Supramolecular Chemistry-I

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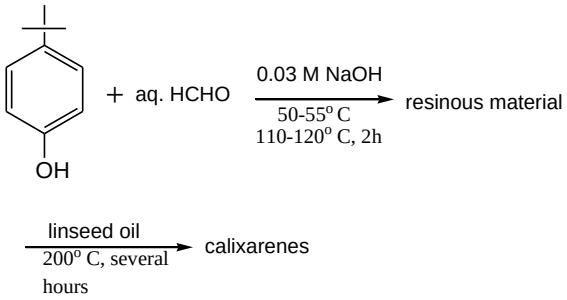
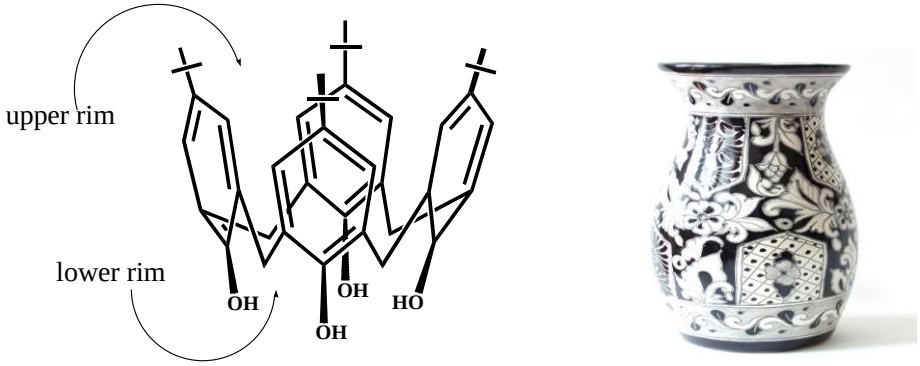
Week - 02

Lecture - 08

Good morning. In my previous class, I introduced the term calixarenes. So, we will take a look at calixarenes in some more details. Calixarenes are a series of macrocyclic phenols. Now, when unsubstituted phenols are reacted with formaldehyde at high temperature, it gives a resinous material called Bakelite. Bakelite is commercially quite useful.

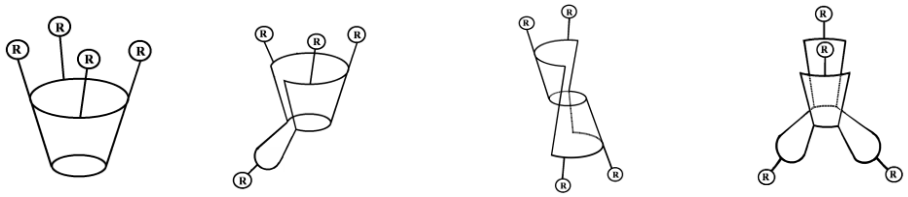


This was discovered around 1870, a long time ago. It took almost a century to find out that if para substituted phenols, specifically tertiary butyl substituted phenols is reacted with formaldehyde at high temperature in some neutral solvent, for several hours several hours, a mixture of products were formed. This mixture of products turned out to be very different from resinous bakelite and it turned out to be mixture of calixarenes. The name calixarene was coined by two people. One of them is Indian, Muthu Krishnan and the other was Gutsche. They gave the name calixarenes. Calix means vase in Greek and arene specifies incorporation of aromatic groups in the macrocycle. Especially, calix-4-arene and calix-5-arene have a three dimensional structure and very much resembles like a flower vase. Larger macrocyclic rings can assume a planar shape in the solid state.



Calix-4-arene

So, the upper rim as shown above and the aromatic groups are hydrophobic in nature and it can accept hydrophobic guests. And, the lower rim is hydrophilic in nature. Obviously, you can see OH groups, therefore, it is hydrophilic. This lower rim can bind metal ions. These molecules are absolutely fascinating. Let me clarify the nomenclature. There are 4 benzene groups (arenes) and so its name is calix-4-arene. So, calix-6-arene should have 6 benzene groups and so on. Now, what caught the imagination of chemists for this kind of molecules? To make drawings is very difficult, but we can make cartoons. I expect you to make cartoons. All calixarenes are conformationally very labile at room temperature that can be monitored by NMR spectroscopy.

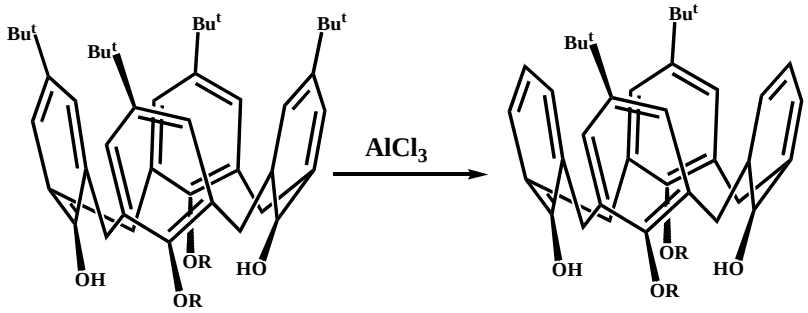


1 2 3 4

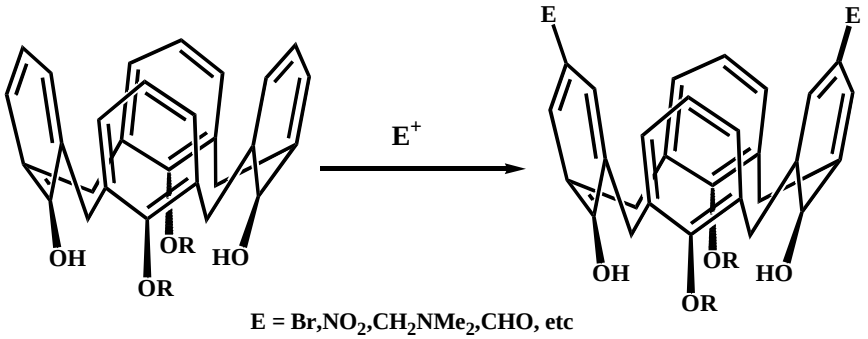
So, we find that calix[4]arene can exist as complete cone (1), one alternate (2), 1,2-alternate (3) and 1,3-alternate (4) conformers at room temperature. There is a methylene spacer between the aromatic groups and one benzene group can invert easily about the methylene spacer. This can give rise to four different conformers as shown in the picture above in the cartoon form. These conformers can be detected by NMR and it caught the imagination of chemists that with these kind of molecules, it was possible to make molecular machines. So, people jumped into this and large number of publications, large amount of results were accumulated. I must tell you that I have made only four conformations possible for calix[4]arene. But, as we go to calix[5]arene, calix[6]arene, there will be large number of conformations possible.

Calixarenes being conformationally mobile, attracted great attention from chemists who wanted to modify the upper and lower rims and the methylene spacers as well. These modifications were designed to impart special properties to these molecules. Making them useful in different fields of supramolecular chemistry.

The *t*-butyl groups at the upper rim can be easily removed by trans-alkylation using $AlCl_3$ and a solvent such as toluene. Subsequent reactions on these substrates allow the introduction[1] of a variety of functional groups. Complete functionalization with groups such as $SO_3^-Na^+$, $CH_2N^+Me_3$, $CH_2PO(ONa)_2$ makes the upper rim hydrophilic. On the other hand, substitution with aromatic or aliphatic groups can deepen the hydrophobic cavity.



Selective functionalization of the lower rim affords regio-controlled introduction of substituents at the upper rim for the synthesis of calixarenes derivatives for various applications.



E = Br,NO_2,CH_2NMe_2,CHO, etc

So, this is a very good supramolecular synthon and is really a milestone in the development of supramolecular chemistry. Thank you.