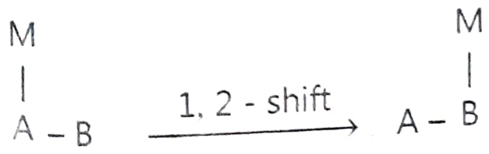
Chapter 3...

Rearrangement Reactions

Contents ...

3.1 Introduction

- A **rearrangement reaction** is a broad class of organic reactions where the carbon skeleton of a molecule is rearranged to give a structural isomer of the original molecule.
- The migration of an atom or group from one position to another within the same molecule is known as molecular rearrangement. The rearrangement involves migration of an atom or group of atoms to an adjacent atom (1,2-shift), or in some cases migration is over longer distances.

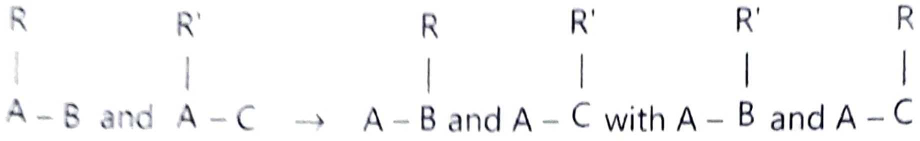


$$\begin{array}{cc} M & \\ | & \\ A & -\ B \end{array} \xrightarrow{1,\,2\text{ - shift}} \begin{array}{cc} & M \\ & | \\ A\ - & B \end{array}$$

where,
A = Migration origin
B = Migration terminus
M = Migrating group

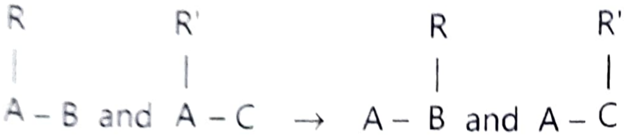
- The atom from which migration begins is known as the migration origin and the atom to which migration group moves is called migration terminus.

- In rearrangement reaction, migrating group shift with its lone pair of electrons called as nucleophilic (anionotropic) rearrangement and migrating group shift without electron pair is called electrophilic (cationotropic) rearrangement. In the rearrangement, if the migration of group is with one electron then it is called free radical rearrangement.
- The most common migrating atoms are carbon, hydrogen or heteroatom. The nucleophilic 1,2-shifts are more common in rearrangement reactions. The rearrangement reaction involves two possible modes of reaction as shown below.

(I) 

$$\overset{\overset{R}{|}}{A}-B \text{ and } \overset{\overset{R'}{|}}{A}-C \rightarrow A-\overset{\overset{R}{|}}{B} \text{ and } A-\overset{\overset{R'}{|}}{C} \text{ with } A-\overset{\overset{R'}{|}}{B} \text{ and } A-\overset{\overset{R}{|}}{C}$$

Intermolecular rearrangement

(II) 

$$\overset{\overset{R}{|}}{A}-B \text{ and } \overset{\overset{R'}{|}}{A}-C \rightarrow A-\overset{\overset{R}{|}}{B} \text{ and } A-\overset{\overset{R'}{|}}{C}$$

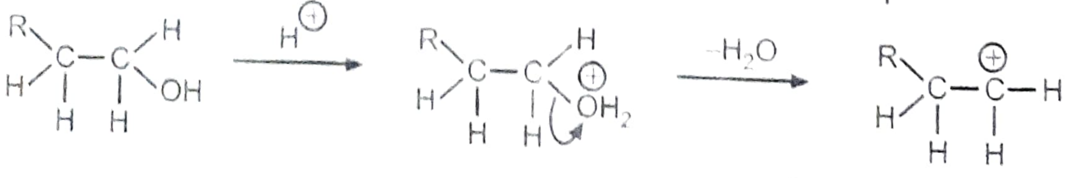
Intramolecular rearrangement

- 'I' type of rearrangements are called as intermolecular rearrangement in which the group R is completely detached from group A and may end up on the B atom or C atom of another molecule. In 'II' type of rearrangement, R going from A to B in the same molecule is called intramolecular rearrangement.

3.2 Types of Rearrangements

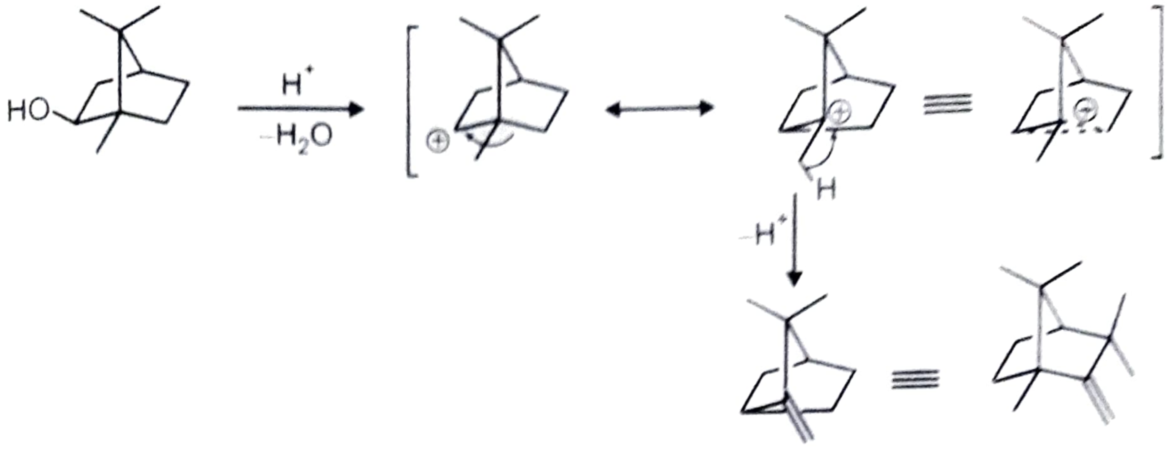
There are two key rearrangement reactions : 1,2-rearrangements and pericyclic reactions.

(i) **1,2-Rearrangements** : In this type of reaction the migrating group carries the electron pair with it, the migration terminus B must be an electron deficient atom with only six electrons in its outer shell. The first step is the formation of a carbocation intermediate. Carbocation can be formed from alcohol (the acid treatment of an alcohol to give carbocation from an intermediate oxonium ion), alkyl halide (reaction with $AgNO_3$) and alkene (electrophilic addition to C=C).

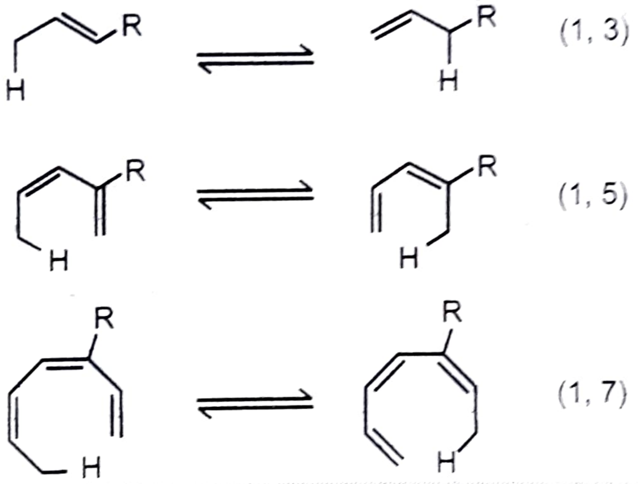


Carbocation intermediate

Examples of these rearrangements are, Beckmann, Baeyer-Villiger, Lossen, Schmidt, Curtius, Pinacol, Wagner-Meerwein Rearrangement :



(ii) **Pericyclic reaction :** A pericyclic reaction is a type of reaction with multiple carbon-carbon bond making and breaking wherein the transition state of the molecule has a cyclic geometry and the reaction progresses in a concerted fashion. Examples of pericyclic reactions are Claisen, Cope, Diels Alder and McLafferty rearrangements.

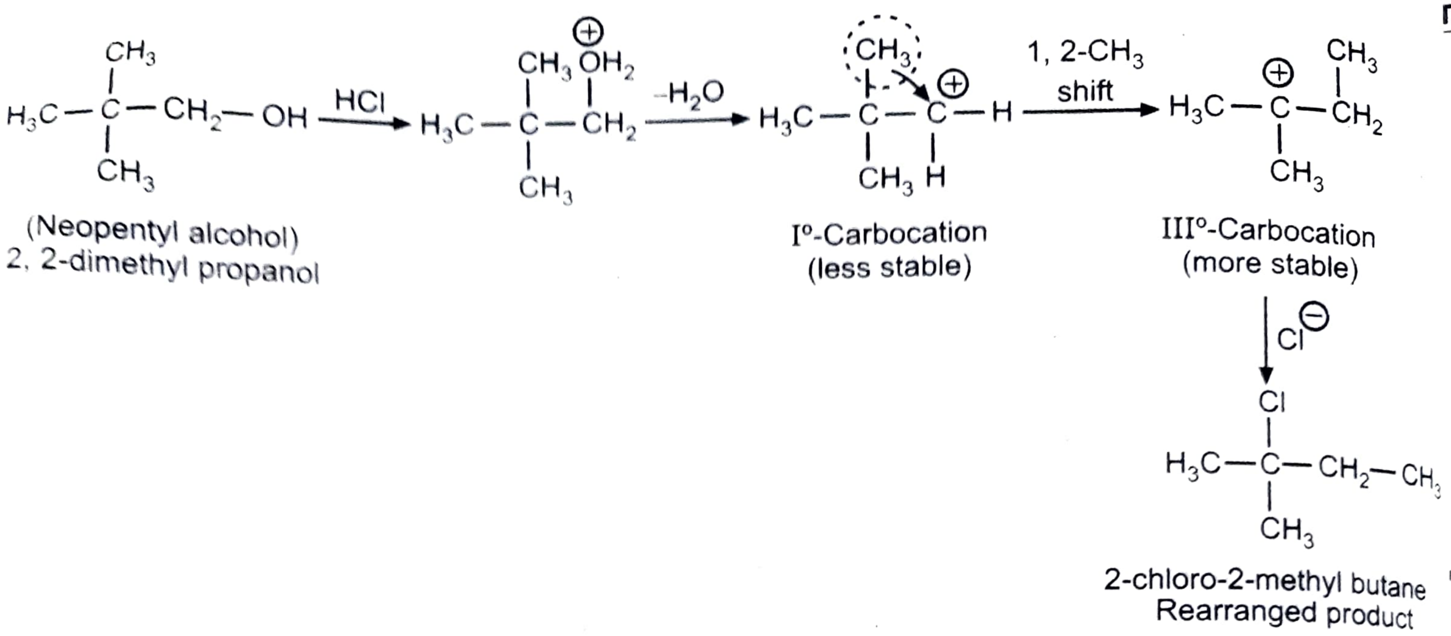


3.3 Types of Reactive Intermediates involved in Different Rearrangements

Rearrangement reactions usually involve carbocation, carbanion, carbene, and electron deficient nitrogen and oxygen intermediates. Carbocation intermediates are most common intermediates in rearrangement reactions.

Rearrangements involving Carbocation Intermediate

- The skeletal rearrangement of carbocation which involves migration of β-alkyl, aryl or σ-bond is called Wagner-Meerwein rearrangement. In most of the carbocation rearrangement reactions, migration of an atom or group occurs due to the formation of more stable carbocation from less stable carbocation. Neopentyl alcohol on treatment with HCl gives the rearranged product 2-chloro-2-methyl butane.

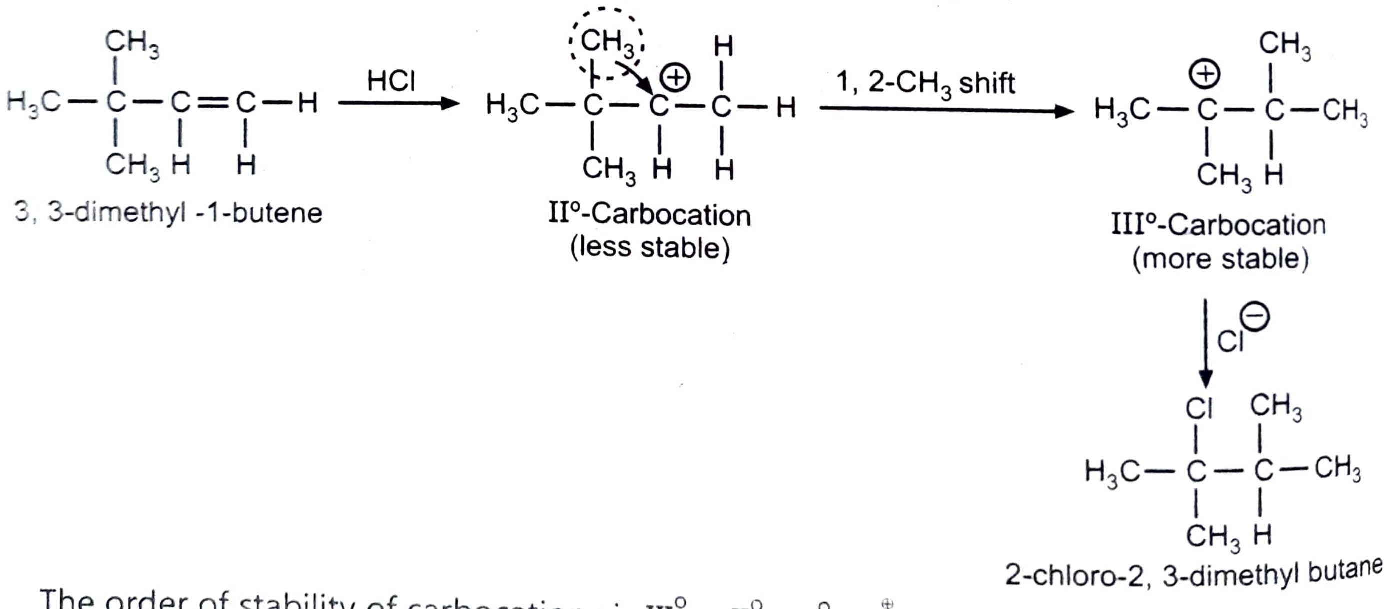

(Neopentyl alcohol)
2, 2-dimethyl propanol

I°-Carbocation
(less stable)

III°-Carbocation
(more stable)

2-chloro-2-methyl butane
Rearranged product

- This rearrangement occurs via carbocation intermediate and involves migration of alkyl group with its lone pair of electrons to an electron deficient carbon atom. It forms more stable carbocation which finally react with nucleophile to give rearranged product.
- In another case, the addition of HCl to 3,3-dimethyl-1-butene forms 3-chloro-2,2-dimethyl butane (an expected product) and 2-chloro-2,3-dimethyl butane (rearrangement product). The rearranged product is the major product.

