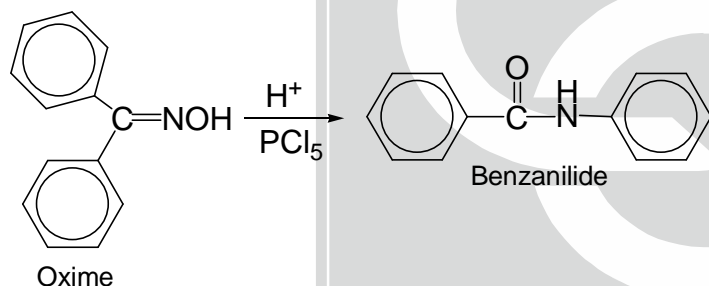


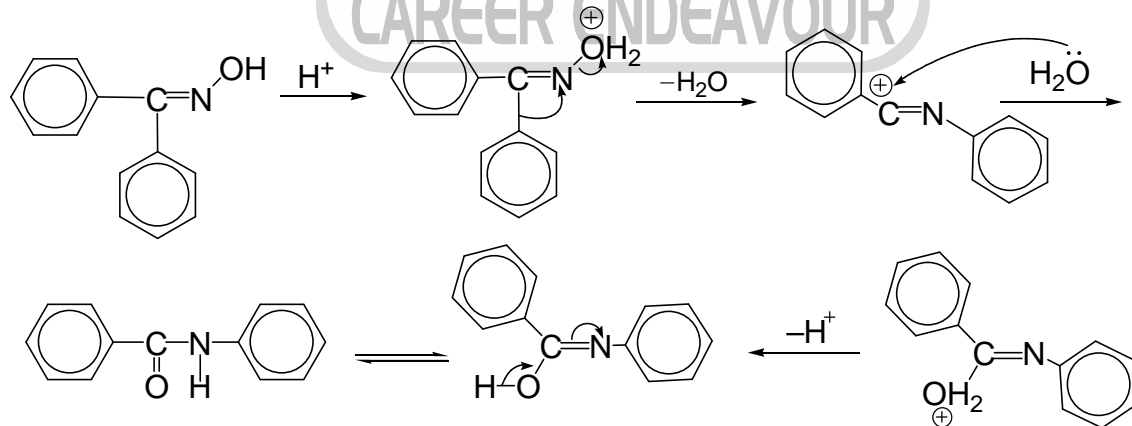
Rearrangement Reactions

7.1. Beckmann Rearrangement

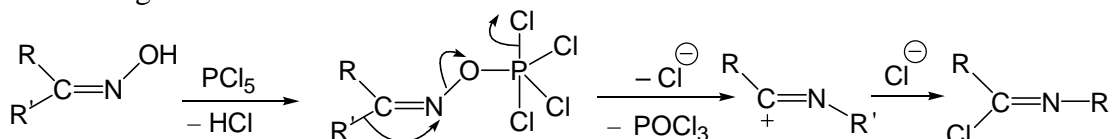
The rearrangement of oxime under the influence of a variety of acidic reagent to N-substituted amide. PCl_5 is commonly used as a catalyst in Beckmann Rearrangement but conc. H_2SO_4 , polyphosphoric acid, formic acid, thionyl chloride, silica etc. have been used successfully. e.g.: Benzophenone oxime is converted into benzanilide in the presence of PCl_5 . The role of these catalyst is to convert the hydroxyl group into a better leaving group.

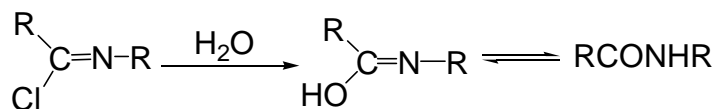


Mechanism :

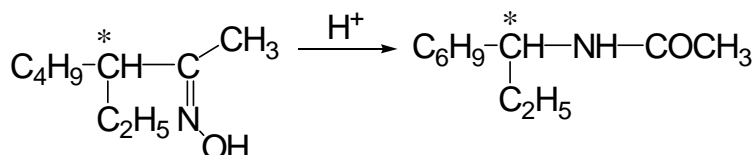
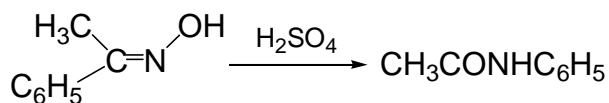


* It has been found that the electron withdrawing substituents ($-\text{R}$ group) attached to the migrating aryl group retard the rate of reaction. The presence of electron donating group ($+\text{R}$ group), on the other hand, has an accelerating influence.





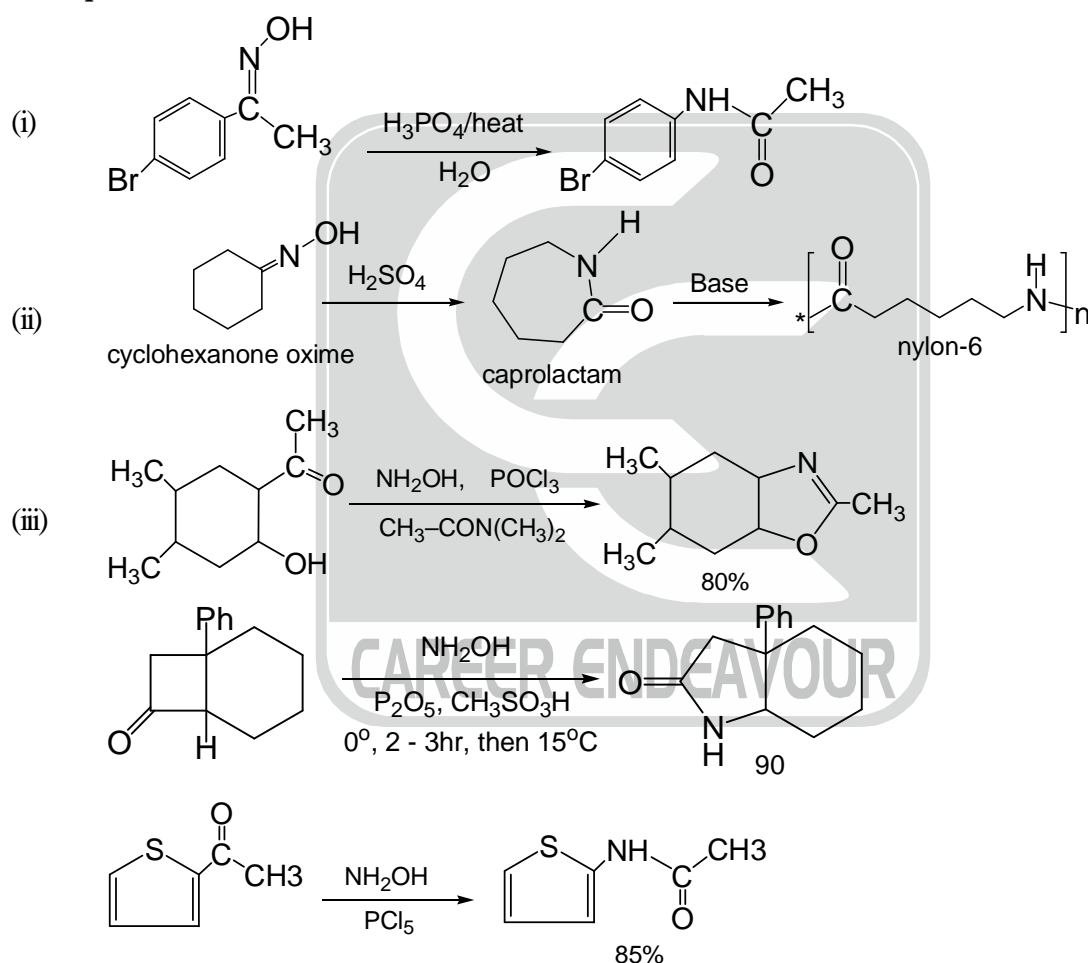
* This rearrangement is highly stereospecific that is the group anti to the oxime hydroxyl group always migrates regardless of relative migratory aptitude of the two groups. The chiral group migrate with retention of configuration.



