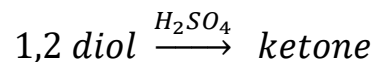


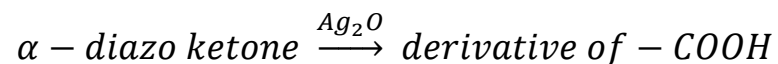
REARRANGEMENT REACTION

➤ FORMULA

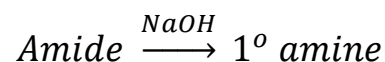
1) Pinacol – Pinacolone



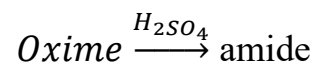
2) Wolf Kishner



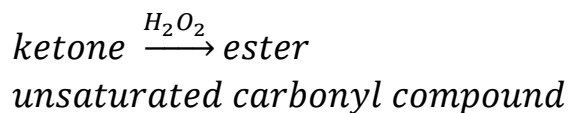
3) Hoffmann Rearrangement



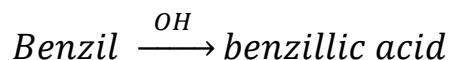
4) Beckmann's rearrangement



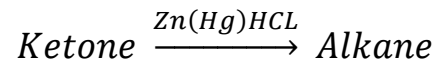
5) Bayer Villiger



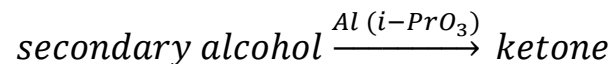
6) Benzilic acid rearrangement



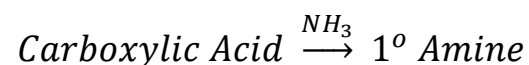
7) Clemmenson reduction



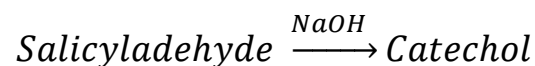
8) Oppenauer oxidation



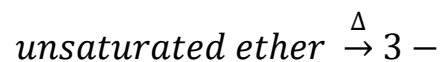
9) Schmidt reaction



10) Dakin reaction

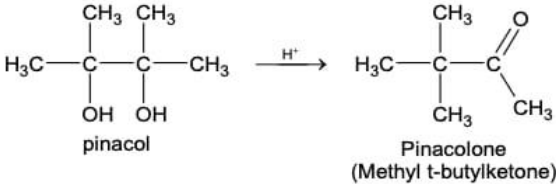
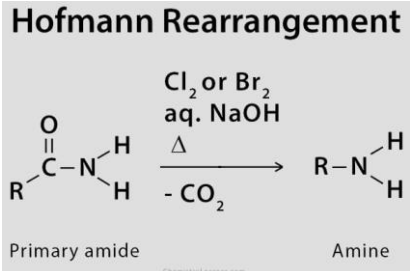


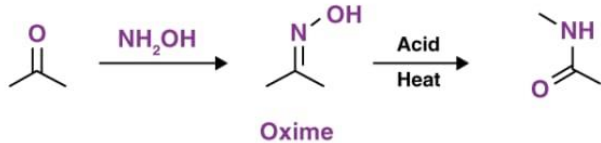
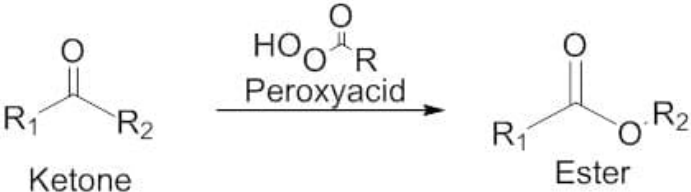
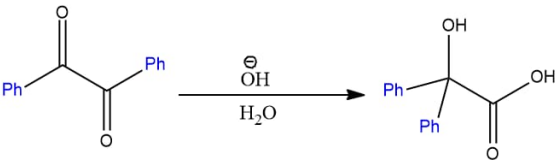
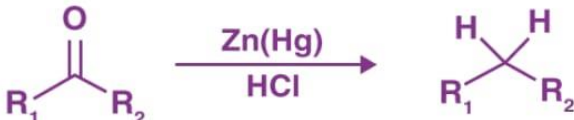
11) Claisen – Schmidt reaction


