



Shree H.N.Shukla College of Science Rajkot

B.Sc. (Sem- 5) (CBCS)

CHEMISTRY: [502]

Unit-1 Chapter-1: Name reaction and rearrangement and reagent

# Index

## Name reaction

Ardnt-Eistert

Bischler–Napieralski

Wolff-Kishner (reaction) Reduction

## Rearrangement

Beckmann Rearrangement

Curtius rearrangement

Baeyer–Villiger oxidation

## Reagent

Lithium aluminium hydride  $\text{LiAlH}_4$

Triphenylphosphine

Sodium amide



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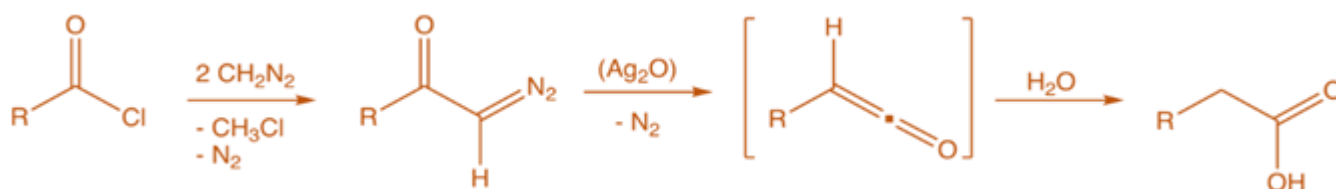
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### Ardnt-Eistert

The Arndt-Eistert synthesis is a series of chemical reactions designed to convert a carboxylic acid to a higher carboxylic homologue. In other words, the homologation process is used to add an additional carbon atom onto a carboxylic acid while generating an acid chloride. In the homologation process, first a carboxylic acid is activated, then, homologated with diazomethane, finally followed by the Wolff-Rearrangement of the intermediate diazoketones in the presence of nucleophiles.

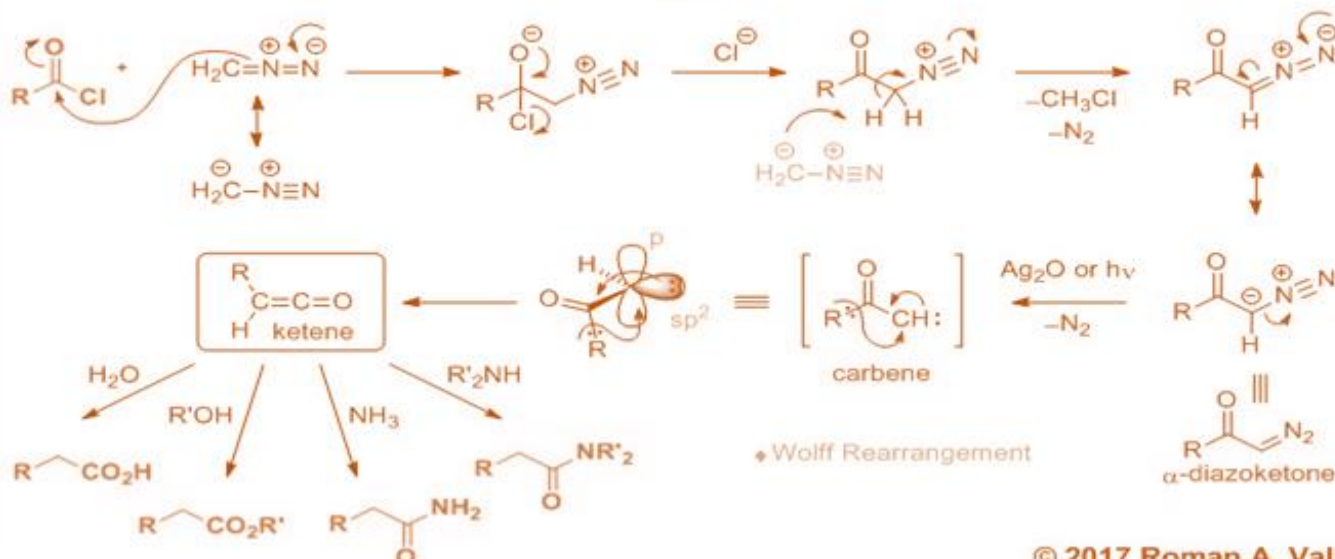
### Reaction



### Mechanism

#### Arndt-Eistert Synthesis

[1935]





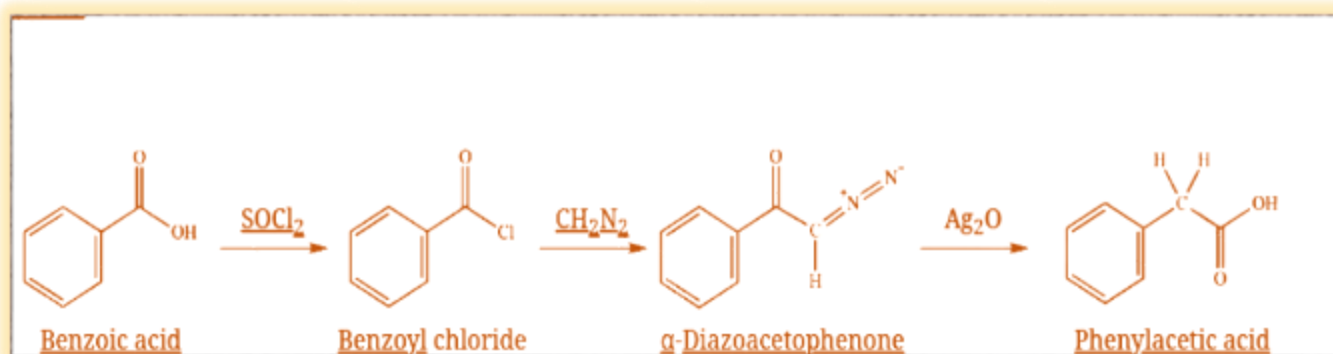
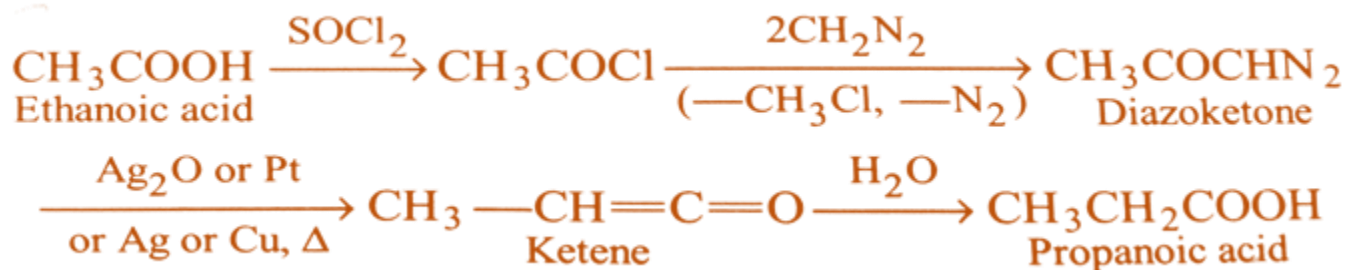
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### Application