methyl - 3- heptyl ketoxime

3- acetamidoheptane (Retention)

Examples:

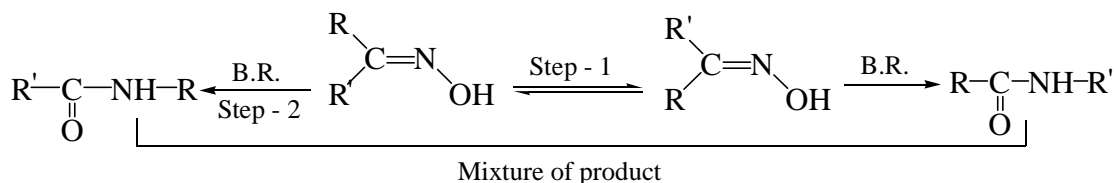


Drawbacks :

(1) Anti - Syn isomerisation of oxime.

(2) Beckmann fragmentation

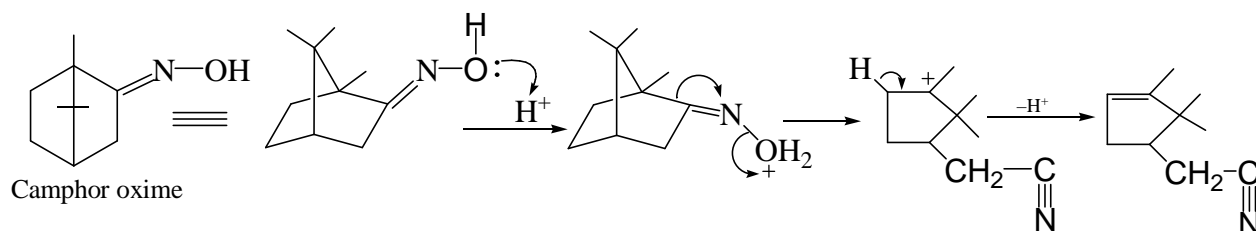
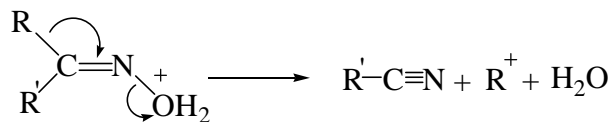
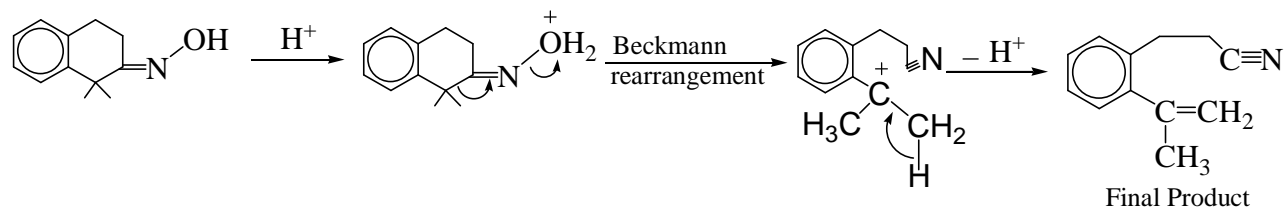
1. **Anti - syn isomerisation :** Some reaction condition can lead to syn-anti isomerization of the oxime occurring at the rate faster than the Beckmann rearrangement then a mixture of product will be obtained.



Rate (Step 1 > Step 2) – Product mixture

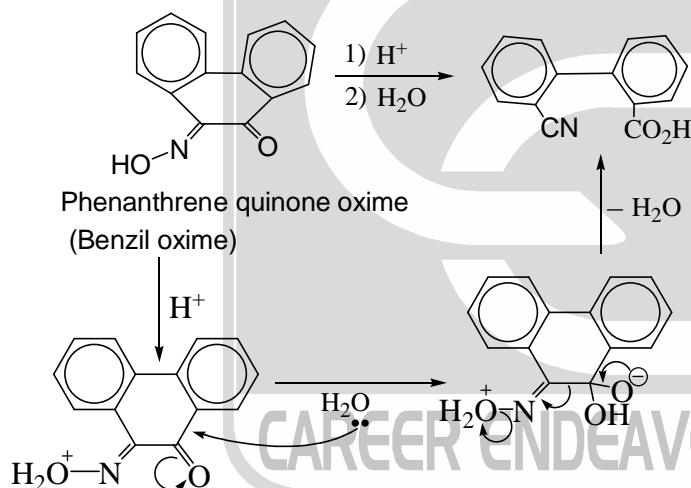
Rate (Step 2 > Step 1) – Pure product

2. **Fragmentation** : A fragmentation reaction occurs if one of the oxime substituent can give rise to a very stable carbocation and subsequent formation of nitrile ($C\equiv N$)



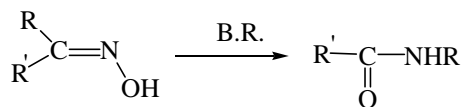
Fragmentation is favoured by reagents like PCl_5 , $SOCl_2$, strong acids. While aryl sulphonyl chloride in pyridine or aqueous alkali encourage rearrangement over fragmentation.

Example:

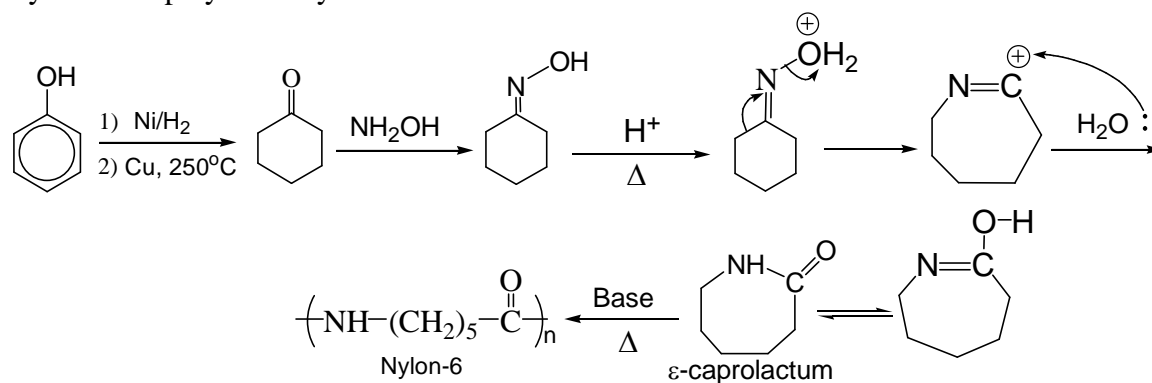


Application:

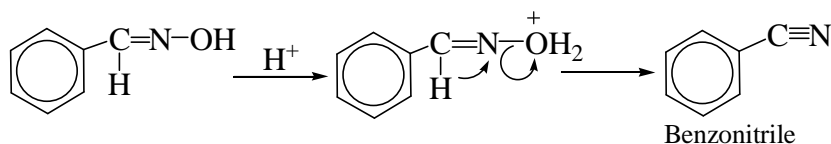
1. Configuration of ketoxime can be obtained.



