Chemistry of non-benzenoid aromatics Part-1

Paper 4201 B

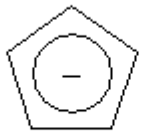
Organic Chemistry (Special-II)

Chemistry of non-benzenoid aromatics

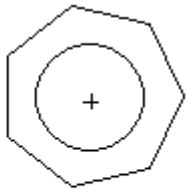
- **Tropones**
- **Tropolones**
- **Azulenes**
- **Metallocenes and**
- **Annulenes**

NON-BENZENOID AROMATICS- *Aromatic systems that are not comprised of benzene ring e.g.,*

Cyclopropenyl ction
2-π electrons



Cyclopentadienyl anion
6-π electrons



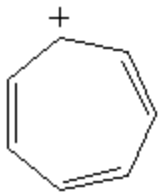
Cycloheptatrienyl cation
6-π electrons

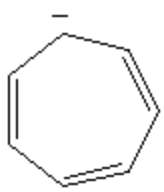
➢ **For a compound to be aromatic it must follow *Hückel's rule : i.e.***

1. Molecule must be ***cyclic and planar***
2. Must have an ***fully conjugated cyclic π electron cloud***.
3. It must ***have (4n + 2) π electrons*** i.e. compounds containing 2, 6, 10, 14, 18, …..π-electrons

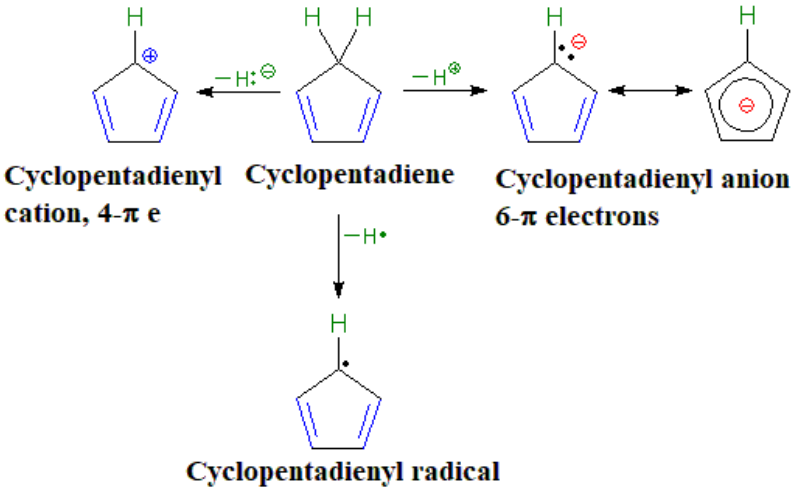
All three conditions should be fulfilled

For example, consider cycloheptatrienyl cation and anion-Both are cyclic, planar and exhibit continuous delocalization of π electrons , yet cycloheptatrienyl cation with 6π electrons is aromatic while cycloheptatrienyl anion with 8π electrons is not aromatic.

Cycloheptatrienyl cation 

 Cycloheptatrienyl anion

- Similarly, ***Cyclodentadiene anion is aromatic*** while, cyclopentadiene (lacks continuous delocalization and (4n + 2) π electrons , cyclopentadienyl radical and cyclopentadienyl cation (both lacking *(4n + 2) π electrons*) are not aromatic.

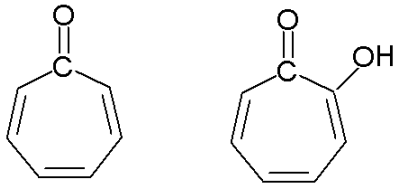


Cyclopentadienyl cation, 4-π e **Cyclopentadiene** **Cyclopentadienyl anion 6-π electrons**

Cyclopentadienyl radical

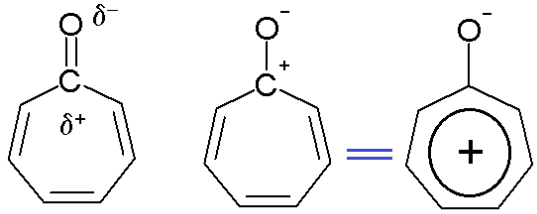
TROPONE AND TROPOLONE

Tropone (*2,4,6-cycloheptatrien-1-one*) and **tropolone** (*2-hydroxy-2,4,6-cycloheptatrien-1-one*) are non-benzenoid aromatic compound.



