

Hello Students my name is Harsha Achari. I am an assistant professor at Government College of Arts, Commerce & Science, Khandola, Marcela-Goa.

This module is for Second year BSc Semester 3, For the course title, Physical chemistry and Organic chemistry and paper code, CHC-103.

Name of the unit Amines and Diazonium salts, module name diazonium salt preparation from aromatic amines and conversion to benzene module no.21.

This module will have an introduction to diazonium salts, Their preparation from aromatic amines and their conversion back to benzene. Once you watch this module, you will be able to explain the term diazonium salt and give its reactions of preparation from aromatic amines and conversion to benzene.

So let us begin. A diazonium salt is an organic compound with the general formula $RN_2^+X^-$, where R stands for an alcohol or an aryl group and X stands for an organic or inorganic anion such as chloride anion, bromide anion, tetrafluoroborate anion.

Diazonium salt. Di refers to two and azo means presence of nitrogen atoms. An ium implies it is cationic in nature. Given below is an example of a diazonium salt, benzene diazonium chloride. The nomenclature is done by naming the hydrocarbon from which the diazonium salt is derived, followed by the anion.

Now let us see its preparation from aromatic amine.

When a primary aromatic when a primary aromatic amine is dissolved in cold, aqueous mineral acid and is reacted with sodium nitrite. A diazonium salt is formed.

Let us see its chemical representation.

Here you have the aromatic amine where AR represents an aromatic ring. It is treated with sodium nitrite, that is $NaNO_2$, and a mineral acid. To give you the diazonium salt with this formula, NaX and two moles of water molecules. This reaction of converting an aromatic amine into diazonium salt is called Diazotization reaction.

Next, let us see the probable mechanism for the preparation of this diazonium salt.

This mechanism is a two step mechanism. in step one, HNO_2 that is nitrous acid is formed when sodium nitrite reacts with a mineral acid here, the oxygen atom of the nitrite anion takes up a hydrogen atom. to gain a positive charge to give such a species. Next, the lone pairs on this oxygen atom is shared to form a triple bond with the nitrogen atom. And finally, since this oxygen atom is carrying a positive charge, it will leave as water molecule to give us the

Electrophile Nitrosonium ion, and this nitrosonium ion will exist in this form in the reaction mixture.

So in step one, we have the formation of the electrophile Nitrosonium ion. In step two, we have the aromatic amine. It will act as a nucleophile and will attack the electrophile nitrosonium ion. To give us a species where in the nitrogen atom of the aromatic amine now gains a positive charge because now it is bonded to four different atoms. Next, one of the hydrogen bonded to the aromatic nitrogen atom will be lost. At the same time, the oxygen atom of the Nitrosonium ion will pick up a hydrogen atom to give us such a species.

Next, another hydrogen will be lost and this hydrogen will be picked up by the same oxygen atom.

to form such a Molecular structure and then it will leave as water molecule. to give us the diazonium salt. In this step two we have finally the formation of the aryl diazonium salt. So to prepare benzene, diazonium chloride, that is the example which was given, We will require an aromatic amine that is Aniline which will be treated with Sodium nitrite and the mineral acid HCl to give us this, benzene diazonium chloride.

Now, this diazonium salts undergo two types of reactions, replacement reaction, and coupling reaction. In replacement reaction, the nitrogen atoms of the diazo group are lost as nitrogen gas and in the coupling reaction, the nitrogen atoms of the diazo group are retained in the product molecule.

Next, let us see the replacement reaction shown by the diazonium salt. So using this replacement reaction, the diazonium salt can be converted to benzene with the help of hypophosphorous acid that is H_3PO_2 to give us benzene wherein the diazo group of the diazonium salt will be replaced by a hydrogen atom to give us benzene molecule.

Let us see its chemical representation. So here is the reaction showing. you have the diazonium salt

reacting with H_3PO_2 in the presence of water molecule to give us the benzene. And here the diazo group is lost as nitrogen gas along with the by product H_3PO_3 , that is phosphorus acid and it's here.

Now let us have a small summary of this module.

So a diazonium salt is an organic compound with the general formula RN_2^+X^- , Where R stands for an alkyl group or aryl group X stands for anion which can be organic or inorganic.

This diazonium salt can be prepared from aromatic amine, and the reaction will be named as diazotization. This diazonium salt undergoes two types of reactions, that is replacement reaction,

and coupling reaction. We saw the replacement reaction using which the diazonium salt can be converted to benzene.

You can go through the following references For more information.

With this I would like to end my presentation.

Thank you.