

Supramolecular Chemistry-I

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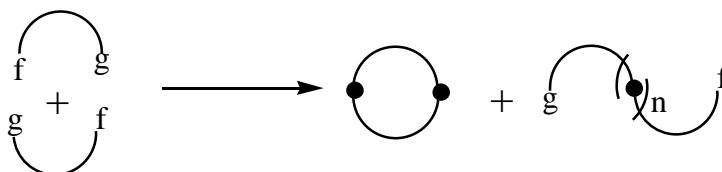
IIT Kanpur

Week - 01

Lecture - 05

Good morning. So, from now on I will discuss what is called supramolecular synthons. There are many supramolecular synthons I will describe and how to extract properties out of them and while discussing those properties out of them you must remember the definition of supramolecular chemistry as we discussed in the very first class.

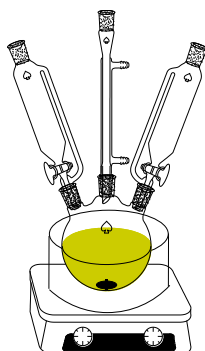
First supramolecular synthon, we will discuss, is known as macrocycles. So, macrocycles very simply I can write like a cyclic compound incorporating donor atoms. When I say macrocycle, it means somewhat big say 12 member onwards and smaller ones sometimes are called mesocycles. This term is not very much in use nowadays, but we are more interested in macrocycles. So, the following is a cartoon of a macrocycle obtained from two acyclic units.



You react two non-cyclic compounds say I have written where **f** and **g** are two functionality in a long chain. So, we want **f** to react with **g**. It can react in two ways as shown giving a desired cyclic product and undesired acyclic oligomers. But these are independent units in solution and while they are in solution then they are moving all around the place. So, what is the probability that this will not form the desired macrocycle? Quite low. Sometimes they can form, but may be less than 1 percent or sometimes 0.01, 0.1 percent and you will get a lot of mixture of linear products.

The question is, how can I increase the desired macrocycle? We can do that sometimes if we have rigidity in the linear components by using aromatic groups. So, then the yield may be somewhat higher. Another method will be using what is known as high dilution technique. What is a high dilution technique? Suppose I take in a round bottom flask with a magnetic starrer and lots of solvent. Now put dropwise the linear compound using a burette. So, it will go on for days we do not need to hang around we

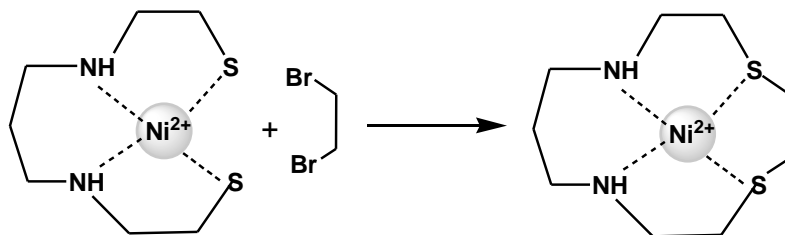
can start this and go after few days we see the everything is gone from here in the burette. There is no need to stay near the experiment as it will go on uninterrupted. In this set-up, when one molecule finds another then they react and the intermediate moves around. Being a very dilute solution will help this molecule to avoid another molecule and it will combine intramolecularly to give the desired macrocycle.



A typical set-up for a high dilution method of synthesis

So, in the high dilution technique all I am doing is I am increasing the residence time of the intermediate.

Then there is another technique: we can use a template that can be a metal ion, an anion or a neutral molecule. Template can be of two types: kinetic template and thermodynamic template. So, let us first discuss kinetic template. What does the template do? It organizes reactants such that it undergoes reaction in a definite direction. Let me show you an example.



An example showing the use of Ni^{2+} ion as a kinetic template

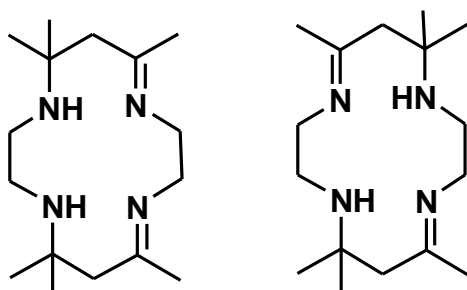
So, suppose I make this complex with a Ni^{2+} salt like nickel chloride, nickel perchlorate, etc., and it is easily available. So, I shall get this square planar complex as shown. Why I have taken Ni^{2+} . Because Ni^{2+} is a d^8 system and d^8 ions will like to form square planar coordination geometry. So, why I do not put Cu^{2+} or Zn^{2+} because these metal ions may not form square planar complex. So, my choice of the template is very

important and when I use metal ion as a template I can use a template which may be metal ion or a non-metallic and anion, sometimes neutral molecules. So, there are different kinds of templating effects are there. Here, I am using a metal ion as a template because metal ion is easily available and you can easily make a complex like this. Now I react this complex with dibromoethane in presence of a base and there are how it will react that depends upon system to system it can react and what I am going to get is a macrocycle.

I can get Ni^{2+} from the cavity if I react with excess cyanide, it will form nickel tetra cyano because that is more stable and Ni^{2+} will go and I will ended up getting the macrocycle. So, this is called a kinetic template effect.

Another template effect is called thermodynamic template effect. Thermodynamic template effect works on the product. Kinetic template effect works on the reactants by arranging the reactive groups suitably.

Let me explain thermodynamic template effect with an example. Suppose I react ethylene diamine means with acetone. Also, acetone is my solvent. All I do is I take ethylene diamine and take acetone as solvent and then reflux it and it will be forming 12 products in the mixture. Out of these 12 macrocyclic products, some ones may not be that stable, others are stable. If I put a Ni^{2+} or Cu^{2+} salt then what will happen? The two products are isolated and others vanish. One difference between the two products : one is cis same side and the other is trans.



The macrocycles are stabilized due to complexation with Ni^{2+} or Cu^{2+} ion

So, out of the 12 product these two products are stabilized in presence of nickel 2 plus or copper 2 plus. So, they get thermodynamic stability in presence of either of these metal ions. So, template by definition is the species which alters the forward reaction in a chemical system and the effect is known as template effect.

So, I finish today with the template effect and now I will start what is known as crown ether from next class. Thank you very much.