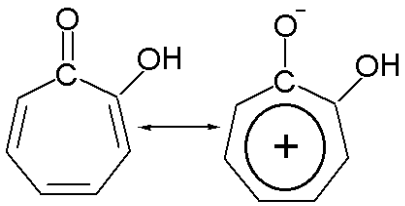
Tropone **Tropolone**

- It was proposed by Dewar that tropones could have aromatic properties as the polarization of C=O group will lead to a partial positive charge (δ+) on the carbon atom and a partial negative charge (δ–) on oxygen (**I**).
- In some extreme cases complete polarization of C=O bond is also possible (**II**) forming a tropylium ion ring which is an aromatic 6 π-electron system (**III**).



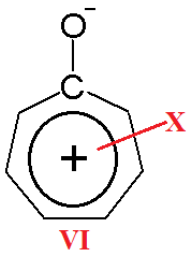
I **II** **III**

- Similarly, tropolone **IV** will also be aromatic by virtue of contribution by structure **V**



IV **V**

- **DIPOLE MOMENT** of numerous troponoids have been measured. They generally show high dipole moment indicating contribution from the polarized form (**VI**)



VI

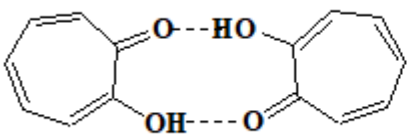
Compound	*Dipole moment (D)*
• Tropone	4.17
• 2-bromotropone	4.92
• Tropolone	3.53
• 3-bromotropolone	3.91

- **THE C=O STRETCHING VIBRATION** (IR spectrum) :

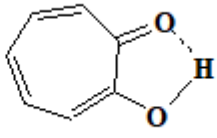
Tropone	**1635 cm^{-1} (liq)**
Tropolone	**1613cm^{-1} (solid)**
	1620 cm^{-1} (liq.)

These stretching frequencies are lower than the usual C=O vibration because ***of high degree of conjugation and high polarity***. This again indicates the greater contribution of structures like (**VI**).

- **THE C-OH STRETCHING VIBRATION TROPOLONE**(IR spectrum) :



Dimeric in solid state forms intramolecular H-bonding

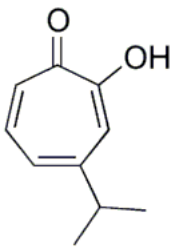


Monomeric in liquid state forms intramolecular H-bonding

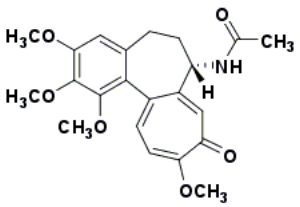
^{1}H NMR: Ring protons in tropone appear at approximately the same filed as that of benzene but those of tropolone appear slightly lower field.

OCCURRENCE

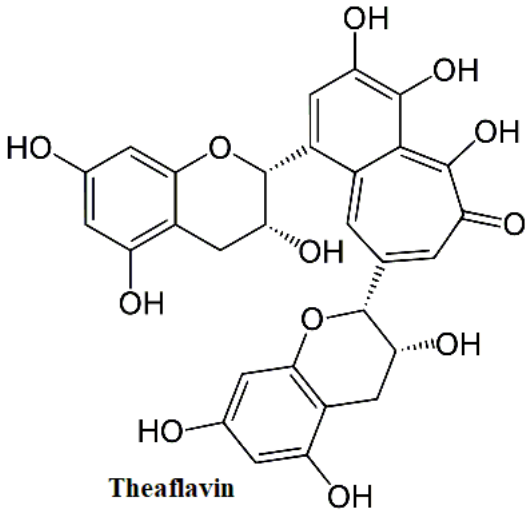
Tropones and tropolones are found in many natural products. Many of these can be isolated from essential oil of trees. e.g., Hinokitiol, (tropolone compound) exhibits antibacterial effect. Alkaloid Colchicine (with a tropolone ring) shows strong antitumor effects.



