CROWN ETHRS

The most interesting recent developments in chemistry is the discovery of macrocyclicpolyethers also called crown ethers. Crown ether is a generic name given to the macrocyclicpolyether containing ethylene bridges separating electronegative oxygen atoms. They typically contain central electron rich hydrophilic cavity with diameter varying from 1.2- 6.0 A°. The hydrophilic cavity is ringed with electronegative binding hetero atoms such as oxygen, nitrogen, sulphur etc., which in turn are surrounded by a collar of -CH2 groups forming a frame work which is flexible and exhibits hydrophobic behavior. The hydrophobic exteriors allow them to solubilize ionic substances into non-aqueous solutions and in membrane media. Such properties facilitate for their use as extractants and membrane carriers. Macrocyclicpolyethers form much more stable complexes than open chain analogues. Apparently, this “macrocyclic effect” is due to the fact that cation is being completely surrounded by a cyclic macrocycle. Thus, when the inorganic cation fits into the cavity of crown ether or sandwiched between two crown ether molecules it becomes a lipophilic species. This property of crown ethers, converting inorganic cation into lipophilic species can Utilized in extractive separation analysis.

Discovery:

The first crown ether was discovered by pure chance. C. J. Pedersen(26) was working as an industrial chemist for Du Pont. A project was initiated in file fell of 1961 by him, to find new vanadium containing catalysts for the polymerization of olefins. Pedersen decided to study the effects of uni- and multidentate phenolic ligands on the catalytic properties of vanadyl group, quinque-dentate ligand selected was bis-{2-(o-hydroxy-phenoxy)ethyl}ether ‘C’ and the synthesis was began according to the route outlined in Fig.-1

