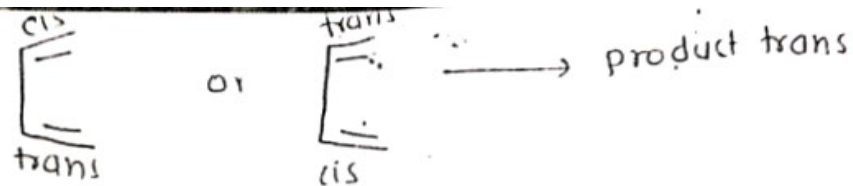
eg:-





## DIENE STEREOCHEMISTRY:





Dienophile stereochemistry →

