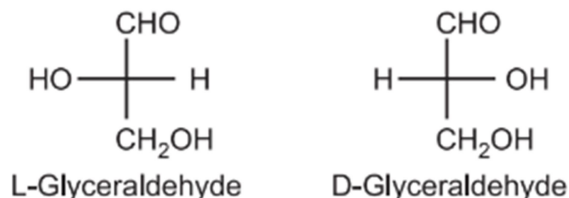
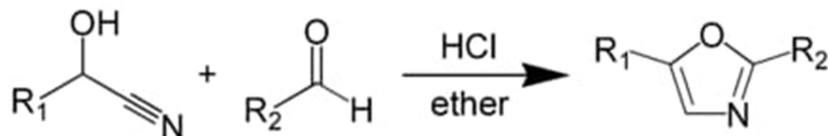


1. **Nomenclature of Optical Isomers:** The D/L system was developed by Fischer and Rosanoff in around 1900. Arbitrarily, (+) glyceraldehyde was defined as being D because the OH group attached to the C2 is on the right-hand side of the molecule. While (–) glyceraldehyde was defined as L because the OH group is on the left-hand side.



The d/l system (named after Latin dexter and laevis, right and left) names the molecule by relating them to the molecule glyceraldehyde. This system of nomenclature represents an older system for distinguishing enantiomers of amino acids and carbohydrates. This arbitrary type of configuration (d/l system) is known as Relative Configuration.

2. The Fischer oxazole synthesis is a chemical synthesis of an oxazole from a cyanohydrin and an aldehyde in the presence of anhydrous hydrochloric acid. The cyanohydrin itself is derived from a separate aldehyde.

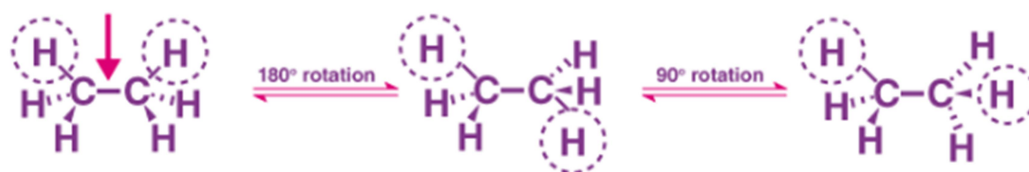


3. Purines are heterocyclic bases. Simply put, these are closed ring structures comprised of at least two different kinds of atoms. Purines are one of three components of nucleotides; phosphate esters of a pentose sugar (either ribose or deoxyribose) in which a purine or pyrimidine base is linked to C1 of the sugar.

The prefix mono- di- or tri- denotes the number of phosphate groups present on the nucleotide. It is important to distinguish the nucleoside; this is the non-phosphorylated form of a nucleotide. It is Nucleoside triphosphates are the monomeric units that act as precursors of nucleic acids.

4. Conformations of Ethane

Ethane is an organic Chemical Compound. It is a colorless and odor gas at a standard temperature. Ethane molecule consists of seven sigma bonds. There will be a change in the shape of the molecule when there is a rotation of about six carbon-hydrogen bonds. But many possible differences occur when there is a rotation about the carbon-carbon bond.



5. Differences between Racemic Mixture and Meso Compound

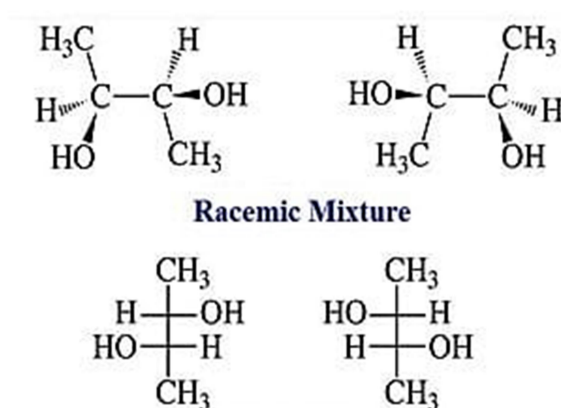
A racemic mixture is a combination of organic compounds known as enantiomers. It is optically inactive due to the presence of equal amounts of non-super imposable mirror images.

A meso compound is a molecule having more than one identical stereocenters and an identical or superimposable mirror image. A meso compound contains an identical mirror image.

The key difference between a racemic mixture and a meso compound is that a racemic mixture contains non-identical isomers whereas a meso compound contains an identical isomer.