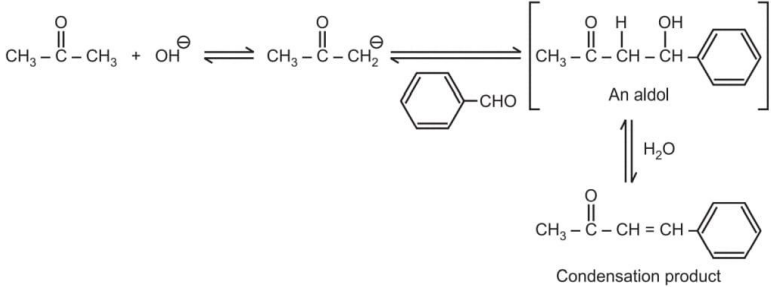
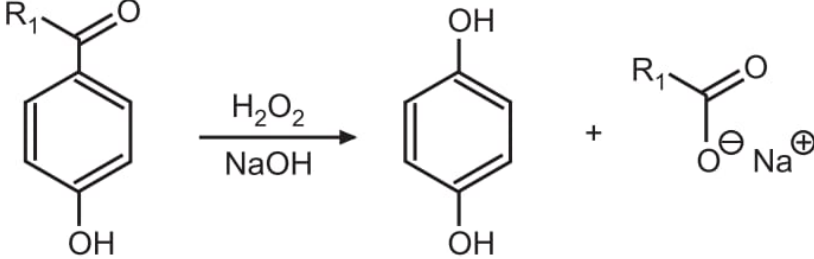
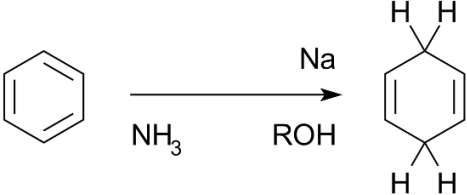


12) Birch reduction



Name	Reaction	Mechanism
Pinacol -> Pinacolone	 <p style="text-align: center;"> $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{CH}_3 \\ \quad \\ \text{OH} \quad \text{OH} \\ \text{pinacol} \end{array} \xrightarrow{\text{H}^+} \begin{array}{c} \text{CH}_3 \quad \text{O} \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \\ \text{Pinacolone} \\ \text{(Methyl t-butylketone)} \end{array}$ </p>	<ol style="list-style-type: none"> 1) Protonation 2) Loss of water molecules 3) Migration 4) Shift of charge 5) Loss of proton
Hofmann Rearrangement	 <p style="text-align: center;"> Hofmann Rearrangement </p> $ \begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{N}-\text{H} \\ \\ \text{H} \end{array} \xrightarrow[\text{- CO}_2]{\text{Cl}_2 \text{ or Br}_2, \text{ aq. NaOH}, \Delta} \begin{array}{c} \text{H} \\ \\ \text{R}-\text{N}-\text{H} \\ \\ \text{H} \end{array} $ <p style="text-align: center;"> Primary amide Amine </p>	<ol style="list-style-type: none"> 1) Abstraction of proton 2) Reaction of intermediate I with Br₂ 3) Loss of proton 4) Migration 5) Hydrolysis 6) Decarboxylation

Backmann rearrangement	 <p style="text-align: center;">Oxime</p>	<ol style="list-style-type: none"> 1) Protonation of oxime 2) Loss of water molecules 3) Hydrolysis 4) Loss of proton 5) resonance
Bayer villiger	 <p style="text-align: center;">Ketone</p> <p style="text-align: center;">Ester</p>	<ol style="list-style-type: none"> 1) protonation 2) nucleophilic attack by h2o2 3) migration of R group 4) loss of proton
Benzilic rearrangement	 <p style="text-align: center;">Benzil</p> <p style="text-align: center;">Benzilic acid</p> <p style="text-align: center;"><small>chemistNotes.com</small></p>	<ol style="list-style-type: none"> 1) loss of OH- 2) migration of Ph group 3) Addition of H-OH
Clemmensen reduction reaction	 <p style="text-align: center;">Clemmensen Reduction Reaction</p> <p style="text-align: right;"><small>© Byjus.com</small></p>	

Oppaneaur oxidation	 <p style="text-align: right; font-size: small;">© Byjus.com</p>	<ol style="list-style-type: none"> 1) Alcohol forms coordination complex 2) Deprotonation 3) Acetone & alcohol bonded to Al 4) Hydride shift 5) Ketone is formed
Claisen Schmidt reaction	 <p style="text-align: center; font-size: small;">Condensation product</p>	<ol style="list-style-type: none"> 1) Strong base is added 2) Nucleophilic attack 3) Carbonyl rearrange to form beta-ketoester
Dakin reaction		<ol style="list-style-type: none"> 1) Addition of nucleophile 2) Rearrangement 3) hydrolysis
Birch reduction		<ol style="list-style-type: none"> 1) Reduction of benzene 2) Protonation 3) Loss of electron 4) Protonation of anion