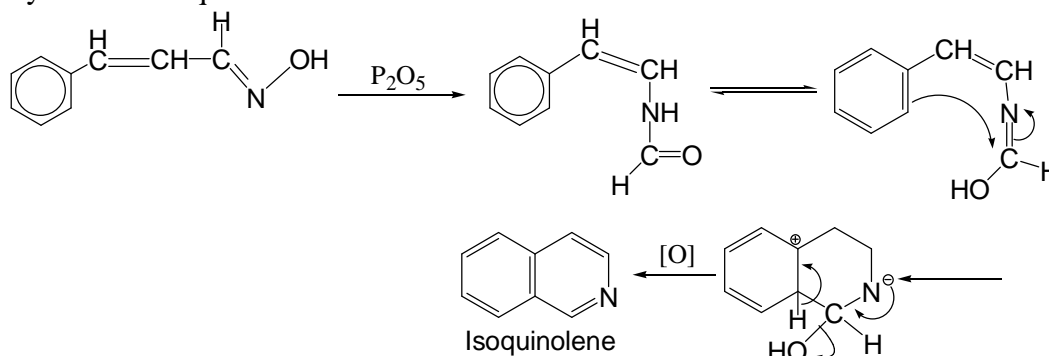
2. Synthesis of polymer – Nylon 6



3. Aldoxime under Beckmann rearrangement condition may dehydrate to nitriles

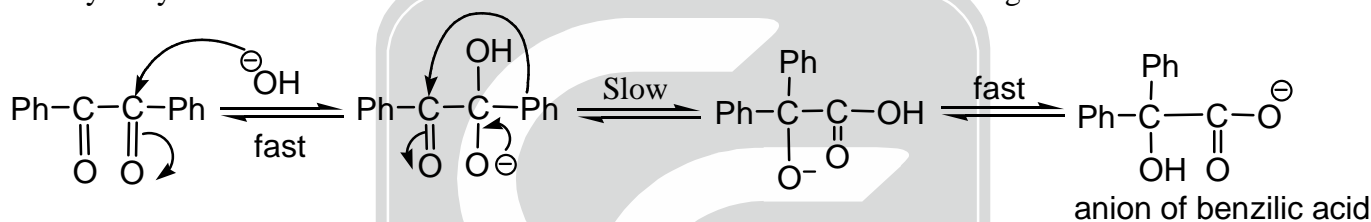


4. Synthesis of isoquinoline :

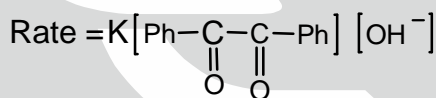


7.2. Benzil-benzilic acid Rearrangement

The base catalysed rearrangement of benzil (obtained from oxidation of benzoin) to produce the anion of a α -hydroxy acid known as benzilic acid is known as Benzil-Benzilic Acid Rearrangement.



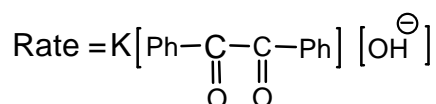
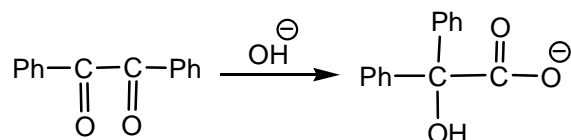
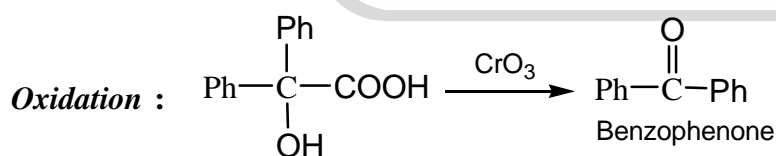
Nucleophilic addition reaction of Ph^- on $\text{C}=\text{O}$



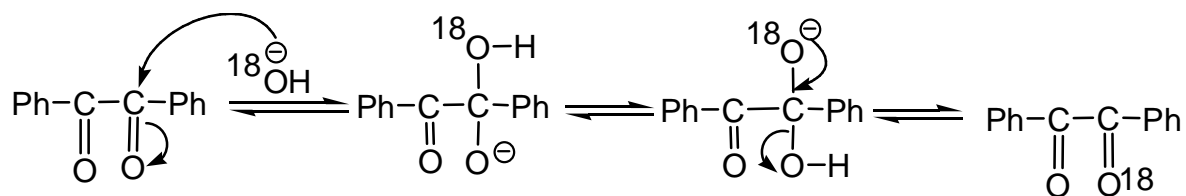
Second order reaction

Properties of Benzilic Acid:

Melting point : 150°C

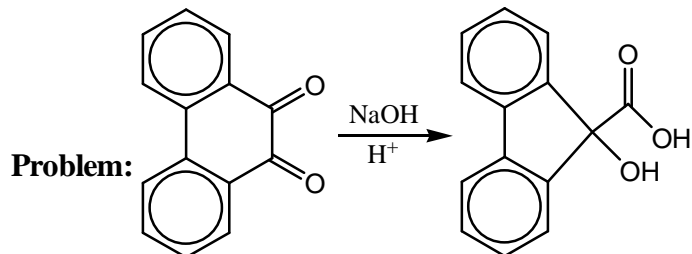


It has been found that when reaction is carried out in ($\text{H}_2\text{O}^{18} \rightarrow {}^{18}\text{OH}^-$) then the benzil exchanges ^{18}O faster than the rearrangement that is why it has been suggested that a fast reversible nucleophilic attack occurs at the carbonyl carbon in the initial step which is followed by rate determining migration of the aryl group.

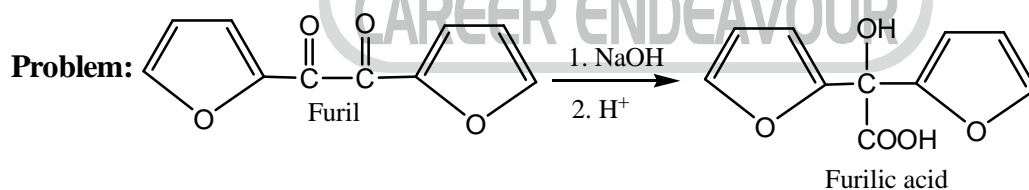
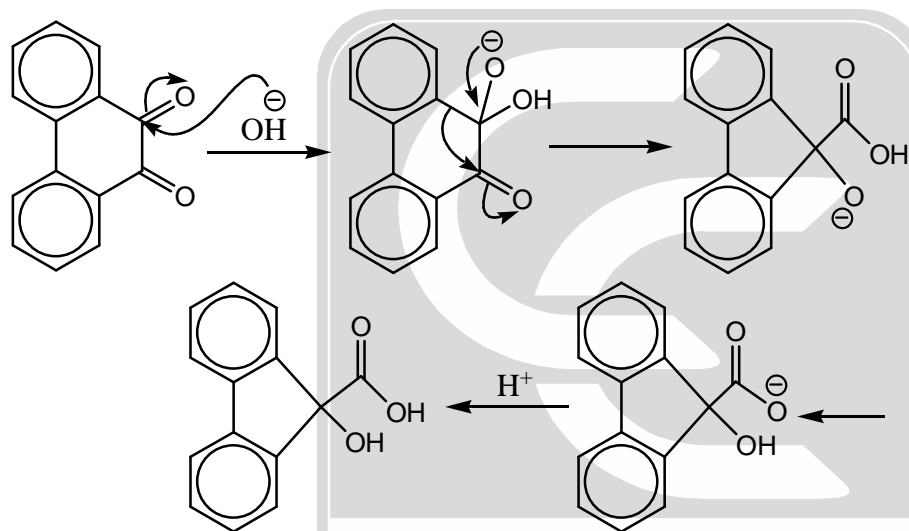