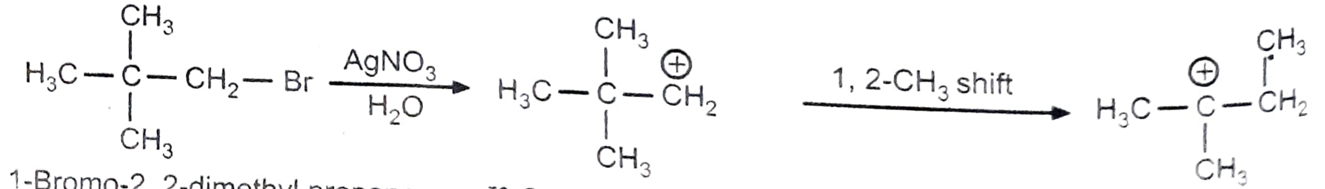

3, 3-dimethyl -1-butene

II°-Carbocation
(less stable)

III°-Carbocation
(more stable)

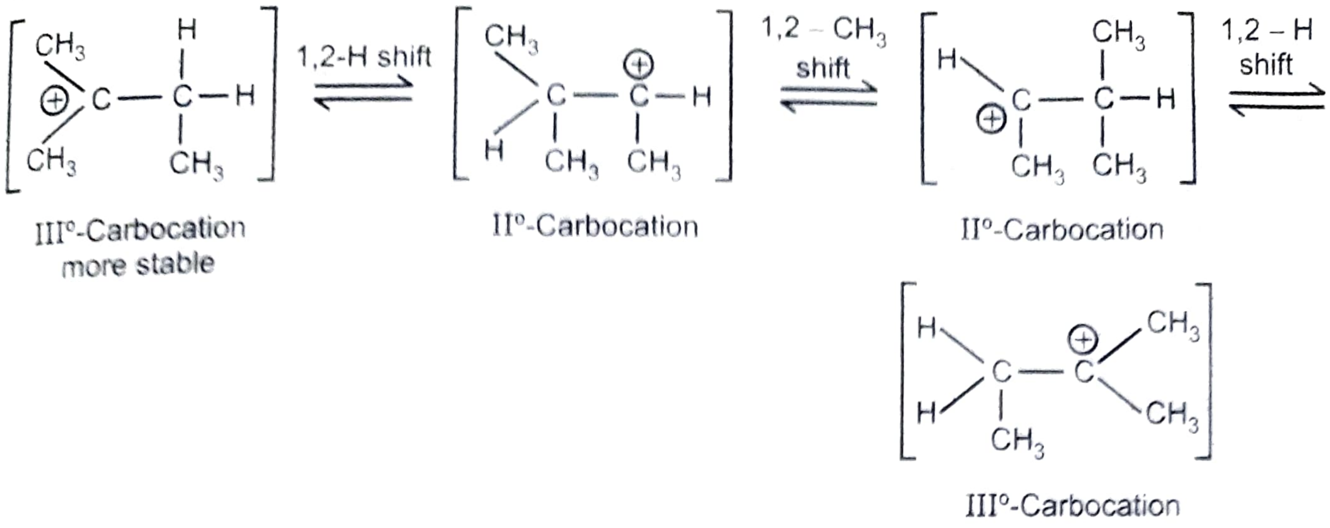
2-chloro-2, 3-dimethyl butane

- The order of stability of carbocations is III° > II° > I° > $\overset{\oplus}{C}H_3$
- The carbocations rearrange only if they become more stable as a result of rearrangement.


1-Bromo-2, 2-dimethyl propane

I°-Carbocation

III°-Carbocation



- Other examples of rearrangements involving carbocation intermediate are Pinacol, semi-pinacol rearrangements.

Rearrangements involving Carbanion Intermediate

Rearrangements involving carbanion intermediates are rare. Some examples of carbanion intermediates in rearrangements are Favorskii, Ramberg-Bäcklund, Stevens and Wittig rearrangements.

Rearrangements involving Carbene

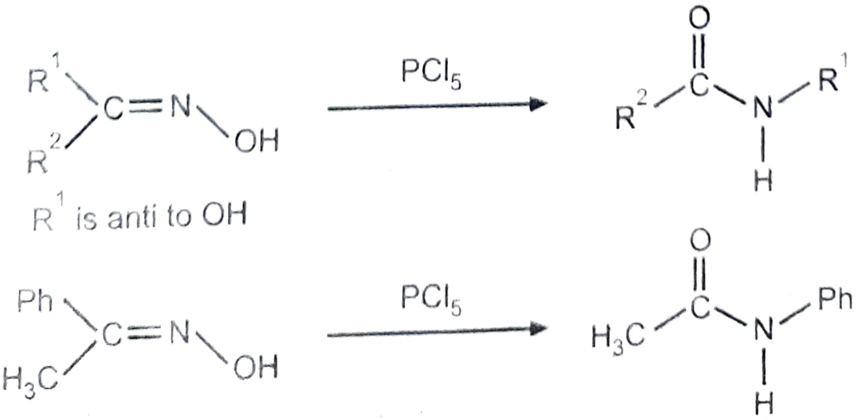
Rearrangement involving carbene intermediates is Wolff rearrangement.

Rearrangements involving Electron Deficient Nitrogen and Oxygen

Rearrangements to electron-deficient nitrogen are Beckmann, Neber, Hoffmann, Curtius, Schmidt, Lossen and Baeyer-Villiger rearrangement.

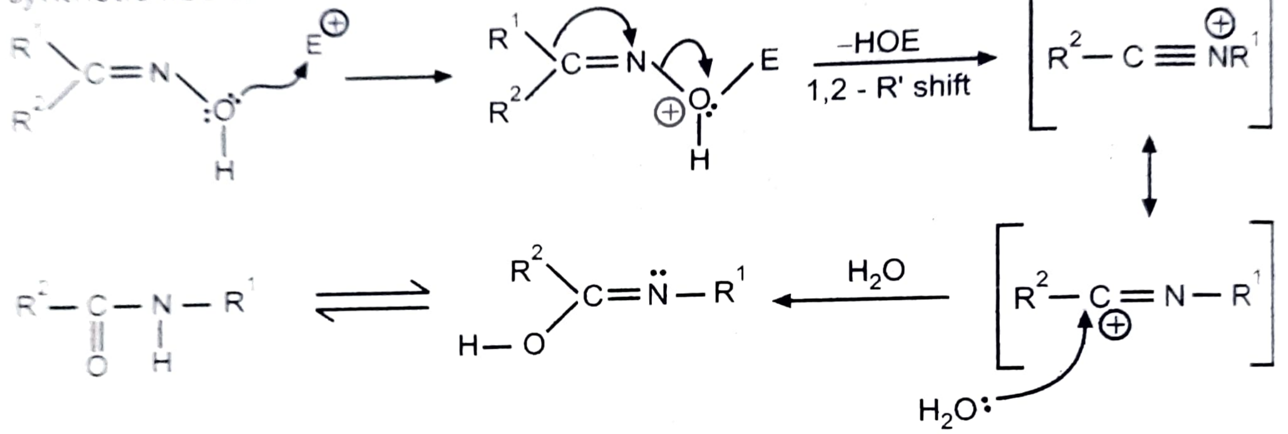
3.4 Beckmann Rearrangement

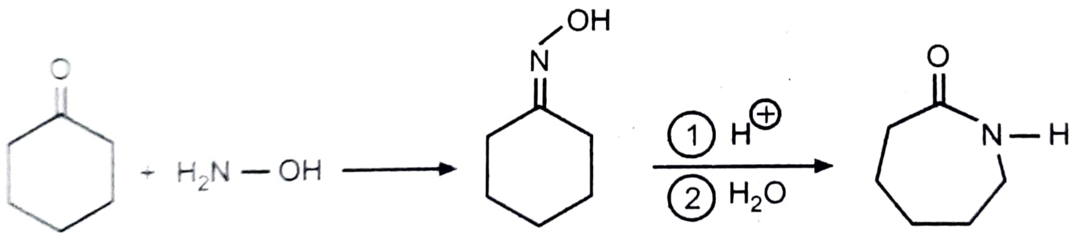
- Rearrangement of oximes to give N-substituted carboxylic amides, the rearrangement of ketoxime under the influence of acidic reagents to yield N-substituted carboxylic amides, is called the *Beckmann rearrangement*. Aldoximes often are less reactive and they form nitrile.



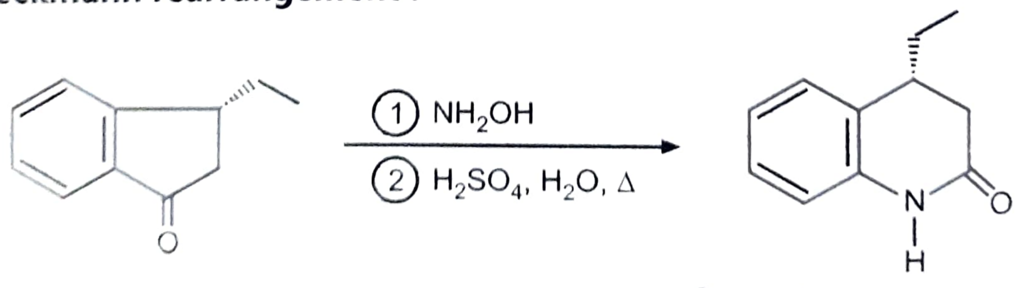
- Upon treatment with a protic acid, the hydroxy group of the oxime is protonated to give an oxonium derivative which can easily lose a water molecule. The anti group migration of the substituent R (together with the bonding electrons) and loss of water proceed simultaneously. The cationic species thus formed reacts with water to give the imin which tautomerizes to a more stable amide tautomer, the N-substituted carboxy amide. As reagents are concentrated sulfuric acid, hydrochloric acid, liquid sulfur dioxid thionyl chloride, phosphorus pentachloride, zinc oxide and even silica gel MoO_3 on sili gel, $RuCl_3$, $Y(OTf)_3$, HCl-HOAc-Ac_2O, $POCl_3$, $BiCl_3$, heat with $FeCl_3$, and polyphospho acid can be used for *Beckmann rearrangement*. Reagents like phosphorus pentachloric (as well as thionyl chloride and others) first convert the hydroxy group of the oxime in a good leaving group.

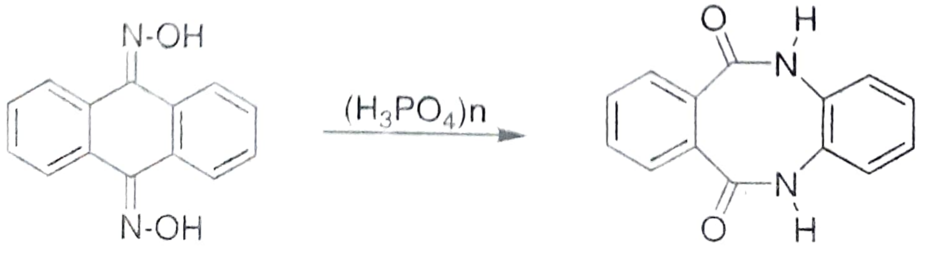
- The reaction with oximes of cyclic ketones leads to ring enlargement and form lactam b ring enlargement. This particular reaction is performed on an industrial scal ε-caprolactam is used as a monomer for polymerization to polyamide for the productio of synthetic fibers.





