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#### **Aldol Condensation**

**<u>Principle:</u>** When aldehydes and ketones having at least one  $\alpha$ -hydrogen are treated with dilute alkali (which act as a catalyst) they form  $\beta$ -hydroxy aldehydes (aldol) or  $\beta$ -hydroxy ketones (ketol) respectively. This reaction is known as aldol condensation.





## Mechanism

#### Step-1:

In reverse order, The hydroxide ion deprotonates the aldehyde.



Step-2:

Here Enolate ion 1 adds to the unreacted aldehyde.



Step-3:

Alkoxide ion 2 is protonated by water.





Step-4:

A small amount of aldol is converted into enolate ion (4) by hydroxide ion





Here Enolate Ion(4) loses a hydroxide ion.







#### **Perkin Condensation**

**<u>Principle:</u>** Perkin Reaction is an organic chemical reaction which was discovered by William Henry Perkin, an English chemist. This reaction yields an  $\alpha$ ,  $\beta$  -unsaturated aromatic acid.

Perkin reaction mechanism includes the reaction between aromatic aldehydes, the aliphatic acid anhydride, and the alkali salt of the acid to give cinnamic acid derivatives. The Perkin reaction is an organic chemical reaction named after its discoverer – William Henry Perkin.

#### **Reaction:**





#### Mechanism:



## **Application:**



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#### Wittig reaction

**Principle:** Wittig reaction is an organic chemical reaction wherein an aldehyde or a ketone is reacted with a Wittig Reagent (a triphenyl phosphonium ylide) to yield an alkene along with triphenylphosphine oxide.

This Reaction is named after its discoverer, the German chemist Georg Wittig. He was also awarded the 1979 Nobel Prize in Chemistry for this discovery.

#### **Reaction:**



#### Mechanism:

**Step 1:** The negatively charged carbon belonging to the ylide is nucleophilic. This carbon proceeds to execute a nucleophilic attack on the carbonyl carbon of the aldehyde or ketone. This leads to the formation of a charge separated (and dipolar) intermediate called a betaine. This step can be illustrated as follows:





Step 2: The betaine intermediate which is formed in step 1 is now subject to the formation of a new oxygen phosphorus bond, yielding another intermediate which has a four-membered ring structure. This step is illustrated below:



Step 3: In the four-membered ring intermediate, the carbon-oxygen bond and the carbon-phosphorus bonds are cleaved. The oxygen takes both the bonding electrons and forms a new double bond with the phosphorus which lost the bonding pair of electrons to the carbon atom. A new carbon-carbon double bond is formed with this electron pair as well, yielding the required alkene product. This step is illustrated below.





## **Application:**





Short Question/Blanks	
1. What condition for Aldol condensation?	<u>α-H present</u>
2. In Aldol condensation which product is yield?	$\alpha$ , $\beta$ –Unsaturated carbonyl compounds.
3. Which types of catalyst used for Perkins reaction?	Sodium acetate(CH <sub>3</sub> -COONa)
4. Give the name reaction Cinnamic acid obtained from benzaldehyde?	Perkins reaction
5. Write the name of wittig reagent?	Methylene triphenyl phosphine
6. The products formed in wittg reaction?	Alkene



#### **Beckmann rearrangement:**

**Principle:** The Beckmann Rearrangement process is a natural reaction that is useful in changing an oxime to that of an amide under some acidic conditions. The reaction eventually starts by the process of protonation of the alcohol group gather shaping a preferred leaving group.

#### **Reaction:**





## **Application:**



#### Benzil-benzylic acid rearrangement

**<u>Principle:</u>** Benzilic acid rearrangement converts a 1, 2-diketone into an  $\alpha$ -hydroxy carboxylic acid containing a rearranged carbon skeleton in presence of alkali like NaOH, KOH etc.



## **Reaction:**



#### Mechanism:



## **Application:**





#### **Hoffmann bromamide Rearrangements**

**Principle:** When an amide is treated with bromine in an aqueous or ethanolic solution of sodium hydroxide, degradation of amide takes place leading to the formation of primary amine. This reaction involving degradation of amide and is popularly known as Hoffmann bromamide degradation reaction. The primary amine thus formed contains one carbon less than the number of carbon atoms in that amide.



#### **Reaction**



#### <u>Mechanism</u>





## **Application:**



Short Question/Blanks	
7. In Beckmann re-arrangement, ketoxime is converted into in which types of amide?	1 <sup>0</sup> Amide
8. Give the name catalyst used for Beckmann re-arrangement	$\underline{\text{Conc.H}_2\text{SO}_4,\text{P}_2\text{O}_5}$
9.Which reagent used in Benzil-Benzilic acid re-arrangement	Alkali(NaOH)
10. How many number of Carbonyl group present in benzyl?	2
11.Give name rearrangement amide into amine.	Hofmann
12.Write chemical formula of Sodium hypobromite	<u>NaOBr</u>