Hinokitiol



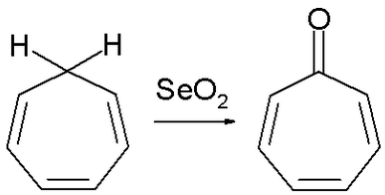
Colchicine



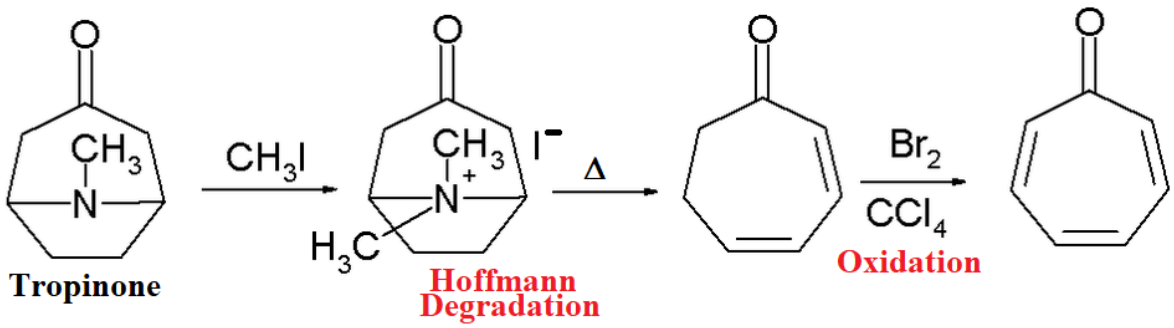
Theaflavin

SYNTHESIS

- By selenium dioxide oxidation of cycloheptatriene



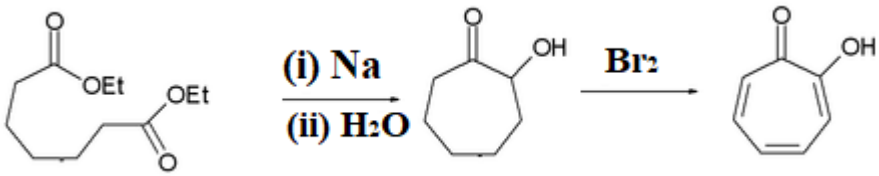
- From tropinone by following the reaction sequence shown below:



Tropinone

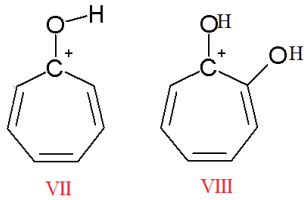
Hoffmann Degradation

- By acyloin condensation of ethyl ester of pimelic acid followed by oxidation by Br_2.

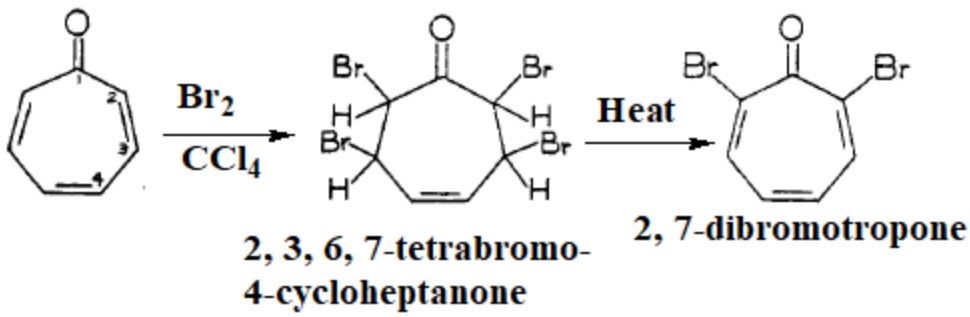


REACTIONS OF TROPONES AND TROPOLONES

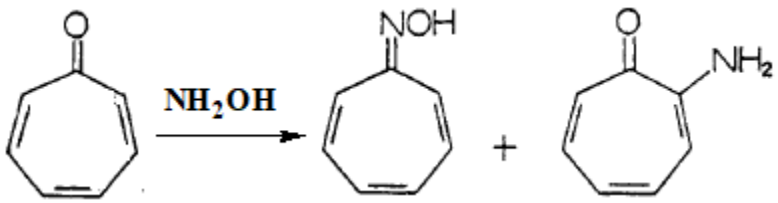
- In the presence of strong acids, tropone and tropolone form conjugate cations (VII and VIII, respectively) :
- They also form picrates



- **Electrophilic and free-radical substitution** should occur at the 2-position for tropone.
- **Bromination of tropone** and its derivatives does go in the 2- position as predicted, but tropones first tend to form addition compounds and later give substitution products by dehydrohalogenation



- **Nucleophilic reaction on tropone**: The reaction of tropone with hydroxylamine yields a mixture of the oxime and 2-aminotropone in proportions depending on the reaction conditions.



- A large number of **tropolone derivatives** with free 5-position undergo azo-coupling, nitrosation (followed by reduction), nitration reaction etc. at 5-position as shown below: