BHARATIYA VIDYA BHAVAN'S SHRI ISHVARLAL L. P. ARTS-SCIENCE AND SMT. J. SHAH COMMERCE COLLEGE, DAKOR-388225, SARDAR PATEL UNIVERSITY, GUJARAT.

Subject Code: US05CCHE21

Subject: Organic Chemistry

Unit 2: Name Reactions

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BHAVANS SCIENCE COLLEGE

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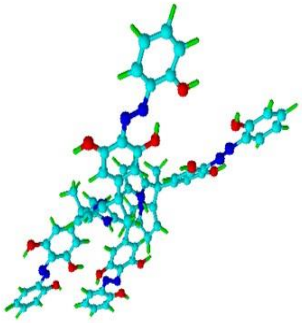
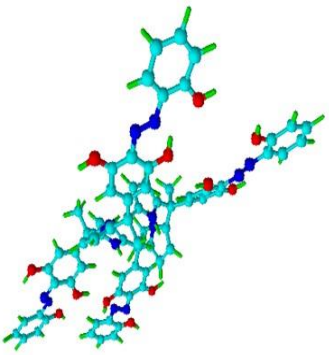
DAKOR-388225





YouTube Channel: THE CALI-X-ARENE

Playlist: B.Sc.V

SARDAR PATEL UNIVERSITY
Programme: B.Sc (Chemistry) Semester: V
Syllabus with effect from June 2020
(30 +70 Marks, 4 hrs per week)

Subject Code: US05CCHE21		**Total Credit: 4**
Title of Subject: Organic Chemistry		
Learning outcomes of the paper: From the study of this paper, student will learnt about basic concept of heterocyclic chemistry, reaction mechanism, Dienes And Macromolecules and Terpenoids. This study will helpful them in further studies and in industries.		
Unit	**Description in detail**	**Weightage (%)**
I	**Heterocyclic Compounds** Heterocyclic systems, Structure of Pyrole, furan and thiophene, Source of Pyrole, furan and thiophene, Electriphilic substitution in Pyrrole, furan and thiophene Reactivity and orientation, Saturated five – membered heterocycle, Structure of pyridine, Sources of pyridine compounds, Reactions of pyridine, Electrophilic substitution in pyridine, Nucleophilic substitution in pyridine, Basicity of pyridine, Reduction of pyridine, Quinoline. The skraup synthesis, Isoquinoline. The Bischler–Napieralski synthesis. Knorr pyrrole synthesis.	25%
II	**Reaction Mechanism** Baeyer Villiger oxidation, Hofmann rearrangement, Mannich reaction, Curtius–Schmidt rearrangement, Benzilic acid rearrangement, Sommlet rearrangement, Birch reduction, Favorskii rearrangement, Benzoin condensation, Beckmann rearrangement, Wittig reaction, Perkin reaction.	25%
III	**Dienes And Macromolecules** Dienes: Structure and properties, Stability of conjugated dienes, Resonance in conjugated dienes, Hyperconjugation, Ease of formation of conjugated dienes, Electrophilic addition to conjugated diene : 1,4- addition,1,2 Vs 1,4-addition, Rate Vs equilibrium, Free-radical polymerization of diene, Polymer and polymerization, Free radical vinyl polymerization, Co-polymerization, Ionic polymerization, Coordination, polymerization, Step reaction, polymerization, Structure and properties of macromolecules. Distinguishing features of addition and condensation polymerization Copolymer, classification of polymers, plastics and resins, Phase system for polymerization (like bulk, solution, emulsion and suspension polymerization).	25%
IV	**Terpenoids** General introduction including nomenclature, General properties of terpenoids, Isolation, Isoprene rule, Classification of terpenoids, General methods for the determination of structure of terpenoids. Introduction, isolation and constitution of Citral, α- terpineol, Camphor, B-carotene.	25%

Unit 2: Name Reaction

1. **Birch Reduction**
2. **Baeyer Villiger Oxidation**
3. **Mannich Reaction**
4. **Witting Reaction**
5. **Sommelet Rearrangement**
6. **Beckmann Rearrangement**
7. **Curtius Rearrangement**
8. **Hoffmann Rearrangement**
9. **Benzil-Benzilic Acid Rearrangement**
10. **Favorskii Rearrangement**
11. **Perkin Reaction**
12. **Benzoin Condensation**

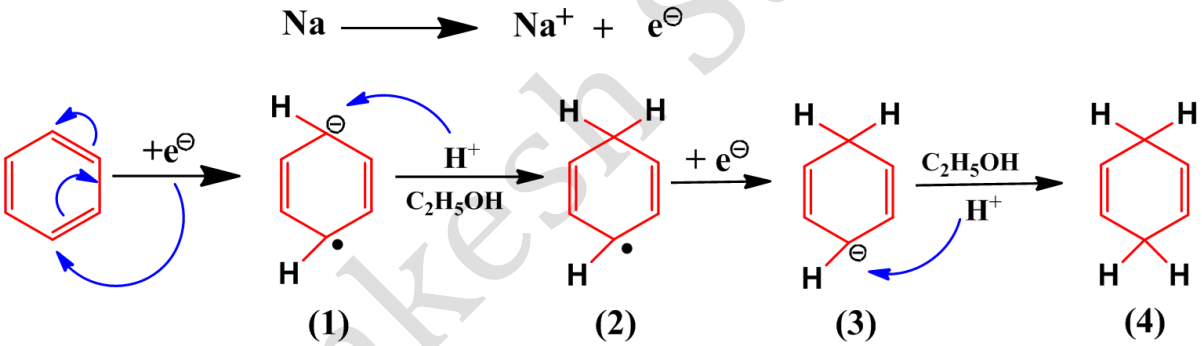
1. Birch Reduction

- **Principle:**

  In Birch reduction, aromatic rings are reduced to1, 4 dienes by alkali metals in liquid ammonia.

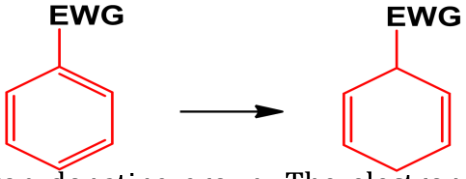
- **For knowledge:**
  - The first thing to note is that when lithium or sodium dissolve in ammonia, they give an intense blue solution. Blue is the colour of solvated electrons: these group 1 metals ionize to give Li^+ or Na^+ and e- $(NH_3)_n$. With time, the blue colour fades, as the electrons reduce the ammonia to NH_2^- and H_2.
  - Birch Reductions use these blue solutions with their solvated electrons as reducing agents. The reduction of NH_3 to NH_2^- and H_2 is quite slow and a better electron acceptor is preference.

- **Mechanism:**



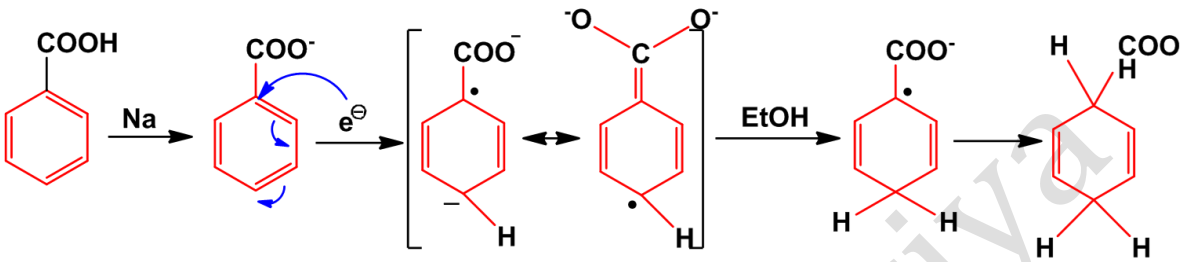
- **Regioselectivity in Birch Reduction:**

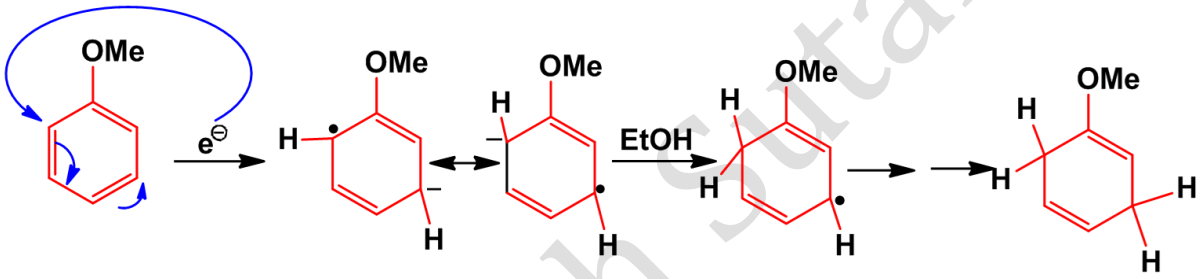
  - The positions of protonation on substituted benzene depend on the nature of the group as illustrated below.
  - Electron withdrawing group: The electron withdrawing groups promote ipso and para position for reduction. These groups activate the ring towards birch reduction. Initially, the protonation occurs at para to the EWG.



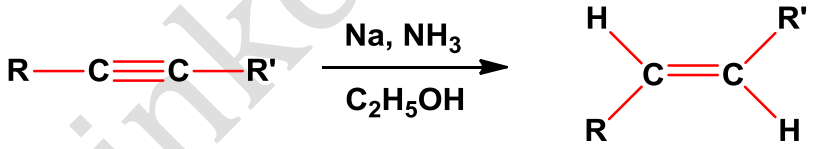
  - Electron donating group: The electron donating groups promote ortho and meta position for reduction. They deactivate the ring for overall reduction compared to the EWG.

➢ The –CHO, -C(O)R, CO_2R act as electron donating groups because they are reduced to $–CH_2O$- prior to the reduction of the ring.

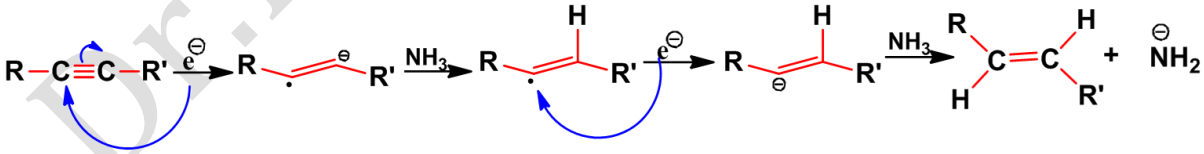




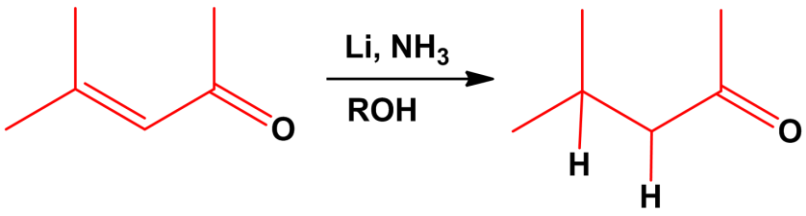
- **Birch Reduction of alkynes:**
  - ➢ Birch Reduction works for alkynes too and reduces them to Trans alkene.



- **Mechanism:**



➢ Dissolving metal reduction of enones gives enolates regiospecifically.



Application:

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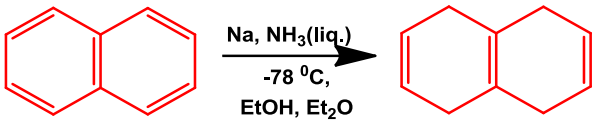

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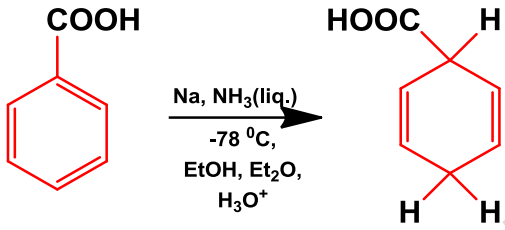

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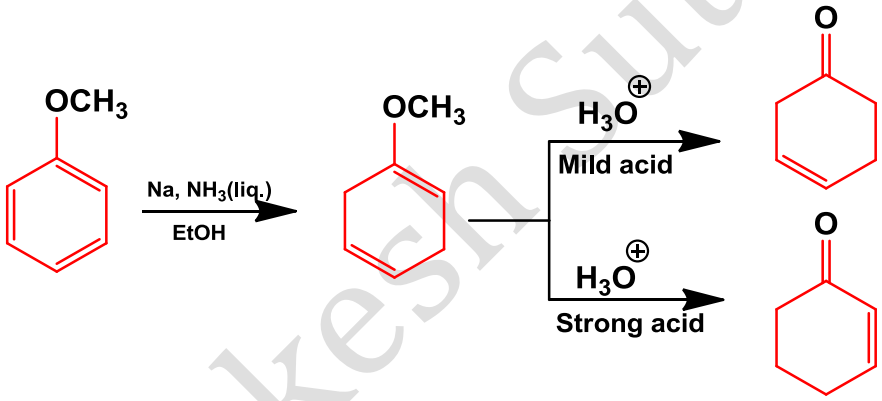

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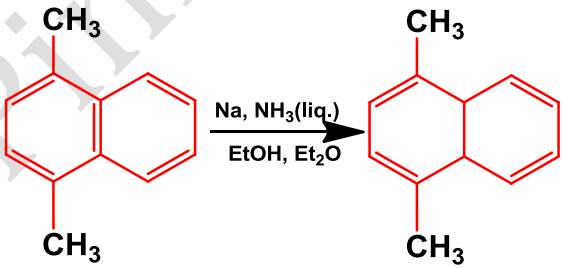

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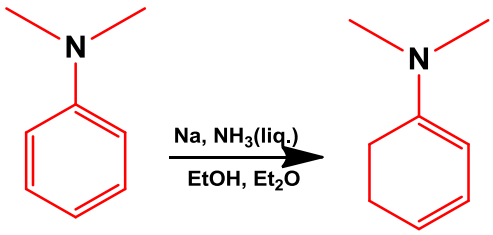

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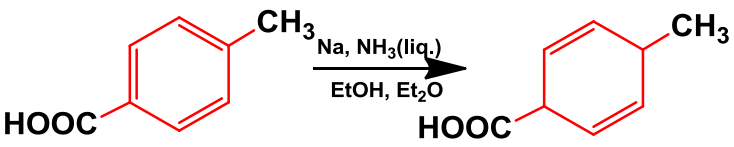

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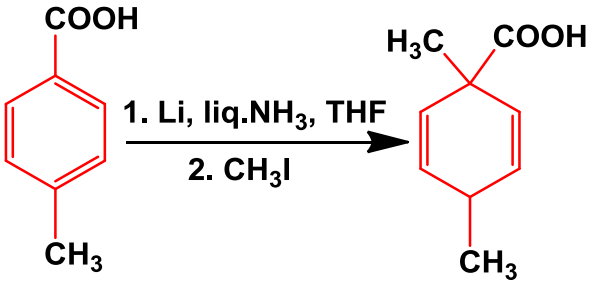

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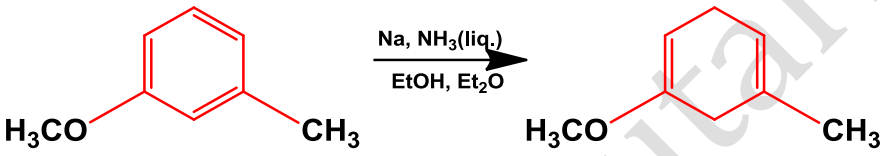

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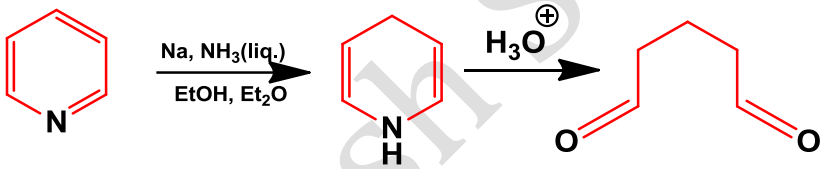

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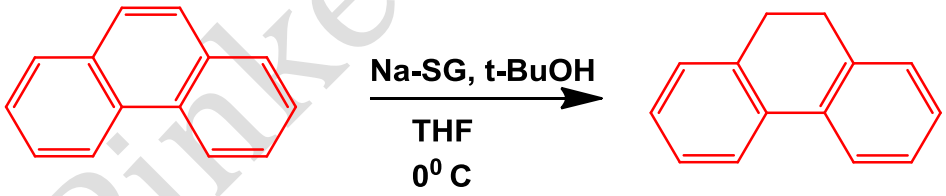
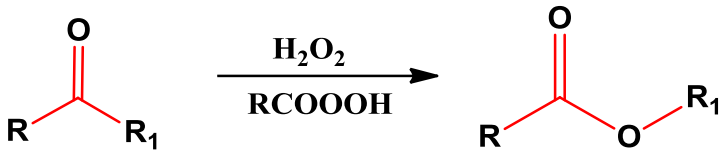


2. Baeyer-Villiger Oxidation:

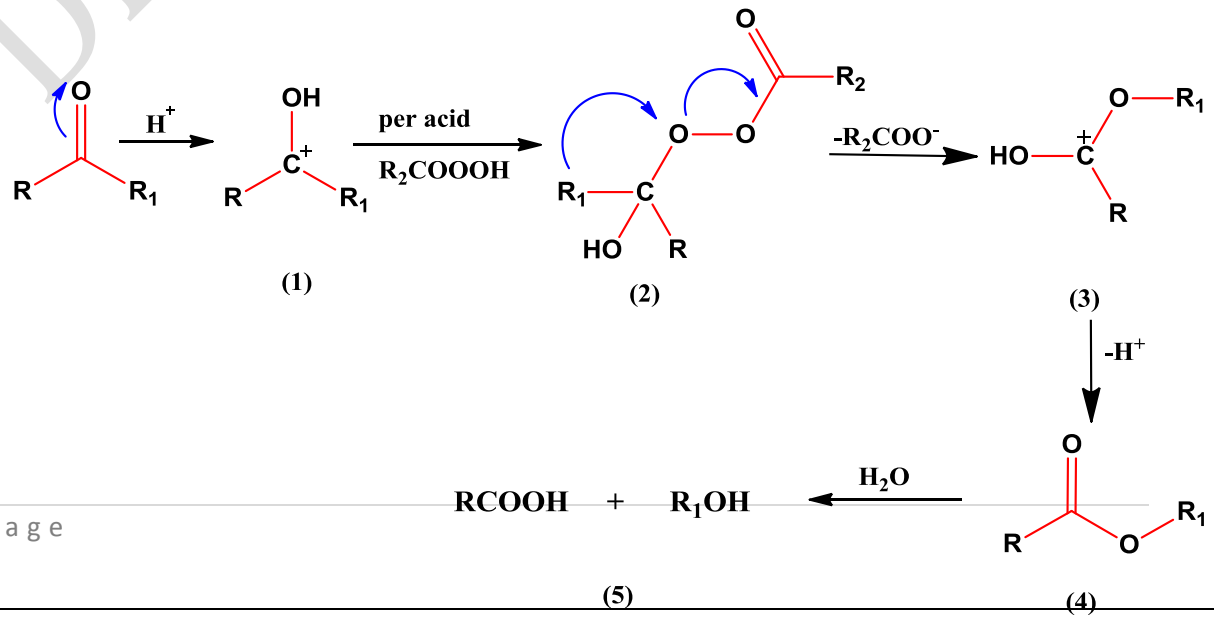
- **Principle:**

  The Baeyer-Villiger oxidation is used to oxidize ketones to esters by using peroxy acids.



Ketone/Aldehyde **Carboxylic ester**

- **Note:**
  - The Baeyer-Villiger rearrangement is a regioselective reaction. In above case, the R' group is assumed to possess greater migratory aptitude and hence only one product is formed preferentially.
  - This reaction involves the oxidative cleavage of C-C bond.
- **Reagents:**
  - Metachloroperbenzoic acid (MCPBA)
  - Peroxyacetic acid (PAA)
  - Peroxytrifluoroacetic acid (TFPAA)
  - Hydrogen Peroxide/BF_3
  - Caro's acid buffered with disodium hydrogen phosphate
  - Sodium percarbonate (Na_2CO_3. 1.5 H_2O_2)
  - Magnesium salt of monoperoxypthalic acid (MMPP)
  - Potassium peroxomonosulphate (Potassium Carbonate) supported on hydrated silica also known as "reincarnated caro's acid".
  - Baeyer-Villiger monooxygenase (an enzyme abbreviated as BVMO)
- **Mechanism:**
  - Initially, the peroxy group is added to the carbonyl carbon to give a criegee like intermediate. Then one of the group attached to carbonyl carbon is migrated on to the electron deficient oxygen atom in a concerted step, which is the rate determination step.



- The substituents which can stabilize the positive charge can migrate readily. The migratory aptitude of various substituents is approximately.

  3^0-alkyl > cyclohexyl > 2^0-alkyl > benzyl > aryl > 1^0-alkyl > methyl

- In case of aldehydes, usually the hydrogen atom is migrated preferentially and thus by furnishing carboxylic acids.

- **Applications:**

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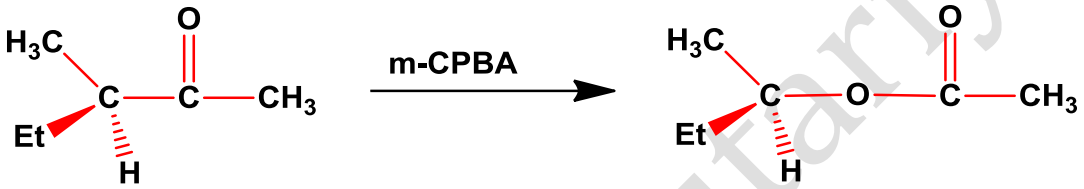

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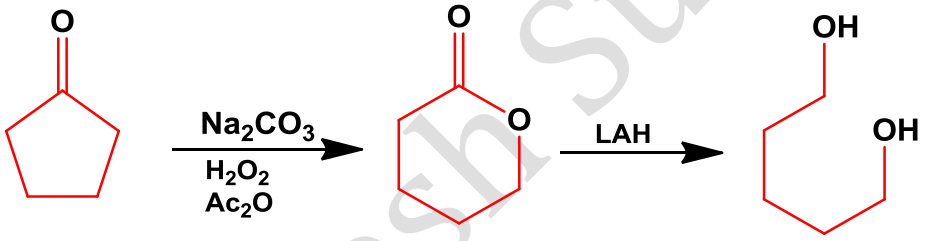

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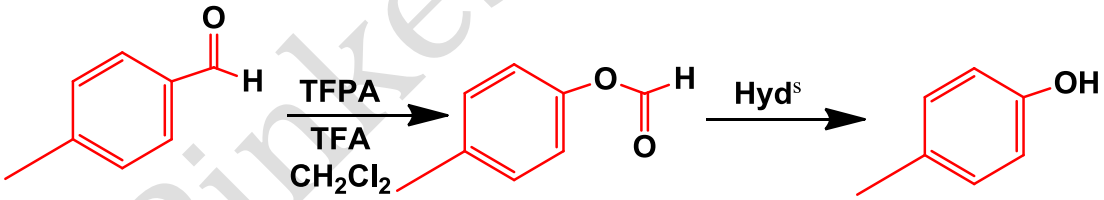

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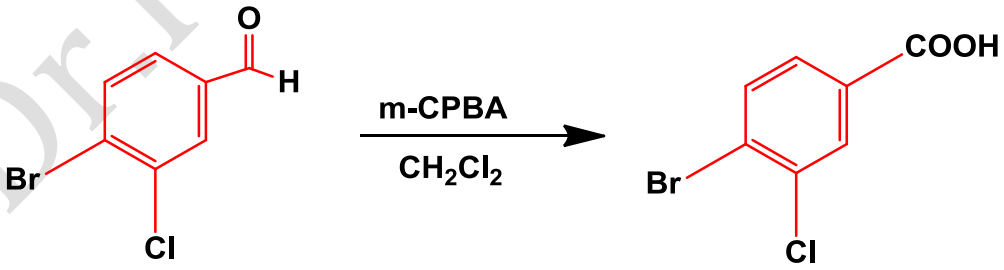

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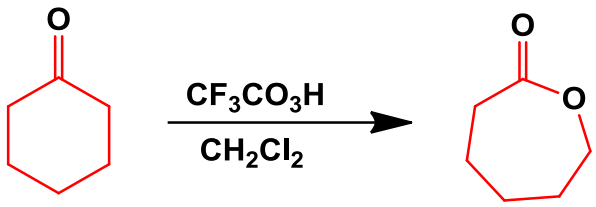

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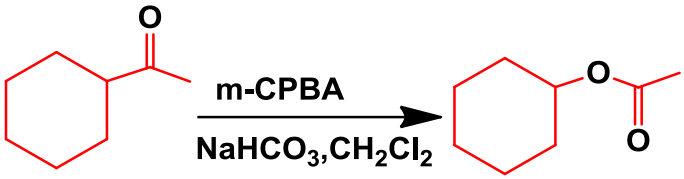

