Supramolecular Chemistry-I

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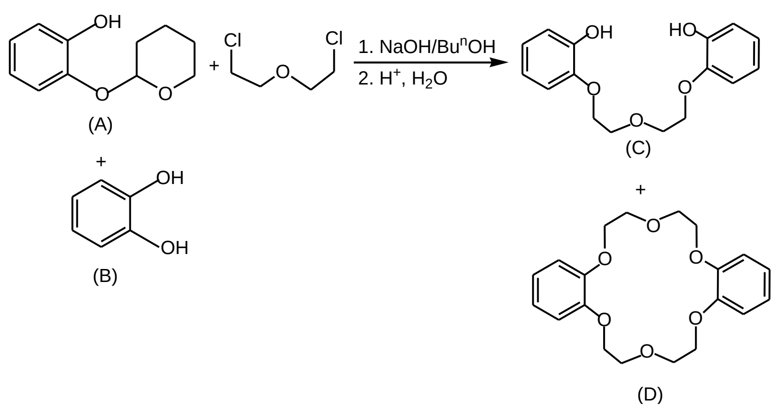
Week - 02

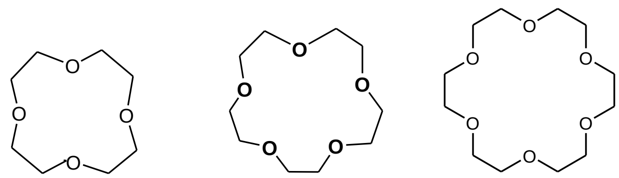
Lecture - 06

Okay, today we will discuss as I said another very important supramolecular synthon that is called crown ether. Synthesis of this compound or rather discovery of this compound was made serendipitously. Charles Pedersen was a scientist in DuPont chemicals in Switzerland. While attempting to prepare a linear diol (C) starting from the catechol derivative (A), he synthesized (Figure 5) the expected diol along with a small amount of the crown ether (D) due to the presence of free catechol (B) as impurity in the reaction mixture.



Tertiary butanol has a higher boiling solvent so you can go up to higher boiling point followed by acid quench in aqueous solution. In the product he obtained a small amount of (D) with unreacted catechol as a yellow greasy product. What did he do? Most people will throw that. Most people will throw such compound but he was a very hard working person and he did not quit. Pederson could recognize that he was on to something important with subsequent characterization of this compound (D) as a colorless compound. So he isolated this in 0.4 percent. He named this compound as dibenzo-18-crown-6. The name he gave like this: there were 2 benzene units, so dibenzo and 18 meant 18 member macrocycle, and 6 meant there were 6 ethereal oxygens in the macrocycle. Since this compound was a nice and a macrocycle, he wanted to find its complexing ability with metals. To his amazement, he found that alkali metals readily form complexes with this and potassium ion could be crystallized where the ion is inside this macrocycle.

Before that it was not known that alkali metal can form coordination compounds with macrocycles or with any ligand. So, this was the first compound of potassium complex and the beginning of the coordination chemistry of alkali metals. Because of this discovery, he got the Nobel prize in chemistry in 1987.