Example of Beckmann rearrangement :



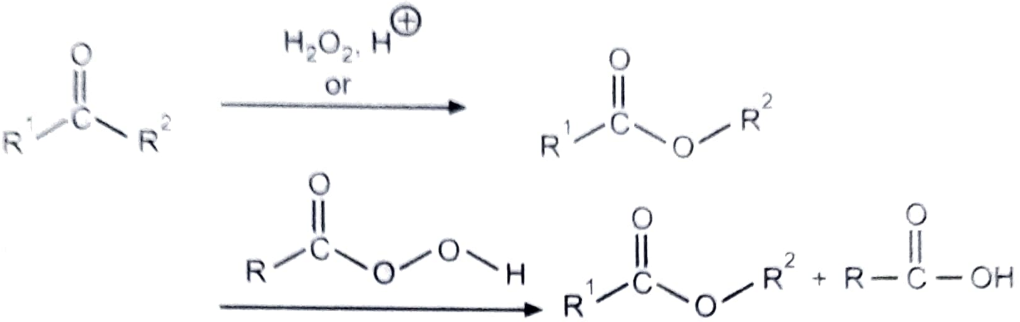


Anthrancene-9,10-dioxime

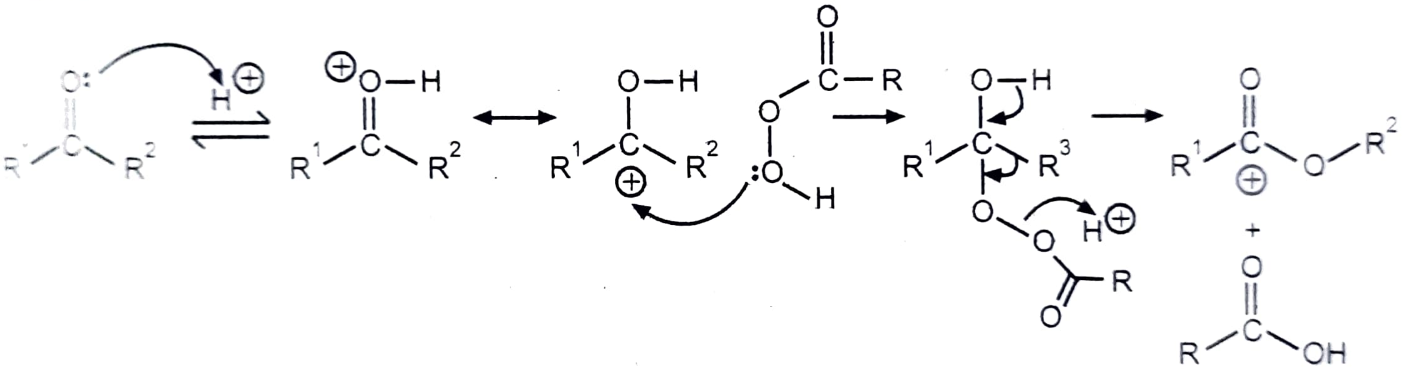
dibenzo[*b*,*f*][1,4]diazocine-6,11(5*H*,12*H*)dione

3.5 Baeyer - Villiger Oxidation

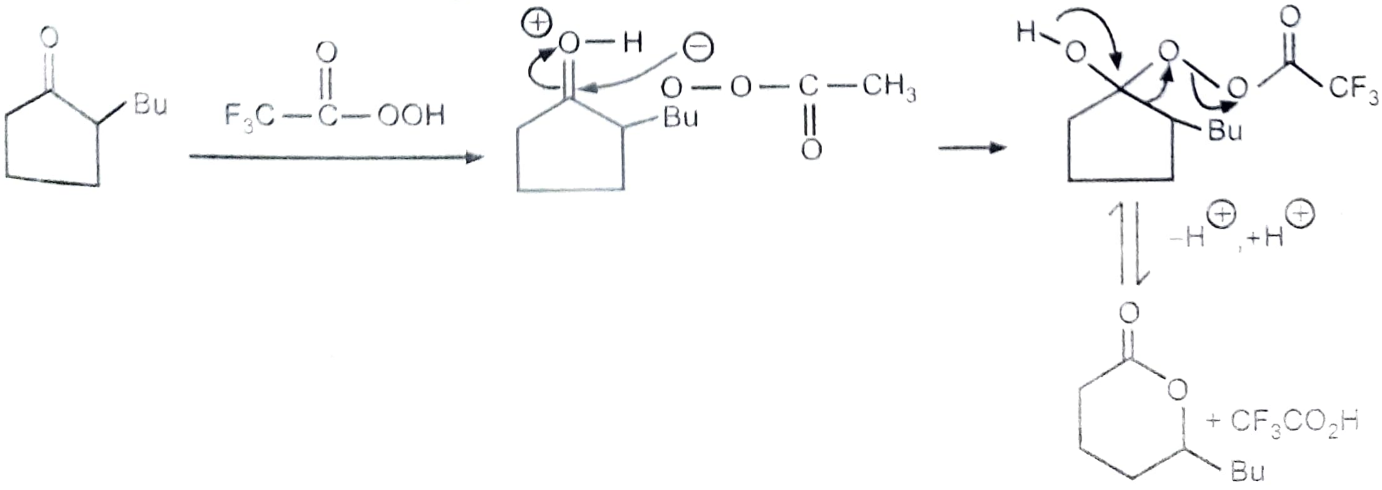
- The treatment of ketones with peroxy acids or with hydrogen peroxide, in the presence of acid catalysts, a formal insertion of oxygen followed by migration of alkyl or aryl group can take place to yield a carboxylic ester. This reaction is called the Baeyer-Villiger rearrangement.



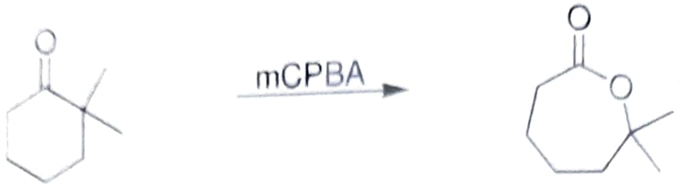
- In a first step, the carbonyl group is taking the proton from acid and protonated to form carbocation intermediate.
- In the second step, the peracid adds to the carbocation to form *Criegee intermediate*.
- In the third step, migration of alkyl or aryl takes place with the elimination of carboxylic acid.

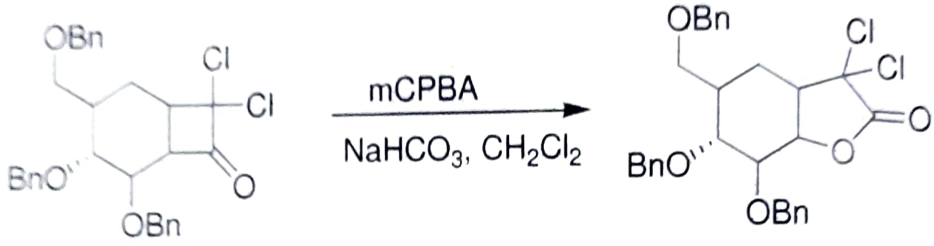


- The ease of migration of substituents R$_1$, R$_2$ depends on their ability to stabilize a positive charge in the transition state. For unsymmetrical ketones the approximate order of migration is $R_3C > R_2CH > Ar > RCH_2 > CH_3$. The CH_3 group has a low migrating ability, and the migrating ability of aryl groups is decreased by electron-withdrawing and increased by electron-donating substituents. The Baeyer–Villiger oxidation of unsymmetrical ketones is regioselective.



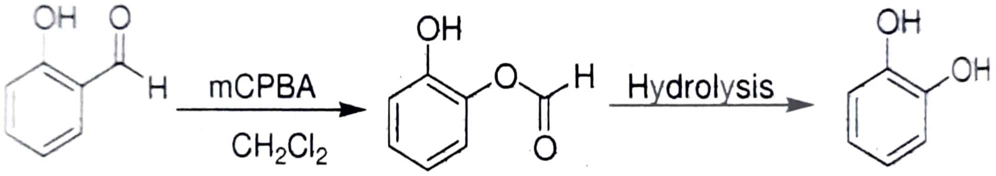
- Cyclic ketones react through ring expansion to yield lactones (cyclic esters). Hydro peroxide has been used to convert cyclic ketones to lactones using a catalytic amoun $MeReO_3$.



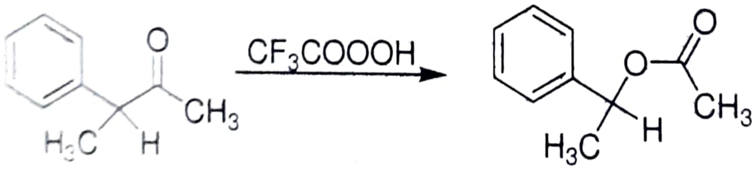


Examples of Baeyer - Villiger Oxidation :

1.



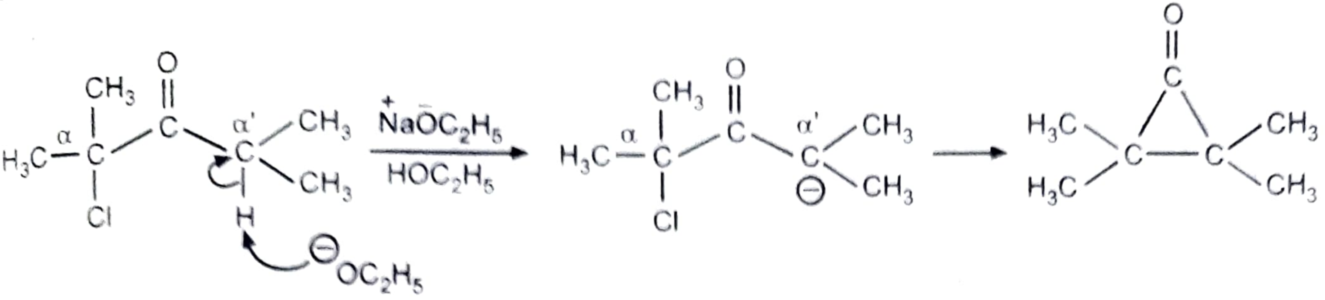
2.



3.6 Favorskii Rearrangement

- α-Halo ketones (chloro, bromo, or iodo) possessing at least one α-hydrogen wh treated with a base (NaOH or NaOEt or $NaNH_2$), can undergo a rearrangement reac via a cyclopropanone intermediate to give a carboxylic acid or an ester or ami depending on the base used. This reaction is called the *Favorskii rearrangement*.
- In the first step, the α-halo ketone is deprotonated by the base at the α'-carbon to g the carbanion, which undergoes a ring-closure reaction by an intramolecular substituti to give the cyclopropanone derivative. The nucleophilic addition of the base to t cyclopropanone intermediate leads to the ring opening. With a symmetrically substitute cyclopropanone, cleavage of either C_α-CO bond leads to the same product. Wi unsymmetrical cyclopropanone, that bond is broken preferentially which leads t thermodynamically more stable carbanion. The carbanion intermediate is protonated t give the final product.

Reaction mechanism :

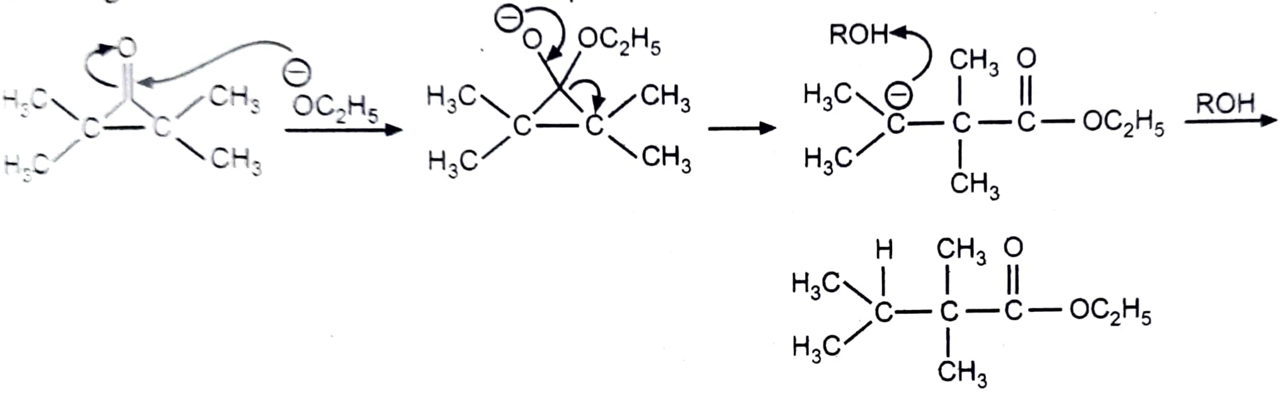


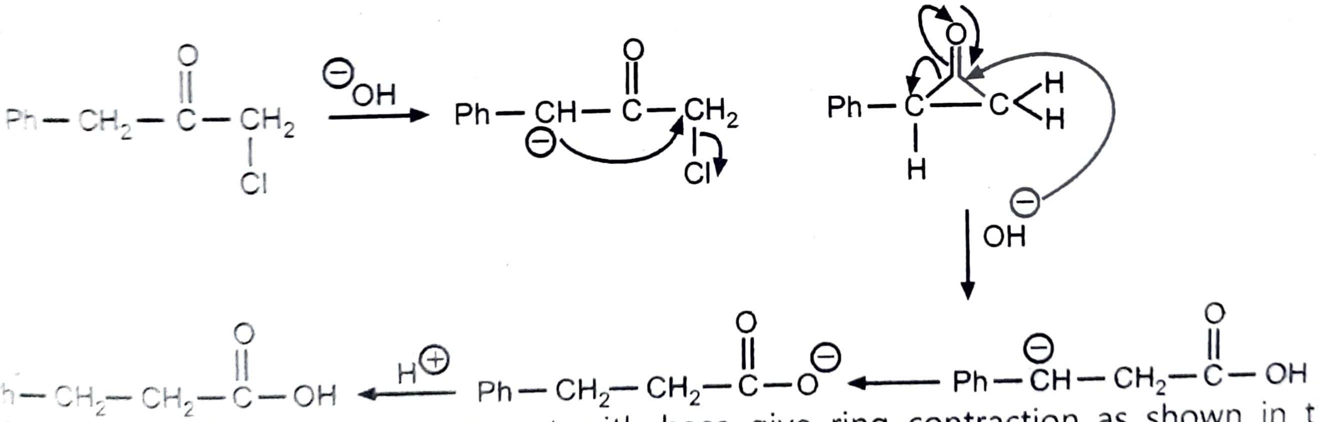
Protons α' to ketone is acidic and sodium ethoxide is strong base that easily abstract the proton to form carbanion as nucleophile

