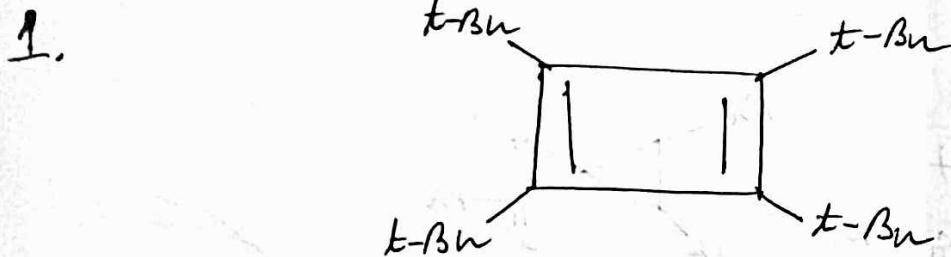
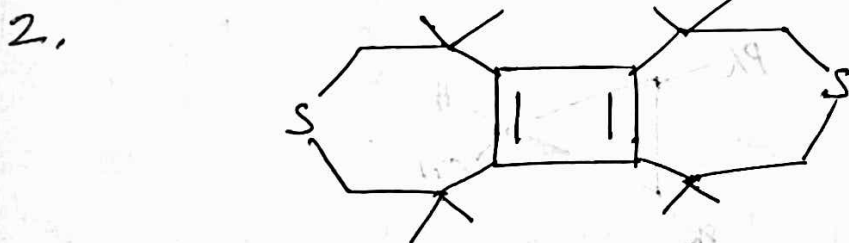


## Cyclobutadienes



This compound is stable at room temperature. Due to the presence of bulky substituents dimerization is sterically hindered.

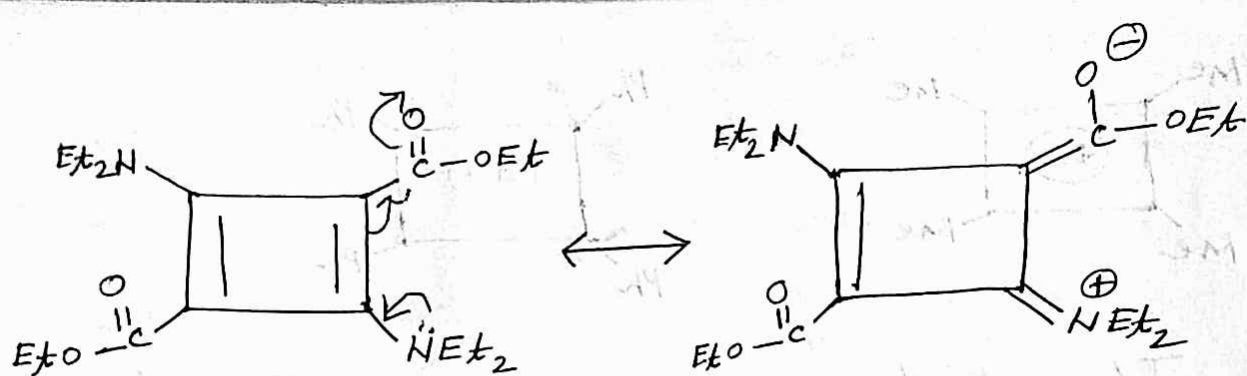
NMR spectra shows that the ring protons ( $\delta = 5.38$ ) is shifted upfield in comparison to the position expected for a nonaromatic compound. This indicates that the compound is antiaromatic.



This compound is stable at room temperature. Due to the presence of bulky substituents dimerization is sterically hindered.

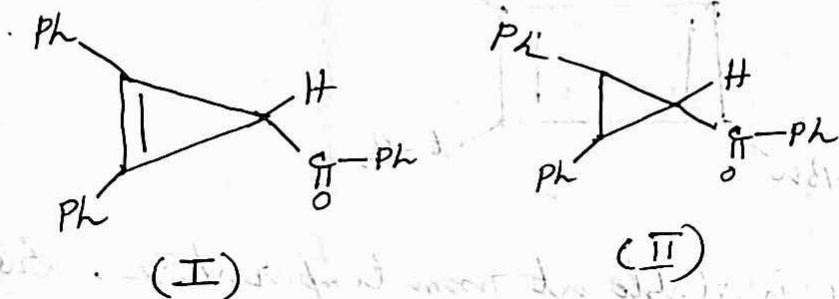
X-ray crystallography showed that the central ring is a rectangular diene with single and double bond lengths of 1.59 and 1.34 Å, respectively. The unusual long single bond distance may be due to the repulsion between the methyl groups.

3.



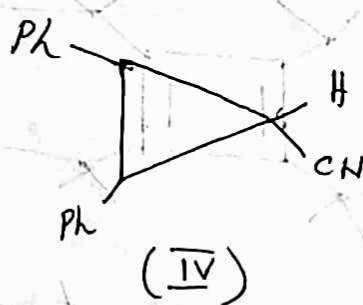
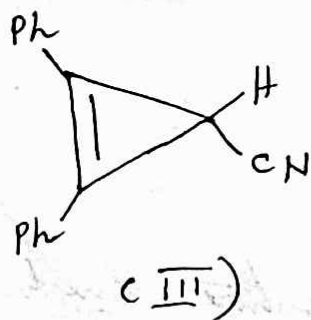
This compound is stable due to the resonance involving electron donating and electron withdrawing groups.

4.



Compound (I) loses its proton about 6,000 times slowly than compound (II). This indicates that (I) is much more reluctant to form cyclopropenyl carbanion than (II), which forms ordinary carbanion.

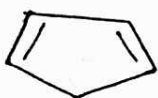
This carbanion of (I) is less stable than the corresponding ordinary carbanion.



Compound (III) loses its proton 10,000 times slowly than compound (IV).

# Cyclopentadiene

E.



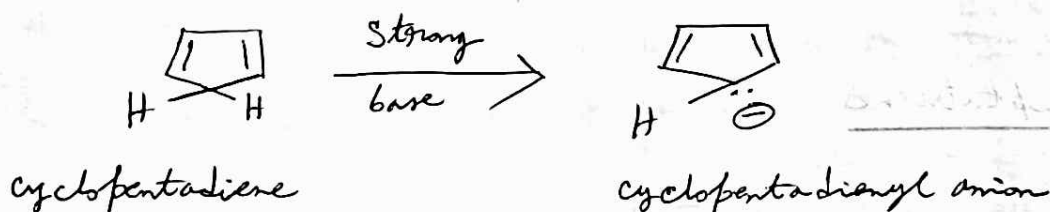
cyclopentadiene

Cyclopentadiene is not aromatic. Firstly, it has not proper number of  $\pi$  electrons and secondly the  $\pi$  electrons can not be delocalized about the entire ring because of the intervening  $sp^3$  hybridized  $-CH_2-$  group with no available  $p$ -orbital.

For this reason, cyclopentadiene is also not antiaromatic.

But, cyclopentadiene is unusually acidic. Its  $pK_a$  value is 16, and it is  $10^8$  times as acidic as a terminal alkyne. It is nearly as acidic as water — why?

Because of its acidity, cyclopentadiene can be converted to its anion by the treatment of moderately strong base.



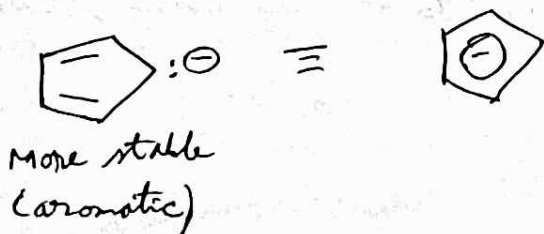
If the  $-CH_2-$  carbon atom becomes  $sp^2$  hybridized after it loses a proton, and the two electrons left can occupy the new  $p$ -orbital.

This new  $p$ -orbital can overlap with the  $p$ -orbitals on either side of it and give rise to a ring with six delocalized  $\pi$ -electrons.

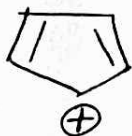
Huckel's rule predicts that the cyclopentadienyl anion (6  $\pi$  electrons) is aromatic.

^ (i.e. to gain the stability)

To achieve the aromaticity, with resonance energy 24-27 kcal/mol, cyclopentadiene shows acidic character.

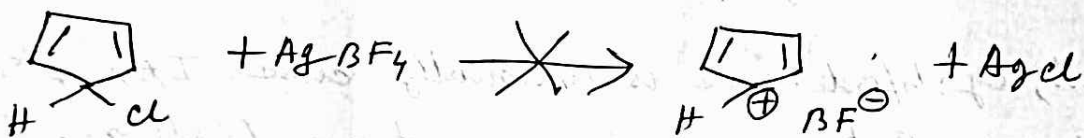


Because, the electrons are delocalized, all of the H atoms are equivalent, and this agrees with what NMR spectrum tells us.



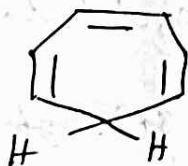
Cyclopentadienyl cation

Cyclopentadienyl cation is a cyclic, planar, conjugated species with  $4\pi$  electrons, i.e. it is antiaromatic and extremely unstable. It does not form.



No reaction occurs

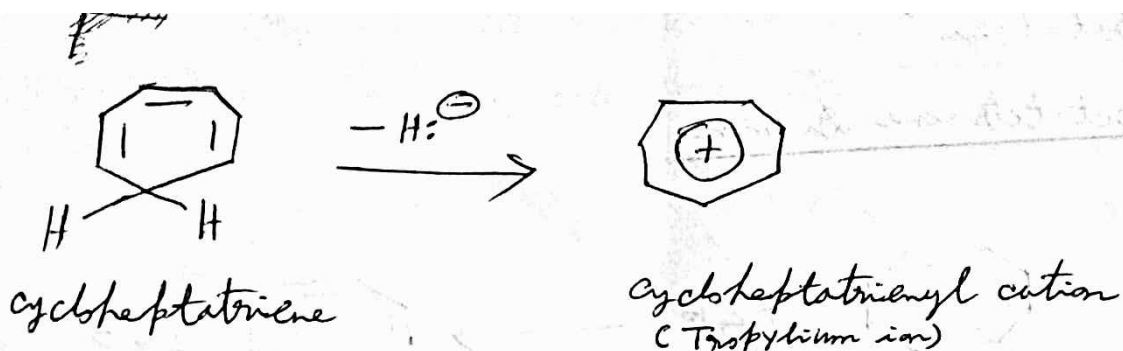
### Cycloheptatriene



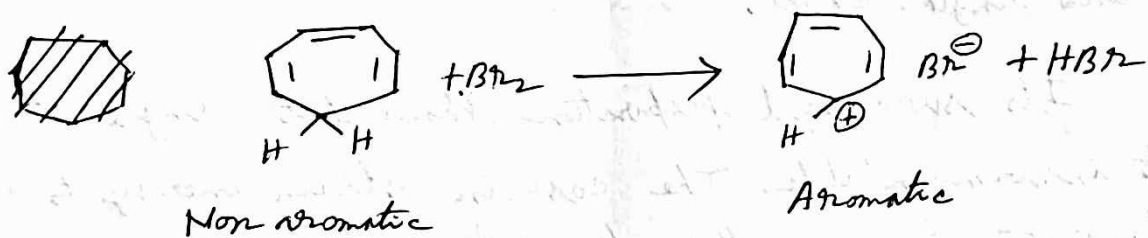
Cycloheptatriene (tropyliene)

Cycloheptatriene has six  $\pi$ -electrons. However, the six  $\pi$ -electrons can not be fully delocalized because of the presence of  $-CH_2-$  group which does not have an available  $p$ -orbital.

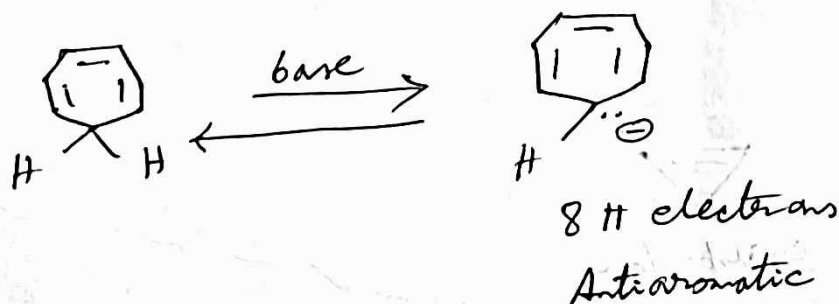
The loss of hydride ion from cycloheptatriene occurs with unexpected ease and the resulting cycloheptatrienyl cation (tropylium ion) is found to be unusually stable.



As a hydride ion is removed from the  $-CH_2-$  group of cycloheptatriene, a vacant p-orbital is created, and the carbon atom becomes  $sp^2$  hybridized. The cation that results has seven overlapping p orbitals containing six delocalized  $\pi$ -electrons. Therefore, this cation is an aromatic cation, and all of its hydrogen atoms should be equivalent. In fact, the NMR spectrum indicates that all seven ~~the~~ H atoms are equivalent.

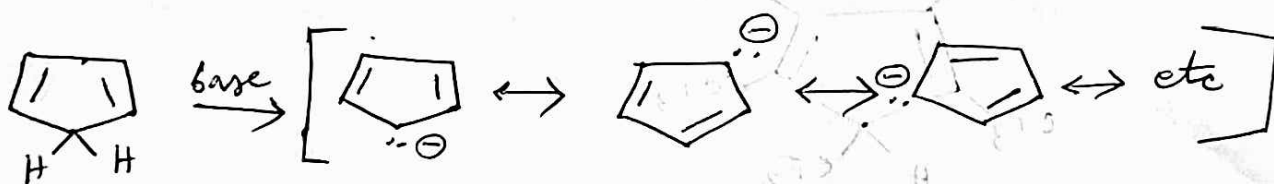


Cycloheptatriene, in sharp contrast to cyclopentadiene, has no unusual acidity. Because, cycloheptatrienyl anion is an antiaromatic species and extremely difficult to prepare due to its instability.



## Further Notes on Cyclopentadiene

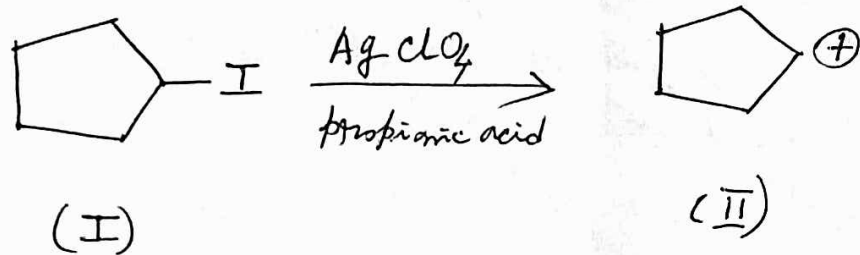
Cyclopentadiene has unexpected acidic properties ( $pK_a = 16$ ) since on loss of proton, the resulting carbanion is greatly stabilized by resonance.



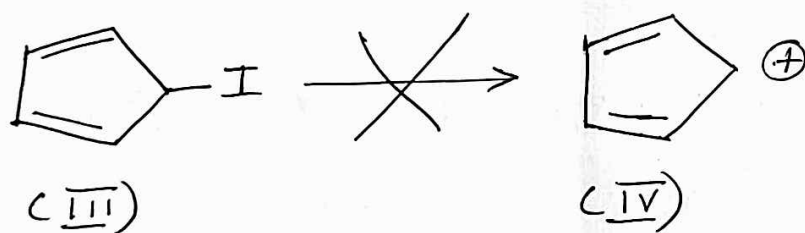
Resonance in this ion is greater than in pyrrole, thiophene and furan, since all five forms are equivalent.

As expected for an aromatic system, the cyclopentadienide ion is diatropic and aromatic ~~by~~ substitutions on it can be achieved.

5.



When (I) is treated with silver perchlorate in propionic acid, the molecule is rapidly solvolyzed.



Under the same conditions, (III) undergoes no solvolysis at all.

If (IV) were nonaromatic, it should be as stable as (II). The fact that it is so much more reluctant to form indicates (IV) is much less stable than (II).