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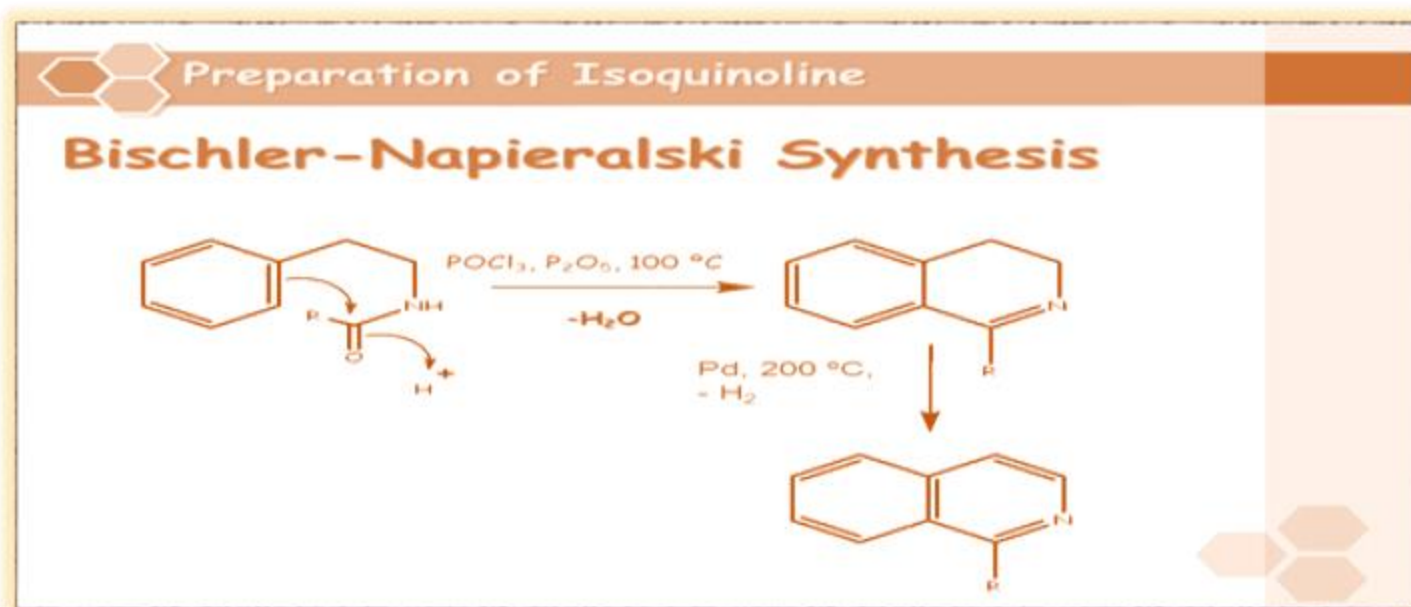
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### Bischler–Napieralski reaction

The Bischler–Napieralski reaction is an intramolecular electrophilic aromatic substitution reaction that allows for the cyclization of  $\beta$ -arylethylamides or  $\beta$ -arylethylcarbamates.



### Bischler–Napieralski reaction mechanism

Two types of mechanisms have appeared in the literature for the Bischler–Napieralski reaction. Mechanism I involves a dichlorophosphoryl imine-ester intermediate, while Mechanism II involves a nitrilium ion intermediate (both shown in brackets). This mechanistic variance stems from the ambiguity over the timing for the elimination of the carbonyl oxygen in the starting amide. In Mechanism I, the elimination occurs with imine formation after cyclization;



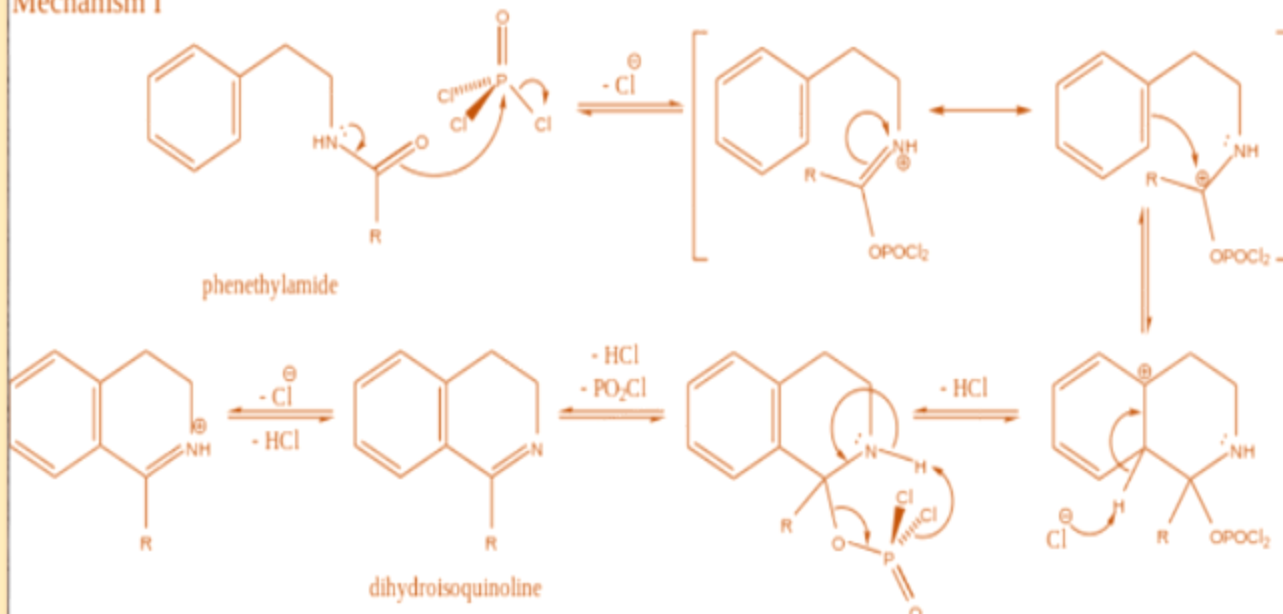
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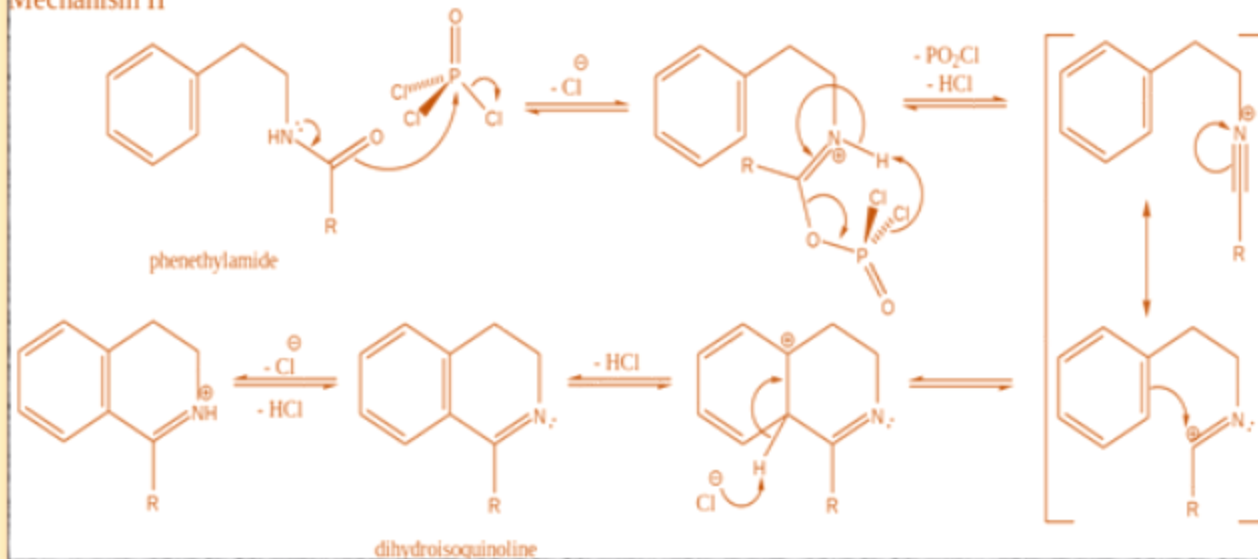
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### Mechanism I