Cl is a leaving group Carbanion attack on the α' carbon atom and substitution reaction takes place to give cyclopropanone

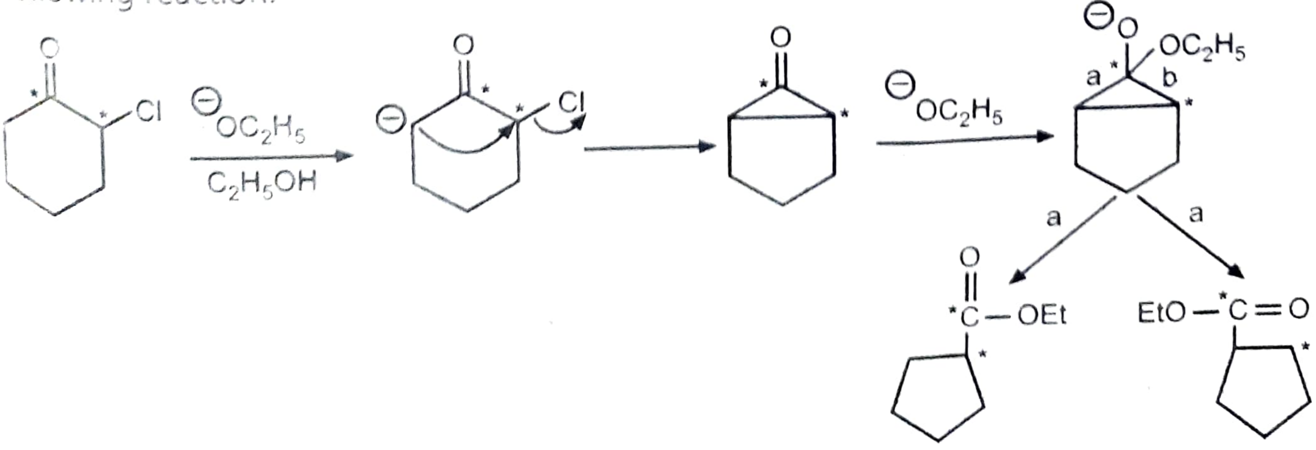
Cyclopropanones are particularly susceptible to nucleophilic addition due to ring strain

- Addition elimination reaction at the carbonyl and cyclopropanone ring opening takes place to generate a stabilised enolate product.



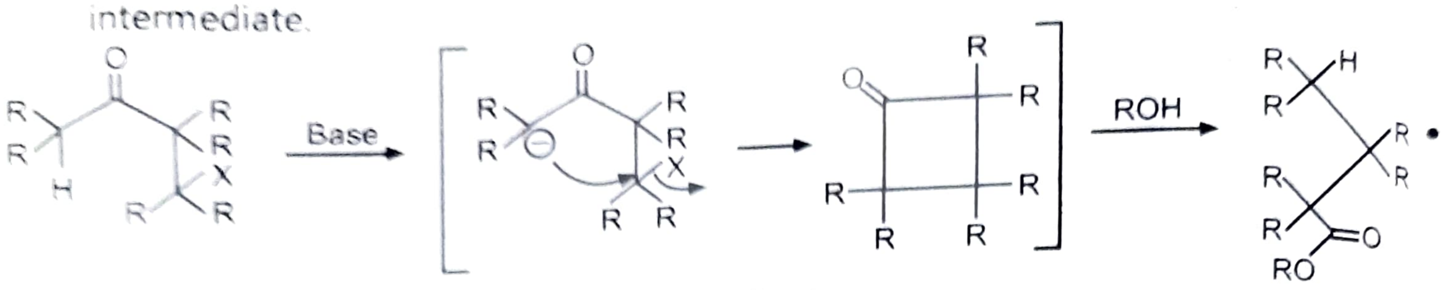


- Cyclic α-halo ketones on treatment with base give ring contraction as shown in the following reaction.



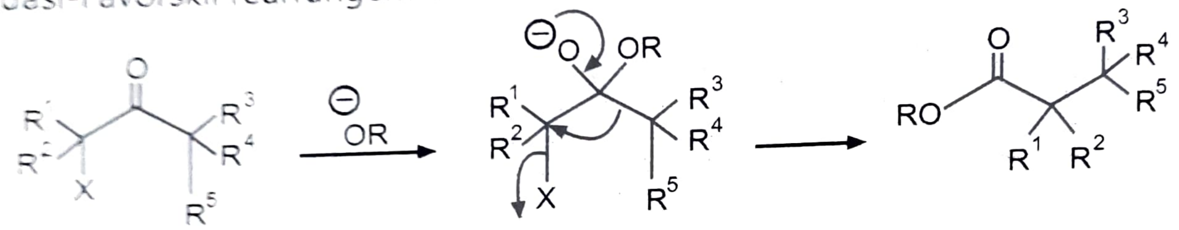
The two important variations of Favorskii rearrangement are :

1. When β-halo ketones are treated with base, in presence of nucleophile the reaction called Homo-Favorskii rearrangement. This reaction takes place via a cyclobutanon intermediate.

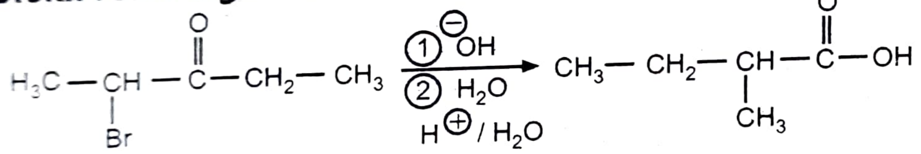


R = alkyl / hydrogen

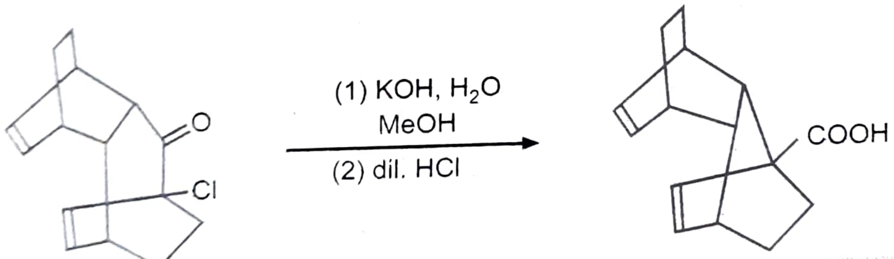
2. If α-haloketone does not have any enolizable hydrogen then the reaction is called a Quasi-Favorskii rearrangement.



Examples of Favorskii rearrangement :

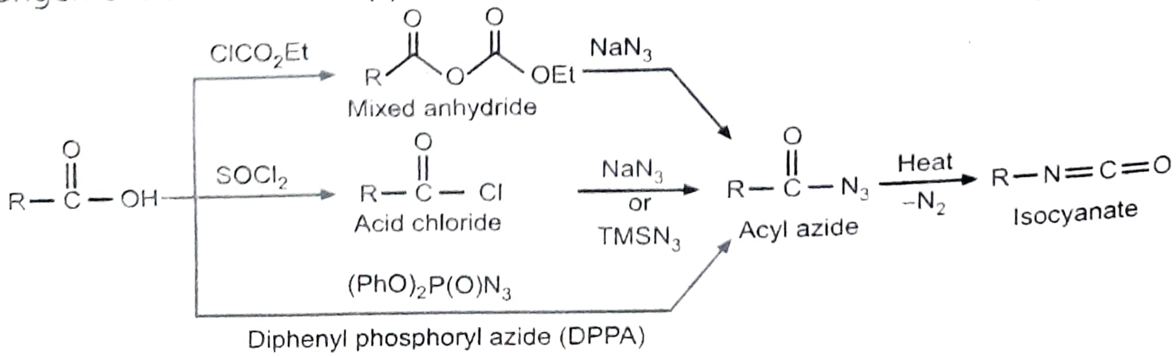


$$H_3C-\underset{Br}{CH}-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \xrightarrow[\text{②}\ H_2O\quad H^{\oplus}/H_2O]{\text{①}\ \overset{\ominus}{O}H} CH_3-CH_2-\underset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-OH$$

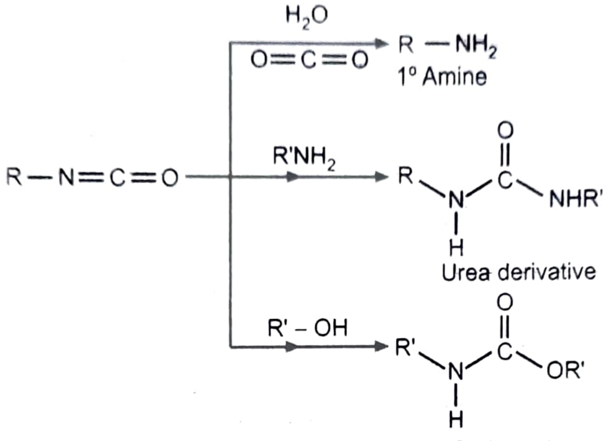


3.7 The Curtius Rearrangement

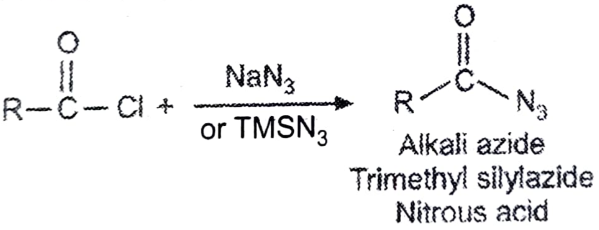
- The Curtius rearrangement involves the thermal decomposition of an acyl azide to yield an isocyanate by loss of N_2. Isocyanate on hydrolysis gives amine. The Curtius rearrangement can thus be applied to convert carboxylic acids into primary amines.

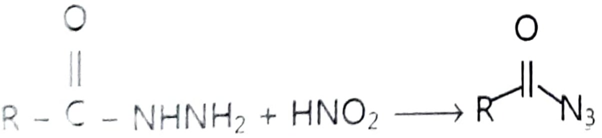


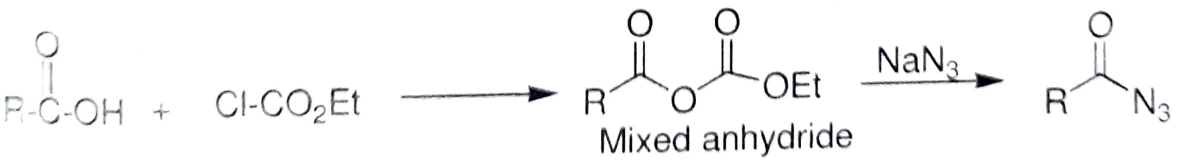
- This reaction can be applied to almost any carboxylic acids such as aliphatic, aromatic, alicyclic, heterocyclic, unsaturated, and containing many functional groups. The required acyl azide can be prepared from the corresponding acyl chloride and azide ion (e.g. with sodium azide) or alternatively from an acyl hydrazine by treatment with nitrous acid or from mixed anhydride.
- Acyl azide can be synthesized from carboxylic acid by using diphenyl phosphoryl azide (DPPA).