exchange of ^{18}O Showing that rearrangement is a slow step

Isolated

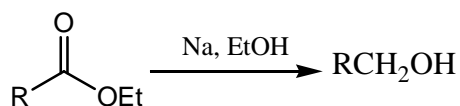


Mechanism: $\text{NaOH} \longrightarrow \text{Na}^+ + \text{OH}^-$

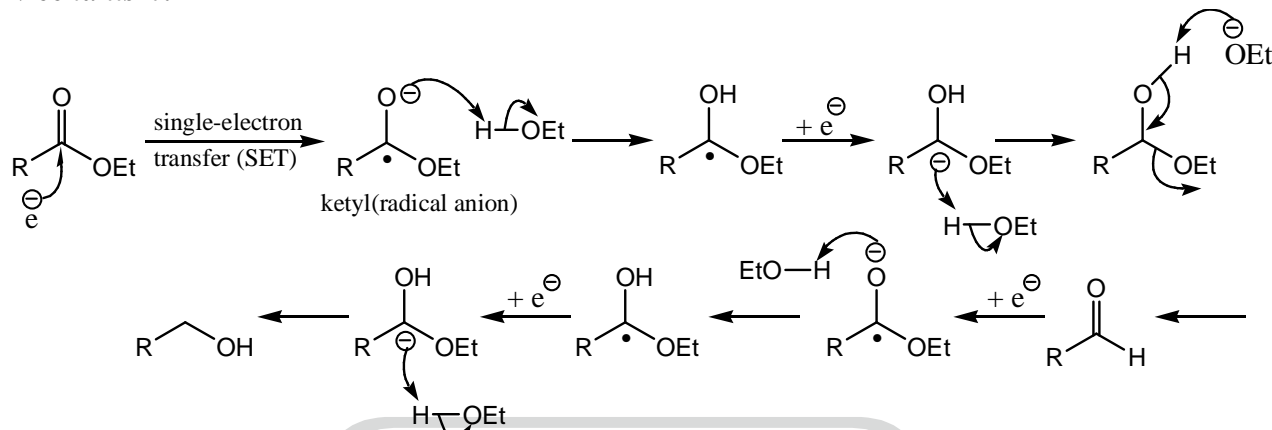


7.3. Bouveault-Blanc Reduction

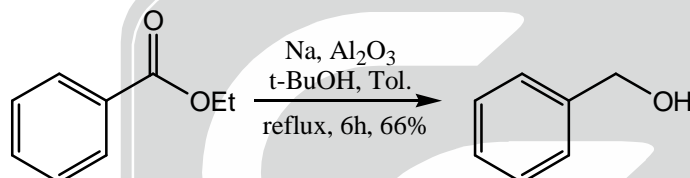
The conversion of esters to the corresponding alcohols using sodium in an alcoholic solvent is known as Bouveault Blanc reduction.



Mechanism:

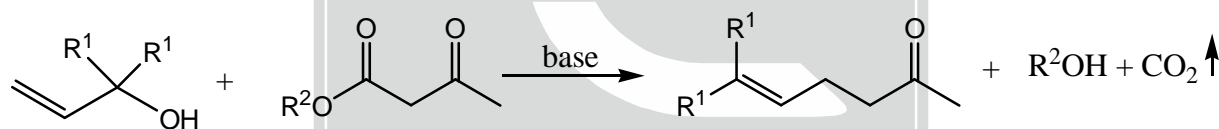


Example:

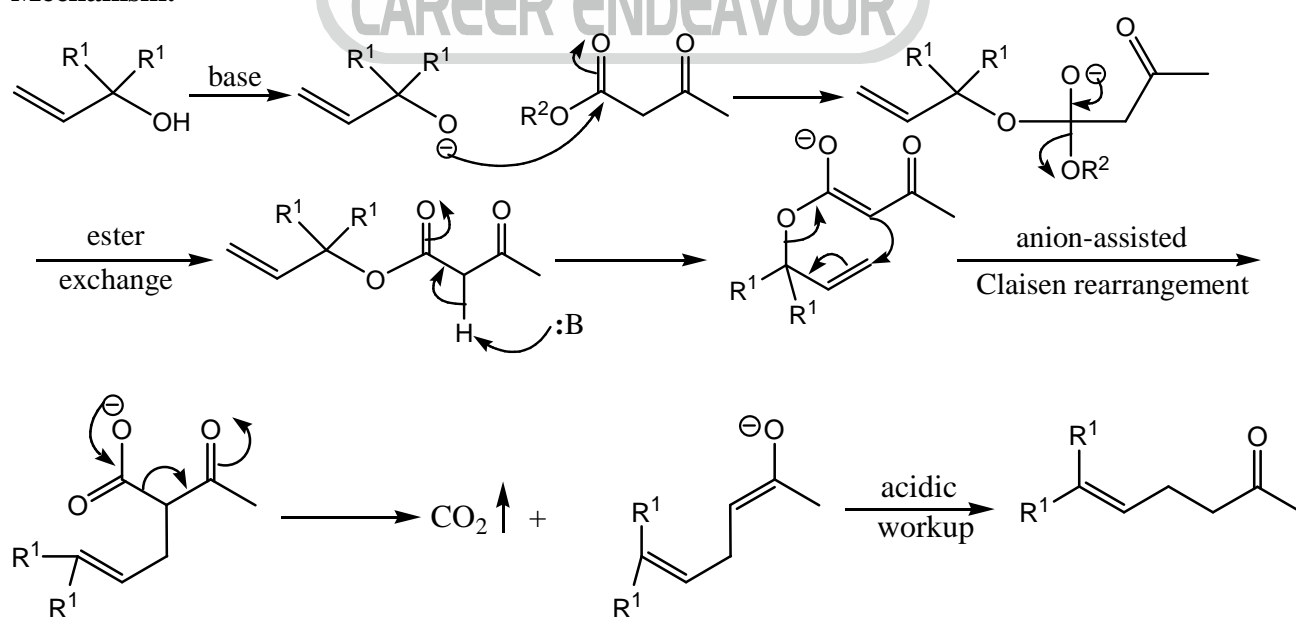


7.4. Carroll rearrangement:

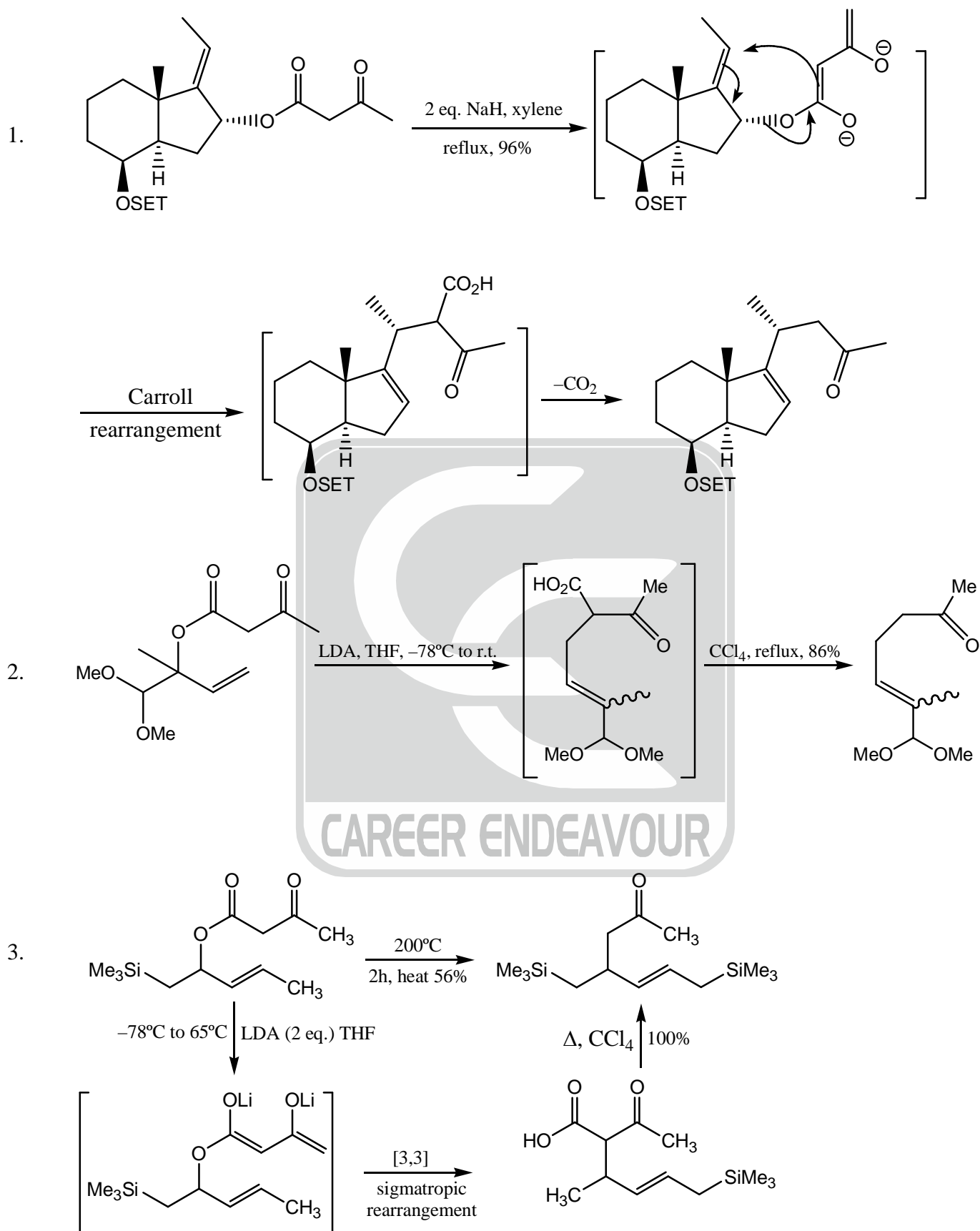
Thermal rearrangement of β -ketoesters followed by decarboxylation to yield γ -unsaturated ketones via anion-assisted Claisen rearrangement. It is a variant of the Claisen rearrangement.

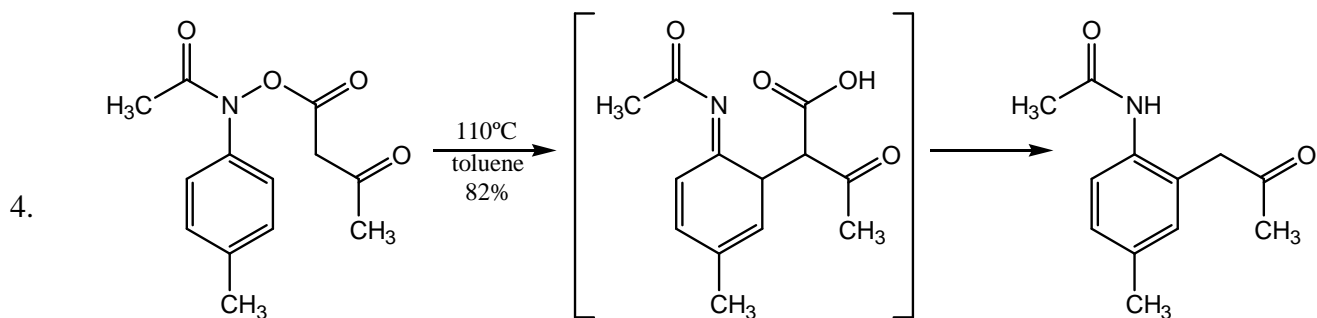


Mechanism:



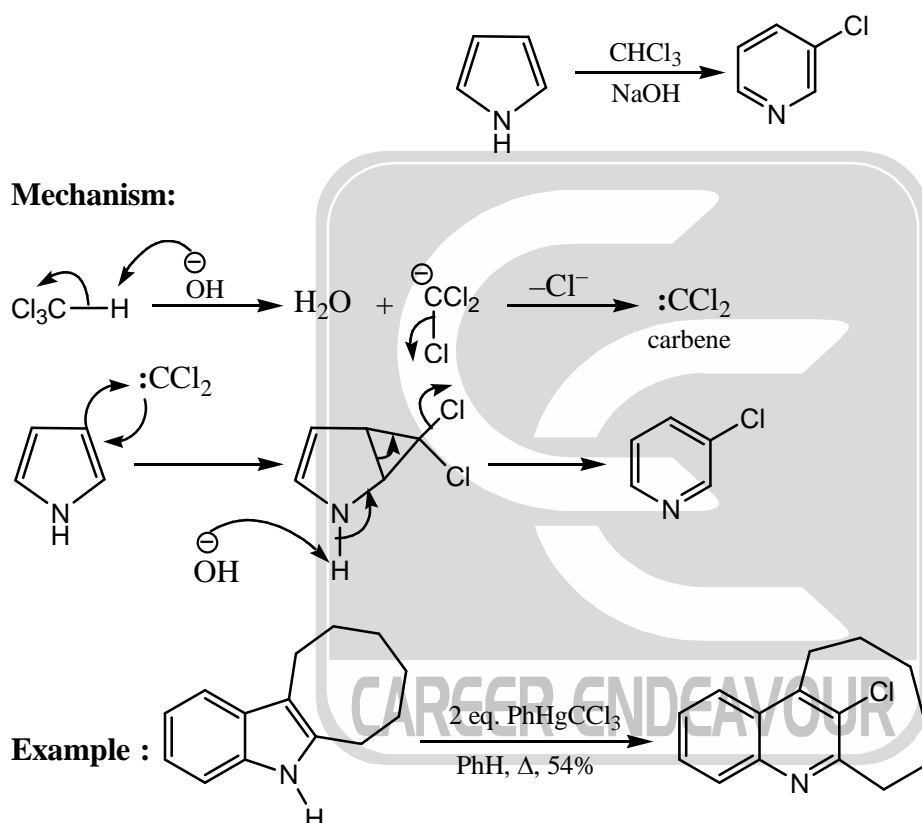
EXAMPLES





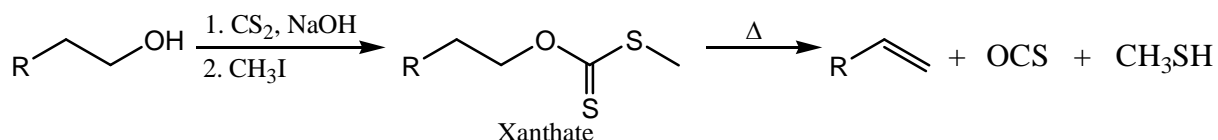
7.5. Ciamician-Dennstedt Rearrangement:

Cyclopropanation of a pyrrole with dichlorocarbene generated from CHCl_3 and NaOH . Subsequent rearrangement takes place to give 3-chloropyridine.