### Mechanism II





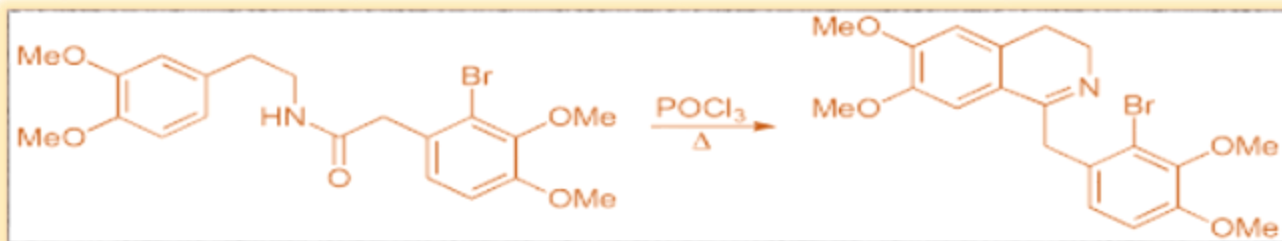
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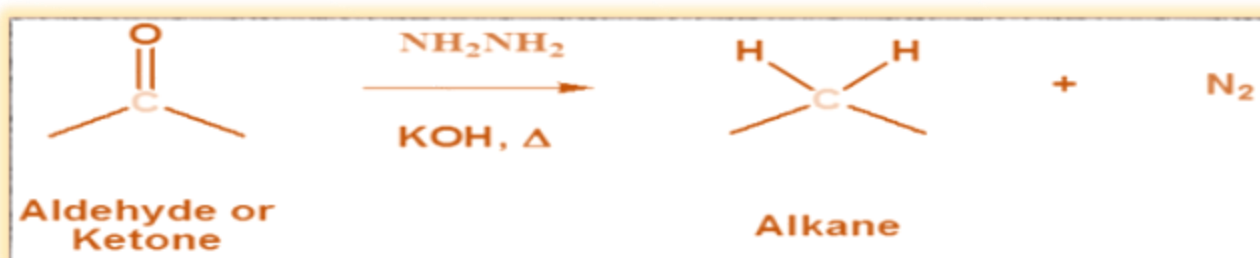
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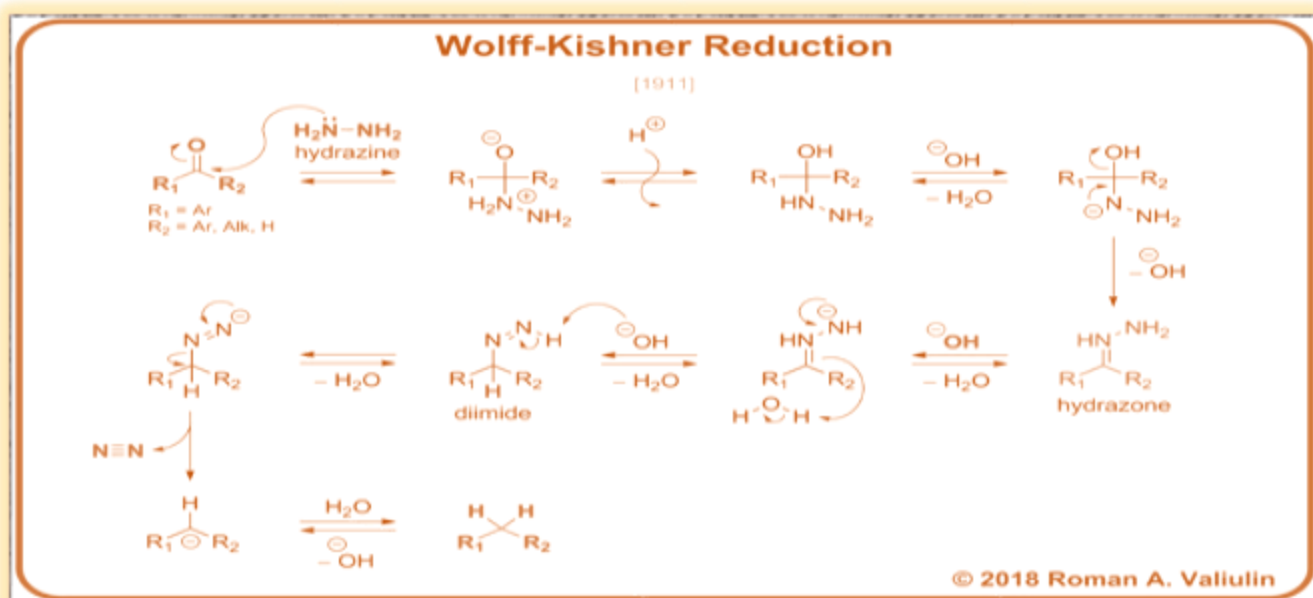