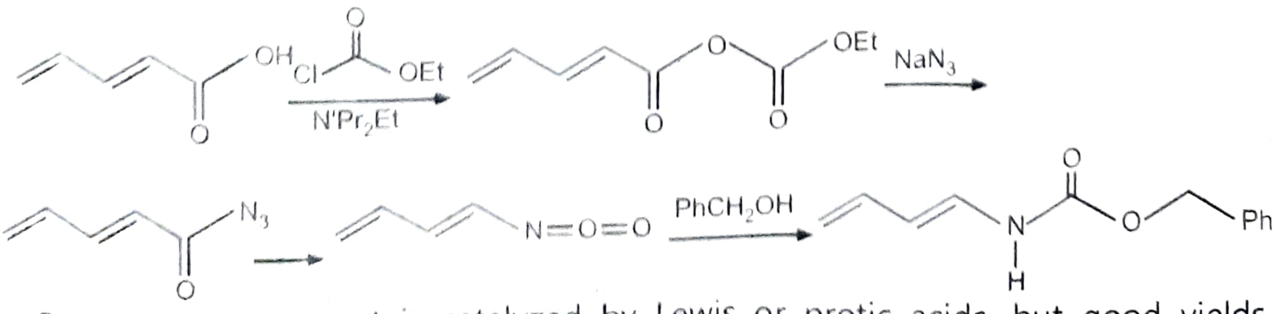


- Loss of N_2 and migration of the group R is likely to be a concerted process, since evidence for a free acyl nitrene RCON in the thermal reaction has not been found.



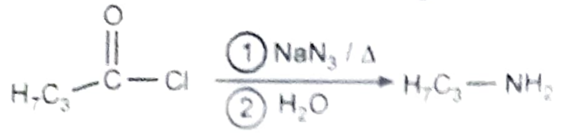






- The Curtius rearrangement is catalyzed by Lewis or protic acids, but good yields of product are often obtained also without a catalyst. Isocyanates are highly reactive and they immediately react with water and form amine. When alcohol is used as a solvent, the isocyanate reacts with alcohol to form carbamate. From reaction in an inert solvent (e.g. benzene, chloroform) in the absence of water, the isocyanate can be isolated.

The examples of Curtius rearrangement are :

①


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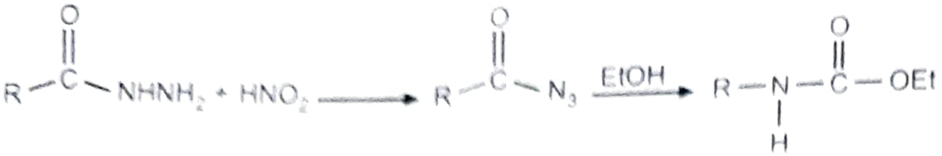

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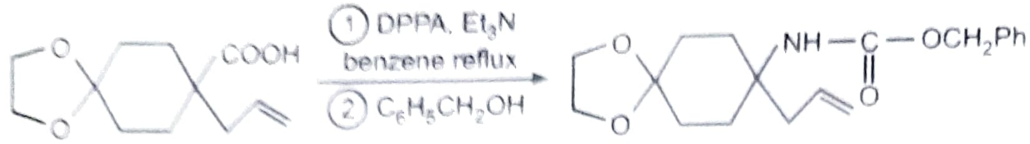
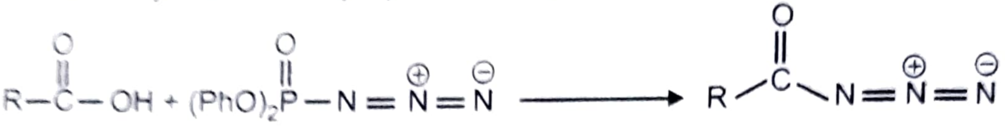
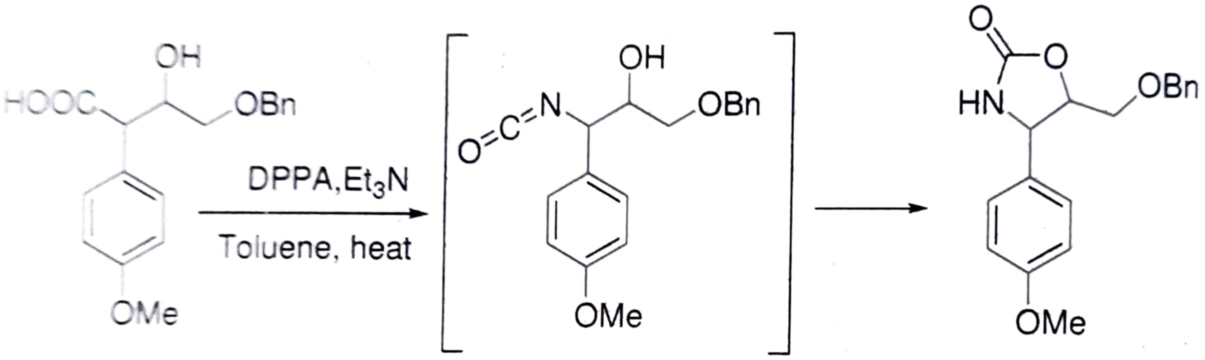


- DPPA is prepared from the corresponding acyl chloride and azide ion (e.g. with sodium azide) or alternatively from an acylhydrazine by treatment with nitrous acid.



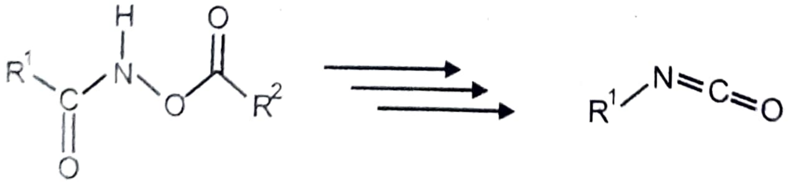
Diphenyl phosphoryl azide (DPPA)

The example of Curtius rearrangement :



3.8 Lossen Rearrangement

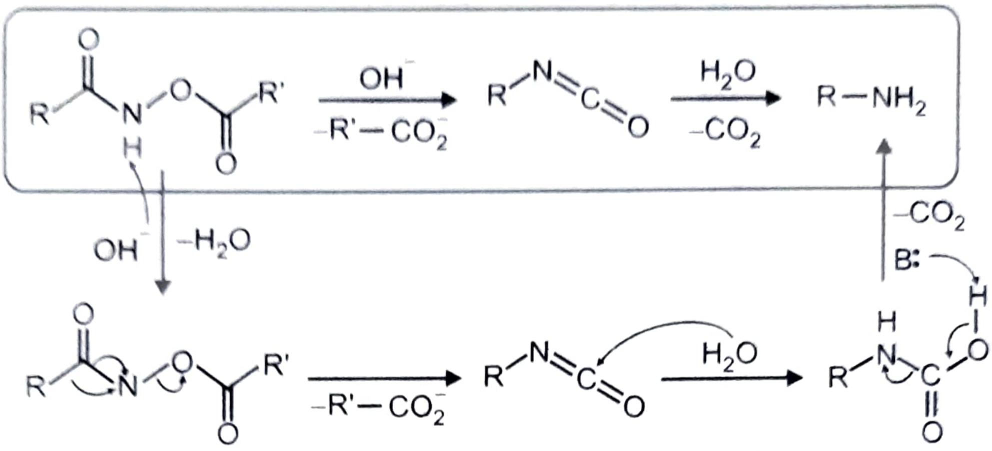
- The **Lossen rearrangement** is the conversion of a hydroxamate ester to an isocyanate. Typically, O-acyl, sulfonyl, or phosphoryl O-derivative are employed. The isocyanate can be used further to generate ureas in the presence of amines or generate amines in the presence of H_2O.



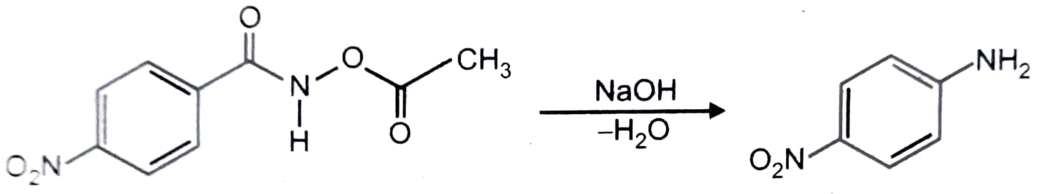
Mechanism :

- In the first step an O-acylated hydroxamic acid derivative is first converted to its conjugate base by abstraction of a hydrogen by a base. Spontaneous rearrangement releases a carboxylate anion to produce the isocyanate intermediate.

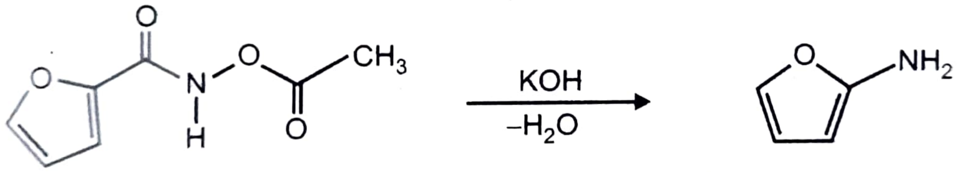
- In the second step the isocyanate is hydrolyzed in the presence of H_2O.
- In the final step, the respective amine and CO_2 are generated by abstraction of a proton with a base and decarboxylation.



Examples of Lossen Rearrangement :



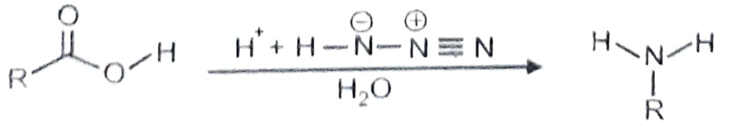
N-acetoxy-4-nitrobenzamide 4-Nitroaniline

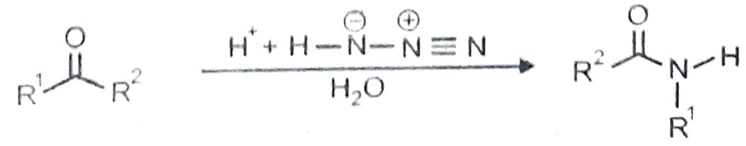


N-acetoxyfuran-2-carboxyamide Furan-2-amine

3.9 The Schmidt Rearrangement

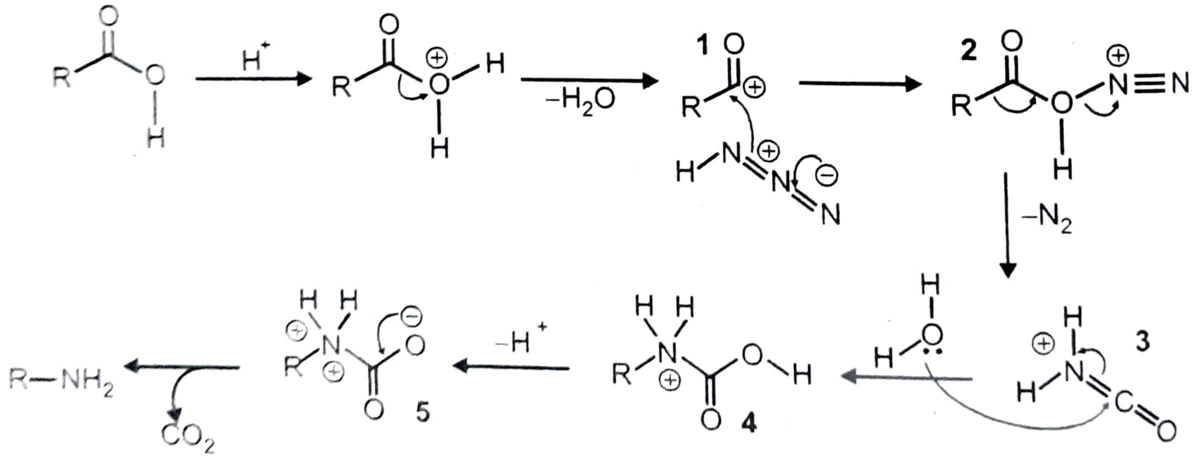
- An azide when reacts with a carbonyl derivative, usually a aldehyde, ketone, or carboxylic acid, under acidic conditions give an amine or amide, with the expulsion of nitrogen is known as Schmidt rearrangement. It is named after Karl Friedrich Schmidt, who first reported the synthesis of benzanilide from reaction of benzophenone and hydrazoic acid. The reaction is effective with carboxylic acids to give amines, and with ketones to give amides.