Definition: A racemic mixture is a mixture of organic compounds known as enantiomers. The equimolar mixture of two enantiomers is called racemic mixture e.g (+) and (-) lactic acid forms (\pm) – lactic acid as a racemic mixture.

A racemic mixture contains chiral compounds. The racemic mixture may be formed from one or more than two asymmetric centers. It is **optical inactive**. The separation of a racemic mixture into D & L form is called resolution. A racemic mixture is a 50:50 combination of a pair of enantiomers with the mixture having zero optical rotation. Racemic compounds are the mixture of dl-compounds which chiral and optically active.



Definition: A meso compound is a molecule having more than one identical stereocenter and an identical or superimposable mirror image.

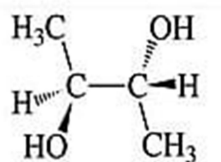
A meso compound has at least two identical asymmetric centers with a plane of symmetry e.g. meso tartaric acid.

A meso compound has **identical mirror images**.

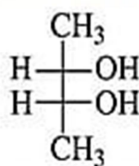
Meso compound is optically inactive due to internal compensation.

Meso compound is a single compound which **cannot be separated into an optically active compound** by the resolution process.

Meso compounds are considered as achiral compounds.



Meso Compound



6. Why study of stereochemistry in chemistry is important.

Stereochemistry is the study of how molecules are affected by the way their atoms are arranged in space. It is also known as 3D chemistry as the word *stereo* means *three dimensional*. Using stereochemistry, chemists can work out the relationships between different molecules that are made up from the same atoms. They can also study the effect on the physical or biological properties these relationships give molecules.

In chemistry, some molecules have more than one isomer. This means that molecules can have different forms. There are two kinds of isomers. Constitutional isomers have the same atoms, but they are joined differently. Stereoisomers have the same atoms, they are joined the same way, but the atoms are arranged differently in space. An important part of stereochemistry is the study of chiral molecules. These molecules look almost identical, except that one molecule is the mirror image of the other.

7. What are the conditions of optical isomerism?

The compound must be asymmetric or having at least one chiral center are essential conditions for optical isomerism. The optical isomerism which is basically a property of compounds displaying identical characteristics in terms of chemical and physical properties but differ in their orientation and rotation of polarised light.

The essential conditions for optical isomerism are as follows:

The compounds should be non-superimposable mirror images of each other.

They should possess similar molecular formulas as well as similar structural formulas.

The compound must possess an asymmetric carbon atom which is bonded to four different groups of atoms or molecules which is normally called chiral carbon.

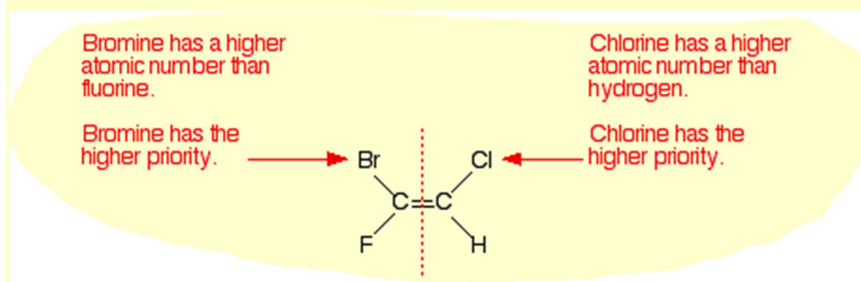
The compound can rotate the plane of polarised light.

Also, the two optical isomers or compounds are called enantiomers and the common example is amino acid alanine which exists as D-alanine and L-alanine.

8. Explain E and Z isomers with suitable example.

(E)- : the higher priority groups are on opposite sides of the double bond.

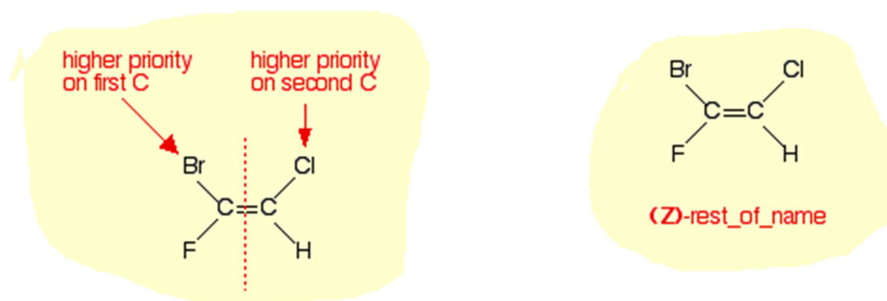
(Z)- : the higher priority groups are on the same side of the double bond.