### Wolff-Kishner (reaction) Reduction

Aldehydes and ketones can be converted to a hydrazine derivative by reaction with hydrazine. These "hydrazones" can be further converted to the corresponding alkane by reaction with base and heat. These two steps can be combined into one reaction called the Wolff-Kishner Reduction which represents a general method for converting aldehydes and ketones into alkanes. Typically a high boiling point solvent, such as ethylene glycol, is used to provide the high temperatures needed for this reaction to occur. Note! Nitrogen gas is produced as part of this reaction.



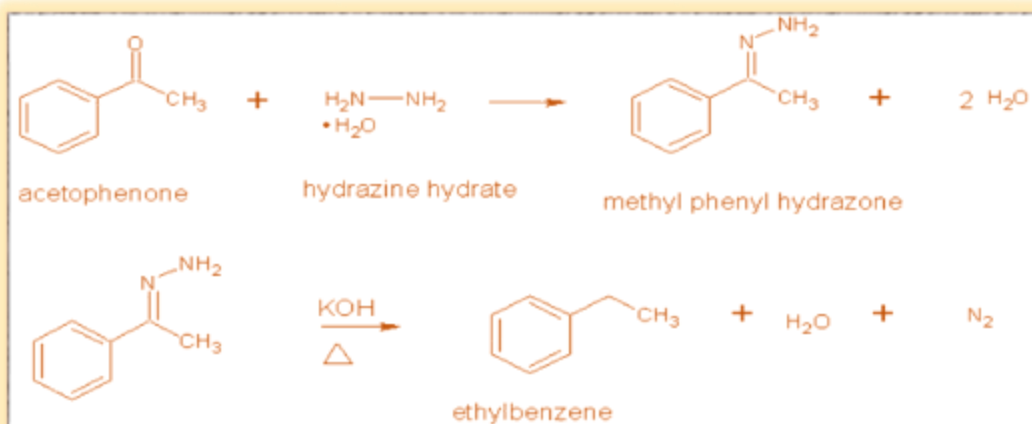
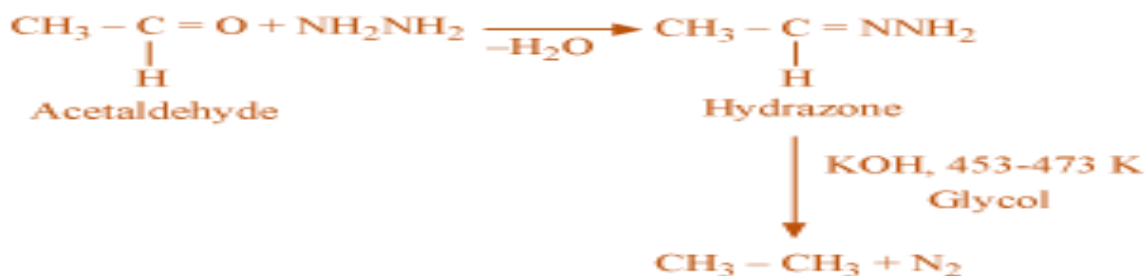
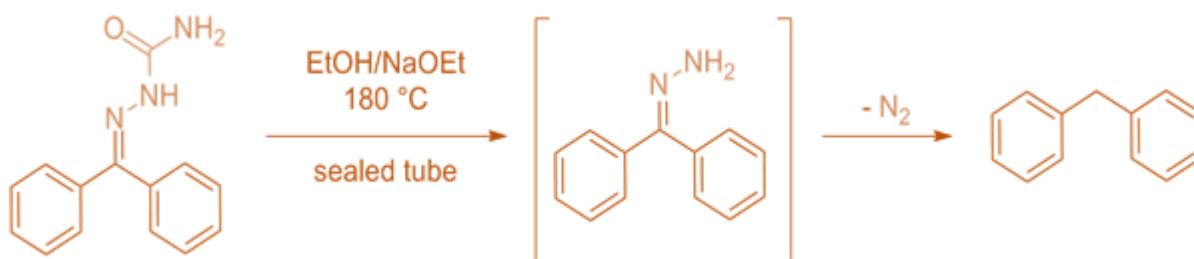
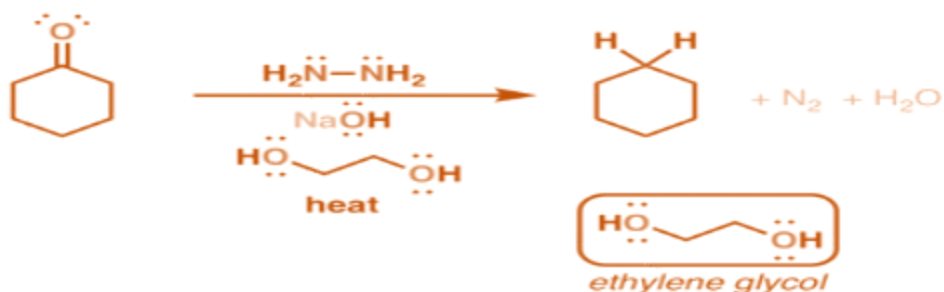
### Reaction mechanism





Application

Example 1: The Wolff-Kishner reaction







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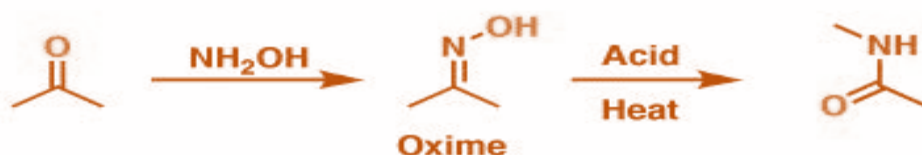
### Beckmann Rearrangement

The Beckmann Rearrangement is a reaction of the oximes that can bring about either nitriles or amides, contingent upon the beginning material. These Oximes that obtained from the ketones develop into amides; oximes got from the aldehydes shape into nitriles.

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.