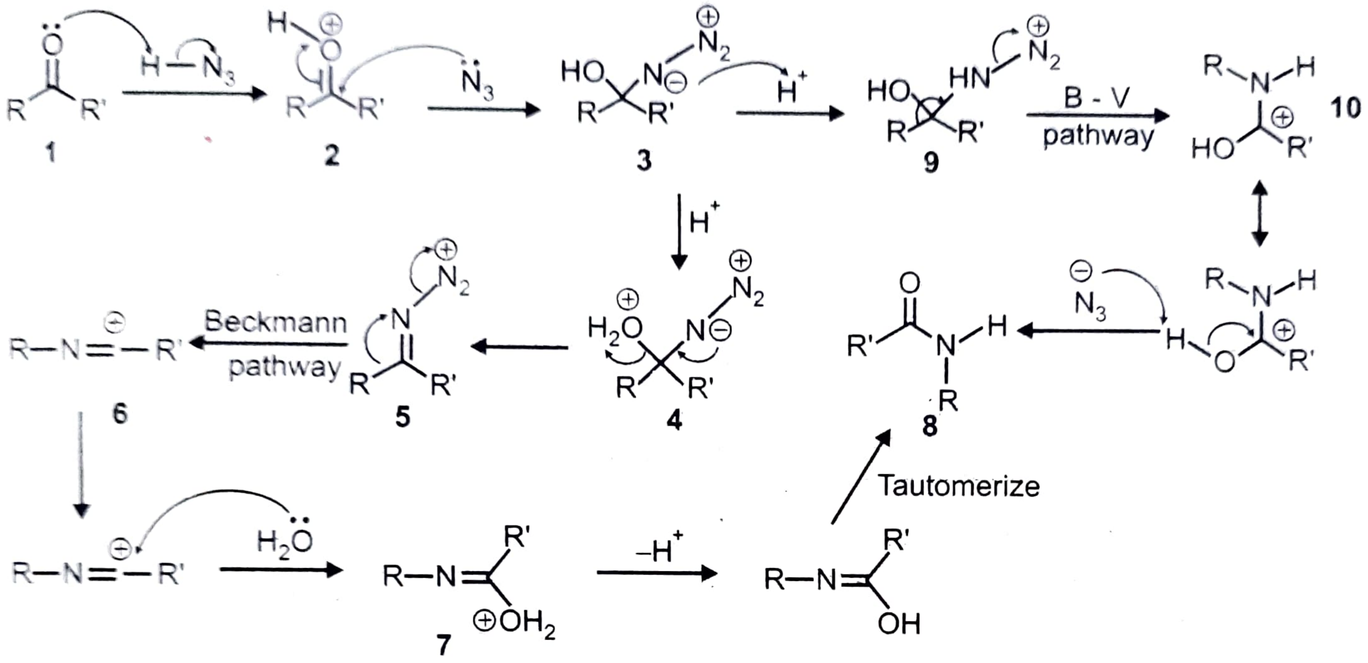
Mechanism :

- The reaction is closely related to the Curtius rearrangement except that in this reaction the acyl azide is produced by reaction of the carboxylic acid with hydrazoic acid via the protonated carboxylic acid, in a process similar to a Fischer esterification. An alternative, involving the formation of an acylium ion, becomes more important when the reaction takes place in concentrated acid (>90% sulfuric acid). (In the Curtius rearrangement, sodium azide and an acyl chloride are combined to quantitatively generate the acyl azide intermediate, and the rest of the reaction takes place under neutral conditions.)
- This mechanism begins with the formation of an acylium ion **1** from the protonation of the carboxylic acid followed by the removal of water.
- This acylium ion is now reacted with hydrazoic acid, leading to the formation of a protonated azido ketone **2**.
- Now, the protonated azido ketone **2** and the R group undergo a rearrangement reaction, resulting in the migration of the carbon-nitrogen bond and the removal of dinitrogen leading to the formation of a protonated isocyanate **3**.
- Now, a carbamate **4** is formed when water is introduced to attack the protonated isocyanate.
- The carbamate **4** is now deprotonated. The subsequent removal of CO_2 yields the required amine.

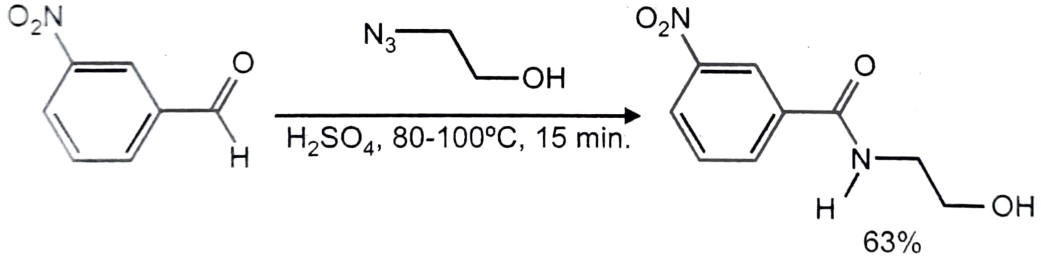


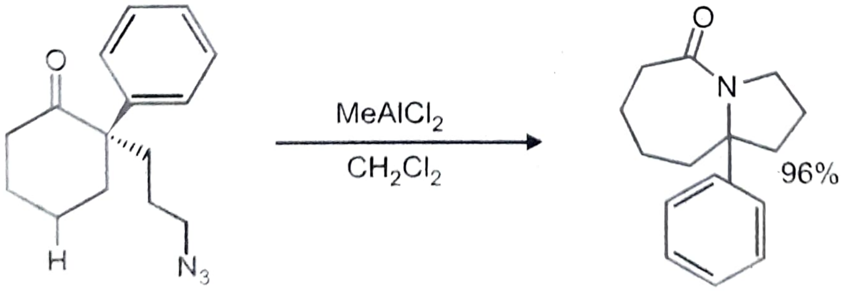
- In the reaction mechanism for the Schmidt reaction of ketone, the carbonyl group is activated by protonation for nucleophilic addition by the azide, forming azidohydrin **3**, which loses water in an elimination reaction to diazoiminium **5**. One of the alkyl or aryl groups migrates from carbon to nitrogen with loss of nitrogen to give a nitrilium intermediate **6**, as in the Beckmann rearrangement. Attack by water converts **6** to protonated imidic acid **7**, which undergoes loss of proton to arrive at the imidic acid tautomer of the final amide **8**.
- In an alternative mechanism, the migration occurs at **9**, directly after protonation of intermediate **3**, in a manner similar to the Baeyer-Villiger reaction to give protonated amide **10**. Loss of a proton again furnishes the amide **8**.

- It has been proposed that the dehydration to **3** to give **5** (and, hence, the Beckmann pathway) is favored by nonaqueous acids like conc. H_2SO_4, while aqueous acids like conc. HCl favor migration from **9** (the Baeyer-Villiger pathway).
- These possibilities have been used to account for the fact that, for certain substrates like α-tetralone, the group that migrates can sometimes change, depending on the conditions used, to deliver either of the two possible amides.



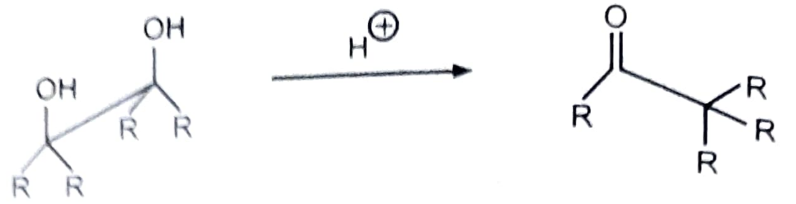
Examples of Schmidt Rearrangement :

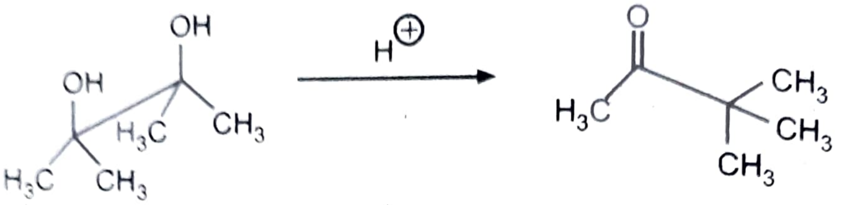




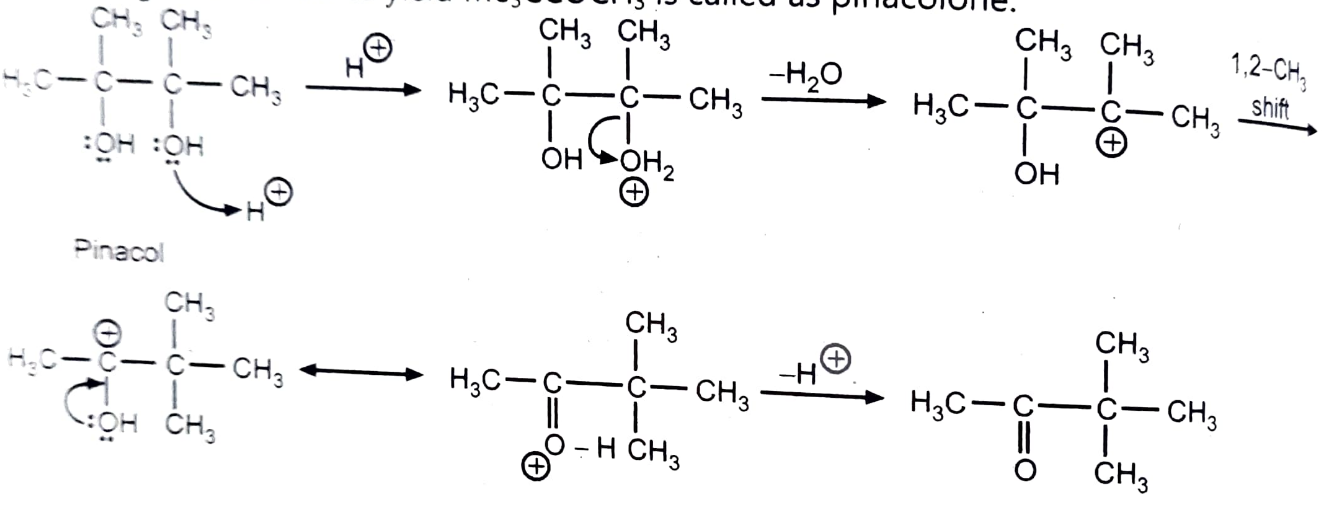
3.10 The Pinacol Rearrangement

- When vicinal diol is treated with a catalytic amount of acid, it can rearrange to give an aldehyde or ketone by migration of an alkyl or aryl group which is called as Pinacol Rearrangement. The pinacol-pinacolone rearrangement reaction or 1,2- migration can be viewed as a special case of the Wagner–Meerwein rearrangement.



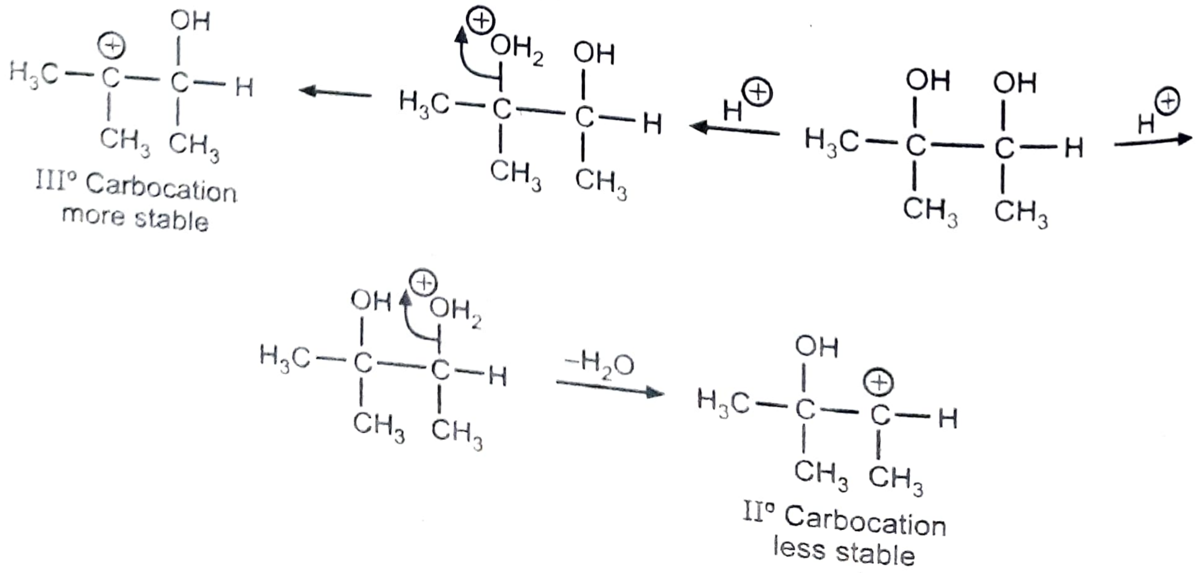


- When $Me_2COHCOHMe_2$ (pinacol) on treatment with acid gives $Me_2COH\overset{\oplus}{C}Me_2$ which on 1, 2-migration of Me to yield Me_3CCOCH_3 is called as pinacolone.