If the two groups with the higher priorities are on opposite sides of the double bond, then this is the (E)- isomer. E comes from the German entgegen which means opposite.



If the two groups with the higher priorities are on the same side of the double bond, that is described as the (Z)- isomer. So you would write it as (Z)-name of compound. The symbol Z comes from a German word (zusammen) which means together.



9. What is partial and absolute asymmetric synthesis?

Asymmetric synthesis is a type of chemical synthesis where a chemical reaction takes place, forming one or more new elements of chirality form in a substrate molecule. We can find this term in two forms as partial asymmetric synthesis and absolute asymmetric synthesis.

Partial asymmetric synthesis is a chemical reaction that involves the formation of less favourable chirality in symmetrical molecules. This term is rarely used in chemistry because this type of chemical reaction has less significance compared to absolute asymmetric synthesis.

For example, for partial asymmetric synthesis, we can give the reaction of optically active styrene oxide with triethyl alpha-phosphonopropionate, which gives 2-phenyl-1-methylcyclopropanecarboxylate, which is chiral. This resultant product has one asymmetric center which is originating from styrene oxide.

Absolute asymmetric synthesis is a chemical reaction that includes the formation of preferential chirality in a symmetrical environment from a symmetric reagent. For example, if we can prepare 2-hydroxypropanenitrile from ethanal and hydrogen cyanide in the absence of other chiral reagents, it gives an excess of one enantiomer over the other.

The key difference between partial and absolute asymmetric synthesis is that partial asymmetric synthesis is the creation of less favourable chirality in symmetrical molecules whereas absolute asymmetric synthesis is the creation of preferential chirality in a symmetrical environment from symmetric reagent.

10. What are stereospecific and stereoselective reactions?

A stereospecific reaction is a reaction where the stereochemistry of the reactant completely determines the stereochemistry of the product without any other option. Therefore, a stereospecific reaction specifies the final product given by a particular reactant. From a stereoisomerically pure reactant, a stereospecific reaction gives 100% of a specific isomer. Let us consider an example in order to understand this concept.

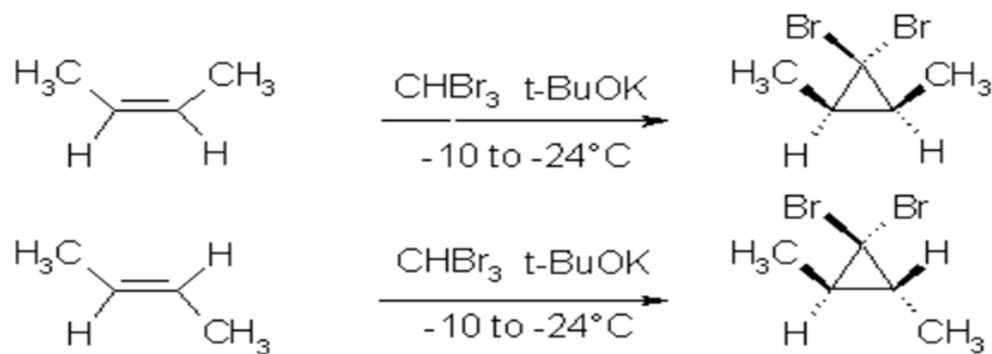


Figure 1: Stereospecific Carbene Addition to an Olefin

Above image shows stereospecific dibromocarbene addition to an olefin. Olefins are alkenes. This reaction is stereospecific because the geometry of the alkene is preserved in the product. *Cis* reactant gives the *cis*-2,3-dimethyl-1,1-dibromocyclopropane whereas *trans* reactant gives *trans* cyclopropane. These are stereospecific addition reactions.

A stereoselective reaction is a reaction where there is a choice of pathway, but the product stereoisomer is formed due to its reaction pathway being more favourable than the others available. The reactants in these reactions give unequal mixtures of stereoisomers as final products.

The selectivity of the reaction pathway depends on differences in steric effects (presence of bulky groups cause steric hindrance) and electronic effects. These effects lead to the formation of different products. There are two types of stereoselective reactions: enantioselective reaction and diastereoselective reaction. **Enantioselective reactions** are reactions that form enantiomers. **Diastereoselective reactions** are reactions that form diastereomers. In order to understand the concept of stereoselective, let us consider an example.

