Welcome to the Bachelor of Science, First Year program in the subject of chemistry for semester one, for the course CHC-101, entitled Inorganic and Organic Chemistry, Section B-organic Chemistry. I am Dr. Durga Kamat, assistant professor at the Department of Chemistry, DCT's Dhempe College of Arts and Science. I am going to take up the module on Wurtz reaction that is preparation of alkanes.

The title of the unit is Aliphatic hydrocarbons, module name alkanes up to five carbons, preparation: Wurtz reaction. In this module, after a brief introduction to Wurtz reaction, we will discuss the mechanism of Wurtz Reaction, limitations of Wurtz reaction and application of Wurtz reaction in preparation of small cyclic alkanes. At the end of this module you will be able to describe the Wurtz reaction, give examples of Wurtz coupling reaction for the preparation of alkanes, explain the mechanism of Wurtz reaction, explain the limitations of Wurtz reaction and describe the use of Wurtz coupling reaction in preparation of small cyclic alkanes.

Wurtz reaction is a sodium mediated coupling of alkyl halides to form an alkane. It is the method used for preparation of alkanes. It is generally carried out by treating 2 moles of alkyl halide with two moles of sodium in presence of anhydrous solvent like dry ether, where X is halogen atom such as chlorine, bromine and iodine. The simplest alkane, which is prepared by this method is ethane. It is prepared by sodium mediated coupling of methyl bromide in dry ether. Please note here that this reaction involves formation of a new carbon carbon bond. Similarly, butane can also be prepared from ethyl iodide and sodium using wurtz reaction.

Wurtz reaction is also known as Wurtz synthesis or Wurtz reductive coupling. Metals such as zinc, manganese or activated copper have also been used to effect Wurtz reaction other than sodium metal.
This is one of the oldest reactions. First reported by Charles Adolphe Wurtz in the year 1855. Wurtz reacted a mixture of two alkyl iodides with sodium. and based on the vapor density, boiling point and formation pathway concluded that he had obtained ethyl butyl, that is hexane.

Now let us discuss the mechanism of Wurtz reaction.Two mechanisms have been proposed for this reaction. One is free radical mechanism and the other is anionic mechanism.

Free radical mechanism involves initial formation of free radicals, followed by their combination to give the expected coupling product. The radical mechanism is supported by experimental evidence, such as the formation of disproportionation products. Anionic mechanism involves 2 mechanistic steps reduction and alkyl coupling. There is an initial transfer of 1 electron from sodium to alkyl halide to form an alkyl radical. The alkyl radical subsequently receives another electron from second sodium to form an alkyl anion. This alkyl anion undergoes regular SN2 substitution with another alkyl halide to form an alkane.

The anionic mechanism is more plausible compared to the radical mechanism as it was found that the alkyl sodium is the actual reaction intermediate which can be trapped almost in quantitative yield.

Now let's see limitations of this reaction.

Richards reported that reaction of ethyl iodide with sodium gave around 51% of butane, which is the desired Wurtz coupling product and side products also were obtained, such as ethane and ethene. These side products were obtained due to disproportionation of the initially formed alkyl free radicals.
Whitemore and Coworkers treated n-hexyl chloride with sodium ethyl to get n-octane and side products ethane and 1-hexene. According to them, these side products were obtained from the action of sodium alkyl as a hydrocarbon base with alkyl halide.

Hence yield of the desired Wurtz coupling product is affected due to formation of other alkane and alkene side products. The Wurtz reaction is useful for synthesis of symmetrical alkanes. If we use different alkyl halides, a mixture of hydrocarbons is obtained, which is often difficult to separate. Primary alkyl halides give good to moderate yield of Wurtz coupling product. Secondary and tertiary alkyl halides give poor yields of Wurtz coupling product.This is due to the side reaction that is elimination reaction which occurs,okay and elimination in secondary and tertiary alkyl highlights is favored over the SN2 displacement reaction, giving the unwanted alkane and alkene.

We have already seen that Wurtz reaction can be used for preparation of alkanes. Wurtz reaction is also used for preparation of small cyclic systems. For example, cyclopropane can be prepared by treatment of 1,3-dibromopropane with sodium in good yield via intramolecular Wurtz reaction. Also, cyclobutane can be prepared from 1,4-dibromo butane using Wurtz reaction, yield of this reaction can be improved by using zinc metal instead of sodium metal.

The classical Wurtz reaction is also useful in the preparation of small bicyclic systems such as bicyclo[1.1.0] butane starting from 1- bromo-3 chlorocyclobutane.

So, to summarize, Wurtz reaction is sodium mediated coupling of alkyl halides to form an alkane and this reaction is useful for preparation of symmetrical alkanes.

These are my references.

Thank you.