The R group transition to that of the leaving species then moves to the nitrogen, bringing about a carbocation and the arrival of a water particle. The water atom attacks the carbocation, and after the process of deprotonation and tautomerization, the amide is obtained.

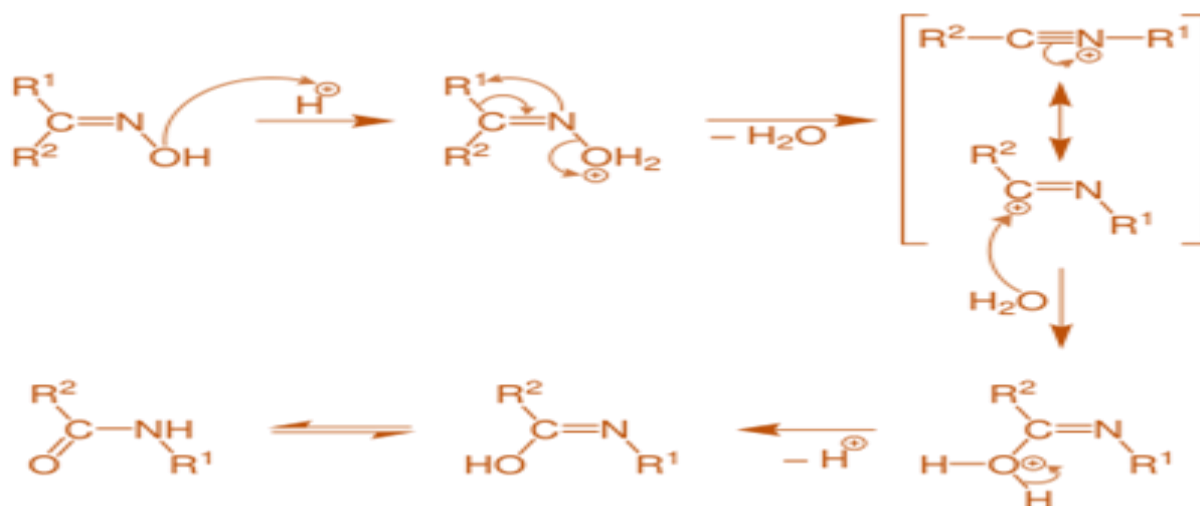
In simple, Beckmann Rearrangement is a reaction where oxime is changed over to an amide. The oxime is processed by treating an aldehyde or a ketone with hydroxylamine. This Beckmann Rearrangement reaction, named after Ernst Otto Beckmann, a German scientist



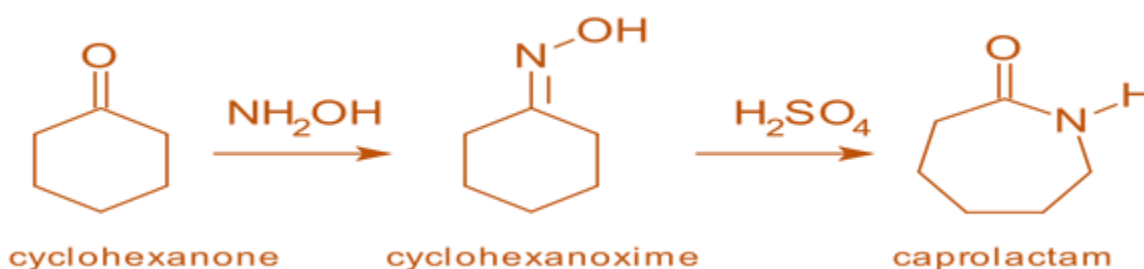


### Reaction mechanism

The Beckmann rearrangement is an organic reaction used to convert an oxime to an amide under acidic conditions. The reaction begins by protonation of the alcohol group forming a better leaving group. The R group trans to the leaving group then migrates to the nitrogen, resulting in a carbocation and the release of a water molecule. This trans [1-2]-shift allows for the prediction of the regiochemistry of this reaction. The water molecule then attacks the carbocation and after deprotonation and tautomerization results in the final amide product.



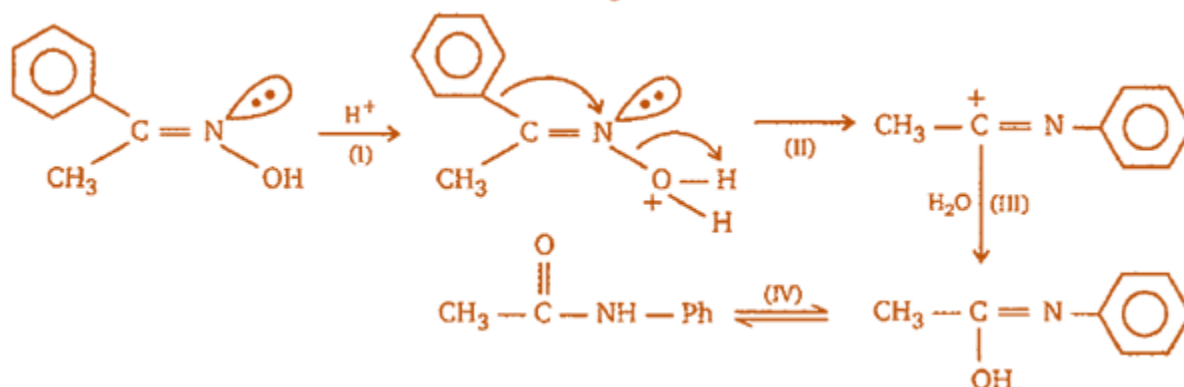
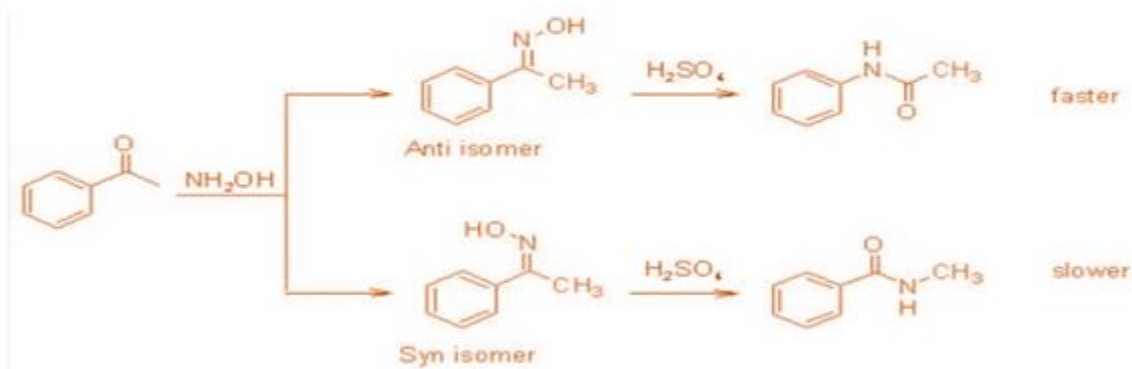
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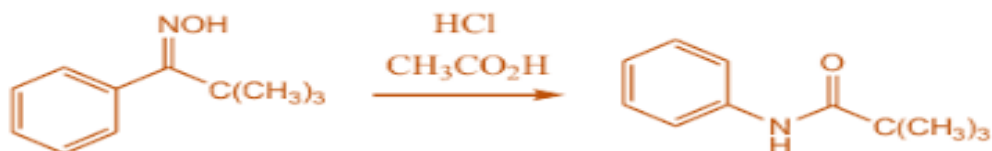


## Migratory aptitude

- The relative migratory aptitudes of different groups in Beckmann rearrangement is illustrated below.



## 2. Beckmann rearrangement



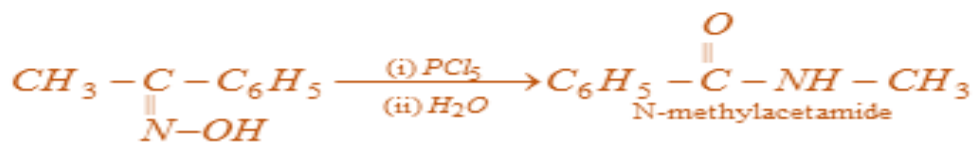
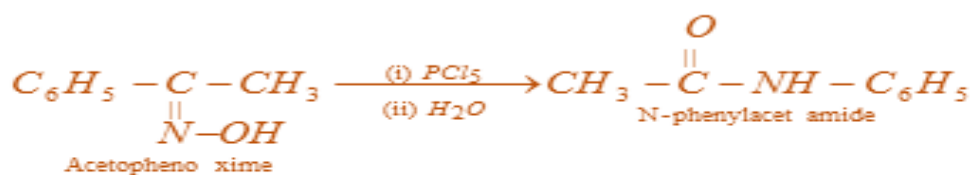


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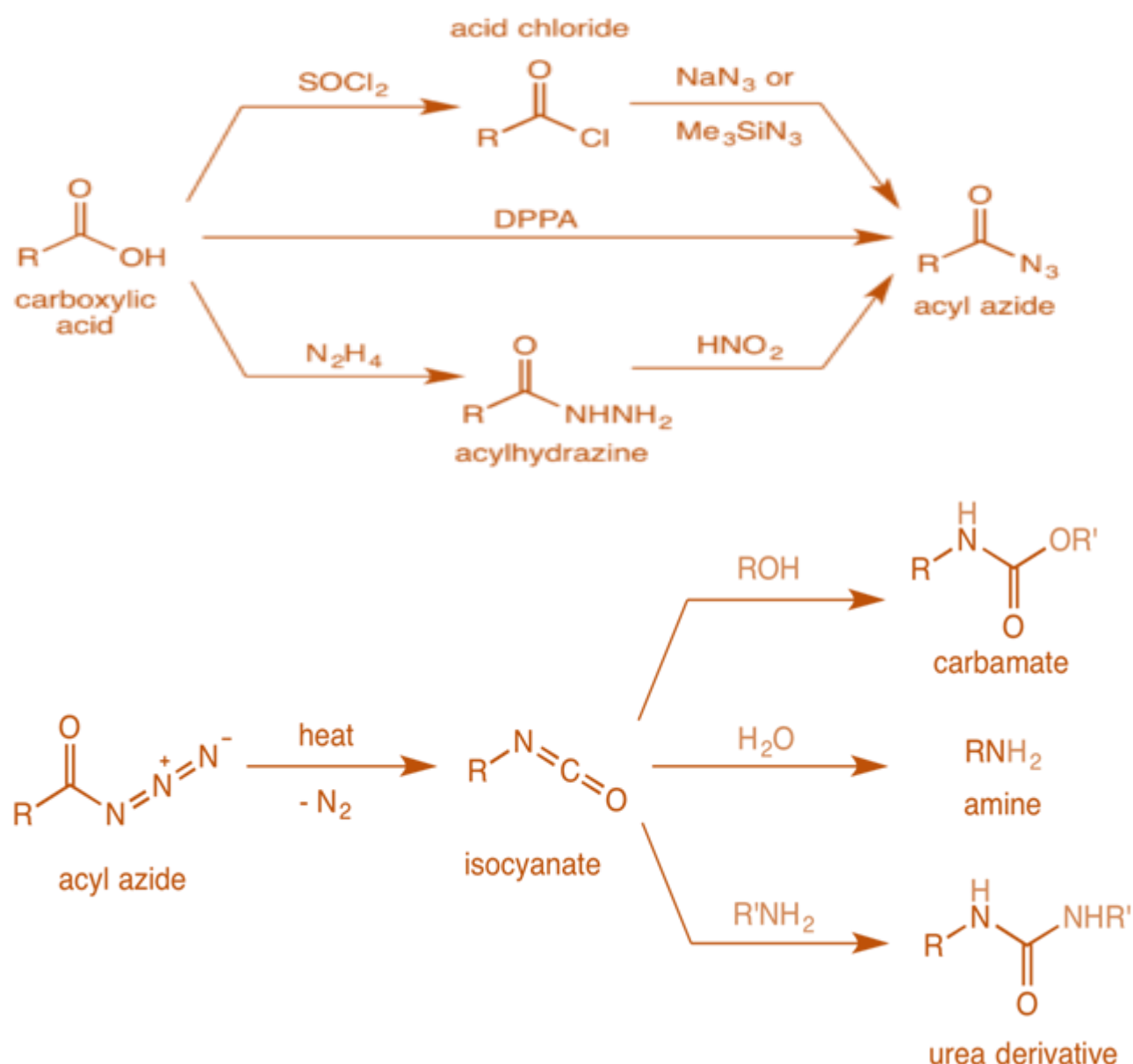
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### Curtius rearrangement

The Curtius rearrangement (or Curtius reaction or Curtius degradation) is the thermal decomposition of an acyl azide to an isocyanate with loss of nitrogen gas.[1][2] The isocyanate then undergoes attack by a variety of nucleophiles such as water, alcohols and amines, to yield a primary amine, carbamate or urea derivative respectively.



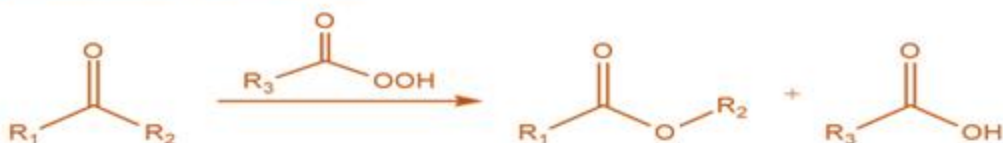




### Baeyer–Villiger oxidation

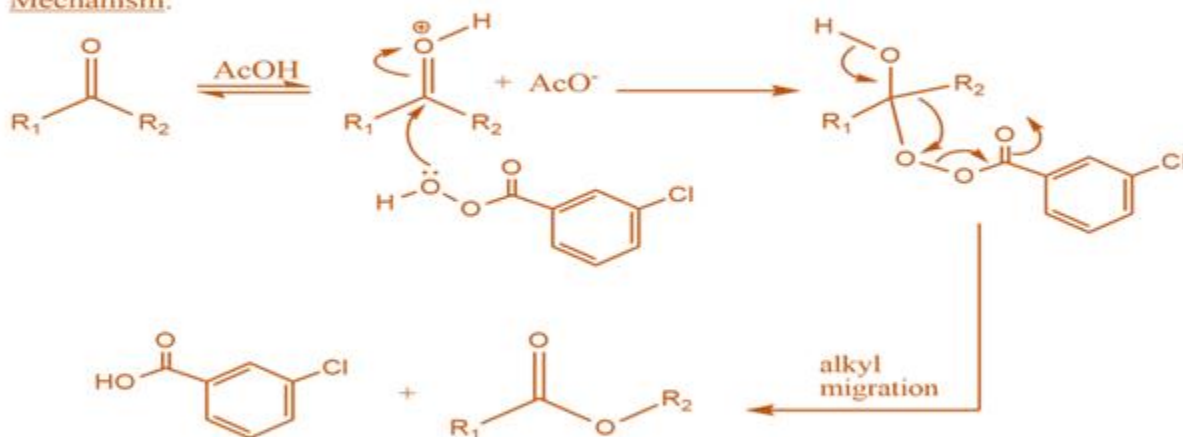
The Baeyer–Villiger oxidation is an organic reaction that forms an ester from a ketone or a lactone from a cyclic ketone, using peroxyacids or peroxides as the oxidant.

#### Baeyer-Villiger Oxidation:

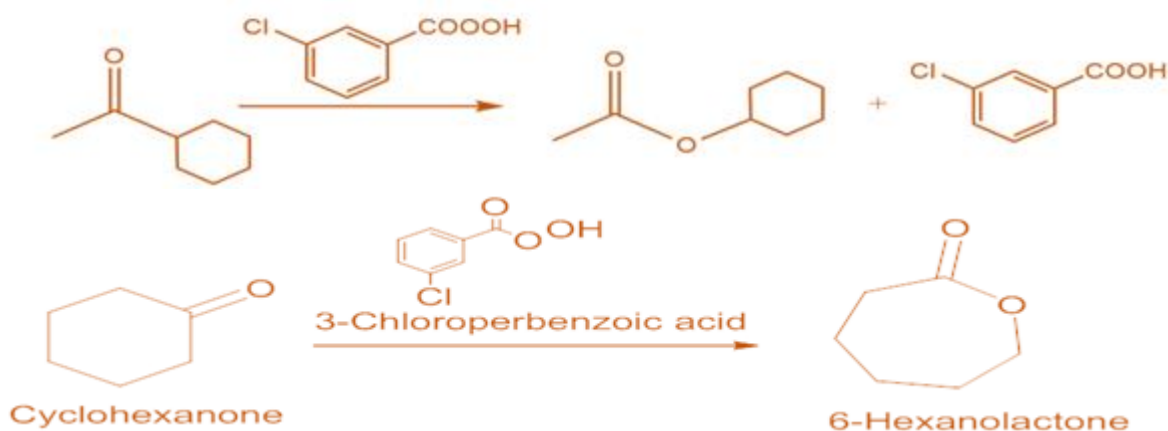


$R_2$  is more electron rich alkyl or aryl group than  $R_1$

#### Mechanism:



#### Example:





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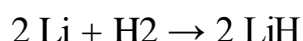
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### Lithium aluminium hydride $\text{LiAlH}_4$

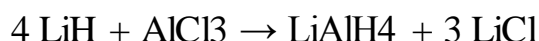
#### Preparation

$\text{LiH}$  is produced by treating lithium metal with hydrogen gas.



This reaction is especially rapid at temperatures above  $600^\circ\text{C}$ .

$\text{LiAlH}_4$  was first prepared from the reaction between lithium hydride ( $\text{LiH}$ ) and aluminium chloride.



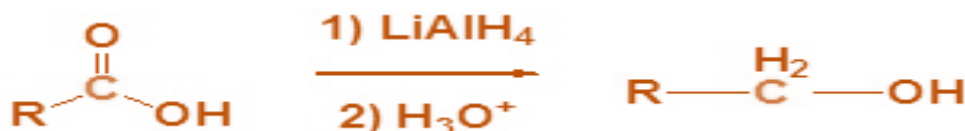
#### Properties

LAH is found as an odorless, greyish or white crystalline solid with a density of  $0.97 \text{ g/mL}$ , and a melting point of  $150^\circ\text{C}$ . It is also available commercially as a dispersion in mineral oil to prevent its violent reaction with atmospheric moisture.

#### Application

Reduction of carboxylic acids and esters

Carboxylic acids can be converted to 1o alcohols using Lithium aluminium hydride ( $\text{LiAlH}_4$ ). An aldehyde is produced as an intermediate during this reaction, but it cannot be isolated because it is more reactive than the original carboxylic acid.







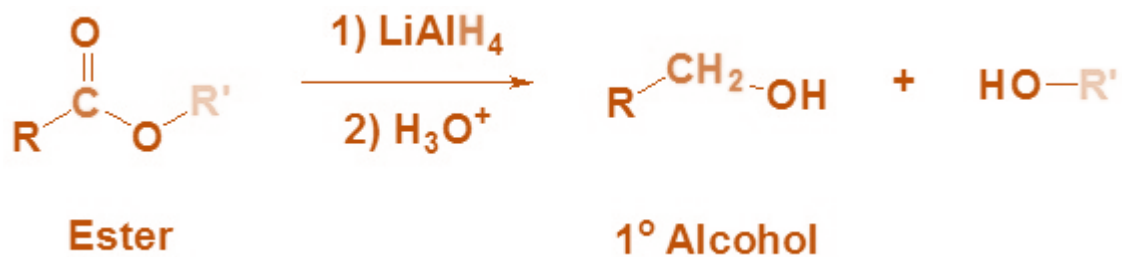
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Esters can be converted to 1° alcohols using  $\text{LiAlH}_4$ , while sodium borohydride ( $\text{NaBH}_4$ ) is not a strong enough reducing agent to perform this reaction.