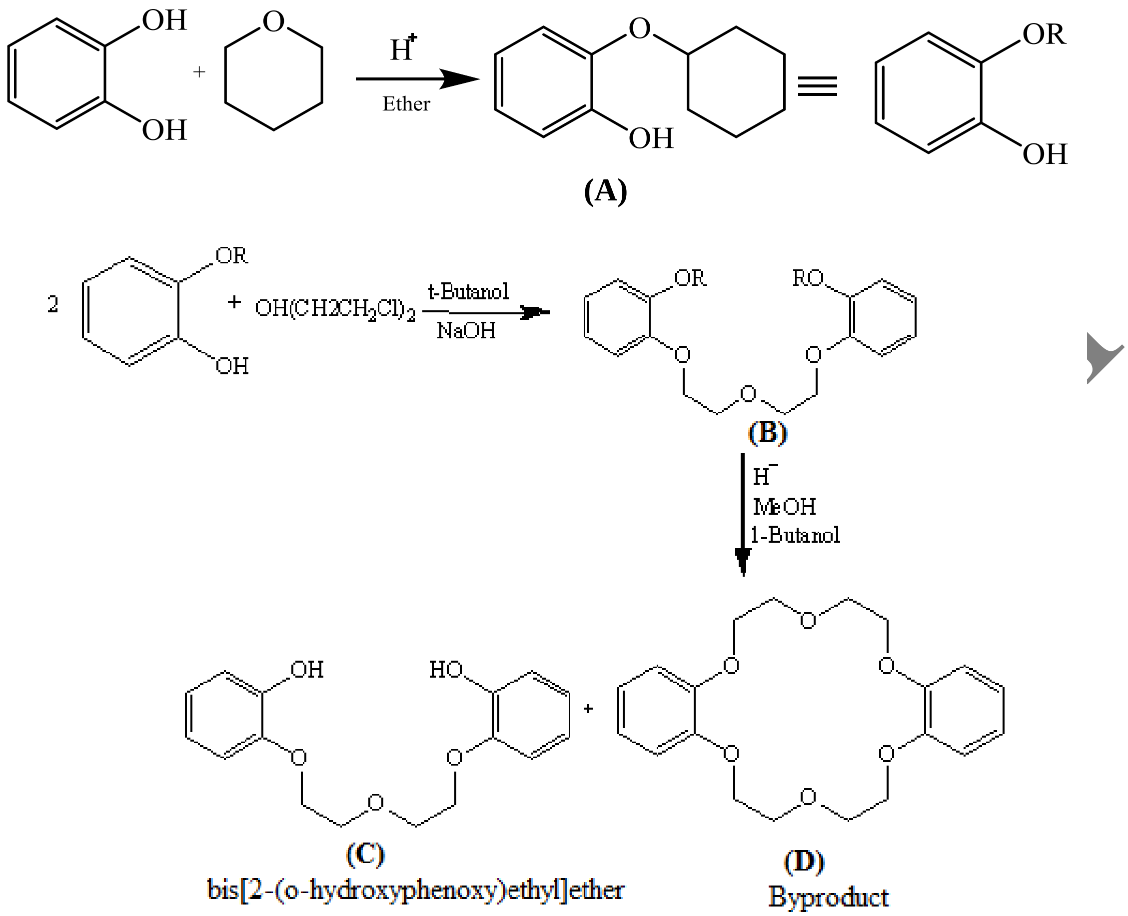


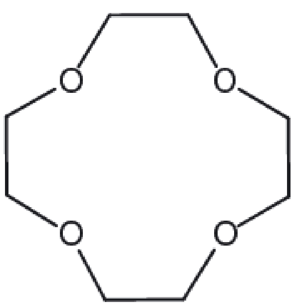
Fig.-1 Synthesis of 1st crownether

Classification:

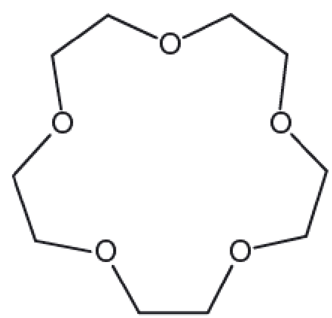
1. **Podands** : Podands are open chain compounds and are characterized by lacking ring and bridge structures.
2. **Coronands**: Coronands are cyclic compounds. Coronands containing oxygen as donor atoms are called crown ethers, these containing oxygen and nitrogen as donor atoms are called as aza-crown ethers and others
3. **Cryptands:** Cryptands are macropolycyclic polyethers and are classified in to bicyclic, tricyclic and tetracyclic.

Nomenclature:

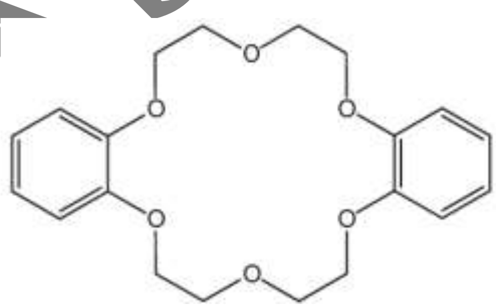
It not always possible to use IUPAC nomenclature for naming the crown ethers as it leads to lengthy names. Thus the conventional IUPAC rules for naming crown ethers are too cumbersome for repeated use. Therefore a system of adhoc name, based upon the number and kinds of hydrocarbon rings, die total number of atoms in the ring, the class name “crown” and the number of oxygen atoms in the polyether ring, was developed for the purpose of naming e.g., 1,4,7,10,13,16-hexaoxa cyclo octadecane is designated as 18-Crown-6. Here number 18 indicates the total number of atoms in the polyether ring while the number 6 denotes the number of donor oxygen atoms in polyether ring. Additional substituents or sites of condensation like dibenzo or dicyclohexano are written first, e.g., Dibenzo-18-Crown-6, Dicyclohexano-18-crown



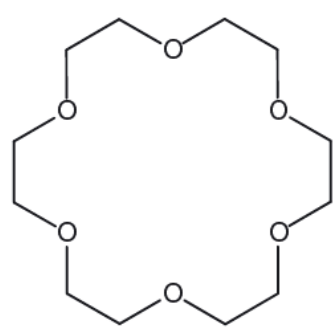
(A) 12-crown-4



(B) 15-crown-5



(C) dibenzo-18-crown-6



(D)18-crown-6

Fig-2 Various Crown Ethers

Physical Properties

1. Crown ethers of the ethylene oxide oligomer type are colorless, odorless, viscous liquids or solids with a low melting point. They are strongly hygroscopic and readily soluble in most organic solvents and in water.
2. Crown ethers with condensed aromatic rings are colorless, barely hygroscopic, crystalline compounds. At room temperature they have poor solubility in water, alcohols, and many other common solvents .They are readily soluble only in halogenated hydrocarbons, pyridine, and formic acid.
3. Crown ethers with alicyclic bridges have much better solubility in hydrocarbons and much poorer solubility in water than the ethylene oxide oligomers .
4. The solubility of crown ethers increases markedly if salts are added, e.g., 25-fold for dibenzo-18-crown-6 in MeOH after addition of KF. The increase depends on the type of salt used. Conversely, presence of thecrown ether increases the solubility of the salt

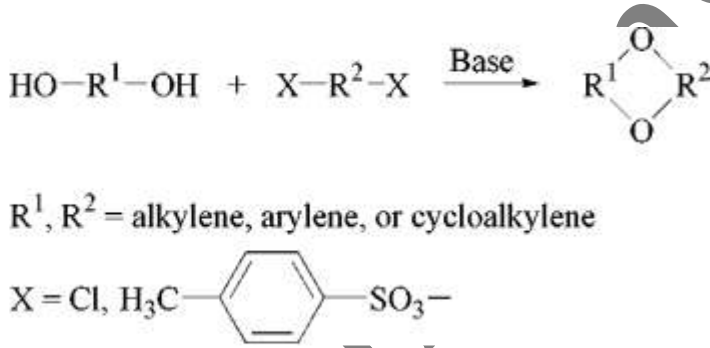
Chemical Properties:

1. Like simple dialkyl ethers, aliphatic and alicyclic crown ethers are chemically stable.
2. Aromatic crown ethers react like anisole or veratrole,i.e., they can be halogenated or nitrated and they react with formaldehyde.
3. Hydrolysis takes place only in special cases.
4. Crown ethers are also thermally stable; dibenzo-18-crown-6(**6**) can be distilled at 380 ◦C without decomposition.
5. With hydrogen ions and in the presence of Lewis acids (AlCl3,TiCl3), oxonium compounds are formed.

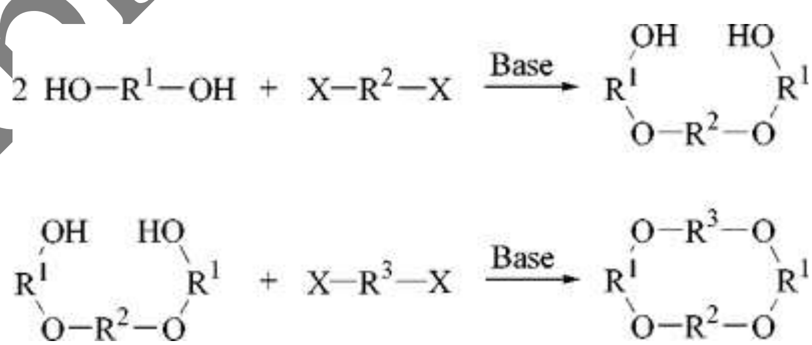
6. The hetero derivatives (**10** – **15**) are usually more reactive than the classical crownethers.
7. Aza analogues are strong bases and react with acids to form salts.

Synthesis:

The most important methods for the production of crown ethers are analogous to theWilliamson ether synthesis . The ether rings are formed by reaction of diols with bifunctional components that possess terminal leaving groups such as chloro or tosylate:



The reaction is carried out in the presenceof a base, e.g., an alkali metal hydroxide or carbonate, cesium fluoride, potassium *tert*butoxide, or sodium hydride. *n*-Butanol, *tert*butanol, tetrahydrofuran (THF), and, less frequently, dimethylformamide (DMF) or dimethyl sulfoxide (DMSO)are used as solvents. Cyclization can take place in a single step or in several steps:



Crown ethers are cyclic polyethere they are cyclic polymers of ethylene glycol, (OCH2CH2)n and are named as x-crown y- where x is the total nujber of atms in the ring and y is the number of oxygens important members of this series are titromus (Y=4) Pentamers (y=5) and the hexamers (y=6) the crown ethers have the property complexes with positive ions the relationship between the crown ether and the ion that it solvate is called a host guest releationship the crown ither act as host and the coordinate cation as the guest the intesor of the complex containsthe oxygen solvated cations but he exterior has hydrocarbon properties (hgydrophobic) . As a result the completed ion is soluble in non-polar organic solvent. The ability of a host moluele to bind specific guests called molecular recognition this property renders crown ethers as potential phase transfer catalysts. The denticity of the polyether influences the affinity of the crown ether for various cations. For example, 18-crown-6 has high affinity for potassium cation, 15-crown-5 for sodium cation, and 12-crown-4 for lithium cation. Crown ethers are not the only macrocyclic ligands that have affinity for the potassium cation. Ionophores such as valinomycin also display a marked preference for the potassium cation over other cations.

Affinity for cations

Apart from its high affinity for potassium cations, 18-crown-6 can also bind to protonated amines and form very stable complexes in both solution the as well as gas phase. Some amino acids, such as lysine, contain a primary amine on their side chains. Those protonated amino groups can bind to the cavity of 18-crown-6 and form stable complexes in the gas phase. Hydrogen-bonds are formed between the three hydrogen atoms of protonated amines and three oxygen atoms of 18-crown-6. These hydrogen-bonds make the complex a stable adduct.

Azacrowns

Macrow cycles containing nitrogen and sulfer atoms have similar propertiesa s do these containing more that one kind of 21- and 18-membered diazacrown ether derivatives exhibit excellent calcium and magnesium selectivities and are widely used in ion-selective electrodes.

Some or all of the oxygen atoms in crown ethers can be replaced by nitrogens to form cryptands. A well-known tetrazacrown is cyclen in which there are no oxygens.