**Supramolecular Chemistry-I**

**Prof. Parimal Kanti Bharadwaj**

**Department of Chemistry**

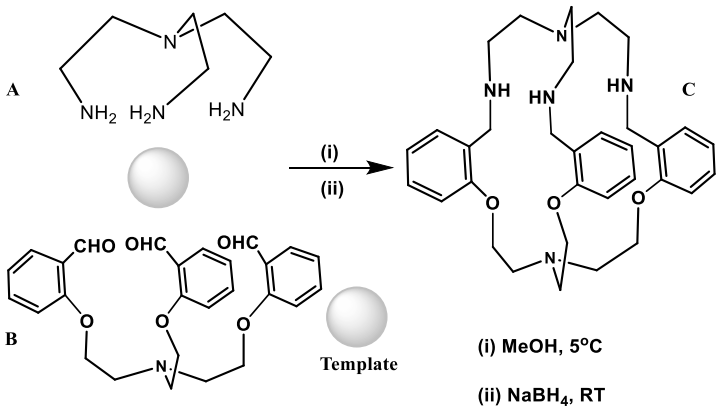
**IIT Kanpur**

**Week - 02**

**Lecture - 10**

Welcome to the class. In the last class, I told you that there are two aspects of the synthesis of cryptands. One is called strategy and the other is methodology. And I discussed that there are five strategies that can be adopted in the synthesis of cryptands starting from non-cyclic starting materials. So, now we will discuss the methodology. I will tell you first the template method.

This is the first method, I will describe and I will tell you in terms of a story ok. We wanted to make this, I said that we introduce first the tripodal coupling that is tripod and two tripods will come ok. So, now why they will come? We have to put a template, so that the template will bind the tripods and bring them closer.




So, I am writing like this, this is my template fine. So, if I put a template then both the reactants will come together; when they are close, they will react and I will get the desired cryptand. So, this was the idea. With this idea we made this starting material, (B) and the other reactant (A) is available commercially. This is called tris 2-aminoethylamine, in short it is called tren. Now, why they will meet? They will meet because I will use a metal ion as template. Then amine and aldehyde will combine to form the Schiff base which upon reduction, it will form the desired cryptand (C).

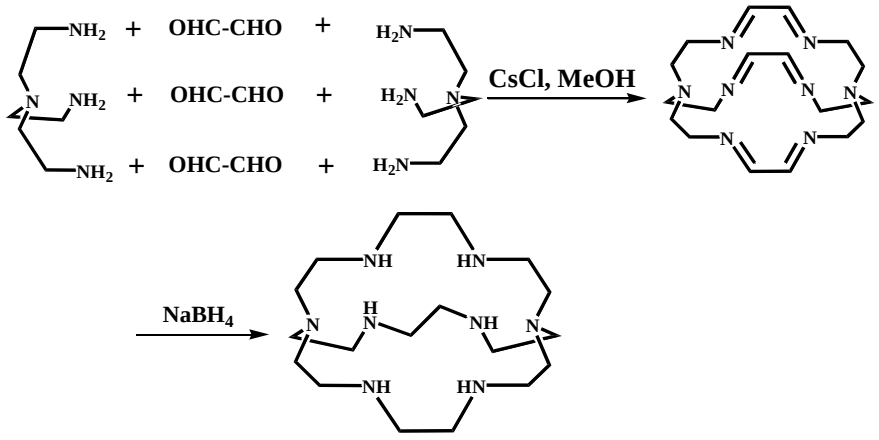
This was our idea. So, for 2 years, we struggled with transition metal ions as template. Then suddenly one bright morning, we decided to start using alkali metal and precisely

we tried with cesium chloride. Cesium chloride has some solubility in methanol, large quantity of methanol we took and we put cesium chloride and it worked very well, we got 40 percent yield. Why was that? That will be clear if you know this Schiff base condensation reaction. The lone-pair on N will make a nucleophilic attack the aldehyde carbon to form the imine, and from the imine, I will get amine by reduction and then I will get a stable cryptand. So, that means, the reaction depends upon the availability of the lone pair on nitrogen for the reaction to go forward. The reaction did not go forward with a transition metal ion as a transition metal ion binds with this amine pretty well. That means, the lone pair is not available for attacking this carbonyl carbon.

Therefore, when we took alkali metal ions, it binds this both oxygen and nitrogen, but very weakly, but what it does? It brings the two parts together and very nicely form imine. So, all the story was is to tell you that when you use template and specially metal ion as a template, you should be very careful about which metal ion you are taking and what reaction you desire. So, with that idea with that idea your choice of template should be very good. We got the cryptand in about 40 percent yield that can be crystallized as a bright colorless crystals like sugar cubes. So, just remember when you adopt the template method we must choose a metal ion properly.

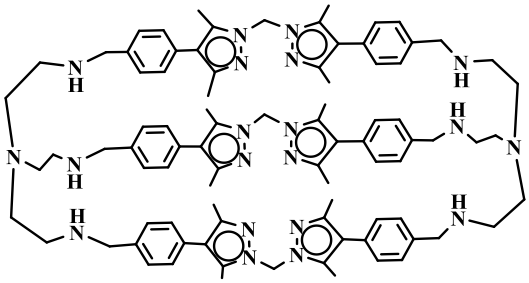
There is another method called high dilution method. I told you about high dilution method earlier when we discussed synthesis of macrocycles. High dilution means the intermediate has enough residence time in the mixture so that it can undergo desired intra molecular condensation not intermolecular. I told you earlier during macrocyclic synthesis that high dilution means it will go for days, sometimes more than one week.

While we are playing with the high dilution method, then one group from US showed that they got good result if the reaction is carried out at low temperature, say $5^{o}$ C. In that condition no templating metal ion was necessary.

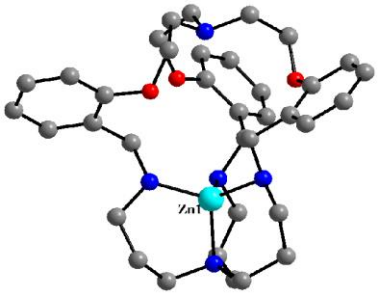



So, this 12 points reactions went smoothly at low temperature! So, there is another method that is low temperature method and why it work I will tell you now. When you

lower the temperature, the degrees of freedom of movement of these 3 amino groups will be drastically reduced. And this amine now will react with the linear aldehyde to give the desired Schiff base. So, low temperature is another very important method. You have to recycle the solvent otherwise you will waste lot of chemicals. Then another method that we use nowadays is low temperature and a template as well. So, when you take both, then sometimes we can get the yield as much as 90 percent. If you tell somebody that some reaction like this we got 90 percent yield he will laugh at us because it is impossible, but indeed if you take a good templating ion at say 5 degree celsius it is possible to get 90 percent yield.

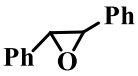
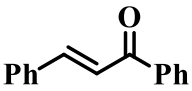
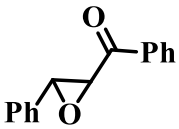
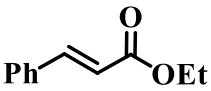
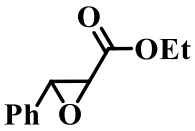
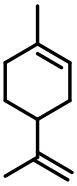
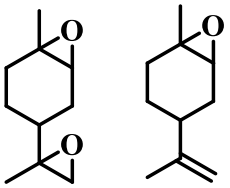
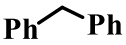
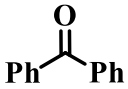
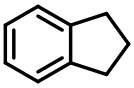
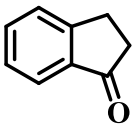
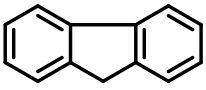
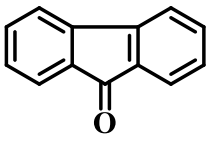


I told you that synthesis of this compound and how this some of the structures are now I will tell you their complexing abilities.

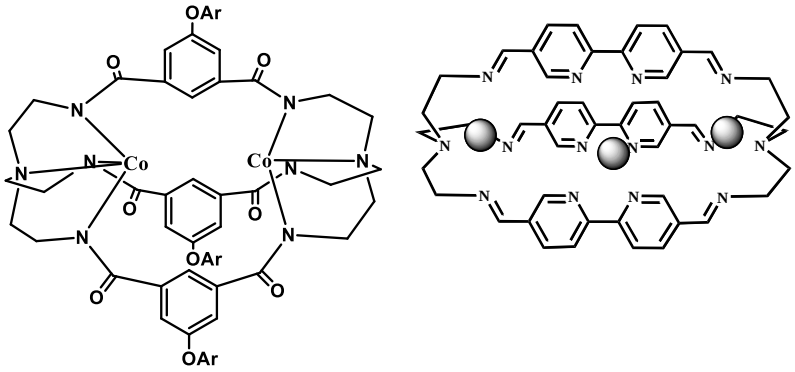



So, 4 nitrogens binds to this $Zn^{2+}$ and it this part is empty there is nothing. So, that something can come and do some chemistry. For example, when you have a cobalt, cobalt or copper then they oxidize olefinic and benzylic in the form of benzylic substrates to their epoxides. So, epoxides can be formed for example, this compound with oxygen, oxygen from air in presence of one aldehyde that is sacrificed isobutyraldehyde sacrificial you can get in very good yield epoxide.

Summary of $Co^{2+}$- and $Cu^{2+}$-Cryptate Catalysed Oxidation of Olefinic and Benzylic Substrates

| Entry | Substrate | Product | Yield % | |
|---|---|---|---|---|
| | | | A | B |
| 1 |  |  | quant. | quant. |
| 2 |  |  | 82 | 60 |
| 3 |  |  | 50 | 36 |
| 4 |  |  | quant. (3 : 1) | 75 (2 : 1) |
| 5 |  |  | 91 | |
| 6 |  |  | 70 | 54 |
| 7 |  |  | 49 | 35 |

A = [**138**⊂Co]$(ClO_4)_2$; B = [**138**⊂Cu]$(ClO_4)_2$




So, that means, in a cryptand we can put one metal depending upon its structure we can put mononuclear cryptate that is known as we can put dinuclear cryptate and we can put trinuclear cryptate as well. So, different types of different numbers of metal ions can be put inside the cavity and that depends upon the length of the cavity, its environment so on and so forth. So, thank you.