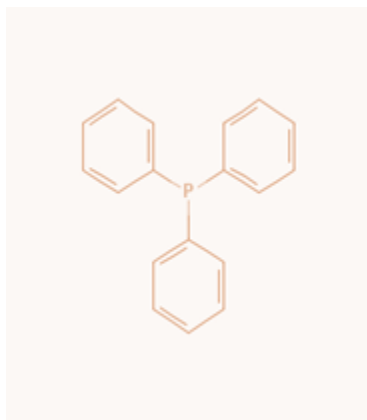


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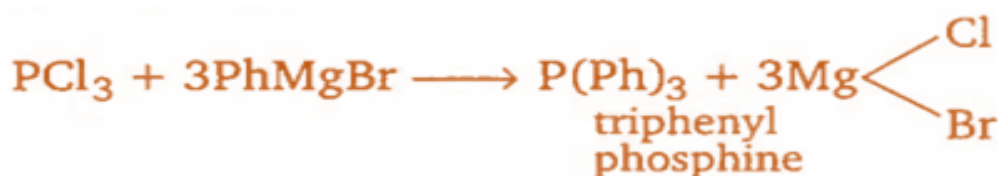
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### Triphenylphosphine

Triphenylphosphine (IUPAC name: triphenylphosphane) is a common organophosphorus compound with the formula  $P(C_6H_5)_3$  - often abbreviated synthesis of organic and organometallic compounds.  $PPh_3$  exists as relatively air stable, colorless crystals at room temperature. It dissolves in to  $PPh_3$  or  $Ph_3P$ . It is widely used in the non-polar organic solvents such as benzene and diethyl ether.

Triphenylphosphine can be prepared in the laboratory by treatment of phosphorus trichloride with phenylmagnesium bromide or phenyllithium. The industrial synthesis involves the reaction between phosphorus trichloride, chlorobenzene, and sodium.



### Application

In organic preparation.

Polymerization initiation.

In a witting reaction, Corey fuchs reaction, Fukuyama amine synthesis.



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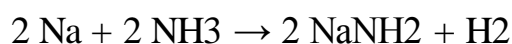
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Sodium amide ( $\text{NaNH}_2$ )

Preparation

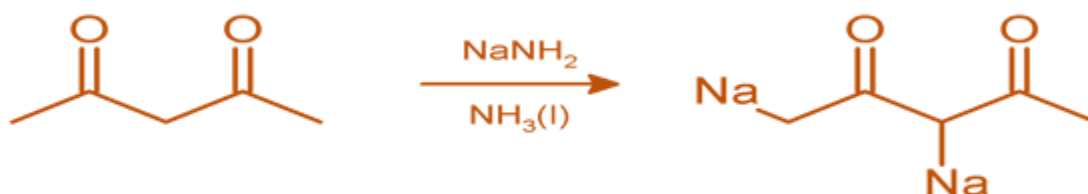
Sodium amide can be prepared by the reaction of sodium with ammonia gas but it is usually prepared by the reaction in liquid ammonia using iron(III) nitrate as a catalyst. The reaction is fastest at the boiling point of the ammonia.



$\text{NaNH}_2$  is a salt-like material and as such, crystallizes as an infinite polymer.

reacts violently with water forming  $\text{NaOH}$  and  $\text{NH}_3$ . The reaction with alcohol is considerably slower, therefore it should be stored in sealed containers which prevent all contact with air. During storage when exposed to the atmosphere sodiumamide rapidly absorbs  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .

use



Dehydrohalogenation[edit]

Sodium amide induces the loss of two equivalents of hydrogen bromide from a vicinal dibromoalkane to give a carbon-carbon triple bond, as in a preparation



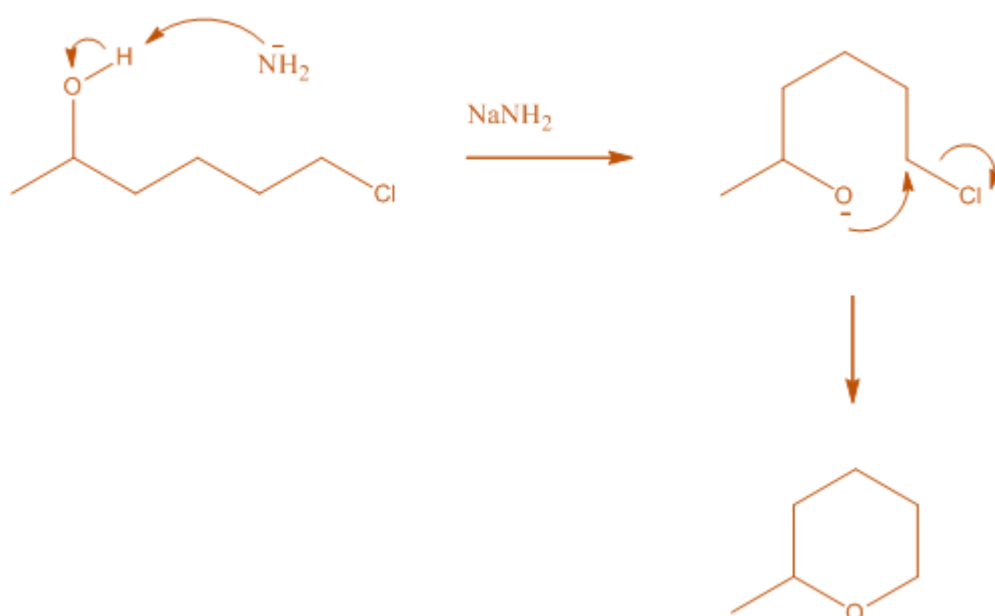
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of phenylacetylene.[8] Usually two equivalents of sodium amide yields the desired alkyne. Three equivalents are necessary in the preparation of a terminal alkynes because the terminal CH of the resulting alkyne protonates an equivalent amount of base.



### Cyclization reactions

Where there is no  $\beta$ -hydrogen to be eliminated, cyclic compounds may be formed, as in the preparation of methylenecyclopropane below.