Schidmit reaction	<p>The diagram shows the reaction of an aldehyde (R-CHO) with a proton (H⁺) and hydrazoic acid (HN=N-NH₂) to form a primary amine (R-NH₂) and water (H₂O). The hydrazoic acid is shown with a positive charge on the terminal nitrogen and a negative charge on the adjacent nitrogen.</p>	<ol style="list-style-type: none"> 1) Protonation 2) Attack of water 3) Loss of water 4) Tautomerism 5) Release of CO₂
Wolf kishner	<p>The diagram illustrates the Wolff rearrangement of a diazoketone. The diazoketone (R₁-C(=O)-C(R₂)-N₂) is shown in resonance with its dipole form. Under conditions of heat (Δ), light (hv), or silver(I) ions (Ag(I)), it undergoes Wolff rearrangement to form a ketene intermediate (R₁-C(=O)-C(R₂)=O). The ketene can then react with water (H₂O) via nucleophilic attack to form a carboxylic acid (R₁-CH(OH)-R₂), or with ethylene (H₂C=CH₂) via [2+2] cycloaddition to form a cyclobutane ring.</p>	<ol style="list-style-type: none"> 1) Protonation 2) Shift of charge 3) Neucleophilic attack 4) Cylcoaddition

USES

1. PINACOL – PINACOLANE :

Pinacolone is used in Pesticides, Fungicides, and Herbicides. Pinacolone is used to prepare the cyanoguanidine drug – pinacidil.

2. HOFMANN REARRANGMENT :

Hofmann rearrangement can be used to prepare anthranilic acid from phthalimide. Anthranilic acid has a wide range of industrial applications including the preparation of perfumes, azo dyes, and saccharin – an artificial sweetener. This rearrangement reaction is also used to convert nicotinic acid into 3-aminopyridine

3. BACKMANN REARRANGMENT :

1. The Beckmann Rearrangement process is a natural reaction that is useful in changing an oxime to that of an amide under some acidic conditions.

2. Beckmann Rearrangement Reaction

It is used in the production of the monomer unit of Nylon 12.

5. BENZILIC REARRANGMENT :

This reaction is used to make benzilic acid and its related esters having essential biological properties. The resulting benzilic acid can be utilized to convert alpha, Beta -unsaturated ketones to saturated ketones.

Similarly, this reaction can be used in the ring contraction.

7. OPPANEUR OXIDATION :

The Oppenauer oxidation is used to prepare analgesics in the pharmaceutical industry such as morphine and codeine.

9. DAKIN REACTION :

Dakin's solution is used to prevent and treat skin and tissue infections that could result from cuts, scrapes and pressure sores. It is also used before and after surgery to prevent surgical wound infections.

4. BAYER VILLIGER :

The Bayer-Villiger oxidation reaction is useful for the following studies: Synthesis of lactones from mesomeric cyclohexanones. Synthesis of 3-hydroxyindole-2-carboxylates. Conversion of non-activated [18F]fluorobenzaldehydes to [18F]fluorophenols with high radiochemical yield.

6. CLEMMENSEN REDUCTION REACTION :

The reaction helps to reduce the aliphatic and mixed aliphatic-aromatic carbonyl compounds. The reduction of Clemmensen is most widely used to transform acyl benzene (from acylation by Friedel-Crafts) to alkylbenzene

8. CLAISEN SCHIDMIT REACTION :

Claisen schidmit reaction used in the pharmaceutical industry and can be hydrogenated to give high quality diesel fuel.

10. BIRCH REDUCTION :

It is particularly useful in aromatic compounds due to its selectivity of reduction of certain double bonds, which are present in one of the starting materials in multi-step total synthesis.

11. SCHIDMIT REACTION :

The Schmidt reaction can be applied to prepare amino acids, diamines, cyclic amides, lactams, and tetrazole. Amino acids are used by the industry in the synthesis of drugs and cosmetics.

12. WOLF KISHNER :

The Wolff rearrangement has been used

- 1). in many total syntheses; the most common use is trapping the ketene intermediate with nucleophiles to form carboxylic acid derivatives. The Arndt-Eistert homologation is a specific example of this use, wherein a carboxylic acid may be elongated by a methylene unit.
- 2). It is used in the production of the monomer unit of Nylon 12. It is used in the production of raw material for Nylon 6. Caprolactam is used as raw material in the production of Nylon – 6.

REFERENCE :

1. Textbook of Organic Chemistry Arjun bahl & B.S.Bahl
2. By google :-
 - a. <https://www.organic-chemistry.org/namedreactions/wolff-kishner-reduction.shtm>
 - b. <https://byjus.com/chemistry/schmidt-reaction/>
 - c. https://en.m.wikipedia.org/wiki/Dakin_oxidation

PREPARED BY :

1. CHOUDHARI KOMAL
SHARADCHANDRA (10)
2. BATWAL BHAGYASHRI GANESH (05)

GUIDED BY : Dr.CHIWADSHETTI N.S
(ASSISTANT PROFESSOR)

SUBJECT : PHARMACEUTICAL
ORGANIC CHEMISTRY III

TOPIC NAME: REARRANGMENT
REACTION

SUBJECT CODE : BP401T

CLASS : S.Y.B PHARM

ACADEMIC YEAR : 2022-23

