Hello everybody, my name is Doctor Richa Sardessai and I'm affiliated to Saint Joseph Vaz College Cortalim.

Today we're going to be studying about the different nucleophilic substitution reactions of alkyl halides. This module is a part of the Bachelor of Science program in Chemistry for first years semester 2. The course code is CHC102 and the course title is physical and organic chemistry section B. The title of the unit is Unit 2 Alkyl and aryl halides and the module name is, Alkyl halides- Reactions: hydrolysis; nitrite and nitro formation; nitrile and isonitrile formation; elimination v/s substitution hydrolysis.

At the end of this module, the student will gain knowledge and understanding of the reactivity of alkyl halides. The student will also be introduced to the concept of ambient nucleophiles. The student will be able to appreciate the difference between substitution reactions and elimination reactions and the conditions which are responsible for the same. This module is broadly divided into 3 sections. The first is an introduction to the reactivity of Alkyl halides.

The second are the different nucleophilic substitution reactions of alkyl halides and the third is the difference between elimination and substitution reactions and understanding the conditions which are responsible for each of them.

So let us first understand the reactivity of alkyl halides. Alkyl halides have a carbon hydrogen bond, which is highly polar. The halogen, being electronegative in nature, tends to pull the electron pair of the bond towards itself. This in turn results it in having a delta negative charge and consequently the carbon to which it is attached gets a delta positive charge. This delta positive charge then makes the carbon susceptible to a nucleophilic attack by any nucleophile which results in the substitution of the halogen by the incoming nucleophile. Having understood this, we now understand further that the alkyl halide can give a number of compounds. By simply adding the nucleophile reacting with it, for example. By reacting the Alkyl halides, I'd buy different nucleophiles we can get alcohols, nitrite, and Nitro alkanes Alkyl nitriles and alkyl isonitriles.

The first set of reaction is the hydrolysis of Alkyl halides. Alkyl halides react with boiling Aqueous alkali as to produce alcohols. For example, methyl bromide reacts with aqueous potassium hydroxide in boiling conditions to give methanol. Similarly, ethyl bromide also reacts with boiling potassium hydroxide to give ethanol.

Now before we further learn about the nucleophilic substitution reactions of alkyl halides, we must understand the different types of nucleophiles that can react with the carbon halogen bond. Let us consider the nucleophile cyano. In this, the negative charge on the carbon may act as the attacking atom towards the electrophilic carbon center. However, it is to be noted that the lone pair of electrons on nitrogen may also act as the nucleophilic center. Similarly, in the case of Nitro group. The negative charge on oxygen can also attack the electrophilic carbon center as well as the lone pair of electrons on nitration can do the same function. Such compounds which have two or more atoms through which they can attack the electrophilic centre are called as ambient nucleophile.

Depending upon which atom undergoes the nucleophilic substitution reaction different types of compounds can be obtained from the same alkyl halides and the same nucleophile, by simply varying the conditions.

The first set of reaction from ambident nucleophile is the nitrite and isonitrile formation. Alkyl halides react with alcoholic potassium cyanide to form alkyl nitrites or alkyl cyanides as they are called. For example, ethyl iodide reacts with alcoholic potassium cyanide to give it as cyanide. However, aqueous solution of alkyl halide when heated with alcoholic silver cyanide forms, alkyl isnitrile Or alkyl isocyanide as they are called. For example, ethyl iodide on reaction with alcoholic silver cyanide gives ethyl isocyanide or isonitrile as they are called.

Another set of ambient nucleophilic reactions are the nitrite and Nitro formation. Alkyl halides react with potassium nitride to form alkyl nitrites. For example, ethyl iodide when heated with alcoholic potassium nitrite forms the nitrite compound. There is aqueous alcoholic solution of an alcohol I with. Silver nitrite forms Nitro alkenes. Again, the same ethyl iodide on reaction with silver nitrite in an alcoholic solution gives ethane. The reason For this observation is that in potassium cyanide The cation and the anion are well separated since it is an ionic compound. Since the anion is well separated, the negative charge on the carbon directly attacks the electrophilic centre of the alkyl halide to generate the cyano compound.

However, in the case of silver cyanide, the bond between the silver and the cyano group is a covalent one which is responsible for the attack via the lone pair of electrons on nitrogen to give the alkyl isocyanide. Similarly, in the case of potassium nitride, the oxygen which bears the negative charge can directly attack the electrophilic carbon to generate the nitrite. However. In silver nitrate, the oxygen is now covalently bonded with silver and is not free to attack the electrophilic carbon and hence the attack takes place through the lone pair of electrons on nitrogen to give the Nitro compound. Having understood this, let us now move on to the elimination versus substitution reactions of alkyl halides, as we have seen alkyl halides undergo various types of nucleophilic substitution reactions.

However, in the presence of a base alkyl halides can undergo beta elimination to generate alkenes. This reaction is called as an elimination reaction. To determine with what compounds are formed when an alkyl halides is treated with a base There are two determining factors ; The first is the nature of the alkyl halides and 2nd is the nature of the base. The first factor, the nature of the alkyl halide is Such that when primary alkyl halide is reacted with sodium ethoxide in ethanol at 55 degrees Celsius, 90% of the substitution products formed, whereas only 10% of the elimination product is formed. However, when a secondary alkyl halide is reacted under the same conditions, 79% of the elimination products form there is only 21% of the substitution product is formed.

When we move to a tertiary alkyl halide under the same set of conditions, it is observed that predominantly only the alkene or the elimination product is formed, whereas the substitution product is hardly 9%. The second factor is the nature of the base. If we consider the reaction of the same alkyl halide under two different conditions, with two different bases, it is observed that when a primary alkyl halide is reacted with an unhindered base like sodium methoxide in methanol then the substitution products predominates. However, when the same alkyl halides is reacted with a hindered base like Potassium tertiary butoxide the elimination product tends to dominate. The reason for this is. The hindered base is unable to effect the substitution due to the crowding of the different methyl groups around it. There is the sodium methoxide can efficiently attack the electrophilic center to give the substitution product and hence that is the one which dominates. Hence, today we understood. The alkyl halides undergo various nucleophilic substitution reactions. Ambident nucleophiles give different products depending upon the reagent used. Finally, the nature of the alkyl halide and the base used will determine the formation of the substitution or elimination products. In case you wish to learn more about this concept, you may refer to these books.

Thank you.