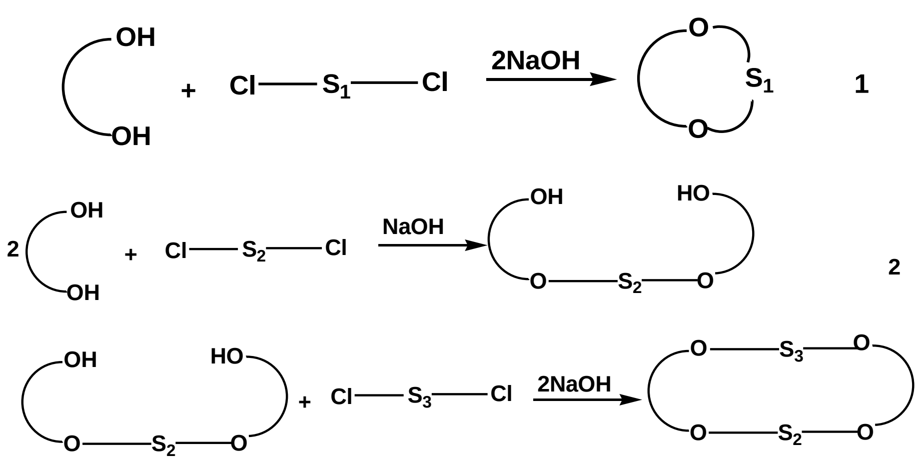


12-crown-4 15-crown-5 18-crown-6

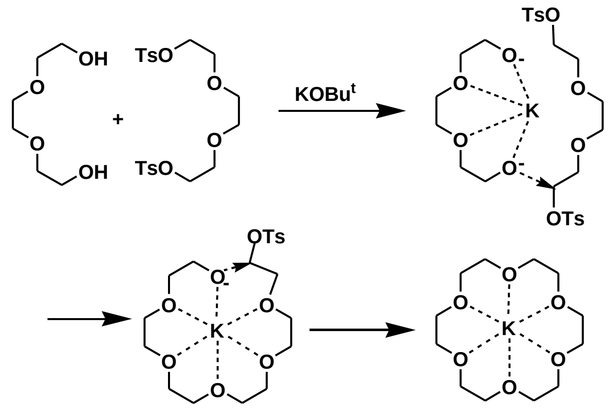
These macrocyclic compounds are known as crown ethers as they take the shape of a crown. I have drawn above three simple crown ethers to appreciate. Crown ethers are ethylene bridged. The nomenclature convention as suggested by Pedersen for the simple compounds involves two numbers. The first number gives the total number of atoms in the macrocycle and the second number gives the number of ethereal O atoms present in the backbone

Discovery of crown ethers was the beginning of alkali metal coordination chemistry. Now let us look at some of the synthetic methods adopted by people. The first method that Pedersen used is still operational.

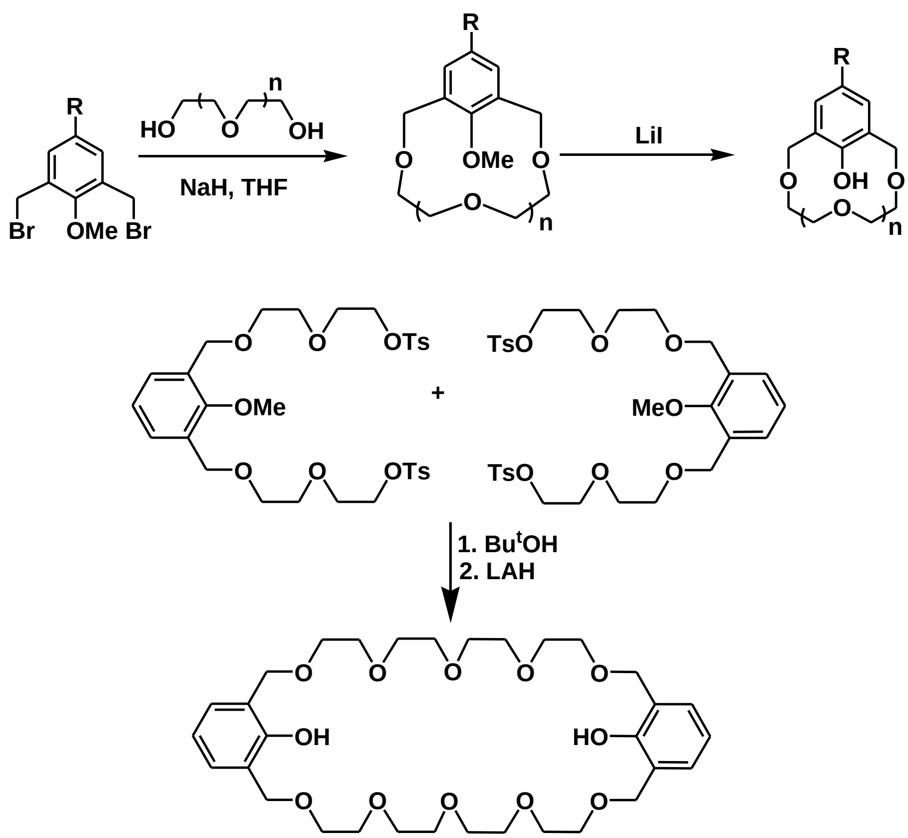
Pedersen proposed the synthesis of crown ethers utilizing Williamson's synthesis in the cyclization step as shown schematically below. However, the crown ethers reported by Pedersen were mostly synthesized adopting the first two methods shown below:



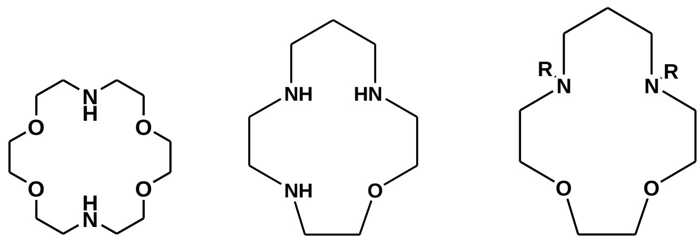
He found that the yield of the product depended upon the base used. Also, use of different leaving groups like tosylate can dramatically increase the yield of the desired product in these cases. Here, potassium ion acts as a template as well.



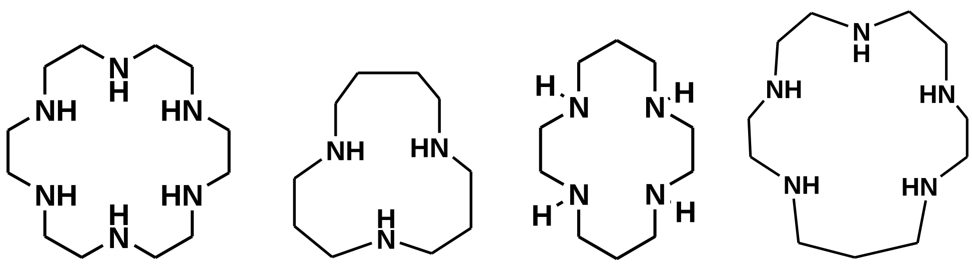
Many crown ethers were synthesized and some of these structures I will share with you; these are available in any book on crown ethers you can get. For example, you take a dihalide and a linear dihydroxo compound in base you will get different kinds of crown ethers.



This group will change to hydroxy group. So, you can get this kind of compounds. That means I am trying to drive home that not only the simple crown ether compounds, but you can get crown ethers of varied structures. Not only the only crown ether, I will show you another compounds are there also. So, these are crown ethers like aza crown ethers.



Aza-oxa crown ethers



Aza crown ethers

These are also formed. So, what I am writing one after another these molecules, these are synthesized by different people, okay and these are supramolecular synthons. How to use them? That we will describe slowly. We will just use it and we will describe slowly to you so that you may appreciate what is the need of making this compound. Why? Our aim in the beginning, the aim of supramolecular chemist or rather chemist was to synthesize macrocycles of different sizes so that we can bring in specificity of binding. alright? If you have nitrogen crown ethers then they bind transition metal ions. If simple crown ethers, they bind alkali metals. Now, if we can synthesize a particular macrocycle, design it such a way that it can specifically bind, it will be great. Specific binding is the key word.

For example, suppose there are so many metal mixture is there. I like to bind only Ni^{2+} from this. We have copper, nickel, zinc, all kinds of metal ions there in a solution. If I can specifically bind say nickel or specifically bind potassium ion so that they can be separated then it is great.

We can do many things. So what things, why it is important? Slowly it will be obvious to you. In the beginning, it is the aim for all of us to make these compounds of different sizes and different donors. I will stop here today and then again I will deal with something else. Thank you.