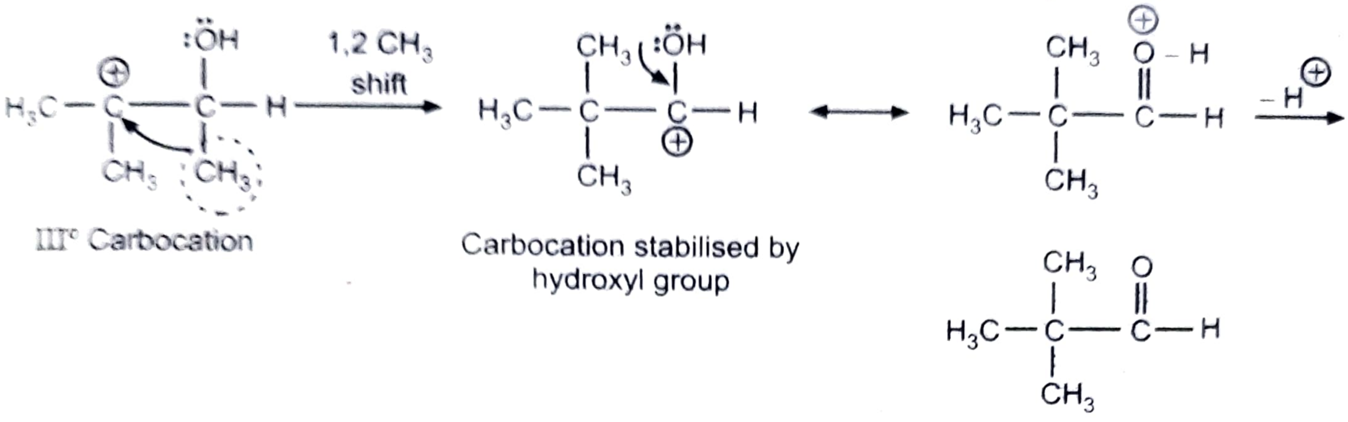


Mechanism :

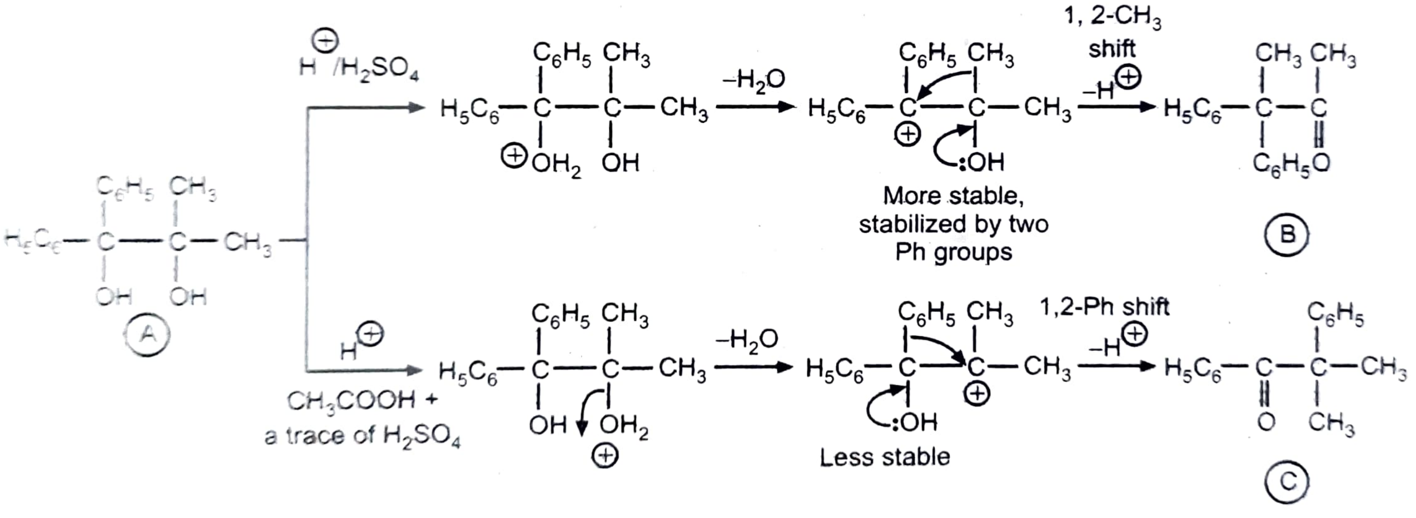
- In the first step one hydroxy group is protonated, and thus converted into a good leaving group. The elimination of water from the molecule proceeds in such a way that the more stable carbocation intermediate is formed.



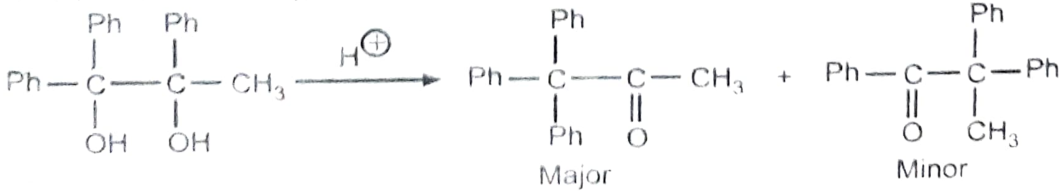
- In the second step, 1,2-shift of a R group to the more stable (III°) carbocation takes place to give a more stable hydroxyl carbocation intermediate. The reaction is intramolecular; the migrating group R is never completely released from the substrate. The driving force is the formation of the more stable rearranged carbocation, which is stabilized by the hydroxy group. In the third step, loss of a proton yields the carbonyl compound.



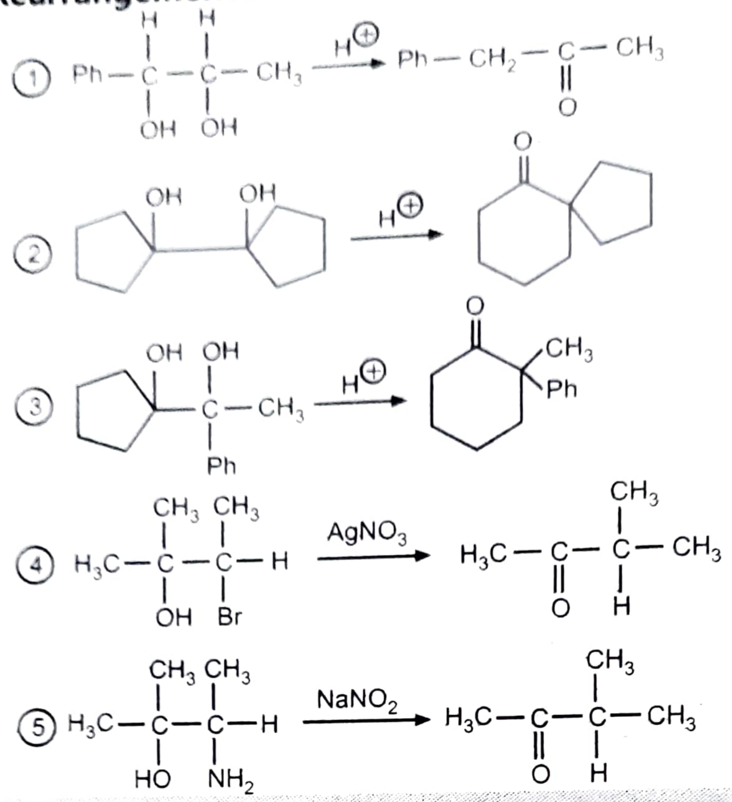
- Reaction with an unsymmetrical diol as starting material may give rise to formation of a mixture of products. Mixtures are product formed, may depend on the reaction conditions, which group preferentially migrates as well as on the nature of the substrate. The order of migration is $R_3C > R_2CH > RCH_2 > CH_3 > H$.



- The action of cold, conc. H_2SO_4 on A produces mainly the ketone B (-CH_3 migration), while treatment of A with acetic acid containing a trace of H_2SO_4 gives mostly C (phenyl migration). If one R is hydrogen, aldehydes can be produced as well as ketones. Generally, aldehyde formation is favored by the use of mild conditions (lower temperatures, weaker acids),



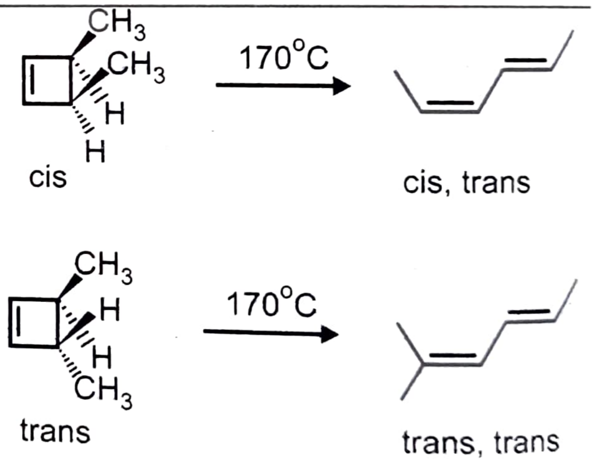
Examples of Pinacol Rearrangement :



3.11 Electrolytic Rearrangements

An **electrocyclic reaction** is a type of pericyclic rearrangement where the net result is one pi bond being converted into one sigma bond or vice versa. These reactions are usually categorized by the following criteria :

- Reactions can be either photochemical or thermal.
- Reactions can be either ring-opening or ring-closing (**electrocyclization**).
- Depending on the type of reaction (photochemical or thermal) and the number of pi electrons, the reaction can happen through either a conrotatory or disrotatory mechanism.
- The type of rotation determines whether the cis or trans isomer of the product will be formed.



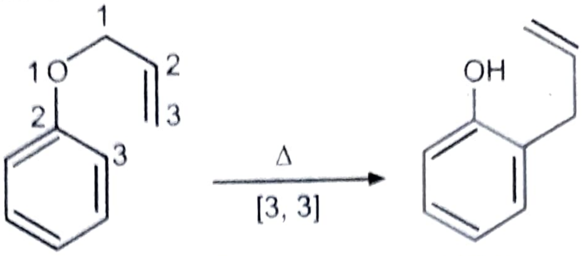
System	Thermally induced (ground state)	Photochemically induced (excited state)
Even number of conjugation	Conrotatory	Disrotatory
Odd number of conjugation	Disrotatory	Conrotatory

3.11.1 The Claisen Rearrangement

- Allylic aryl ethers, when heated, rearrange to *ortho*-allylphenols, this reaction is called the Claisen rearrangement. If both *ortho* positions are filled, the allylic group migrates to the para position (para-Claisen rearrangement).

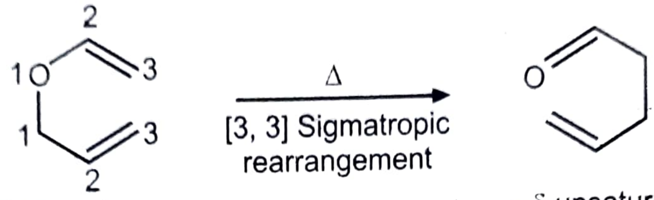
- The Claisen rearrangement reaction is a concerted pericyclic [3,3] sigmatropic rearrangement reaction. A carbon–oxygen bond is cleaved and a carbon–carbon bond is formed followed by tautomerization to the stable aromatic allyl phenol.

①



Allyl phenyl ether Sigmatropic rearrangement Ortho allyl phenol

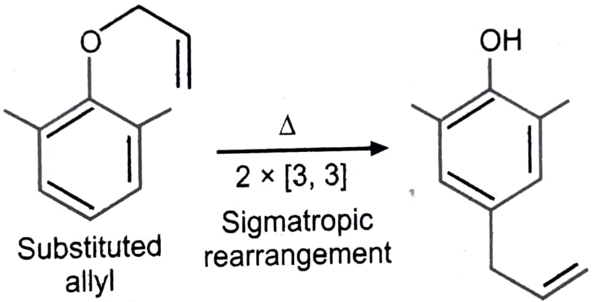
②



Allyl vinyl ether

γ-δ unsaturated carbonyl compound

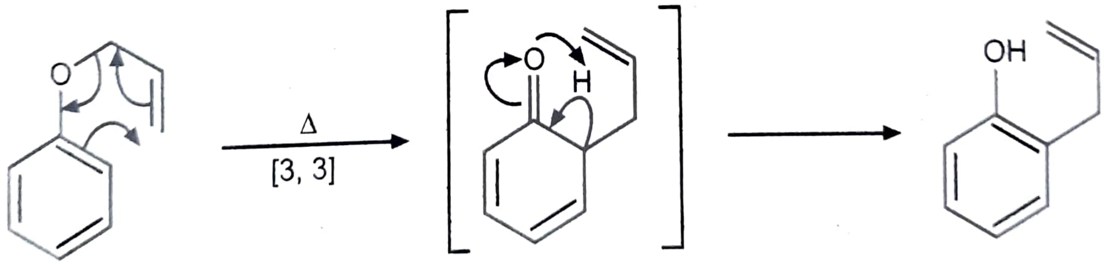
③

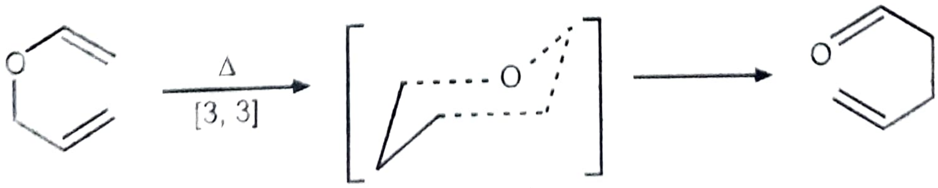


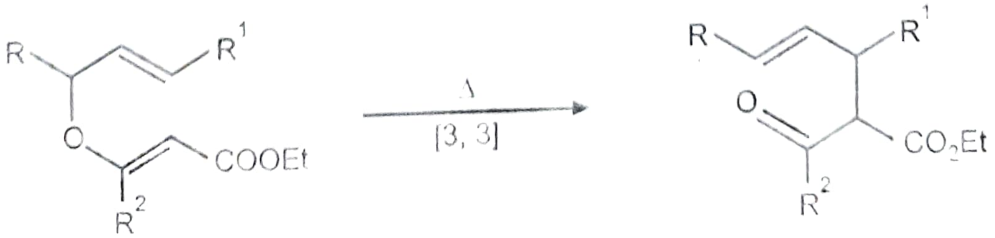
Substituted allyl phenyl ether

Para allyl phenol

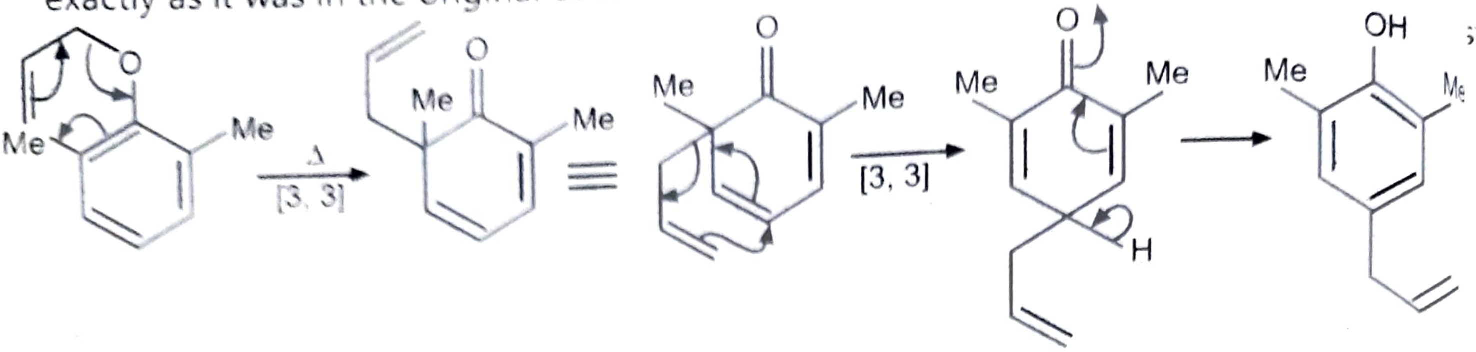
- Allylic ethers of enols (allylic vinylic ethers) also undergo the Claisen rearrangement.





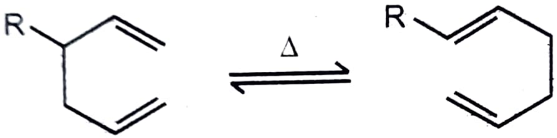


- In the ortho migration, the allylic group always undergoes an allylic shift. Whereas in th para-Claisen rearrangement there is never an allylic shift. The allylic group is foun exactly as it was in the original ether.

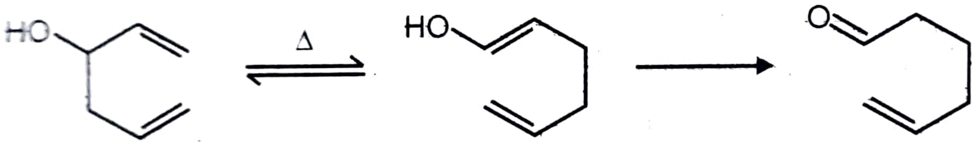


3.11.2 The Cope Rearrangement

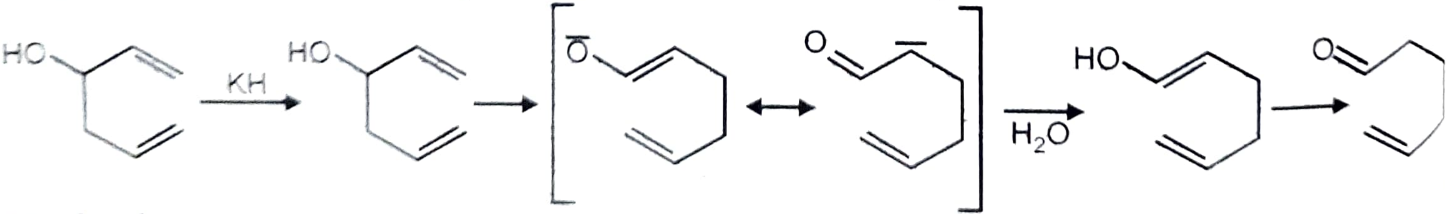
- The Cope Rearrangement is the thermal isomerization of a 1,5-diene leading to regioisomeric 1,5-diene. The main product is the thermodynamically more stabl regioisomer.



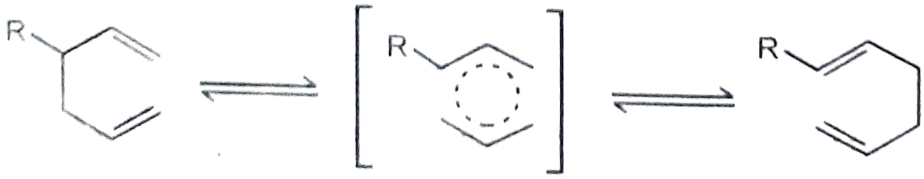
- The Oxy-Cope has a hydroxyl substituent on an sp^3-hybridized carbon of the startin isomer.



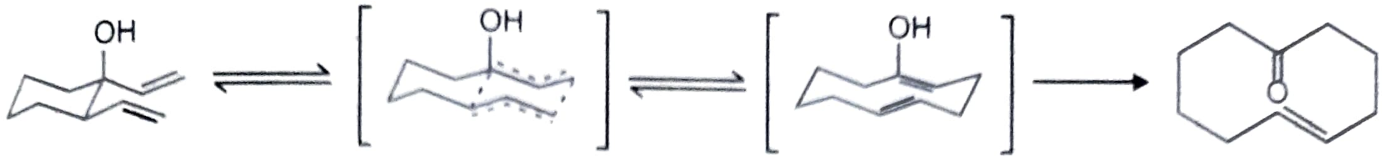
The driving force for the neutral or anionic Oxy-Cope Rearrangement is that the produc is an enol or enolate (resp.), which can tautomerize to the corresponding carbony compound. This product will not equilibrate back to the other regioisomer. The Oxy-Cope Rearrangement proceeds at a much faster rate when the starting alcohol is deprotonated e.g. with KH. The reaction is then up to 10^{17} times faster, and may be conducted at room temperature. Aqueous work up then gives the carbonyl compound.

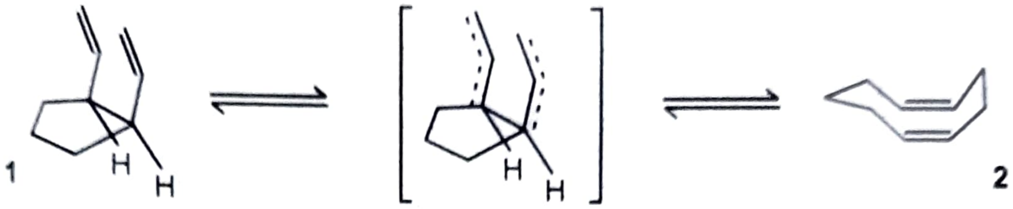


Mechanism :

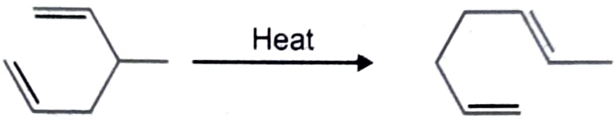


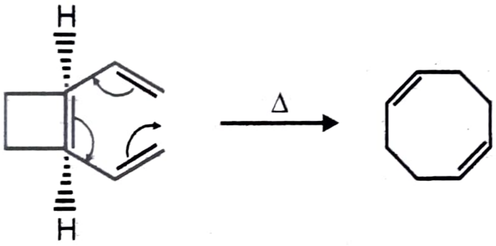
Two transition states are possible, and the outcome of the reaction can be predicted on the basis of the most favorable overlap of the orbitals of the double bond, as influenced by stereoelectronic factors:





Examples of Cope and Oxy-Cope Rearrangement :

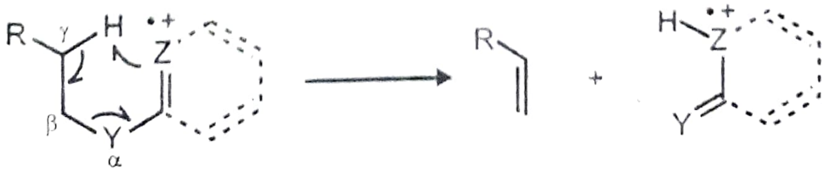




3.11.3 The McLafferty Rearrangement

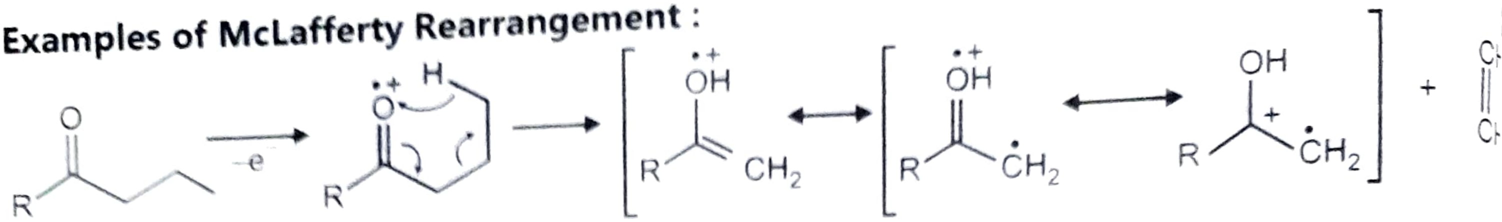
- The McLafferty-Rearrangement is observed in compounds in which at least one abstractable gamma (γ) hydrogen is present with respect to a pi (π) bond. When such compounds are ionized as molecular ions, in mass spectrometer, usually by the Electron Ionization (EI) method. The resultant molecular ion undergoes a special type of rearrangement. The hydrogen at gamma (γ) position transfers to the carbonyl functional group followed by the hemolytic cleavage of the C_α-C_β sigma bond. This rearrangement finally results in the formation of an olefin without any charge and an enol radical cation as products.
- This rearrangement is widely observed in Aldehydes, Ketones, Carboxylic acids, Esters, Amides, Imines, Cyanides, Alkenes, and Alkynes. The McLafferty Rearrangement is helpful in the identification and characterization of various organic molecules.

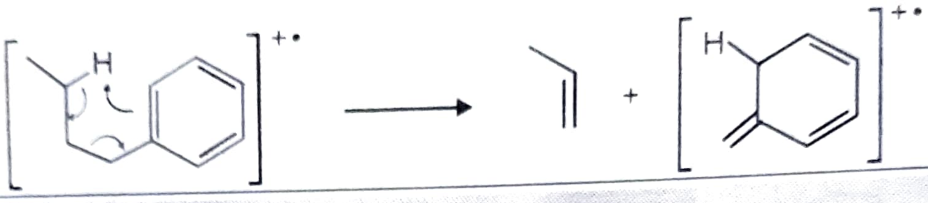
Mechanism :



Z, Y = C, N, O

Examples of McLafferty Rearrangement :





Exercise

(A) State True or False Questions :

(1) In rearrangement reaction, migrating group shift with its lone pair of electro called as electrophilic rearrangement.

(2) The skeletal rearrangement of carbocation which involves migration of β-alkyl, ar or σ-bond is called Wagner-Meerwein rearrangement.

(3) Rearrangement involving carbanion is Favorskii rearrangement.

(4) Vicinal diol on treatment with a catalytic amount of acid, rearrange to give aldehyde or ketone is called as Baeyer Villiger rearrangement.

(5) Allylic aryl ethers, when heated, rearrange to *ortho*-allylphenols, this reaction called the Cope rearrangement.

(6) The McLafferty-rearrangement is observed in compounds in which at least o abstractable gamma (γ) hydrogen is present with respect to a pi (π) bond.

(7) Allylic ethers of enols (allylic vinylic ethers) also undergo the Claisen rearrangemen

(8) The Cope rearrangement is the thermal isomerization of a 1,5-diene.

(9) In Pinacol rearrangement, the order of migration is $R_3C < R_2CH < RCH_2 < CH_3 < H$

(10) In Lossen rearrangement, azide reacts with a carbonyl derivative, usually aldehyde, ketone, or carboxylic acid, under acidic conditions to give an amine amide.

(11) When β-halo ketones are treated with base, in the presence of nucleophile reaction is called Quasi-Favorskii rearrangement.

(12) In pericyclic rearrangement the net result is one pi bond being converted into o sigma bond or vice versa.

(13) In Baeyer Villiger rearrangement, for unsymmetrical ketones the approximate ord of migration is $R_3C > R_2CH > Ar > RCH_2 > CH_3$.

(14) In Beckmann rearrangement, aldoximes often are more reactive than ketoximes ar they form nitrile.

ANSWERS

1. False	2. True	3. True	4. False	5. False	6. True	7. True
8. True	9. False	10. False	11. False	12. True	13. True	14. Fals