

Hello students, I am Dr. B. L. Malik, Associate professor from PE SSRS in College of Arts and Science for Moody, Ponda, Goa. Today we're going to study in organic chemistry section A something about name reactions, and rearrangement. In this part under module name, reactions and mechanism, we're going to study Wolff rearrangement in detail with the mechanism & applications.

When you are going to study this module, you will come to know formation of ketene & α – diazo carbonyl compound. You will also understand the reaction and mechanism of Wolff rearrangement. You will study different applications of Wolff rearrangement.

Let us try to understand the rearrangement in details. It can be defined as thermal or photochemical or catalytic conversion of α – diazo ketone to ketene by liberation of Nitrogen with rearrangement. The reaction was discovered by German chemist Ludwig Wolff in 1910. General presentation of the reaction is as follows.

It shows acetyl chloride is reacting with diazomethane to give intermediate α – diazoketone which rearranges to corresponding ketene by liberation of Nitrogen. Wolff rearrangement gives ketene as an intermediate which undergoes nucleophilic reaction with weakly acidic nucleophiles like water, alcohol, ammonia, primary and secondary amines to give carboxylic acid, derivatives of esters, amides, mono substituted amides, and di substituted amides, respectively.

The acyl halide required in the reaction can be easily prepared from carboxylic acid by using thionyl chloride or any other chlorinating agents.

The general reactions are shown below. When carboxylic acid reacts with Thionyl chloride we get corresponding acid halide with liberation of SO_2 & HCl . We can also have reaction of carboxylic acid with phosphorus pentachloride or phosphorus trichloride giving corresponding acyl halide. Out of these three methods, the first one is supposed to be the most useful because the side products SO_2 & HCl are gases which can be released in the atmosphere or can be absorbed in the proper solvent so that we get the corresponding acyl halide as a single product.

The mechanism of the reaction is shown here. The acyl chloride is converted to α -dizoketone by reaction with diazomethane which exists itself into two resonating structures which are shown here. This α -dizoketone reacts with Silver oxide to give ketene with loss of Nitrogen.

So initially, α -dizoketone loses proton. What we get is carbon, and this carbon rearranges itself to this more stable reactive species, where oxygen is having a negative charge. This negative charge rearranges, or it comes back to oxygen, then alkyl group along with electron pair migrates to carbon, and carbon nitrogen bond breaks very in. This pair of electron goes to this positively charged nitrogen, and the nitrogen is liberated and what we get is corresponding ketene.

This structure, whatever shown here is of alkyl ketene, where alkyl group R is bonded to carbon. When the rearrangement is carried out in presence of different solvents Ketene is directly converted to different products. Let us try to understand all these reactions.

With water It gives corresponding carboxylic acid with one carbon more than the starting acid chloride. See general reaction is written here as

needed. Let us try to understand this with some simple examples. Acetyl chloride reacting with diazomethane giving methyl ketene which on hydrolysis with water gives propanoic acid. Phenyl acetyl chloride reacts with diazomethane gives benzyl ketene which on hydrolysis with water gives 3-phenyl propanoic acid with one carbon more than the starting acid chloride.

Let us try to understand hydrolysis with alcohols. With alcohols it hydrolyzes giving corresponding Ester. So methyl ketene on reaction with Ethylalcohol will give ethyl propionate. Phenyl ketene on reaction with ethyl alcohol gives ethyl phenyl acetate.

We can also carry out hydrolysis of ketene with ammonia which gives corresponding amides. The general reaction is given here. Methyl ketene on reaction with ammonia gives Propanamide $\text{CH}_3\text{-CH}_2\text{-CONH}_2$ where CONH_2 is amide group, Substituted amines would result into corresponding substituted amides. The general reaction is given here. If we take the corresponding alkyl ketene, it reacts with mono, substituted amine giving N alkyl amide. We can also have the reaction where methyl ketene reacting with methyl amine to give N-methylpropanamide or Phenyl ketene reacting with methyl amine giving corresponding N-methyl Phenyl acetamide.

Secondary amines also can react, giving corresponding N,N Disubstituted Amide. The general reaction is given along with specific reactions. Methyl ketene on reaction with dimethyl amine gives corresponding N,N dimethyl propanamide and N,N dimethyl phenyl acetamide.

There are some important applications of Wolff rearrangement. 1. Homologation of carboxylic acid, meaning carboxylic acid can be converted into its higher homologues. For example, if we take Acetic acid, it is converted to Propanoic acid. Acetic acid contains 2 carbons, through Wolff

rearrangement we can convert acetic acid to propanoic acid which contains 3 carbons in total.

Second application is 2 + 2 cycloaddition reaction wherein addition of ketene, which contains a carbon carbon double bond to another compound containing carbon carbon double bond. Two carbons of ketene and two carbons of other compound are involved and what we get 2 + 2 cycloaddition reaction, giving a corresponding cyclic compound.

Students if you want to know certain more information about this, the references are given at the bottom of this presentation. You can go through these references and you will get more idea about this particular reaction in details.

Thank you.