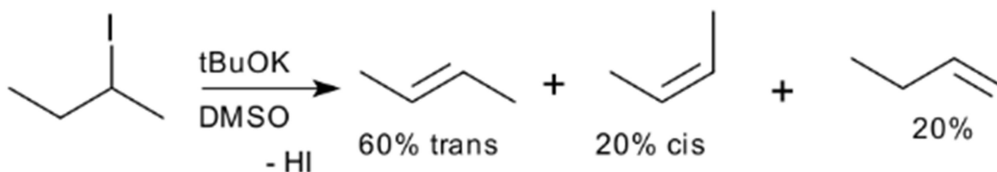


Figure 2: Stereoselective Dehalogenation

Dehalogenation is the removal of a halogen atom. The above image shows a reaction of dehalogenation that takes place as a stereoselective reaction. It gives multiple products. But the trans isomer is given about 60% since it has the least steric effects and electronic effects.

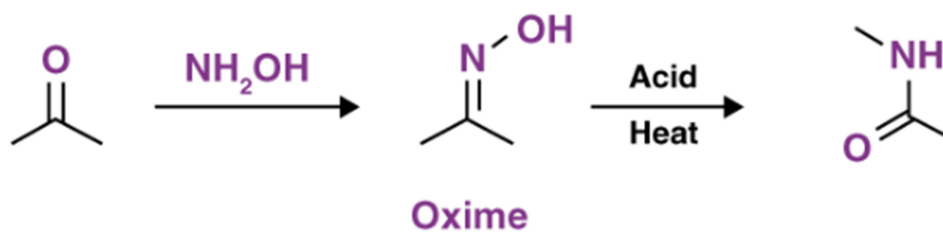
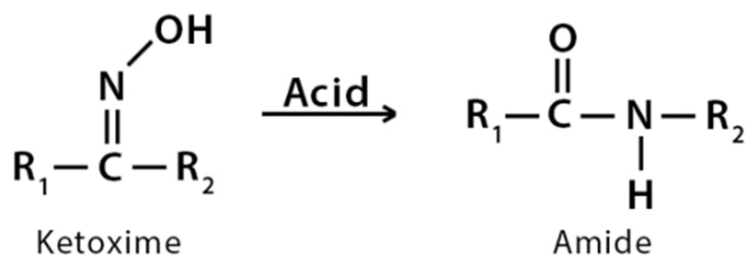
Stereospecific Reactions: A stereospecific reaction is a reaction in which the stereochemistry of the reactant completely determines the stereochemistry of the product without any other option.

Stereoselective Reactions: A stereoselective reaction is a reaction in which there is a choice of pathway, but the product stereoisomer is formed due to its reaction pathway being more favourable than the others available.

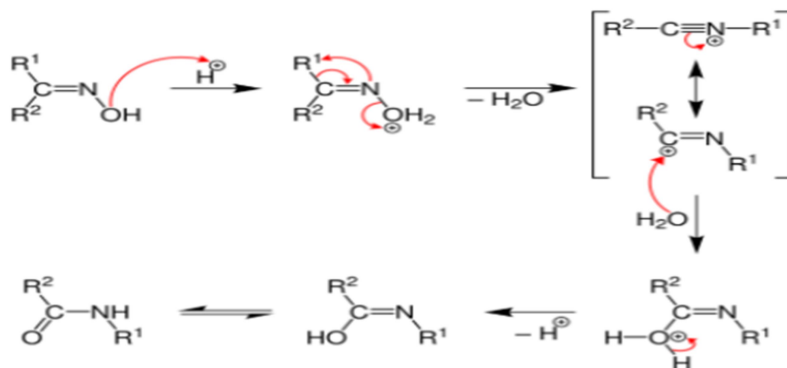
11. Explain the Beckmann rearrangement reaction with examples.