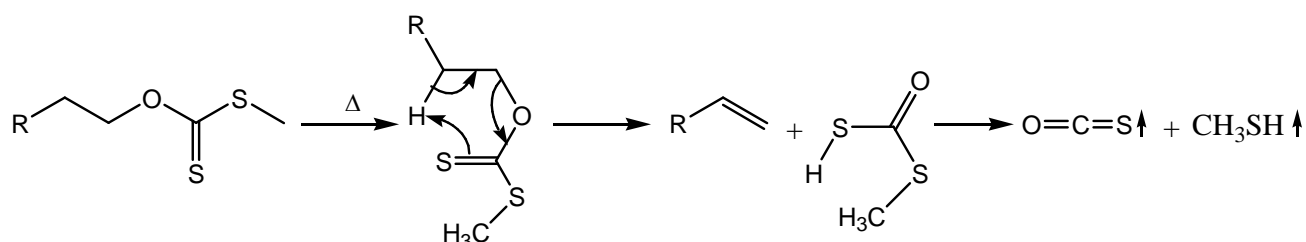


7.6. Chugaev Elimination

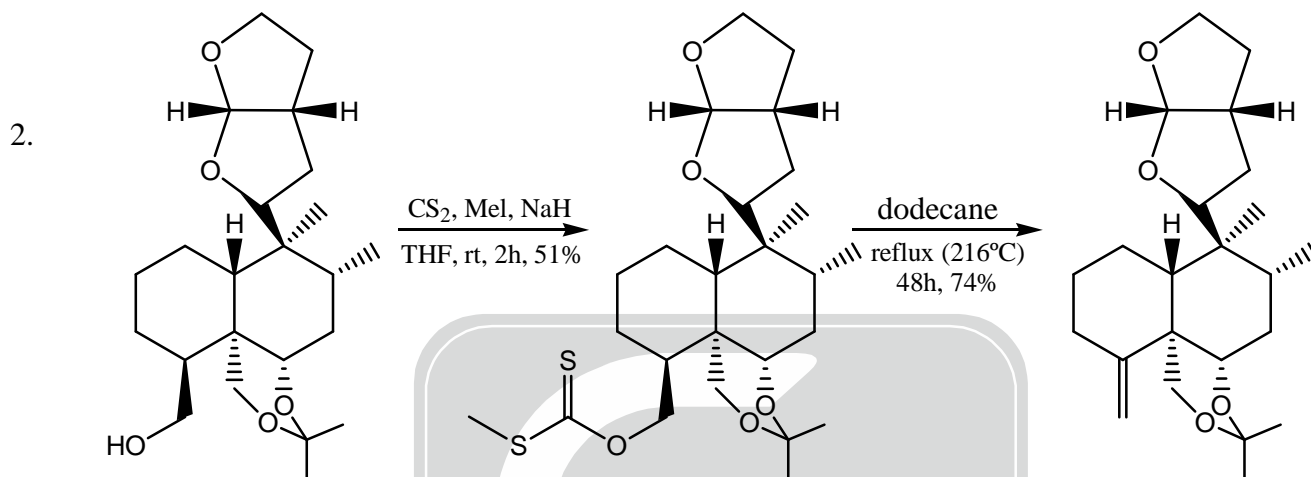
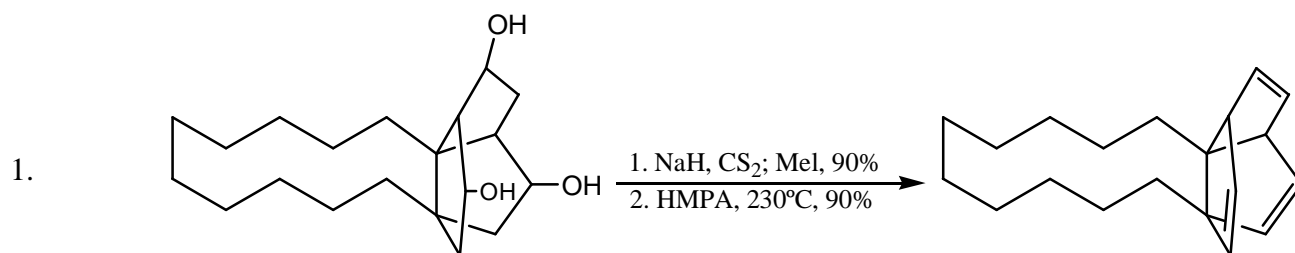
Thermal elimination of xanthates to olefins is known as Chugaev elimination.



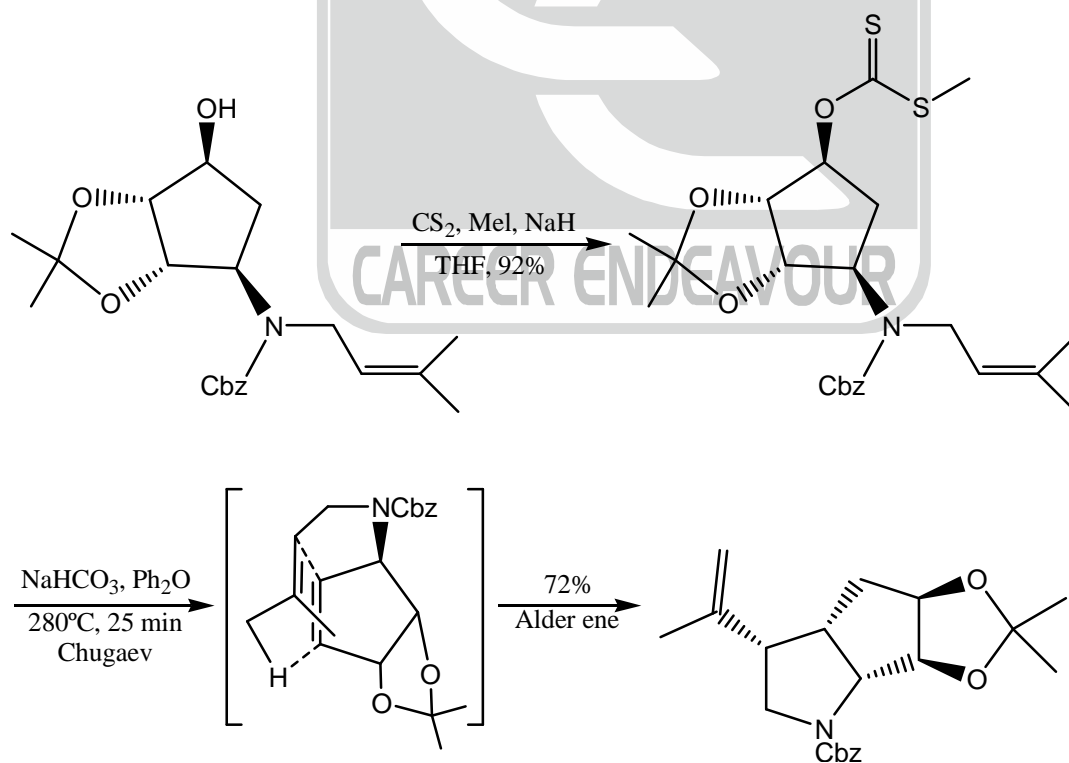
Mechanism:



EXAMPLES

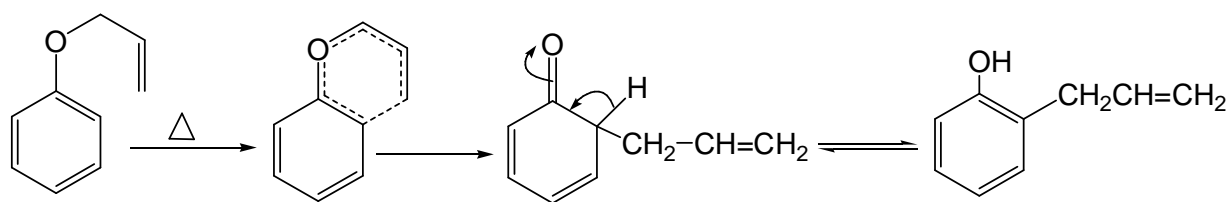


3. This reaction is an example of Chugaev syn-elimination is followed by an intramolecular ene reaction.



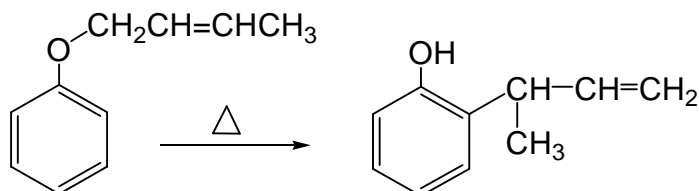
7.7. Claisen Rearrangement

Rearrangement of allyl aryl ether into *o* or *p*-allyl phenol through sigmatropic rearrangement. The allyl group migrate from oxygen to the ring preferably at ortho position.



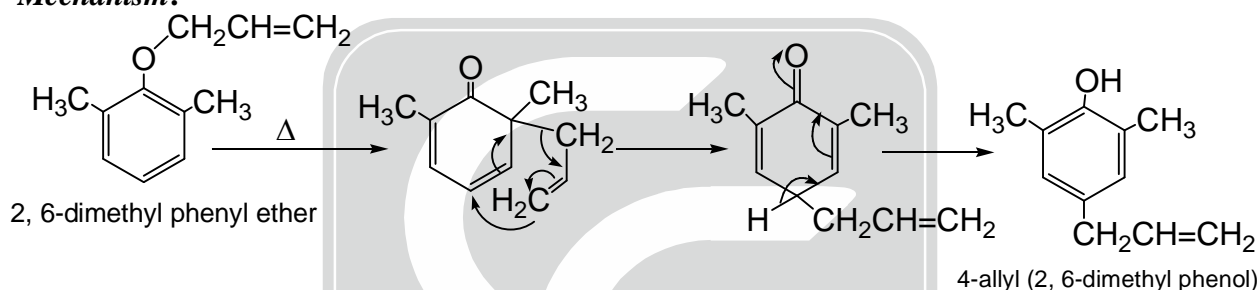
2-allyl phenyl ether cyclic transition state cyclohexadienone

o-allylphenol

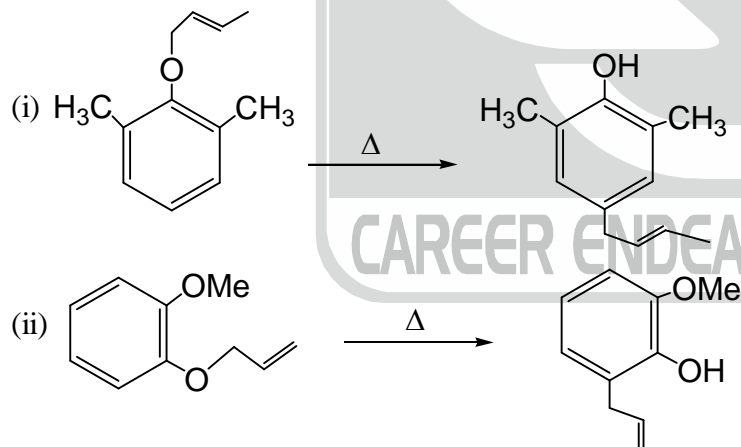


2-butenyl phenyl ether 2-(1-methyl(-2-propenyl)) Phenol

Mechanism:

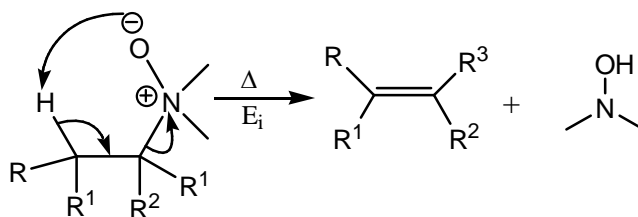


Example:



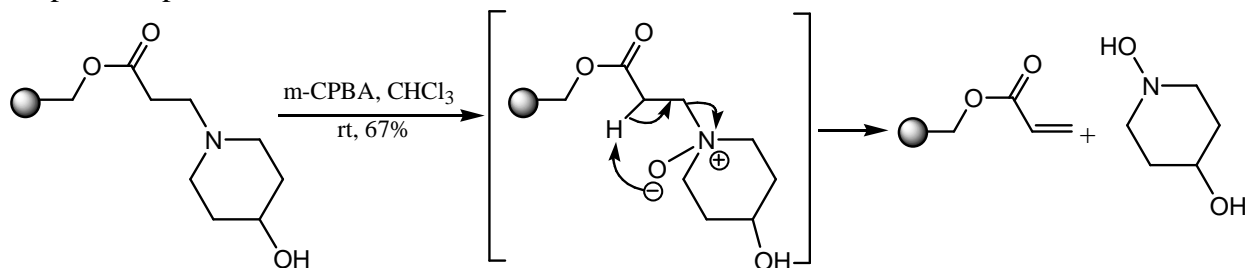
7.8. Cope Elimination Reaction

This reaction includes thermal elimination of N-oxides to olefines and N-hydroxyl amines.

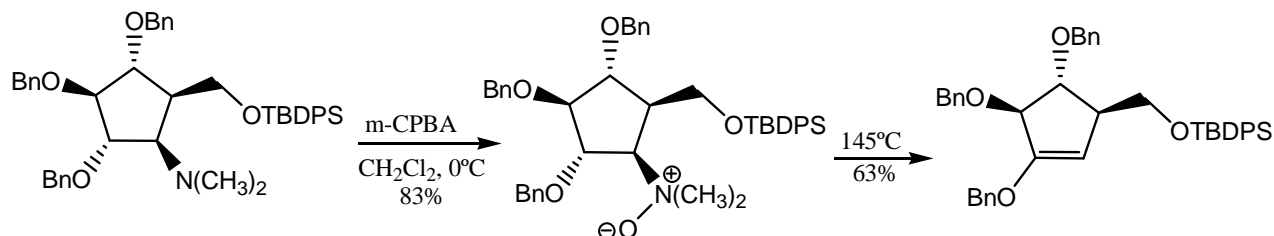


PROBLEMS

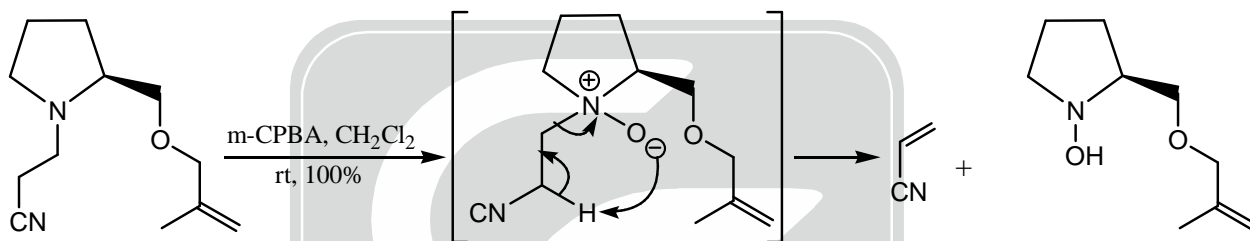
1. Solid-phase Cope elimination.



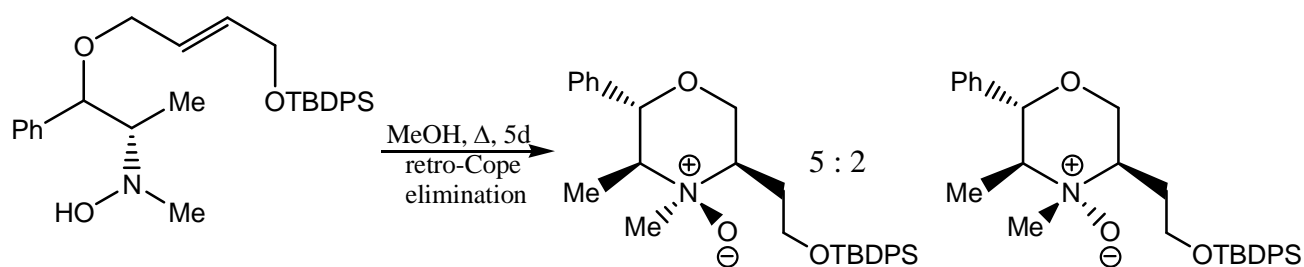
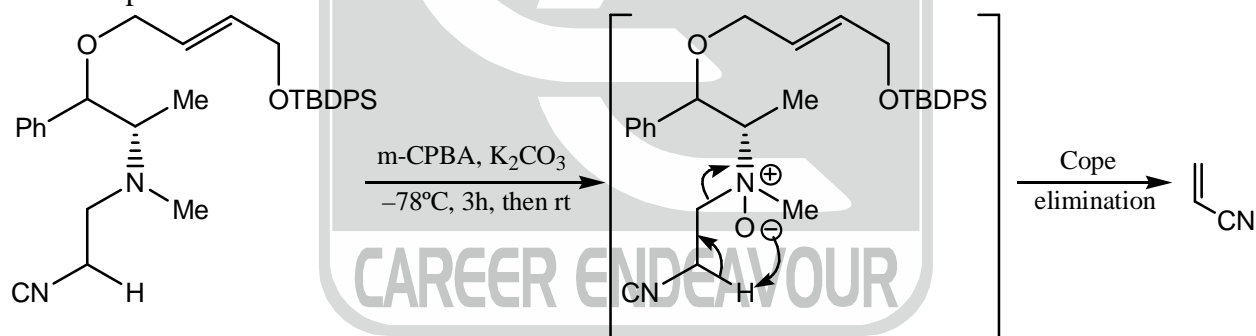
2.



3.

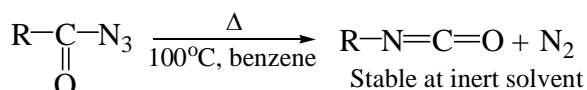


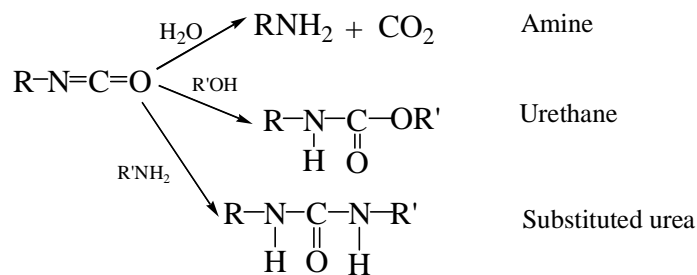
4. Retro-Cope elimination:



7.9. Curtius Rearrangement

It involves the decomposition of acyl azides in an inert solvent (benzene) by heating to isocyanate; the temperature required is around 100°C . The isocyanate can be converted to amine by adding H_2O , to urethane by adding alcohol and to substituted urea by adding amine. The conversion of acyl azide to isocyanates uses Curtius rearrangement followed by conversion to amines, urethanes, etc. is known as Curtius rearrangement.

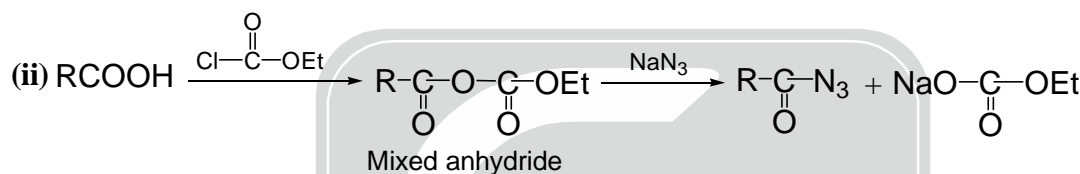
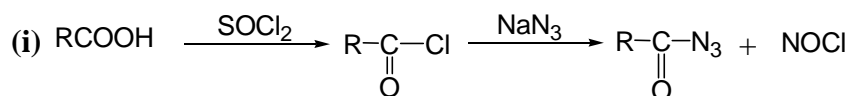
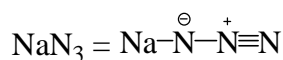




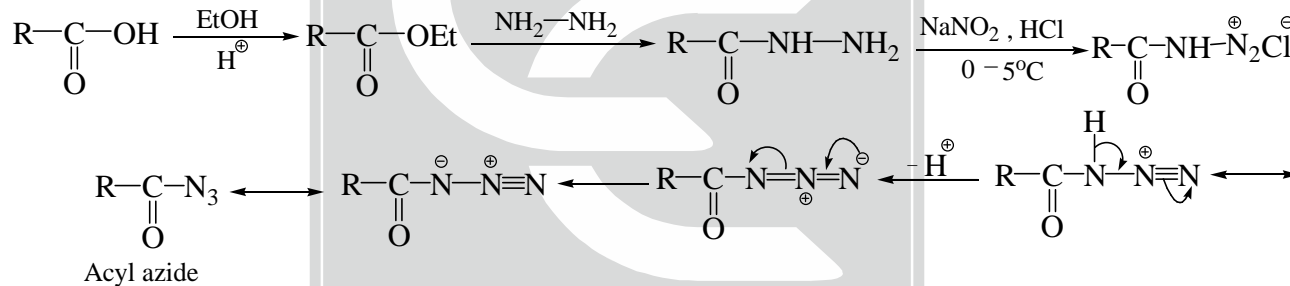
Ester of carbonic acid is called urethane.

The reaction is general and can be applied to aliphatic, aromatic, heterocyclic and unsaturated acids. The other functional group remain unaffected during the reaction.

1. **Acyl azide preparation :** Reacting sodium azide (NaN_3) with a reactive acylating agent made from acid.



2. **By diazotisation of acyl hydrazide :**



3. **Using diphenyl phosphoryl azide :**



Mechanism :

The rearrangement is a concerted process in which the migration of the R group is accompanied by the loss of N_2 . So removal of N_2 is driving force and also derives the reaction forward. The migrating group retains the stereochemical consideration (If chiral during the rearrangement. like that of Hoffmann rearrangement) No cross over products are obtained suggesting that it is strictly intramolecular process. Since there is no evidence for the formation of the $\text{R}-\overset{\cdot\cdot}{\text{C}}-\overset{\cdot\cdot}{\text{N}}$, hence the rearrangement step is concerted.