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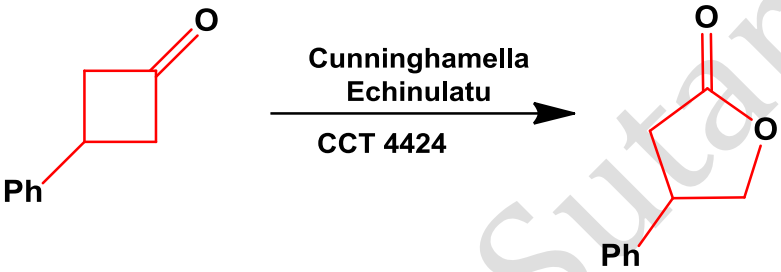

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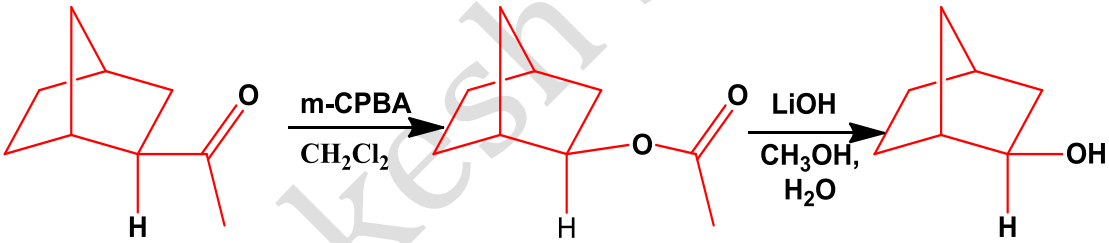

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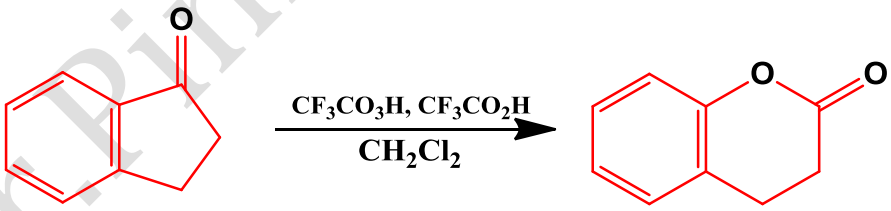

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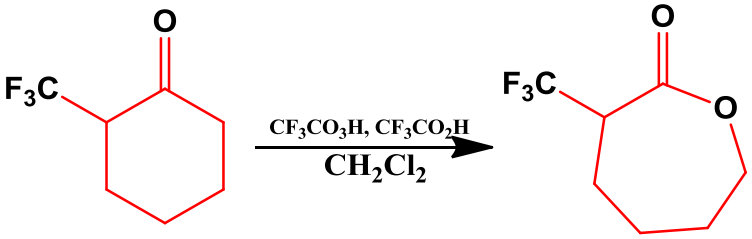

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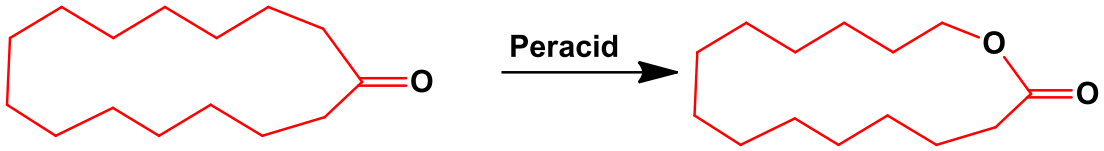

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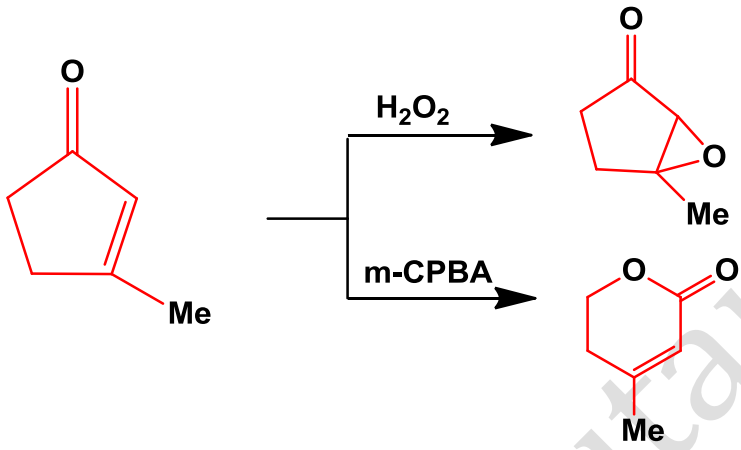
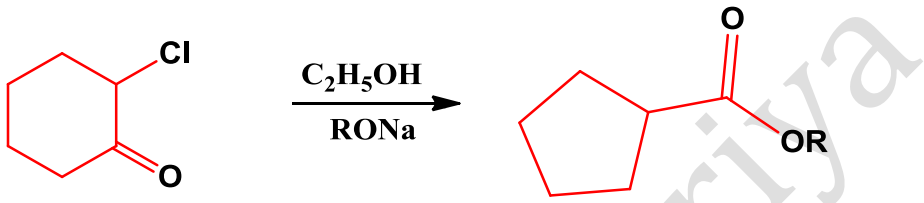


3. Favorskii Rearrangement:

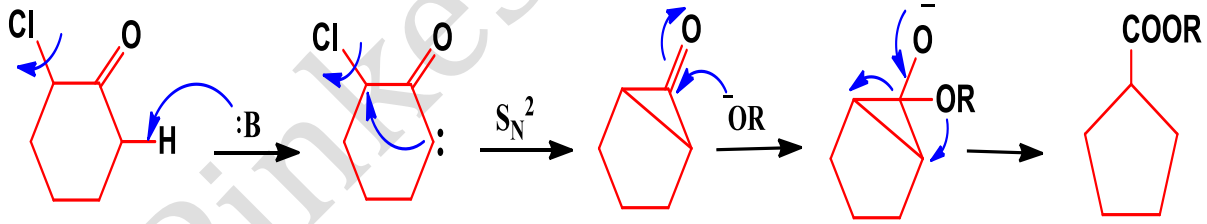
- **Principle:**

  Treatment of an α-haloketone with an alkoxide gives an ester product. In this reaction, the product has a rearranged carbon skeleton but the same number of carbon atoms as the reactant. This reaction is called Favorskii Rearrangement.

- **Reaction:**



- **Mechanism:**
  - The mechanism involves cyclopropane intermediate.
  - Base abstracts the α-hydrogen from substrate to give the carbanion, which undergoes intramolecular SN2 displacement of the halide ion. The resulting cyclopropanone intermediate is opened under the reaction conditions to give the more stable anion, which takes proton from solvent to make final product, ester.



- **Application:**

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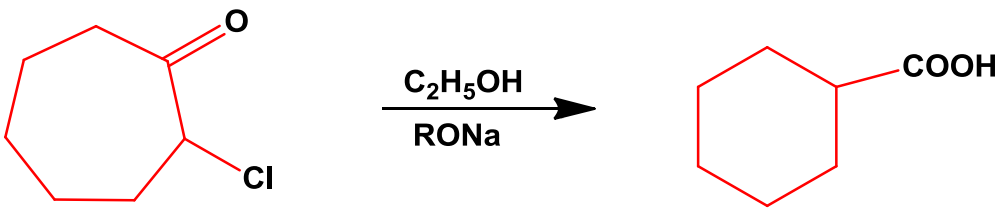
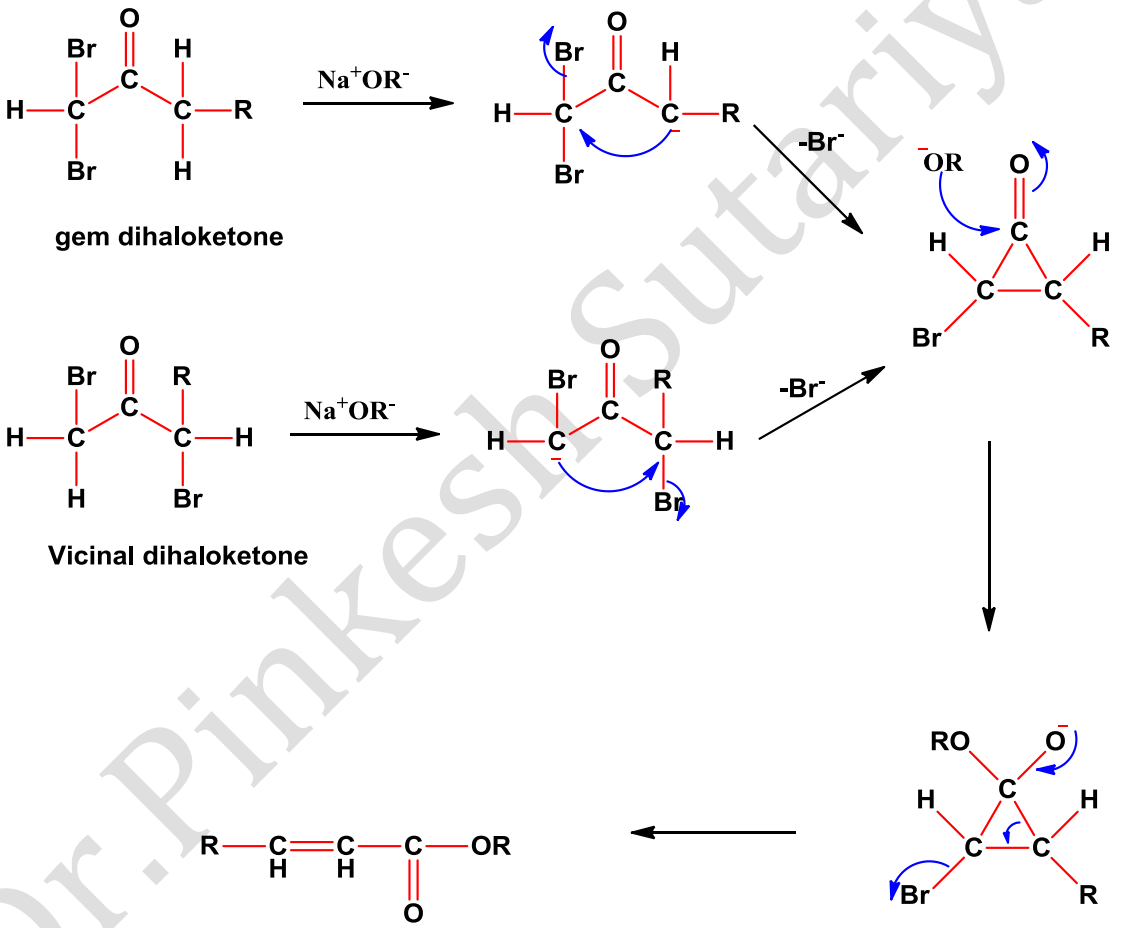


➢ **Favorskii Rearrangement of gem and vicinal dihaloketones:**

Favorskii rearrangement of gem and vicinal dihalokeones gives the same product i.e., α,β-unsaturated ester.



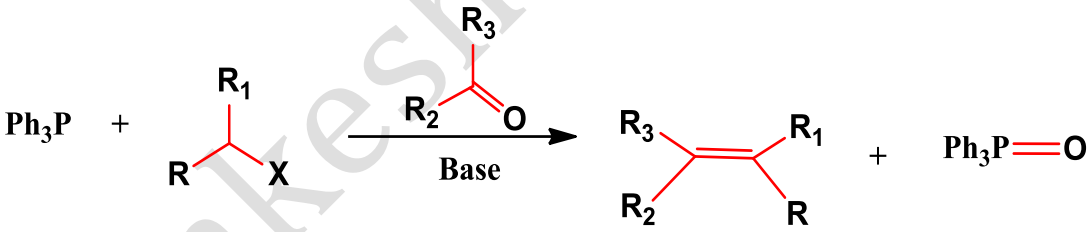
4. Wittig Reaction:

- **Principle:** The Wittig reaction or Wittig olefination is a chemical reaction of an aldehyde or ketone with a triphenyl phosphonium ylide (often called a Wittig reagent) to give an alkene and triphenylphosphine oxide.

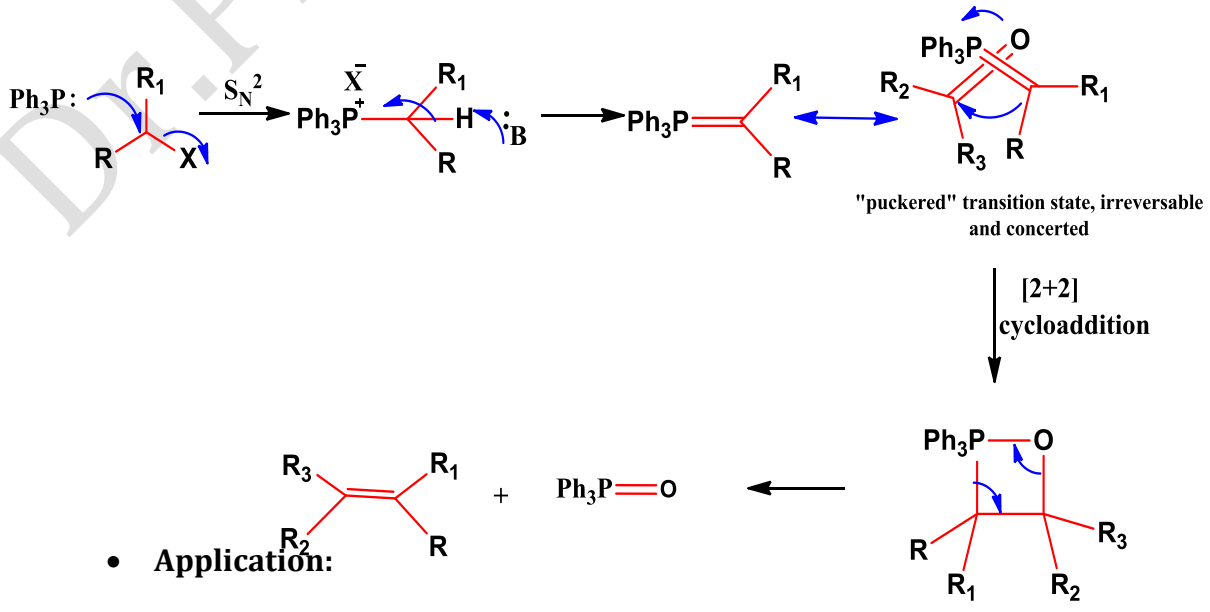
  An ylide or ylid is a neutral dipolar molecule containing a formally negatively charged atom (usually a carbanion) directly attached to a heteroatom with a formal positive charge (usually nitrogen, phosphorus or sulfur), and in which both atoms have full octets of electrons. The result can be viewed as a structure in which two adjacent atoms are connected by both a covalent and an ionic bond; normally written X+–Y–. Ylides are thus 1,2-dipolar compounds, and a subclass of zwitterions.

  They appear in organic chemistry as reagents or reactive intermediates.

- **Reaction:**



- **Mechanism:**



- **Application:**

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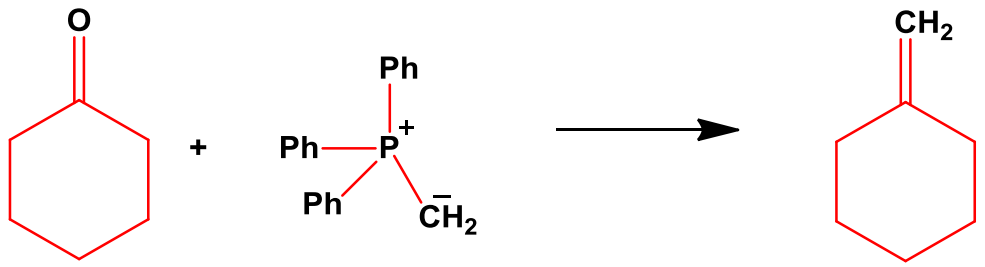

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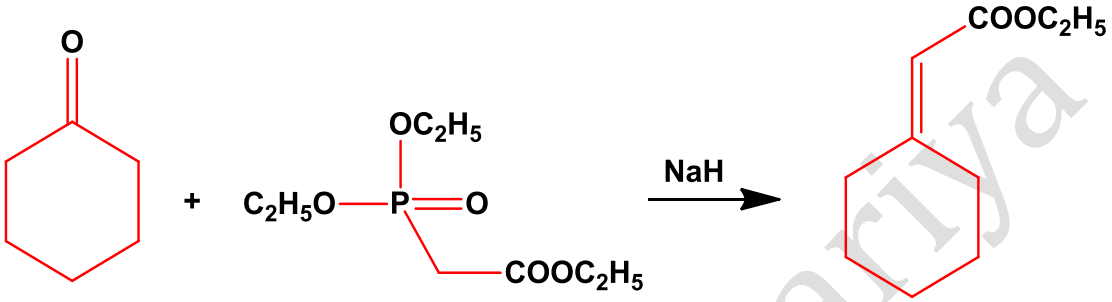

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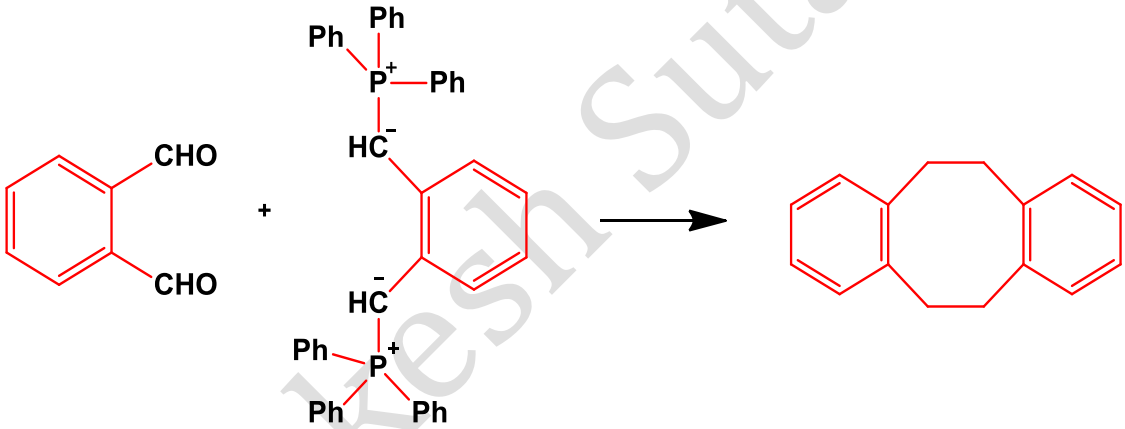
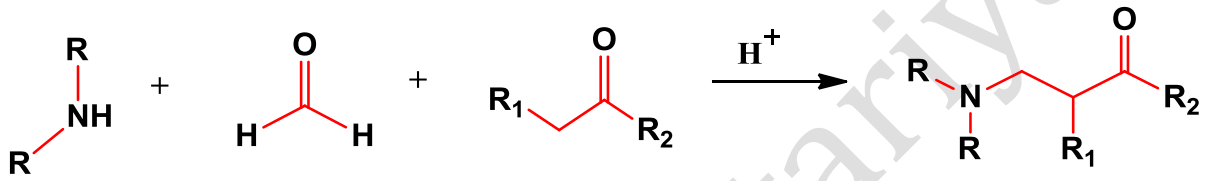


5. Mannich Reaction:

- **Principle:**

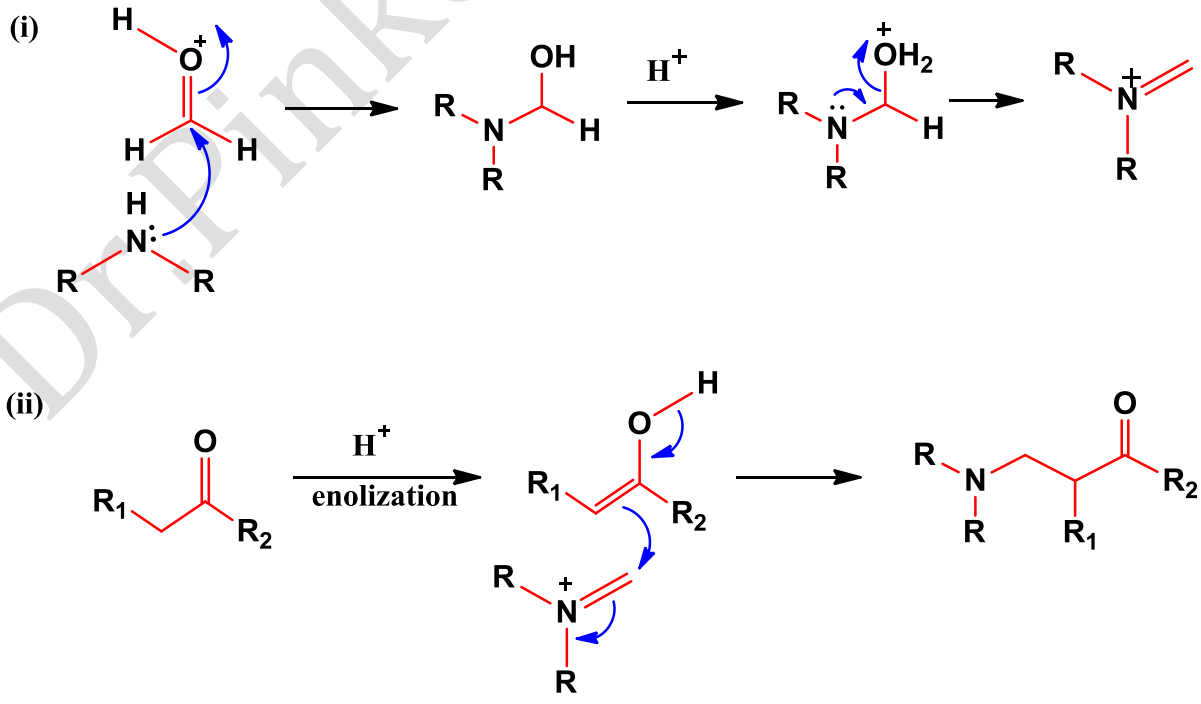
  Compound containing at least one active hydrogen atom (ketones, nitroalkanes, β-keto-ester, β-cyano-acids etc.) condenses with formaldehyde and rimary or secondary amine or ammonia to give the product known as Mannich base and the reaction is called Mannich Reaction.

- **Reaction:**



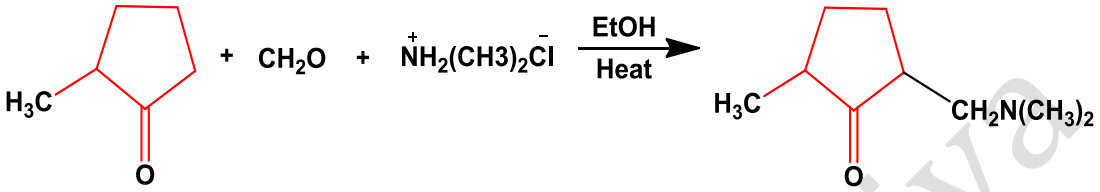
- Formaldehyde has been most common but other aldehydes have also been used successfully.
- The Mannich reaction also proceeds with the other activated hydrogen compounds such as indole, furan, pyrrol and phenols.

- **Mechanism:**



- **Application:**

1.



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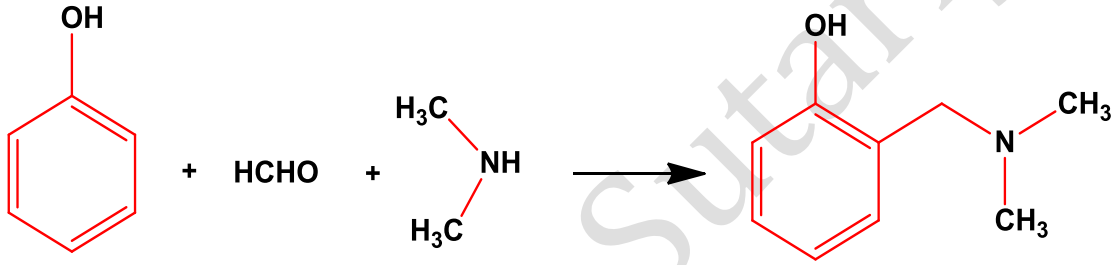

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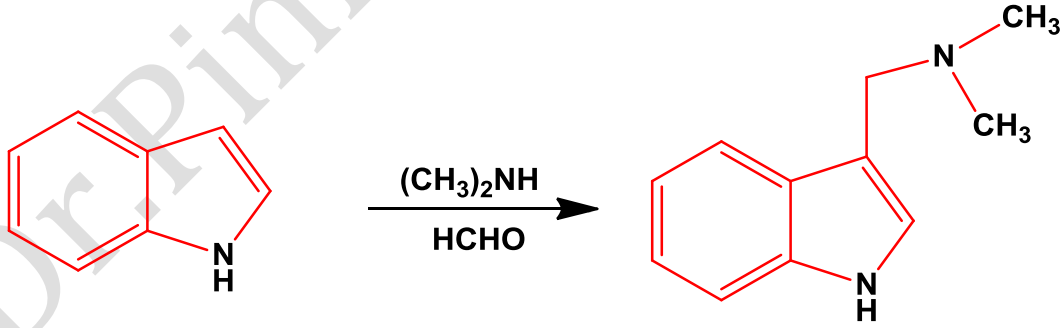
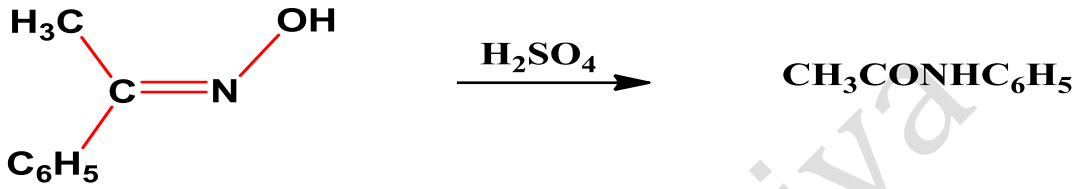


6. Beckmann Rearrangement:

- **Principle:**

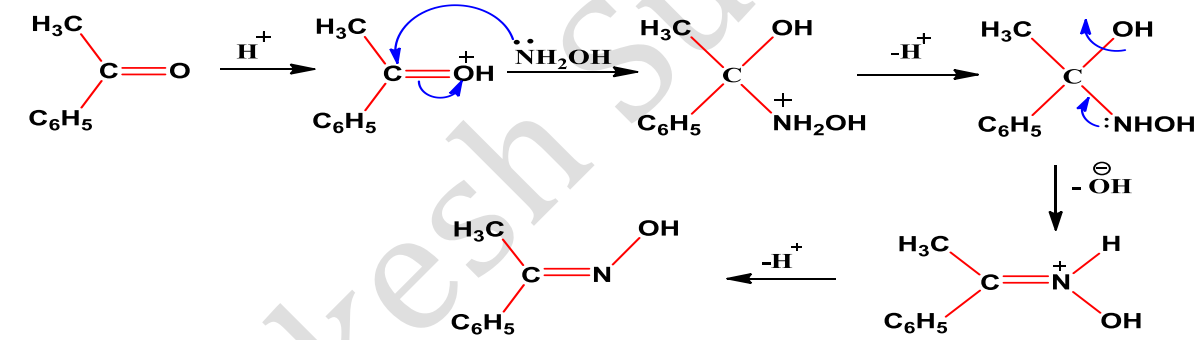
  The conversion of a ketoxime to nitrogen substituted amine in the presence of acid catalyst (e.g., PCl5, P2O5, SOCl2, POCl3, H3PO4 and H2SO4) is known as the Beckmann rearrangement.

- **Reaction:**
  - Benzophenone oxime gives benzanilidine in the presence of H2SO4.

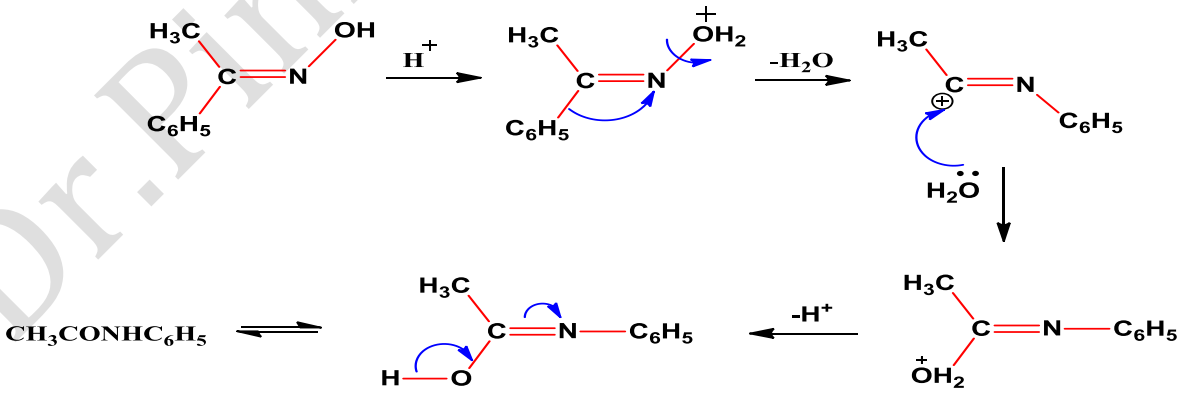


- **Mechanism:**

(i) Oxime Formation

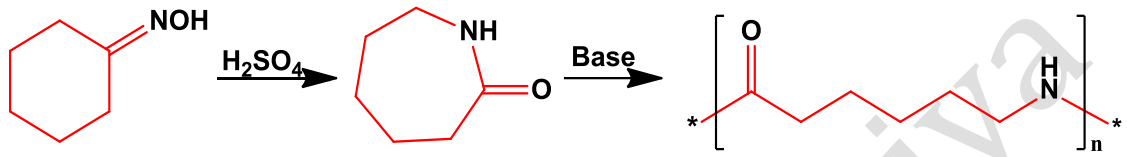


(ii) Rearrangement



- **Beckmann Rearrangement is highly stereospecific:**
  - Beckmann rearrangement is highly stereospecific in that the migratory group always approaches to nitrogen atom from the opposite side of oxygen atom.
  - Only R migrates because it is on the opposite side of leaving group (H2O or oxygen atom) i.e., the group which is anti or trans to the –OH group, migrates to the electron deficient N atom.
- **Application:**

1.



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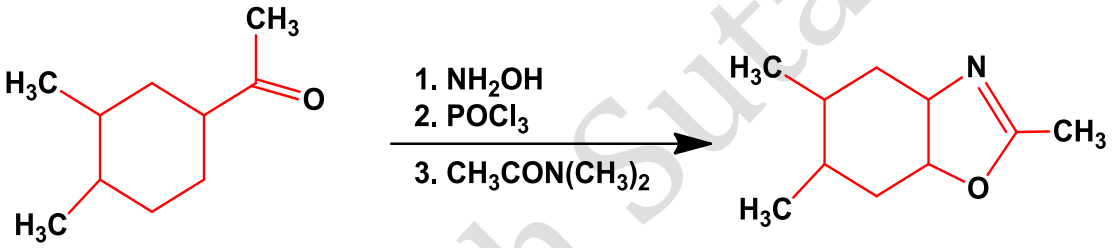

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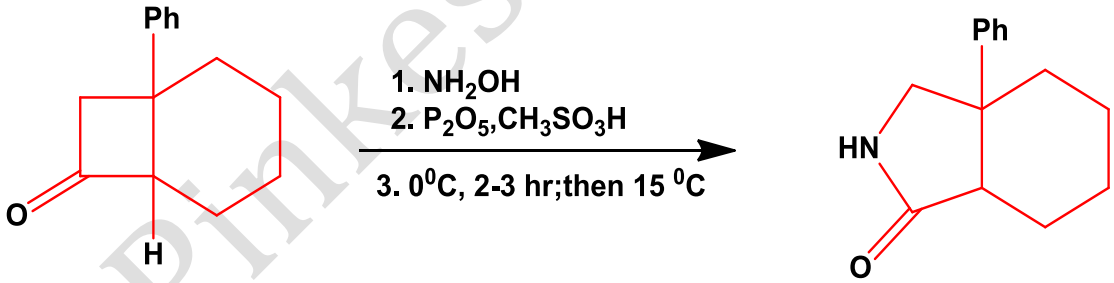

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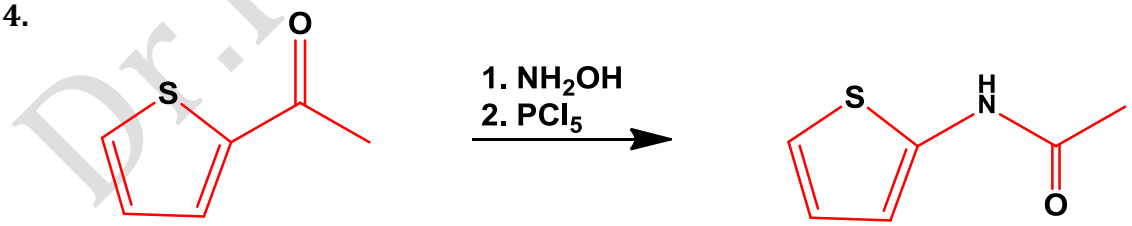
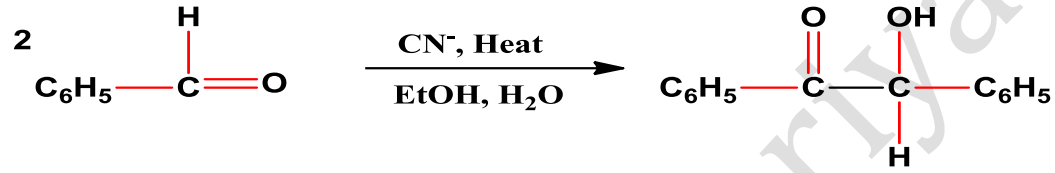


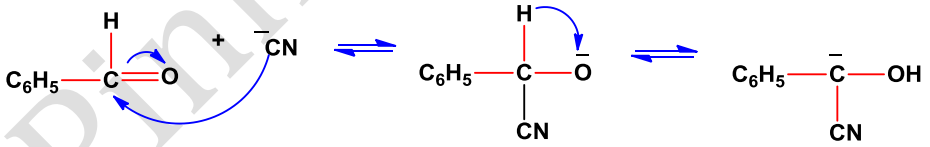
7. Benzoin Condensation:

- **Principle:**
  - **The self-condensation of aromatic aldehyde (with α-hydrogen)** in presence of cyanide ions as a catalyst to α-hydroxy ketone (benzoin) is called benzoin condensation.
  - Benzoin belongs to a class of compounds called acycloins.
  - The reaction is not successful with aliphatic aldehydes under these conditions.
- **Reaction:**

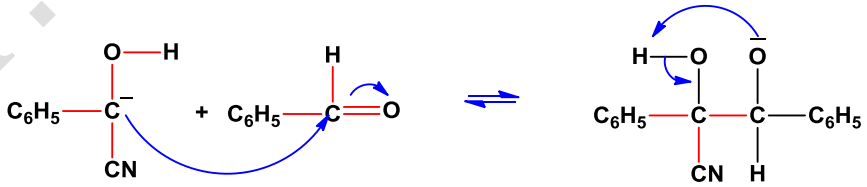


- **Mechanism:**
  - Cyanide ions attack the carbonyl group to give carbanion. Cyanide group with its electron withdrawing nature makes aldehydic hydrogen more acidic.
  - First carbanion is less stable. So, it is converted to more stable carbanion as it is stabilized by benzene ring.
  - The anion attacks another aldehyde carbonyl to form the link between the two molecules.
  - The deprotonation-protonation steps give the alkoxide anion. Finally, cyanide ion departs to give benzoin.

(i)

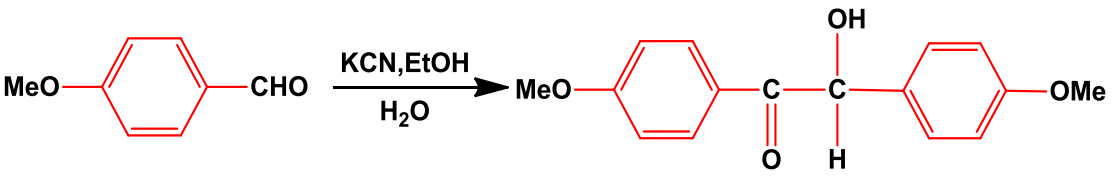


(ii)



- **Application:**

1.



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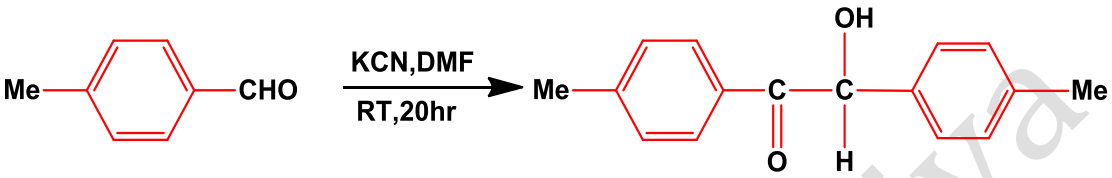

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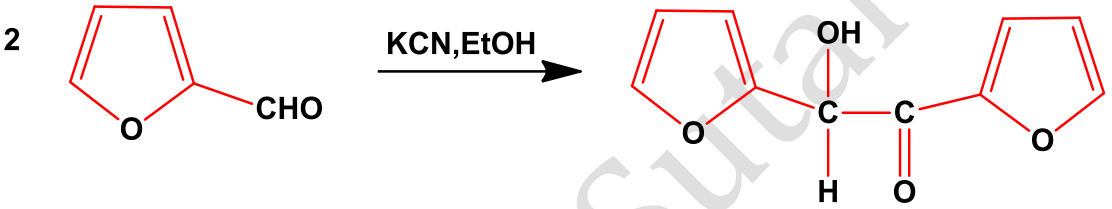
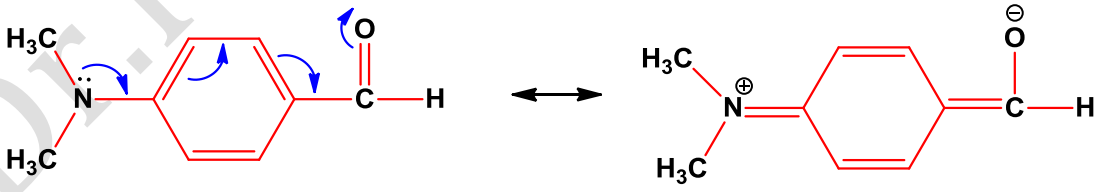
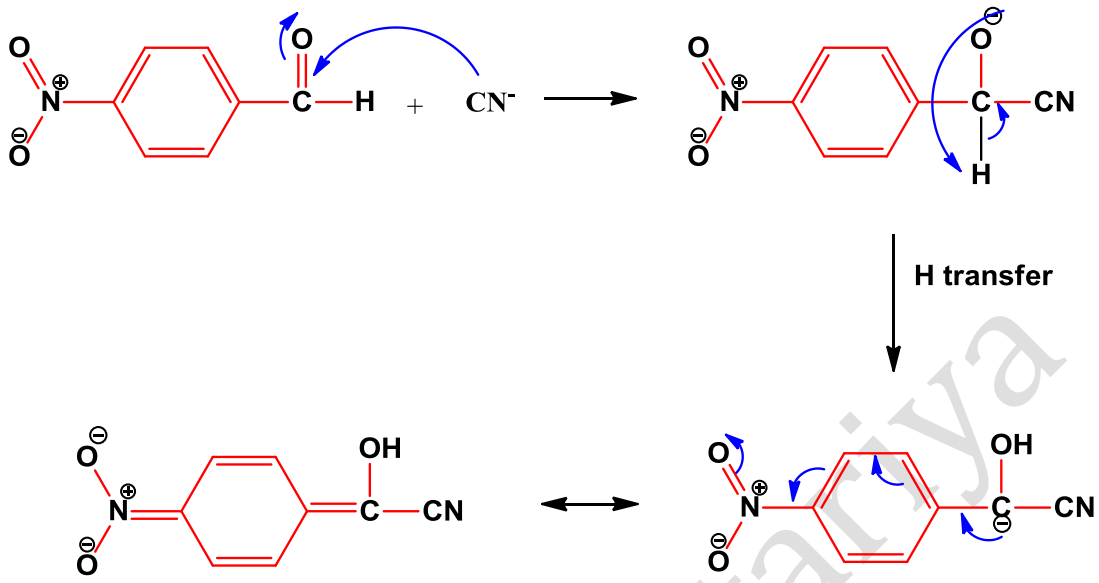


➢ **p-N,N-dimethylaminobenzaldehyde and p-nitrobenzaldehyde donot undergo self condensatior under benzoin conditions. Explain.**

- Due to resonance in p-N,N-dimethylamino benzaldehyde, the carbonyl carbon is not suffieciently electrophilic and hence it cannot undergo attacked by the CN^-.



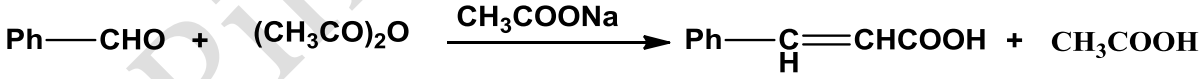
- Similarly because of resonance, the cyano hydrin anion of p-Nitrobenzaldehyde is not nucleophilic enough to attack on another aldehyde molecule.



8. Perkin Reaction:

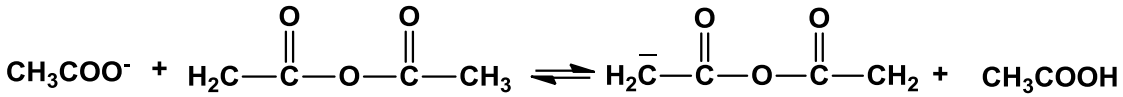
- **Principle:**
  - An aromatic aldehyde is condensed with acid anhydride in the presence of base to form an α, β- unsaturated acid. This reaction is known as Perkin Condensation.
  - The reaction is carried out by refluxing equimolar quantities of the aldehyde and salt of acid with excess amount of anhydride.

- **Reaction:**



- **Mechanism:**
  - The anhydride provides the carbanion under the influence of base, which attacks the carbonyl carbon of aldehyde.
  - Abstraction of proton from active methyl group by base, followed by elimination of hydroxyl group. Its hydrolysis gives α,β-unsaturated acid.

(i)



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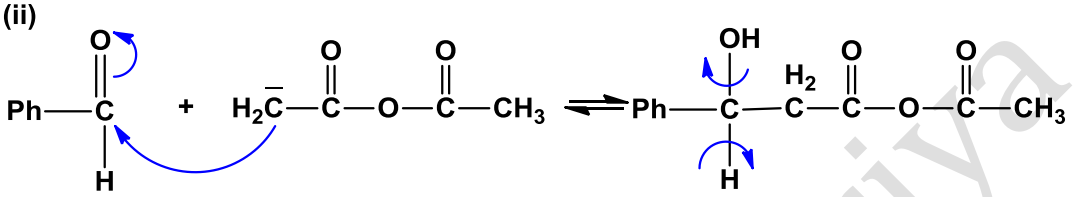
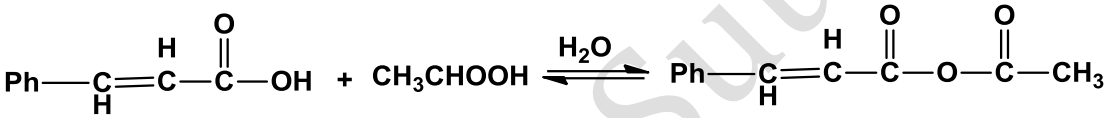
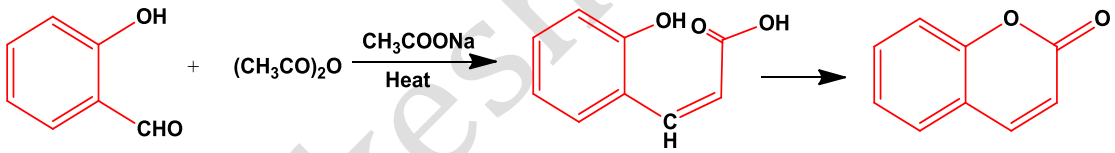




- **Application:**

1.



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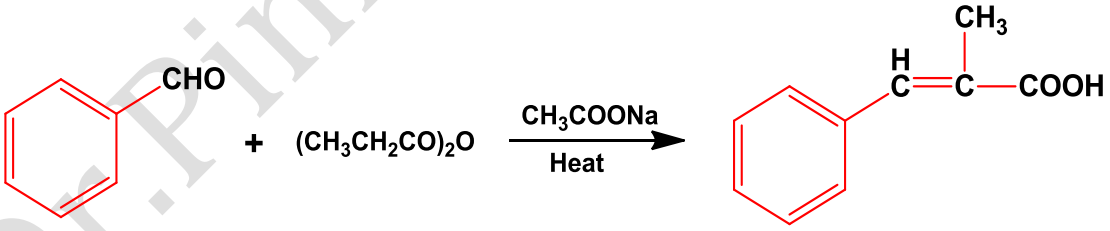

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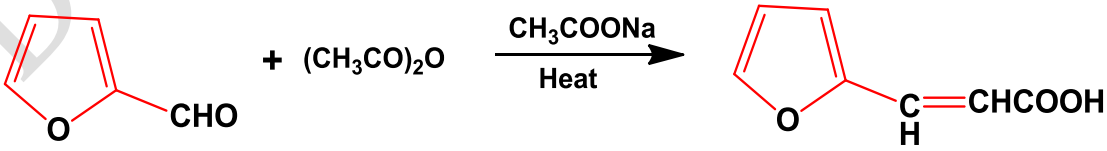
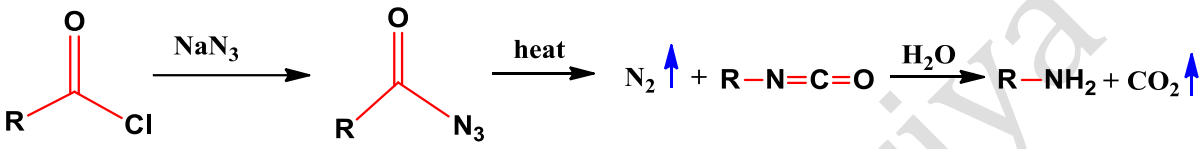


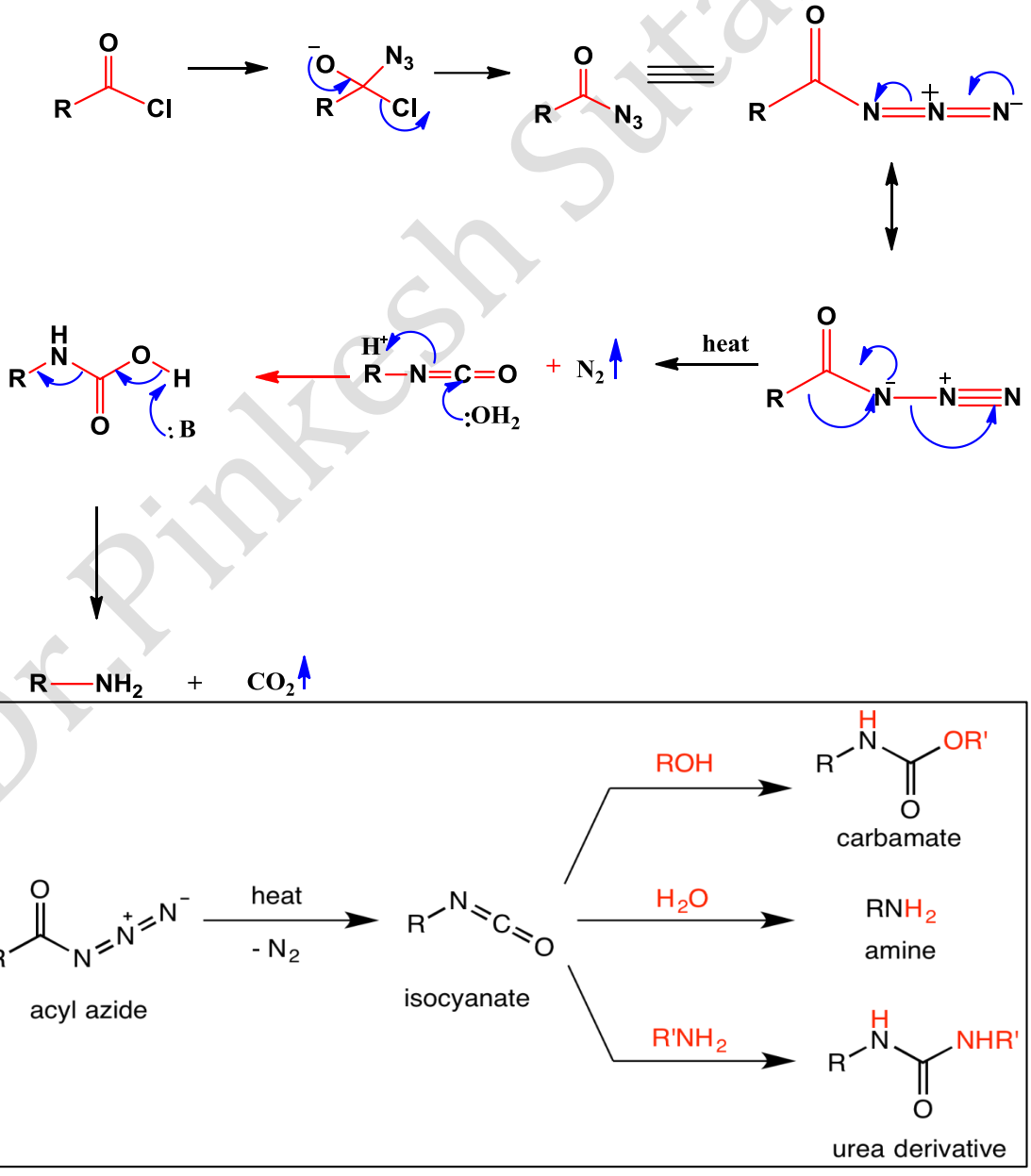
9. Curtius- Schmidt Rearrangement:

- **Principle:** The Curtius Rearrangement is the thermal decomposition of carboxylic azides to produce an isocyanate. These intermediates may be isolated, or their corresponding reaction or hydrolysis products may be obtained

- **Reaction:**



- **Mechanism:**

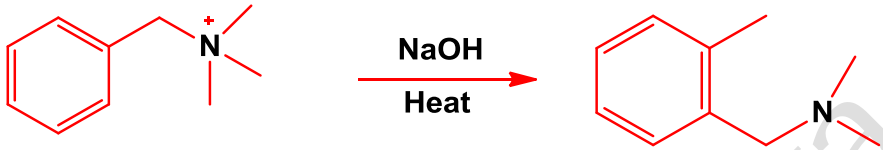


10. Sommelet-Hauser Rearrangement:

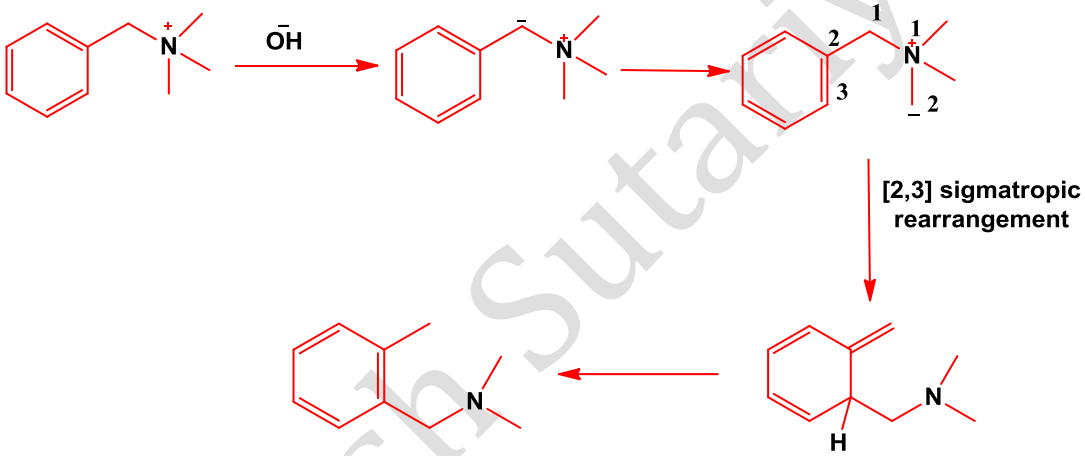
- **Principle:**

  The reaction of tetraalkylammonium halides containing a benzyl hydrogen to 3^0-amine in the presence of strng base is called the Sommelet rearrangement.

- **Reaction:**

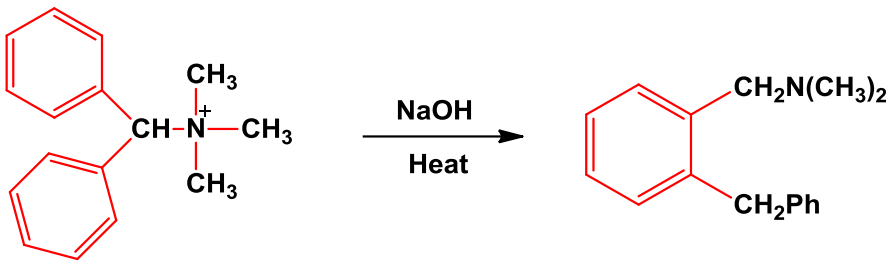


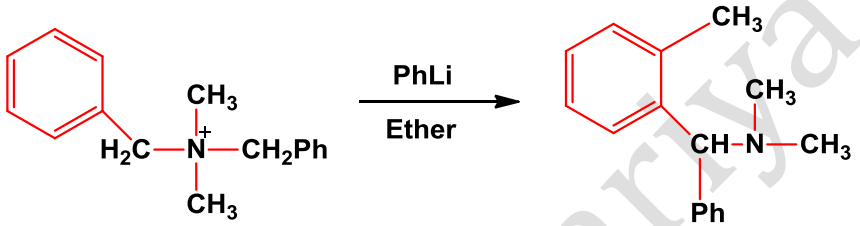
- **Mechanism:**

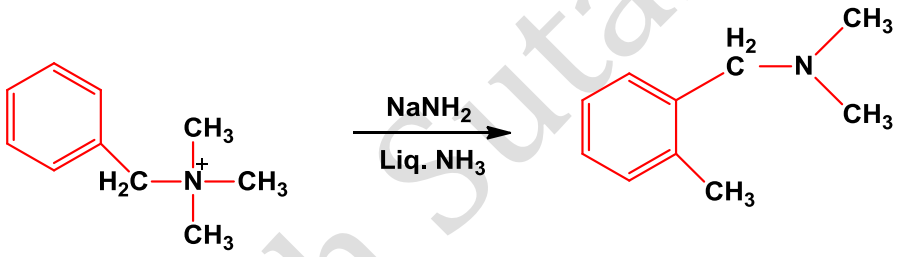


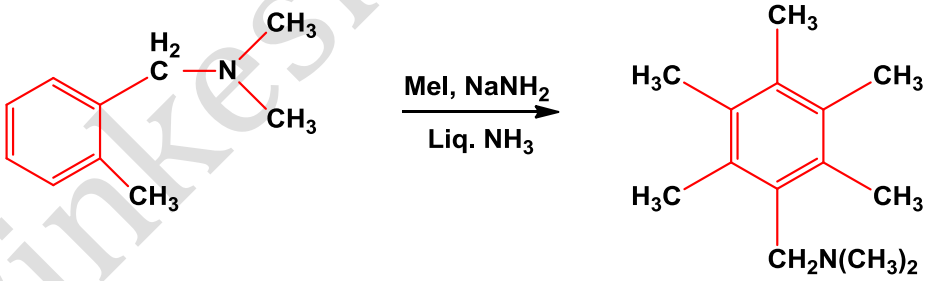
- Ylide (I) is more stable ylide than (II) because of the possibilities of resonance and is formed at low temperature.
- Both ylide are exist in equilibrium and the rquilibrium is displaced to the less stable ylde as the reaction progresses at higher temperature.
- Scientist Hauser has provided some independent support. He argued that if the sommelet rearrangement really proceeded via an intermediate ylide (less stable) compounds, than the compounds in which ortho positions are occupied by some groups should be isolated without aromatization.

- **Application:**

1. 

2. 

3. 

4. 

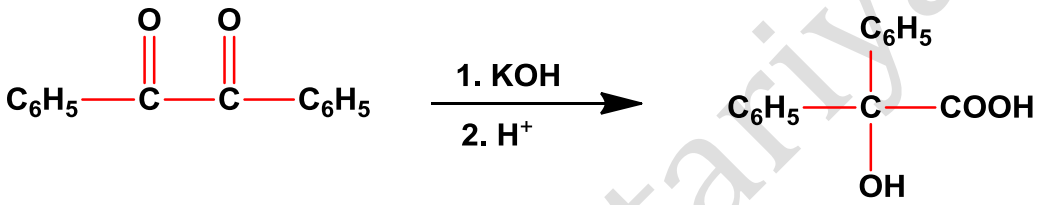
11. Benzilic acid Rearrangement:

- **Principle:**

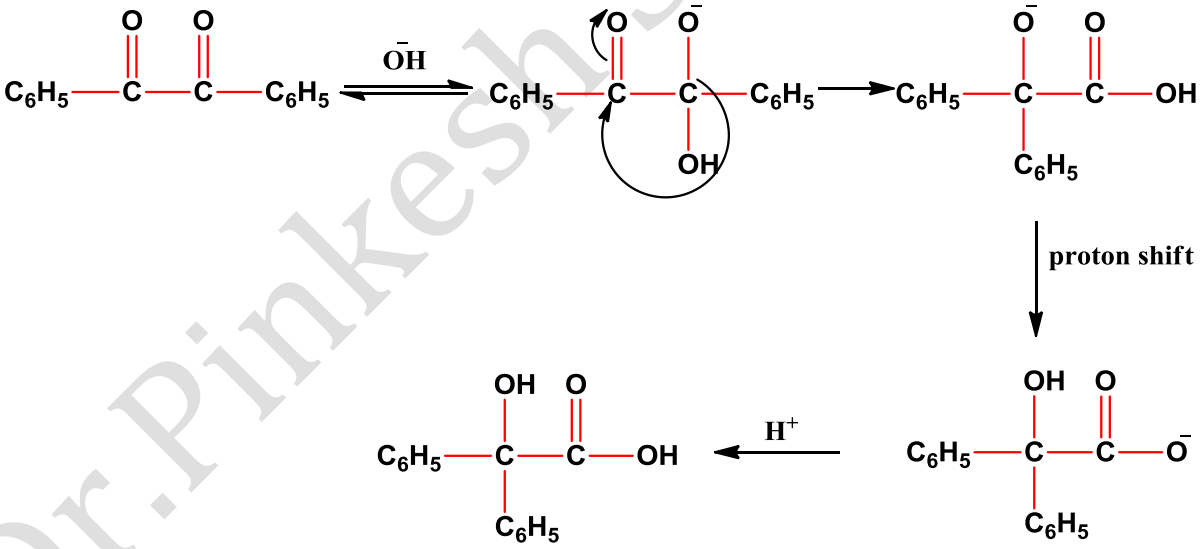
  The rearrangement of 1,2-diketones in the presence of strong base to α-Hydroxyacid is known as Benzilic acid rearrangement.

  (1,2-diketone) $\xrightarrow[\text{(ii) acid}]{\text{(i) Strong base}}$ (α-Hydroxyacid)

- **Reaction:**

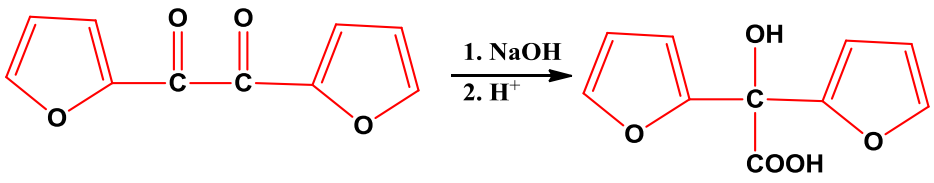


- **Mechanism:**



- **Application:**

1.



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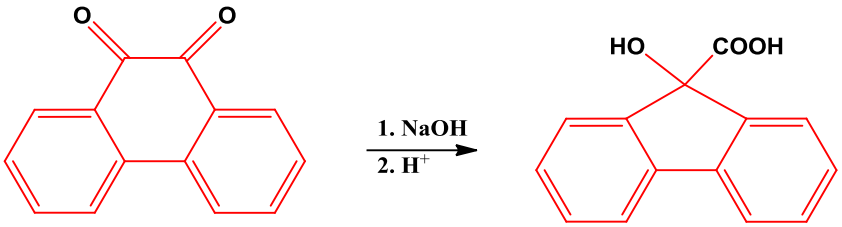

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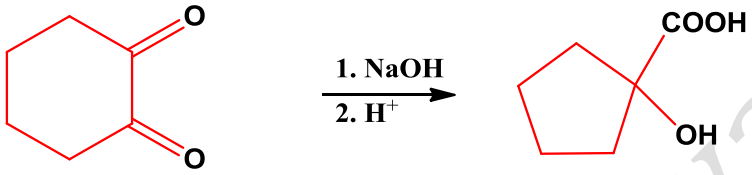
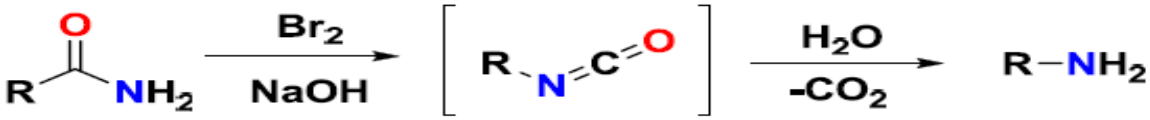
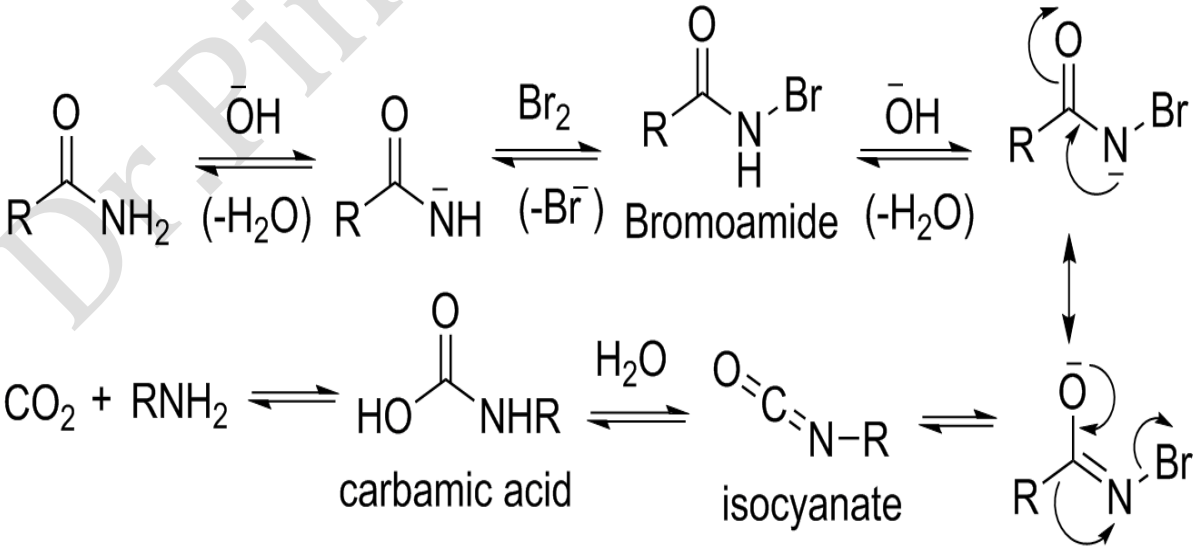


12. Hoffmann Rearrangement

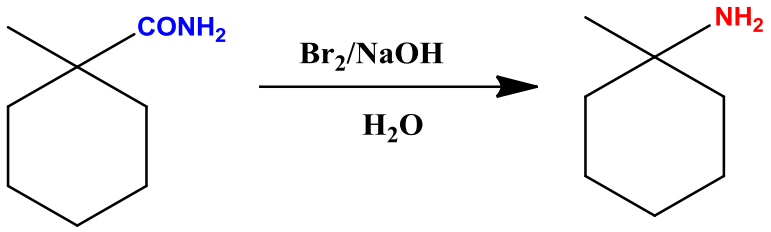
- **Principle:** The Hofmann rearrangement is the organic reaction of a primary amide to a primary amine with one fewer carbon atom.

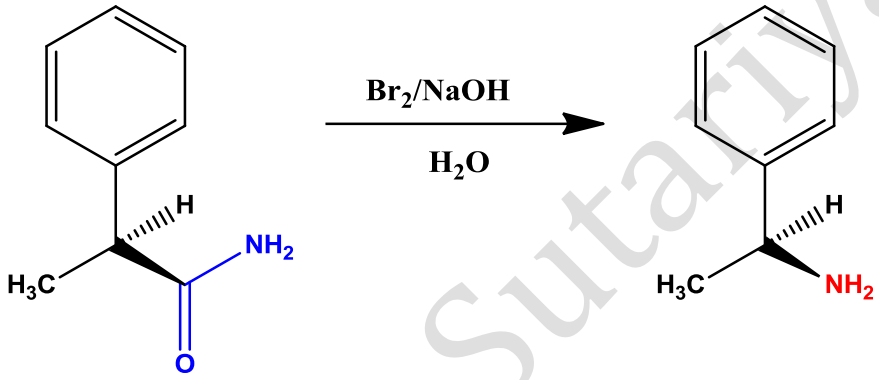


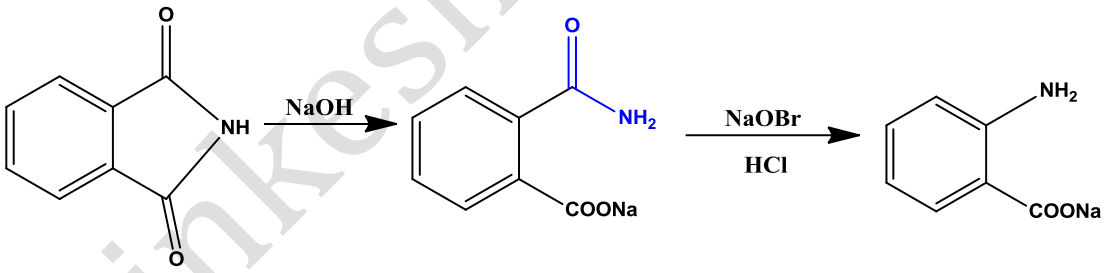
Mechanism:



- **Application:**







Multiple Choice questions

1. The conversion of trans alkene from alkyne is known as _____

(A) Beckmann Rearrangement	(b) **Birch Reduction**	(C) Witting Reaction	(D)Hoffman Rearrangement

2. Which of the following is not C to N migration rearrangement?

(A) Hoffman Rearrangement	(b) Curtius Rearrangement	(C) Beckmann Rearragement	(D) **Favorskii Rearrangement**

3. The Conversion of Alpha-Hydroxy acid from Diphenyl ketone is known as_____

(a) Perkin Reaction	(B) Mannich Reaction	(C) **Benzil-Benzilic Acid Rearrangement**	(D) Sommelet Rearrangement

4. The conversion of benzanilide from benzophenone oxime is known as_____

(A) Hoffman Rearrangement	(b) **Beckmann Rearrangement**	(C) Curtius Rearrangement	(D) Witting Reaction

5. Five member Cyclic ester is known as _____

(a) Beta Lactone	(B)**Gamma Lactone**	(C) Delta Lactone	(D) Alpha Lactone

6. Conversion of aniline from benzamide is known as_____

(A) **Hoffman Rearrangement**	(b) Perkin Reaction	(c) Witting Reaction	(D) Beckmann Rearrangement

7. The conversion of alpha hydroxy ketone from two moles of benzaldehyde is known as__

(A) Perkin Reaction	(B) **Benzoin Condensation**	(C) Birch Reduction	(D) Benzil-Benzilic acid rearrangement

8. The conversion of alpha, beta unsaturated acid from benzaldehyde is known as_____

(A) **Perkin Reaction**	(B) Benzoin Condensation	(C) Birch Reduction	(D) Benzil-Benzilic acid rearrangement

9. Which of the following is P-Ylide reaction_____ ?

(A) Sommelet Rearrangement	(B) Hoffman Rearrangement	(C) **Witting Reaction**	(D) Curtius Rearrangement

10. Which of the following is N-Ylide reaction_____ ?

(A) **Sommelet Rearrangement** (B) Hoffman Rearrangement (C) Witting Reaction (D) Curtius Rearrangement

11. In birch reduction, which of the following intermediate is generated?

(A) Free Radical (B) Carbanion (C) **Free Radical and carbanion** (D) Carbocation

12. The conversion of geminal dihaloketone to alpha, beta unsaturated ester is known as_____

(A) **Favorskii Rearragement** (B) Benzoin Condensation (C) Benzil-Benzilic acid rearrangement (D) Curtius Rearrangement

13. Which of the following intermediate is generated in favorskii rearrangement?

(A) Nitrene (B) **Carbanion** (C) Carbocation (D) Free Radical

14. The reaction of isocynate with alcohol will give____

(A) Urea derivative (B) **carbamate** (C) amine (D) amide

15. The reaction of acid chloride with sodium azide/water will give_____

(A) amide (B**) amine** (C) carbamate (D)urea derivative

Long Questions

1. Preparation of trans alkene from alkyne with its mechanism.
2. Regioselectivity in birch reduction with presence of electron donating and withdrawing group.
3. p-Nitro toluene is reacted under birch reduction, what will be the product ?
4. What is Ylide? Give comparison of p-Ylide and N-Ylide reactions.
5. What is lactone? Explain its preparation with mechanism.
6. Compare Curtius and Hoffmann rearrangement with suitable examples.
7. What is Condensation reactions? Explain benzoin condensation reaction.
8. Reaction of germinal and vicinal dihaloketone under basic conditions, what will be the product?
9. Preparation of N-N dimethyl xylene via [2,3] sigmatropic rearrangement.
10. What will be the product when aromatic aldehyde is reacted with acetic anhydride and sodium acetate?
11. What is mannich base? Explain it with suitable examples.
12. Explain: Beckmann rearrangement is highly stereospecific.
13. Explain (Any reaction) with its principle, mechanism and applications.

Short Questions

1. What is Ylide?
2. What is [2,3] sigmatropic rearrangement? Give one example for it.
3. Give migratory aptitude for Baeyer villiger oxidation?
4. What is lactone? Give its nomenclature.
5. What will be product when isocynate is reacted with water, alcohol and ammonia?
6. What is the meaning of C to N migration?
7. What will be the product when enone is reacted under birch condition?
8. Will chirality is affected in Baeyer villiger oxidation reaction?
9. Will chirality is affected in Hoffmann product?
10. Define Carbocation, Carbanion, Nitrene and Free radical.
11. Difference between Hoffmann and Curtius rearrangement.
12. What is lactum? Give its nomenclature.
13. Give preparation of Nylon-6.
14. Give principle (Of any name reaction)

Definitions (Just for Knowledge)

1. **Carbocation**: A **carbocation** is a molecule in which a carbon atom has a positive charge and three bonds. We can basically say that they are carbon cations. Formerly, it was known as carbonium ion. **Carbocation** today is defined as any even-electron cation that possesses a significant positive charge on the carbon atom.
2. **Carbanion**: A **carbanion** is an anion in which carbon is trivalent (forms three bonds) and bears a formal negative charge (in at least one significant resonance form). Absent π delocalization, carbanions assume a trigonal pyramidal, bent, or linear geometry when the carbanionic carbon is bound to three (e.g., methyl anion), two (e.g., phenyl anion), or one (e.g., acetylide anion) substituents, respectively. Formally, a carbanion is the conjugate base of a **carbon acid**.
3. **Nitrene**: In chemistry, a nitrene or imene (R–N) is the nitrogen analogue of a carbene. The nitrogen atom is uncharged and univalent, so it has only 6 electrons in its valence level—two covalent bonded and four non-bonded electrons. It is therefore considered an electrophile due to the unsatisfied octet. A nitrene is a reactive intermediate and is involved in many chemical reactions. The simplest nitrene, HN, is called imidogen, and that term is sometimes used as a synonym for the nitrene class.
4. **Inductive Effect**: In chemistry, the inductive effect is an effect regarding the transmission of unequal sharing of the bonding electron through a chain of atoms in a molecule, leading to a permanent dipole in a bond. It is present in a σ (sigma) bond as opposed to electromeric effect which is present on a π (pi) bond. The halogen atoms in alkyl halide are electron withdrawing and alkyl groups are electron donating. If the electronegative atom (missing an electron, thus having a positive charge) is then joined to a chain of atoms, usually carbon, the positive charge is related to the other atoms in the chain. This is the electron-withdrawing inductive effect, also known as the -I effect. In short, alkyl groups tend to donate electrons, leading to the +I effect. Its experimental basis is the ionization constant.
5. **Mesomeric Effect**: The mesomeric effect in chemistry is a property of substituents or functional groups in a chemical compound. It is defined as the polarity produced in the molecule by the interaction of two pi bonds or between a pi bond and lone pair of electrons present on an adjacent atom.

6. **Hyperconjugation Effect**: Hyperconjugation is the stabilising interaction that results from the interaction of the electrons in a σ-bond (usually C-H or C-C) with an adjacent empty or partially filled p-orbital or a π-orbital to give an extended molecular orbital that increases the stability of the system.
7. **Resonance Effect**: The resonance effect is the polarity produced in a molecule by the interaction between a lone electron pair and a pi bond or the interaction of two pi bonds in adjacent atoms. It is usually found in molecules with conjugated double bonds or in molecules having at least one lone pair and one double bond.

REFERENCE

1. Organic Reaction and Mechanism (Third Edition), Narosa Publication by V.K.Ahluwalia.
2. Wikipedia and Organic Portal

Things To Do for improvement in Organic Chemistry

- *Prepare your handwritten notebook for reading.*
- *Practise each reaction's application with given mechanism.*
- *Just try to find out what is the effect, intermediate, migration and stability.*
- *For organic make a simple chart which only include principle and try to memorise each day.*

-Dr. P.G.Sutariya