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

Beckmann Rearrangement

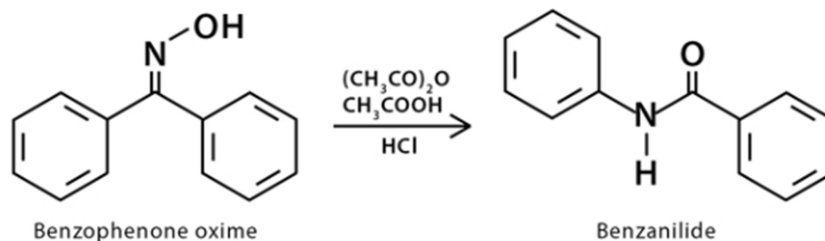


Mechanism:



Example:

Beckmann Rearrangement For Benzophenone Oxime



Applications:

Some uses of this reaction are as below-

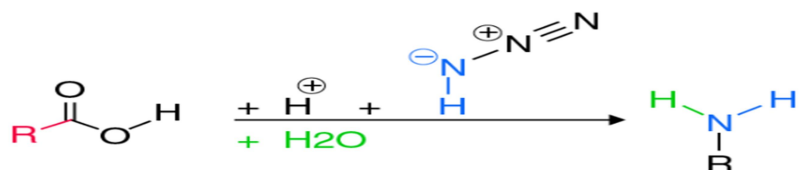
- It is used in the industries for the synthesis of paracetamol. This integration is achieved by the process of conversion of a ketone to a ketoxime with the help of hydroxylamine.
- It is mainly used in the synthesis of various steroids and drugs
- The Beckmann Rearrangement synthesis is helpful in the production of some chloro bicyclic lactams.

12. Give reaction and mechanism for Schmidt rearrangement.

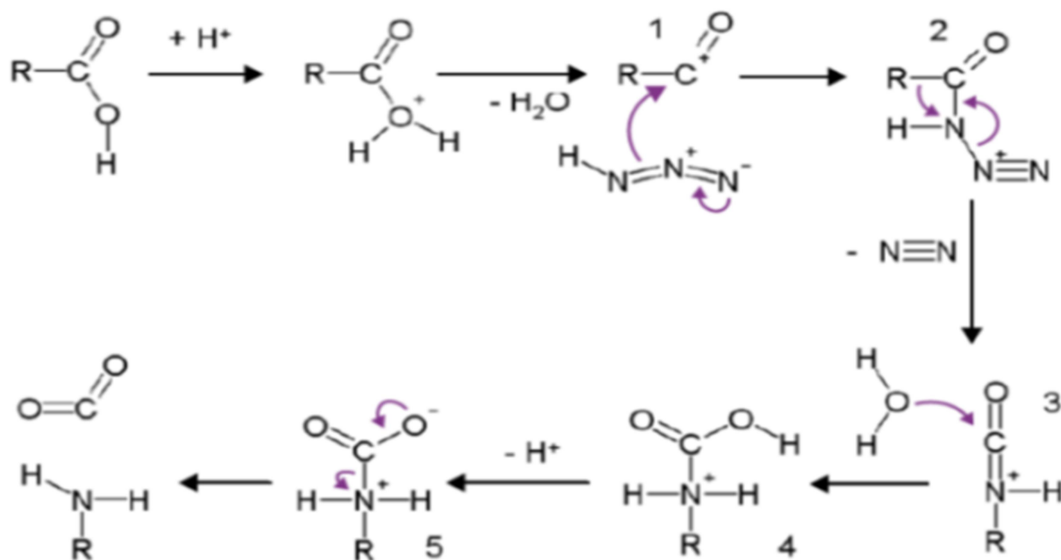
The Schmidt Reaction can be employed to either get amides by reacting the azide with a ketone or to get an amine by reacting the azide with a carboxylic acid.

Schmidt Reaction for Carboxylic Acids

The chemical reaction wherein amines can be produced from an azide and a carboxylic acid can be shown as follows:



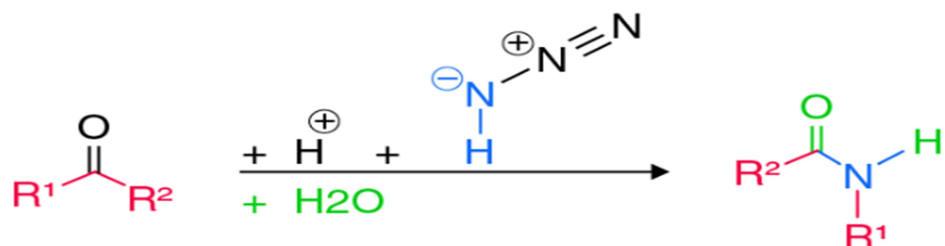
Reaction Mechanism for amine:



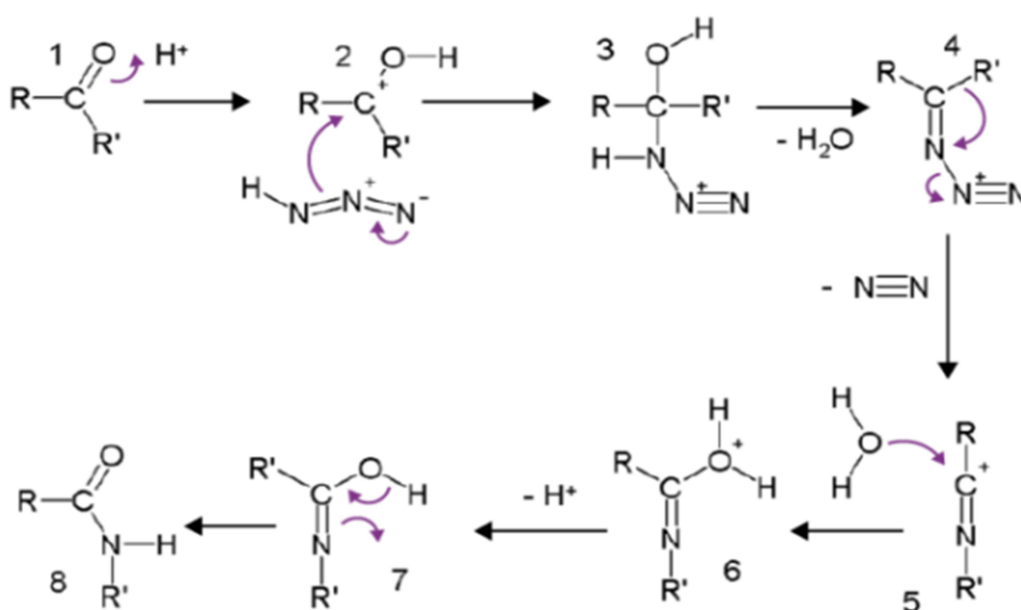
- This mechanism begins with the formation of an acylium ion from the protonation of the carboxylic acid followed by the removal of water.
- This acylium ion is now reacted with hydrazoic acid, leading to the formation of a protonated azido ketone.
- Now, the protonated azido ketone and the R group undergo 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.
- Now, a carbamate is formed when water is introduced to attack the protonated isocyanate.
- The carbamate is now deprotonated. The subsequent removal of CO₂ yields the required amine.

Schmidt Reaction for Ketones

Another example of the Schmidt Reaction is when an amide is produced from the chemical reaction between an azide and a ketone. This reaction can be illustrated as follows:



Reaction Mechanism for amide:

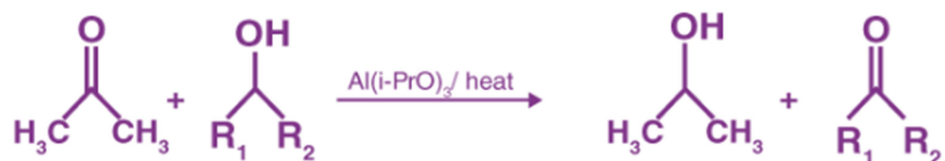


- This Mechanism begins with the protonation of the ketone, leading to the formation of an O-H bond.
- The subsequent nucleophilic addition of the hydrazoic acid leads to the formation of an intermediate.
- Water is now removed from this intermediate via an elimination reaction, forming a temporary imine.
- An alkyl group which was a part of the original ketone now migrates from the carbon to the nitrogen belonging to the imine. This results in the elimination of dinitrogen.
- Now, water is used to attack the resulting compound, and the subsequent deprotonation yields a tautomer of the required amide.
- The relocation of a proton belonging to the tautomer of the amide gives the final amide product.

13. Give short note on Oppenauer oxidation.

Oppenauer Oxidation is the process of conversion of secondary alcohols to ketones by selective oxidation.

It is an aluminium alkoxide catalysed the oxidation of a secondary alcohol to the corresponding ketone. This is reverse of the Meerwein Ponndorf Verley reduction. It is a very good method to oxidize allylic alcohols to α , β - unsaturated ketones.



Oppenauer Oxidation Mechanism

1. In the first step, alcohol coordinates with aluminium isopropoxide to form a complex
2. This complex reacts with ketone to form a six-membered transition complex
3. The alpha-carbon of the alcohol is converted to the carbonyl carbon from the aluminium-catalyzed hydride shift.
4. The acetone proceeds over a six-membered transition state.
5. The desired ketone is formed after the hydride transfer

Mechanism of Oppenauer oxidation

Step 2:

