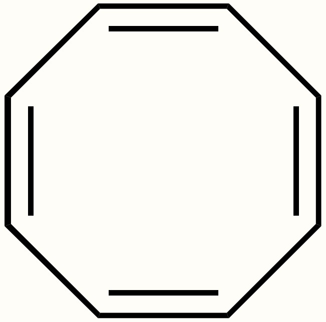
Lecture 25
Organic Chemistry 1

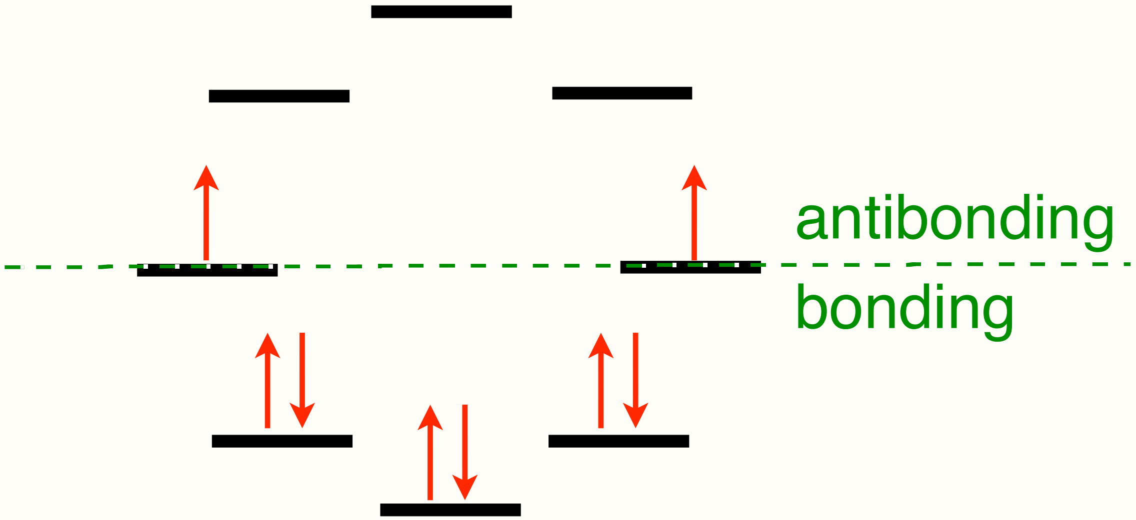
Professor Duncan Wardrop

April 6, 2010

Self Test Question

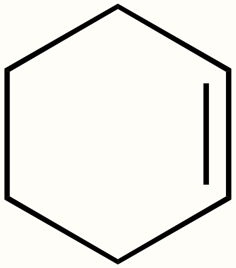
Below is the molecular orbital diagram for cyclooctatetraene; only the energy levels for each MO are indicated, not the MOs themselves. List the number of π-electrons in cyclooctatetraene and the number of π-electrons that would be required to fill the MO diagram below so that the system were aromatic, respectively.



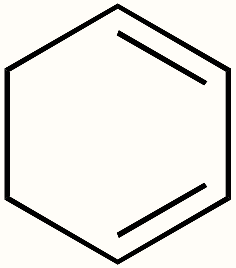


A. 8,3
B. 16, 10
C. 10, 3
D. 8,8
[✓ E.] 8, 6

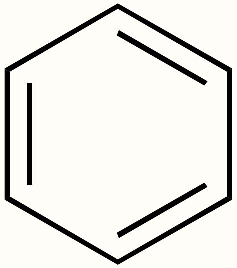
Aromaticity: Observations



120 kJ/mol



231 kJ/mol

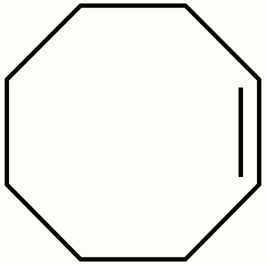


208 kJ/mol

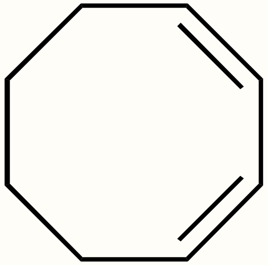
Observation: Heat of hydrogenation of benzene is 152 kJ/mol less than three times that of cyclohexene.

Hypothesis: Cyclic conjugation imparts *extra stability* compared to acyclic π-system (more MO *net bonding*).

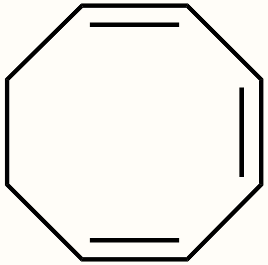
Aromaticity: Observations



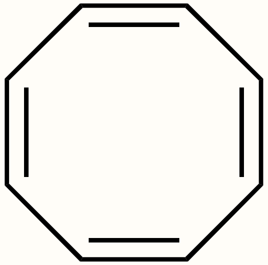
97 kJ/mol



205 kJ/mol



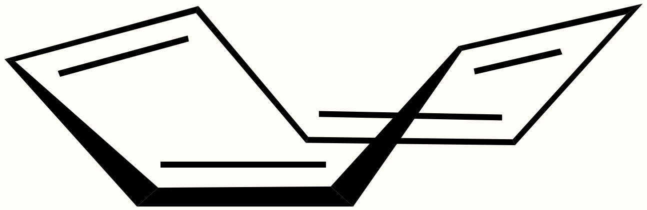
303 kJ/mol



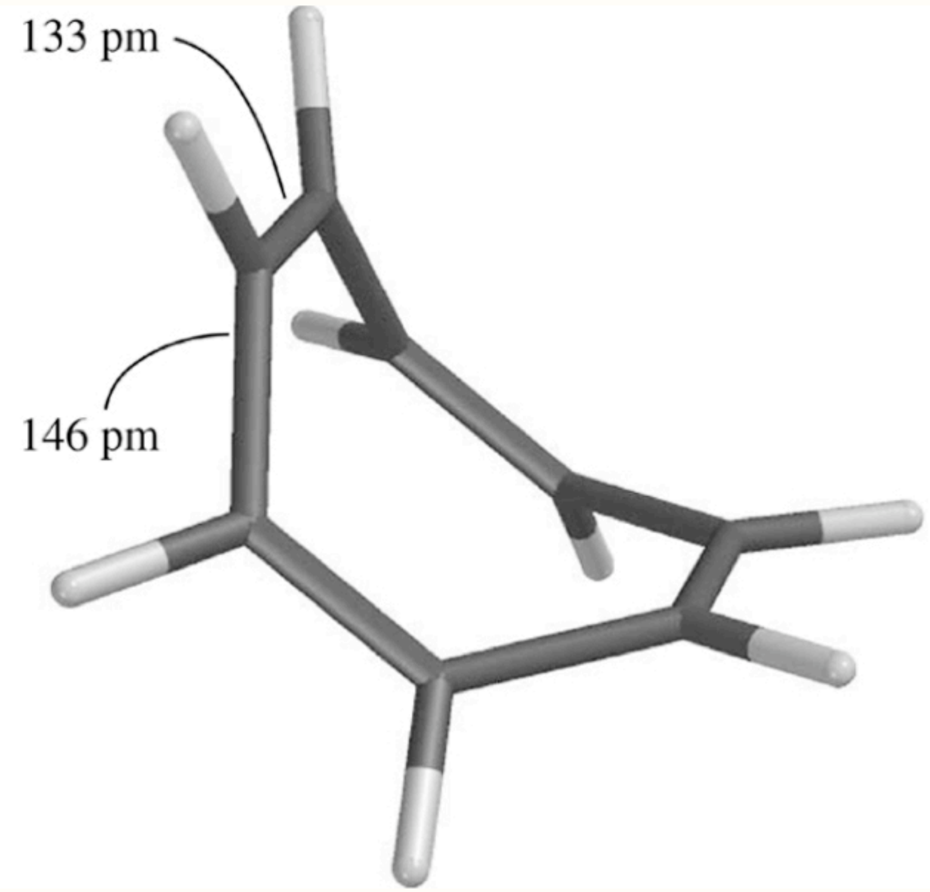
410 kJ/mol

Observation: Heat of hydrogenation of cyclooctatetraene is even greater than four times that of cyclooctene.

Aromaticity: Observations

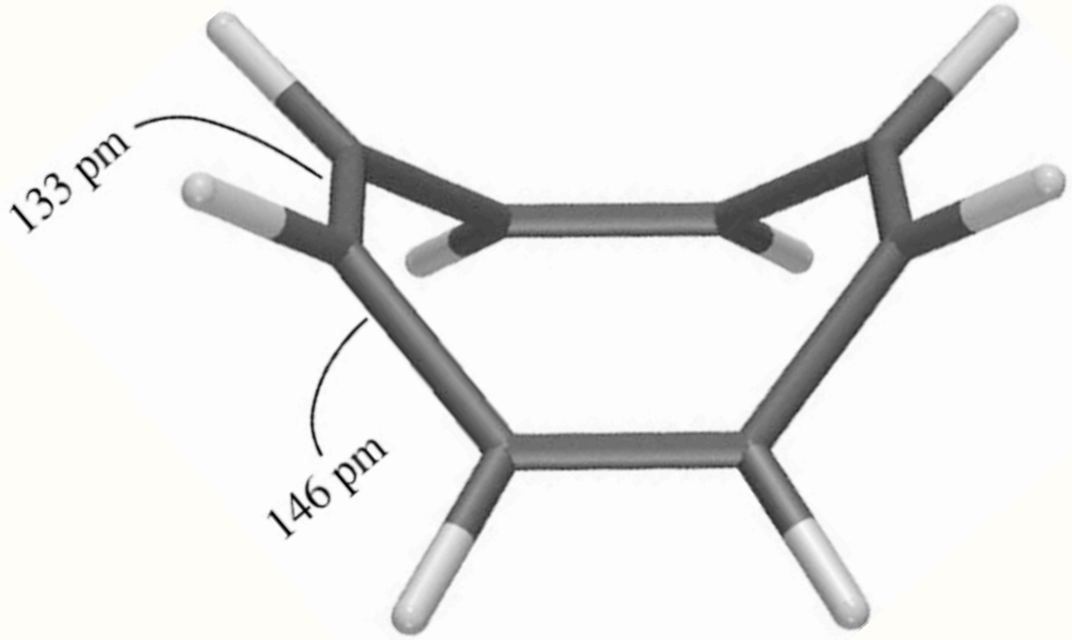


"tub" conformation



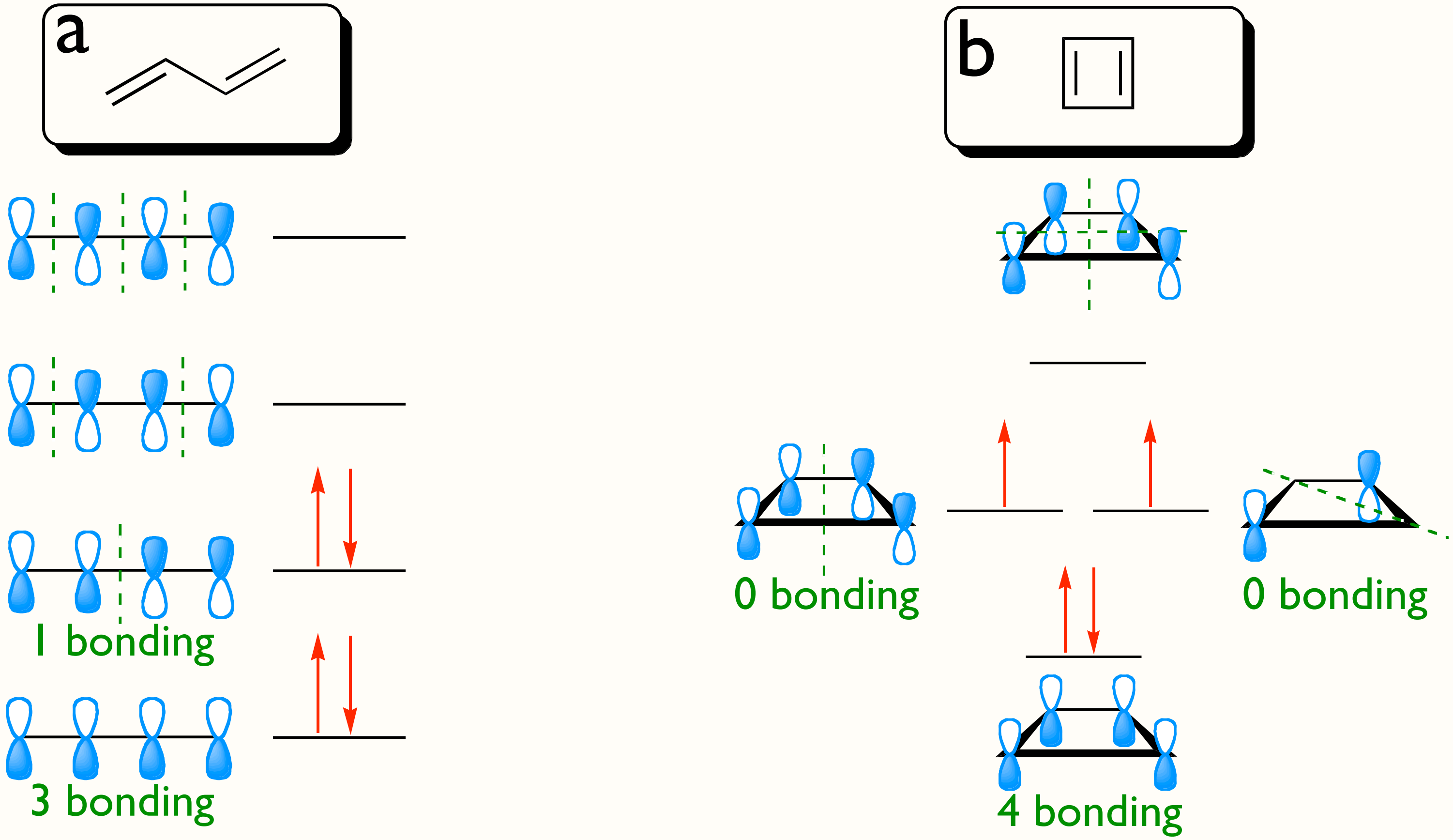
Observation: In order to avoid cyclic conjugation, cyclooctatetraene adopts a non-planar conformation.

Cyclooctatetraene Adopts A Bucket Conformation



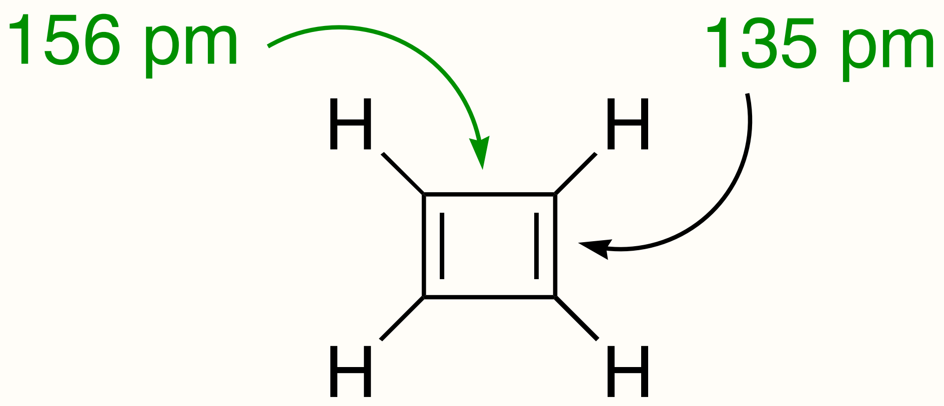
Observation: In order to avoid cyclic conjugation, cyclooctatetraene adopts a non-planar conformation.

Aromaticity: Observations



Observation: The filled MOs for cyclobutadiene contain the same amount of *net bonding* than the acyclic 1,3-butadiene; no extra stability = not aromatic

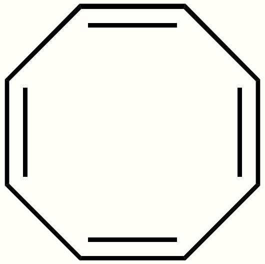
Aromaticity: Observations



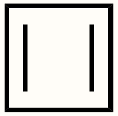
Observation: MO orbital calculations give two different bond lengths for cyclobutadiene suggesting no delocalization of the alkenes; act as if not conjugated

Observation: Cyclobutadiene is very difficult to prepare; it is very high in energy (unstable)

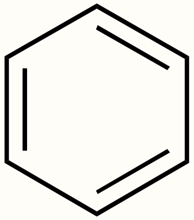
Aromaticity: Initial Conclusion



antiaromatic
(when planar)



antiaromatic
(when square)



aromatic

antiaromatic: destabilized by cyclic delocalization of π-electrons

aromatic: extra stabilization by cyclic delocalization of π-electrons

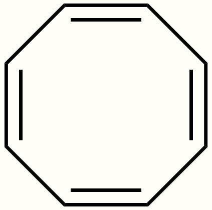
Conclusion: Aromaticity depends on the number of π-electrons that can be cyclically delocalized

Hückel's Rule

Aromatic: compounds that posses extra stability as a result of cyclically delocalized π-systems with an odd number of electrons *pairs* ($4n + 2$; n = integer).

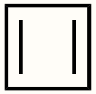
Antiaromatic: compounds that are destabilized as a result of cyclically delocalized π-systems with an *even* number of electron *pairs* ($4n$; n = integer).

4 π-electron pairs
8 π-electrons



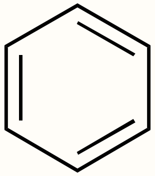
antiaromatic
(when planar)

2 π-electron pairs
4 π-electrons



antiaromatic
(when square)

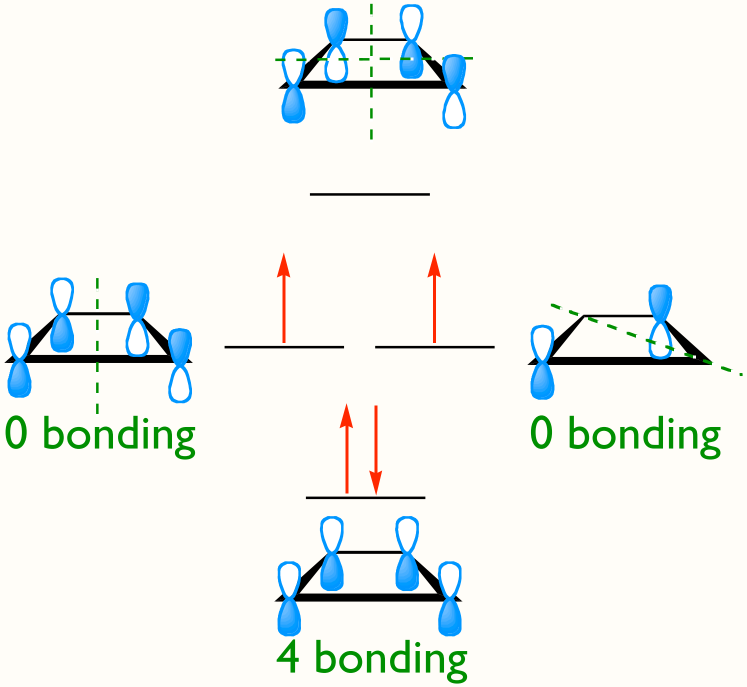
3 π-electron pairs
6 π-electrons



aromatic

Hükel's Rule

There can only be one lowest MO with zero nodes. Therefore, there is always an *odd* number of *bonding* MOs. An odd number of *bonding* MOs requires an odd number of π-electrons to fill a closed shell.



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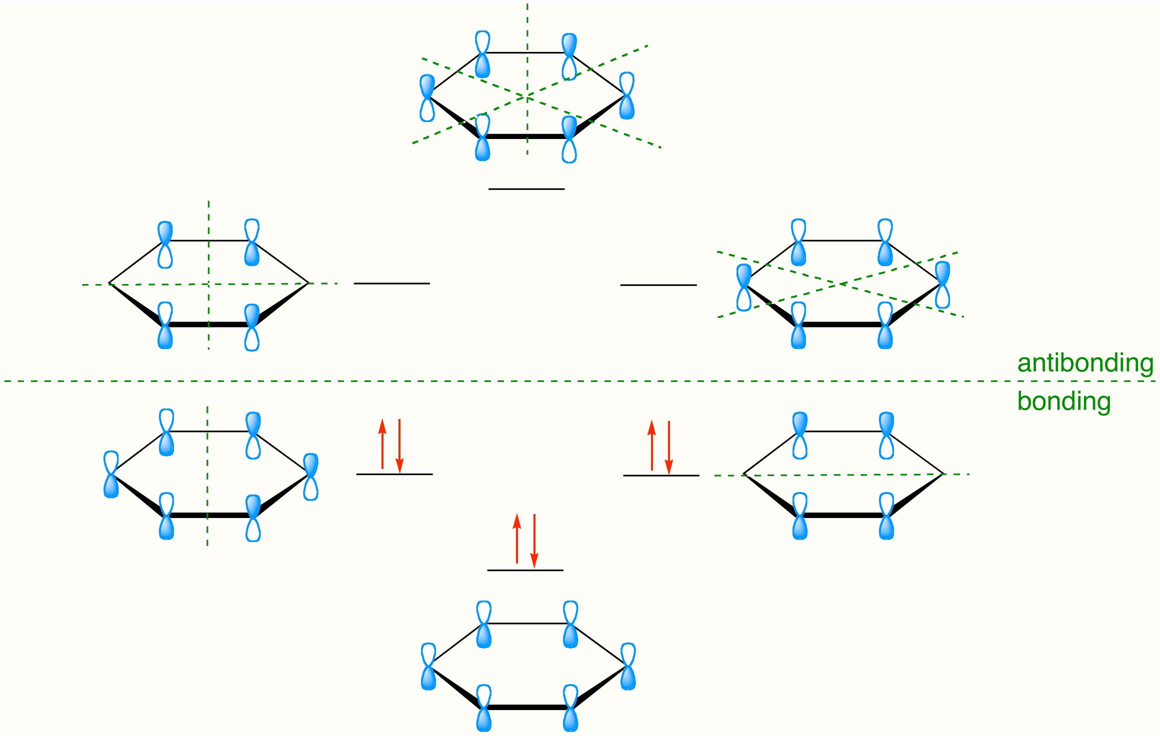
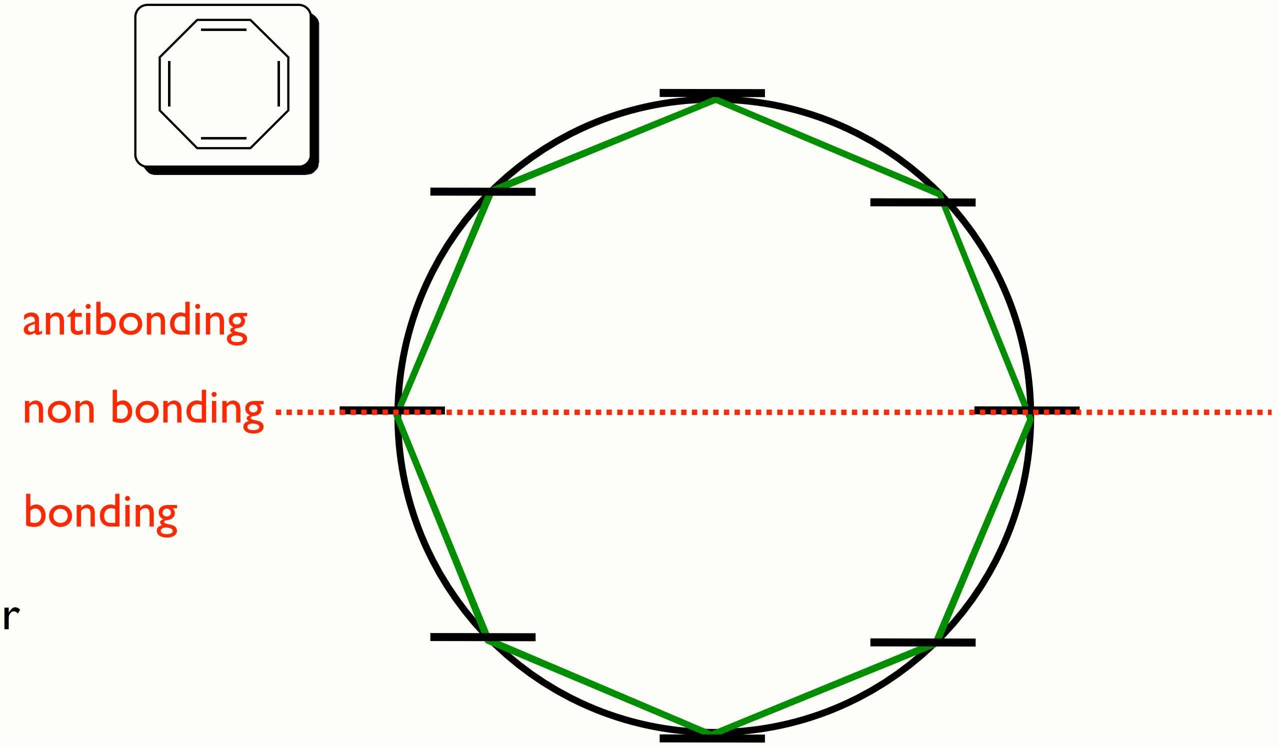


Frost Circle

Frost Circle: a mnemonic for determining the number and relative energies for the π-molecular orbitals of cyclically conjugated systems.

Steps:

1. Draw a circle.
2. Inscribe a regular polygon inside the circle so that one of the corners is at the bottom.
3. Draw a horizontal line at each vertex intersecting the circle. *These are the energy levels of the MOs.*
4. Draw a dotted-line through the center of the circle. *This represents the boundary between bonding and antibonding orbitals. Orbitals coinciding with this line are nonbonding.*



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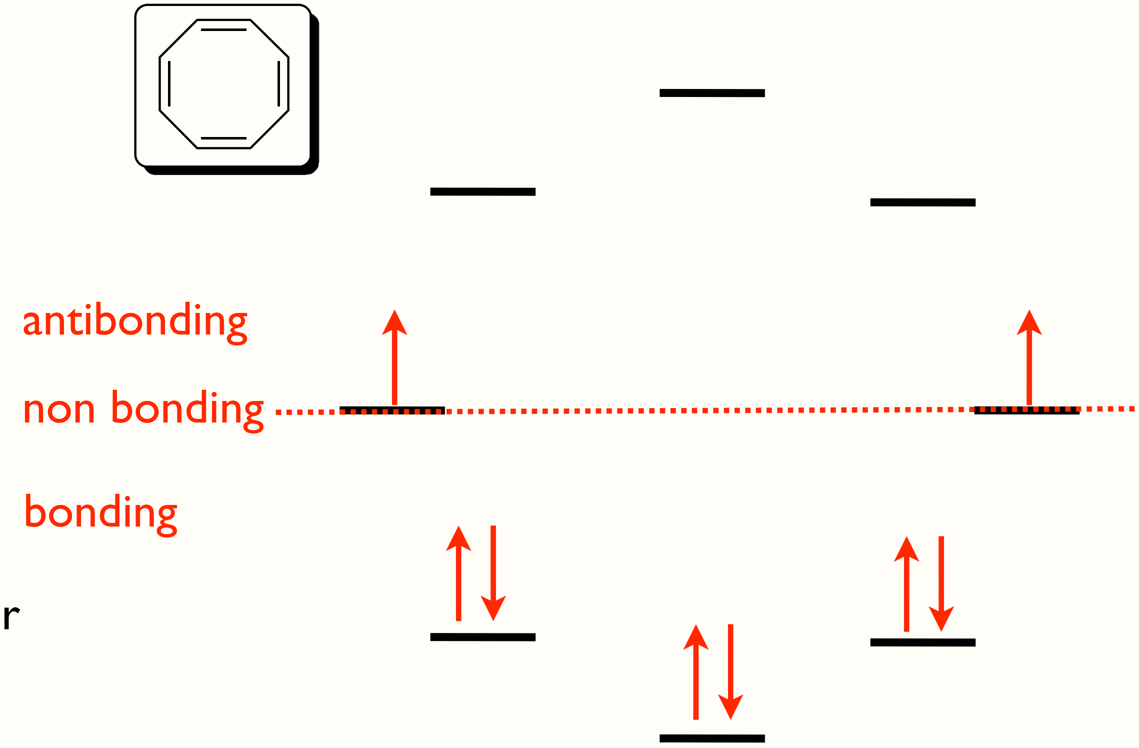
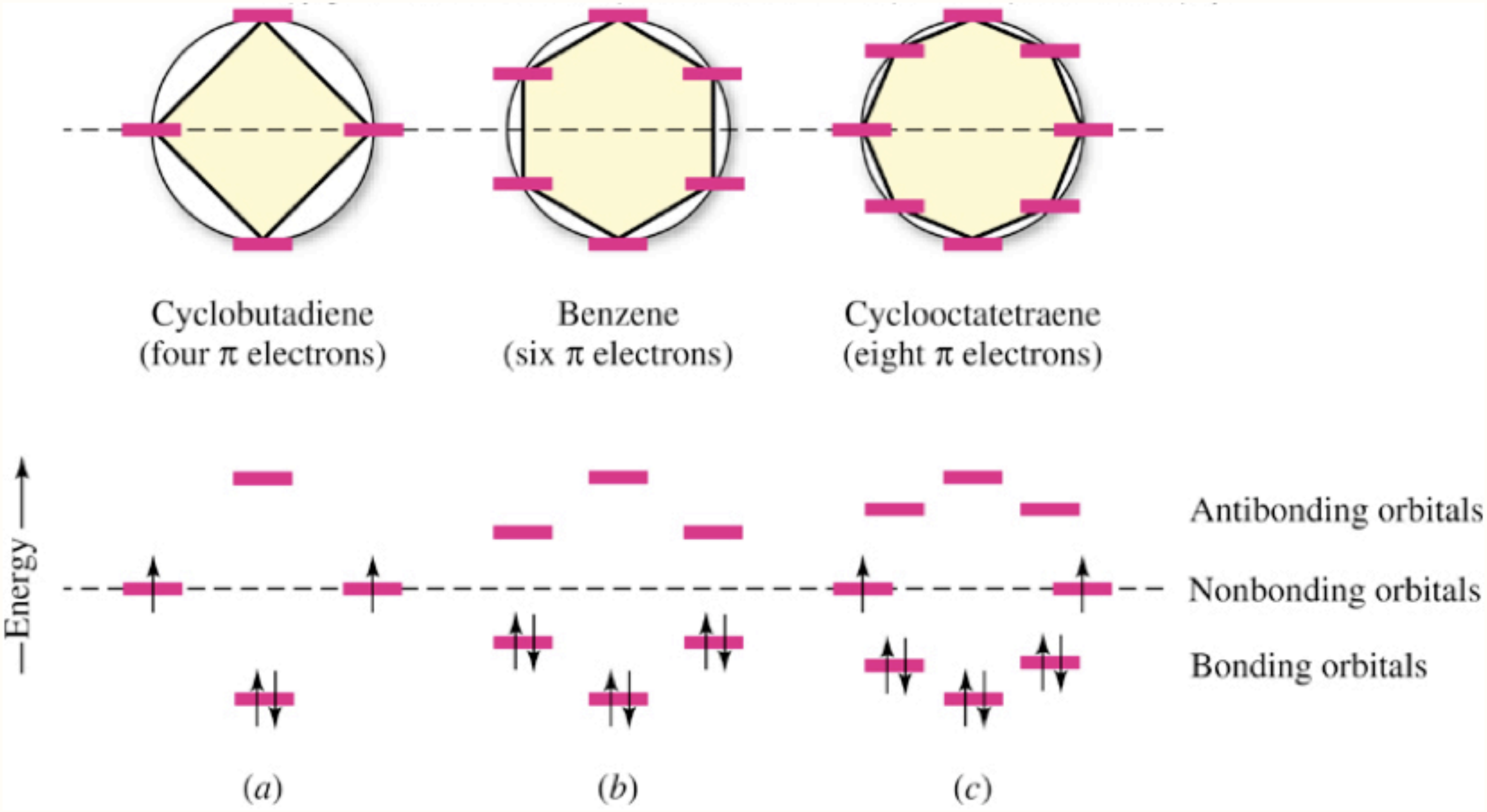
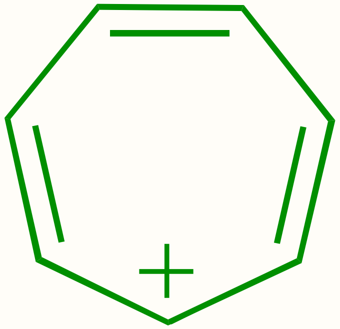


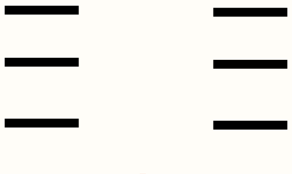
Frost Circles



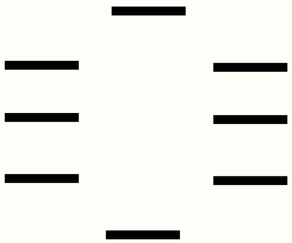
Self Test Question

Which MO diagram best represents the fully conjugated cycloheptatrienyl carbocation (a.k.a. tropylium cation)?

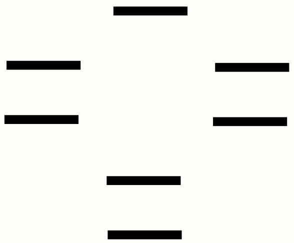




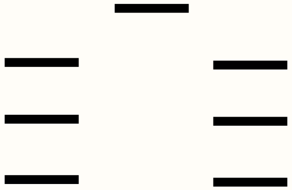
[✓ A]



B

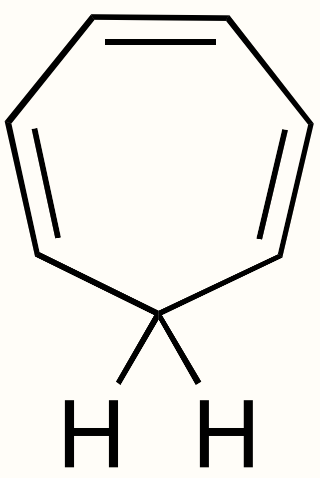


C

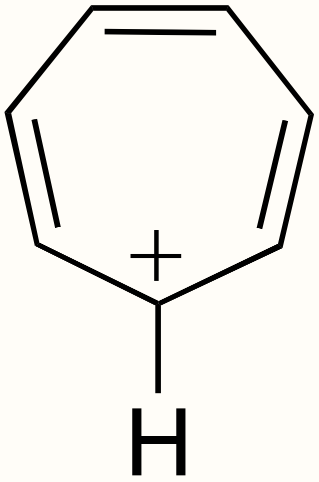


D

Aromatic Effects on Properties



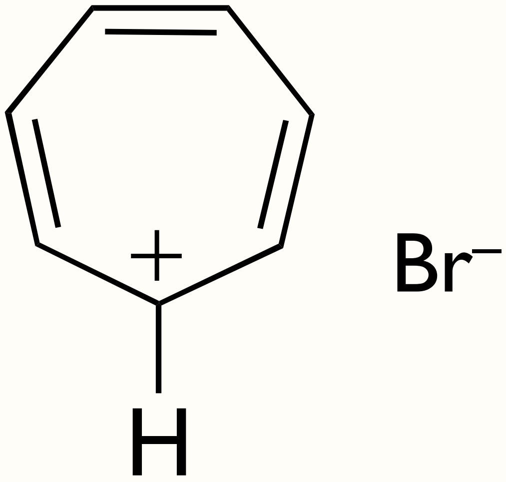
6 π-electrons
not fully conjugated =
not aromatic



6 π-electrons
fully conjugated =
aromatic

Aromatic Effects on Properties

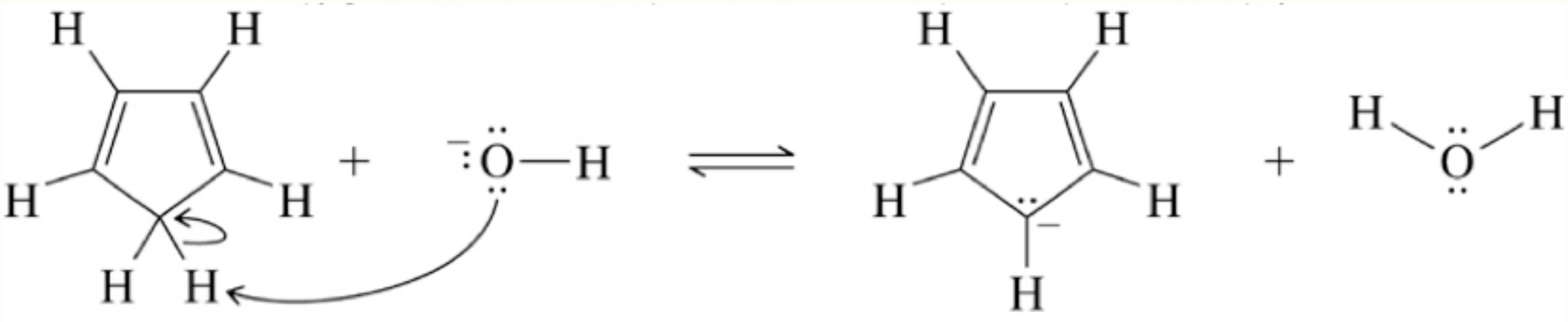
- tropylium cation is so stable, that tropylium bromide is ionic rather than covalent
- high mp = 203 °C
- soluble in water
- insoluble in diethyl ether



6 π-electrons
fully conjugated =
aromatic

Aromatic Effects on Properties

Cyclopentadiene is only a slightly weaker acid that water; it's conjugate bases is exceptionally stable since it is aromatic.



Cyclopentadiene
$pK_a = 16$

Hydroxide
ion

Cyclopentadienyl anion
aromatic

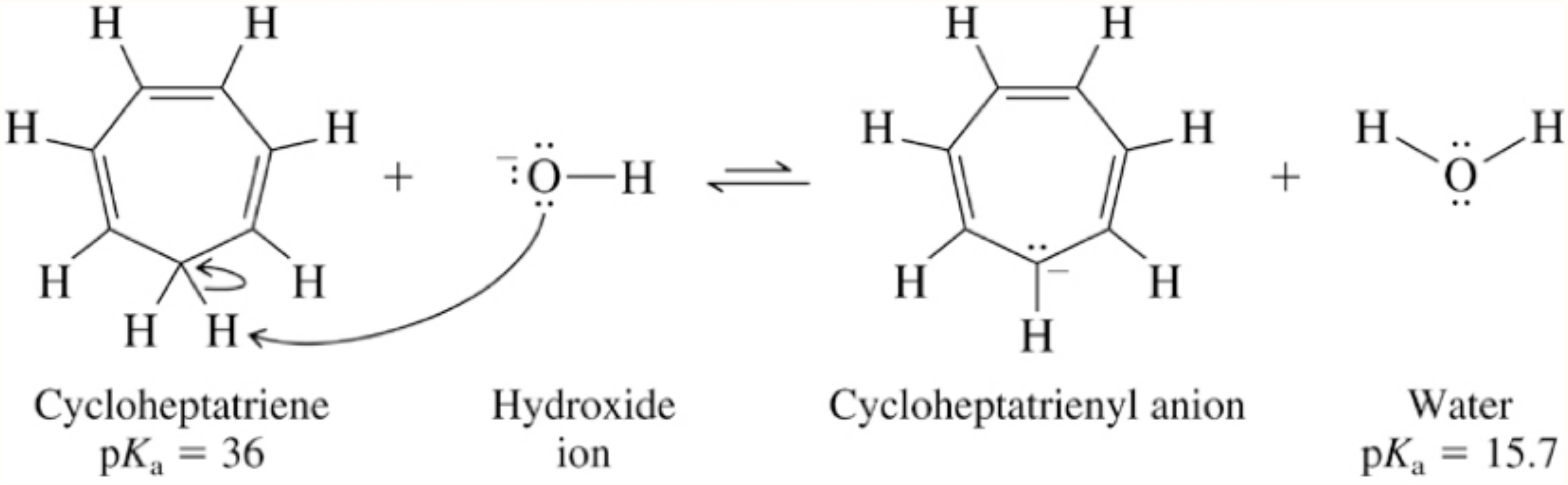
Water
$pK_a = 15.7$

$$Keq = 10^{-[pKa(left)\ -\ pKa(right)]}$$

$$Keq = 10^{-0.7}$$

Aromatic Effects on Properties

The conjugate base of cycloheptatriene is antiaromatic. Consequently, cycloheptatriene is a much weaker acid than cyclopentadiene.



$$Keq = 10^{-[pKa(left) - pKa(right)]}$$

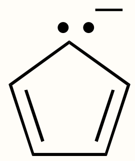
$$Keq = 10^{-20.3}$$

Self Test Question

Which of the following species is antiaromatic?

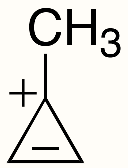
√ cyclic conjugation
√ odd e– pairs (4n+2)
= aromatic

A



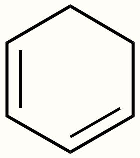
√ cyclic conjugation
√ odd e– pairs (4n+2)
= aromatic

B



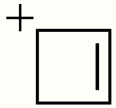
X no cyclic conjugation
X even e– pairs (4n)
= neither

C



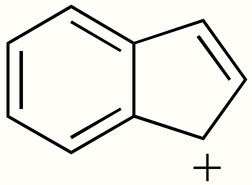
X no cyclic conjugation
√ odd e– pairs (4n+2)
= neither

D



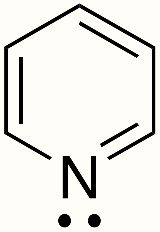
√ cyclic conjugation
√ even e– pairs (4n)
= antiaromatic

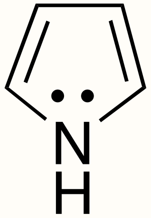
[✓ E]

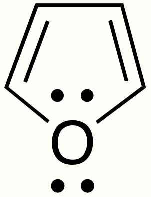


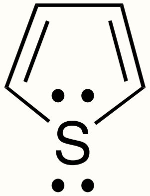
Heterocyclic Aromatic Compounds

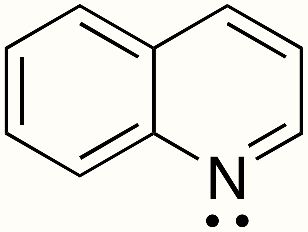
Heteroatom: any atom other than C or H; typically, but not limited to N, O, Si, P, S, Se

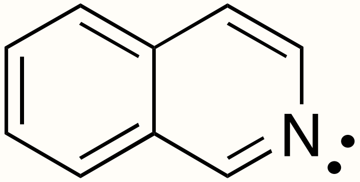

pyridine

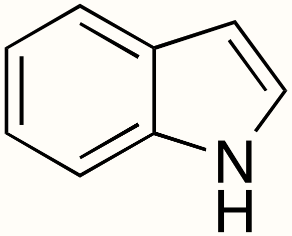

pyrole


furan


thiophene

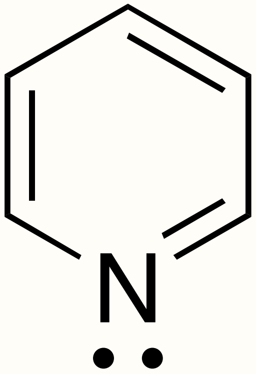

quinoline


isoquinoline

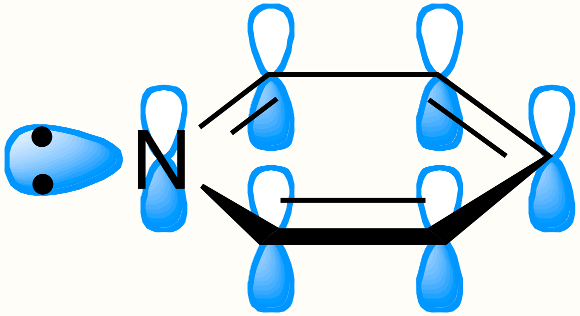

indole

There are more examples in your text; I will only ask you to know these 7.

Hükel's Rule and Lone Pairs on Heteroatoms



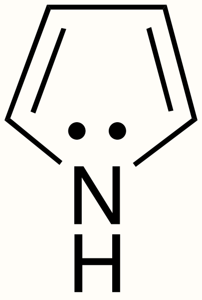
pyridine



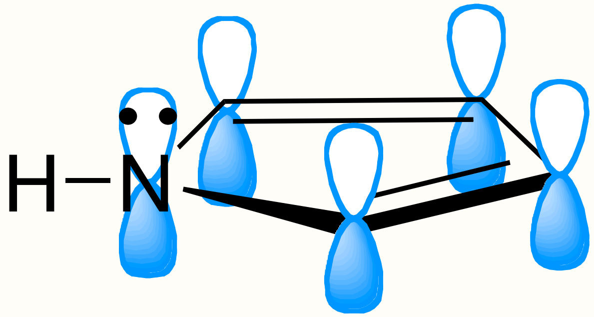
***convention**: lone pairs that are not part of the aromatic π-system are written outside of the ring; lone pairs that are part of the aromatic π-system are written inside the ring*

- 6 π-electrons in the ring
- lone pair of electrons on nitrogen is in an sp2-hybridized orbital that is perpendicular to ring π-system
- lone pairs must be in coplanar orbitals to delocalize
- lone pair is not counted in Hükel's rule

Hükel’s Rule and Lone Pairs on Heteroatoms



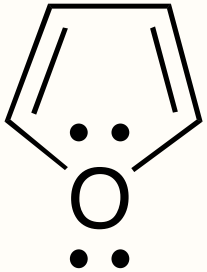
pyrole



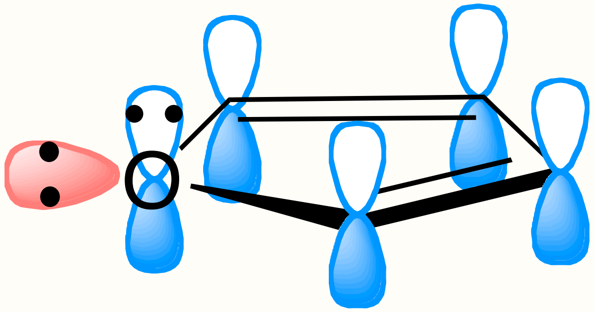
***convention**: lone pairs that are not part of the aromatic π-system are written outside of the ring; lone pairs that are part of the aromatic π-system are written inside the ring*

- lone pair on nitrogen does participate in ring π-system so that ring is aromatic and more stable
- lone pair of electrons on nitrogen is in an pure p-orbital that is coplanar to the ring π-system
- lone pair is counted in Hükel’s rule

Hükel's Rule and Lone Pairs on Heteroatoms



furan

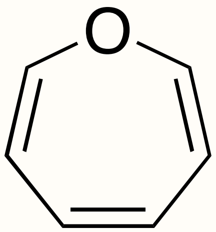


convention: *lone pairs that are not part of the aromatic π-system are written outside of the ring; lone pairs that are part of the aromatic π-system are written inside the ring*

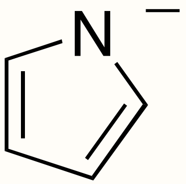
- only one lone pair is in a pure p-orbital coplanar to the ring π-system (is counted in Hükel's rule)
- the second lone pair is in an sp2-hybridized orbital perpendicular to the ring π-system (not counted in Hükel's rule)

Self Test Question

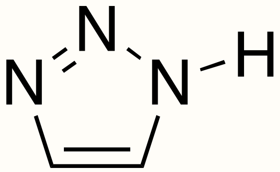
Which compound below is either not aromatic or antiaromatic? *Lone pairs are not shown.*



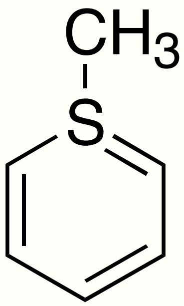
A



B



C



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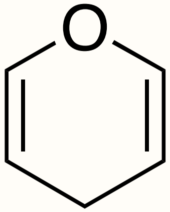
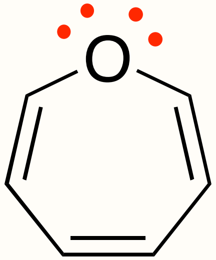


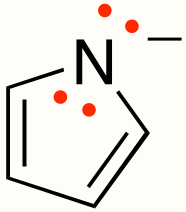
E

Self Test Question

Which compound below is neither aromatic or antiaromatic, i.e. is non-aromatic



A



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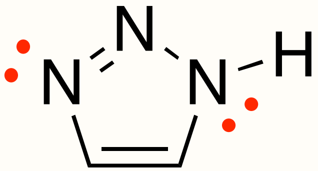

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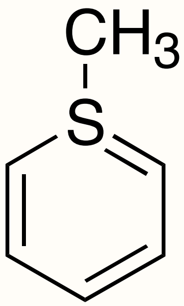

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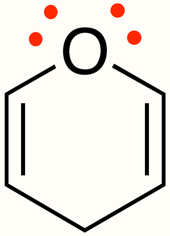


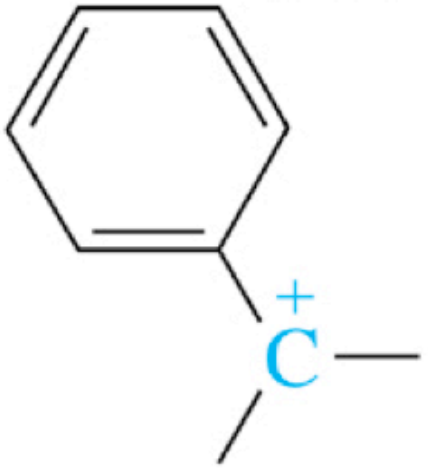
[✓ E]

Reactions of Functional Groups Attached to Aromatic Rings

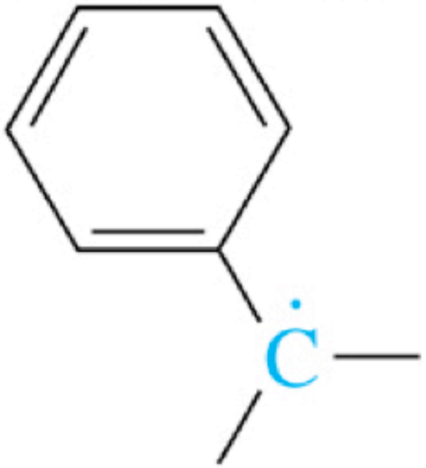
Sections: 11.12-11.17
You are responsible for sections 11.10, 11.11, 11.13,11.18, 11.21, 11.23, 11.24

Conjugation with Benzene

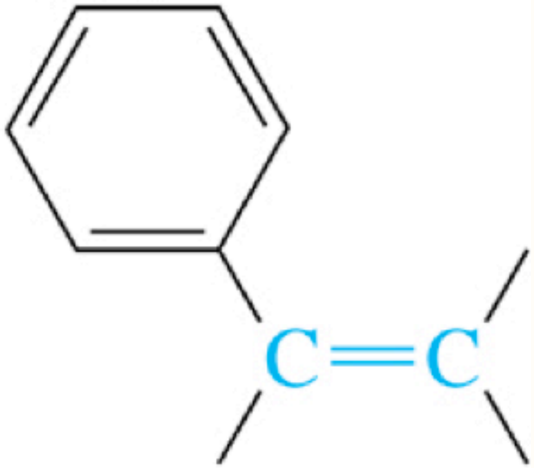
benzyllic carbon: carbon atom attached to a benzene ring
benzyllic hydrogen: hydrogen attached to a benzyllic carbon



Benzylic carbocation



Benzylic radical



Alkenylbenzene

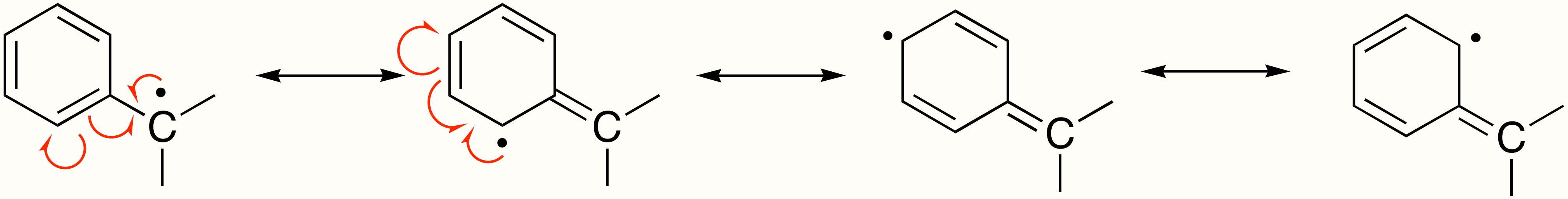
Free Radical Halogenation

benzyllic carbon: carbon atom attached to a benzene ring
benzyllic hydrogen: hydrogen attached to a benzyllic carbon

- benzyllic radical is analogous to an allylic radical
- both are stabilized by resonance
- benzyllic is more stabilized than allylic because more resonance structures
- see lecture 23 (April 7) for reactivity of allylic systems

Free Radical Halogenation

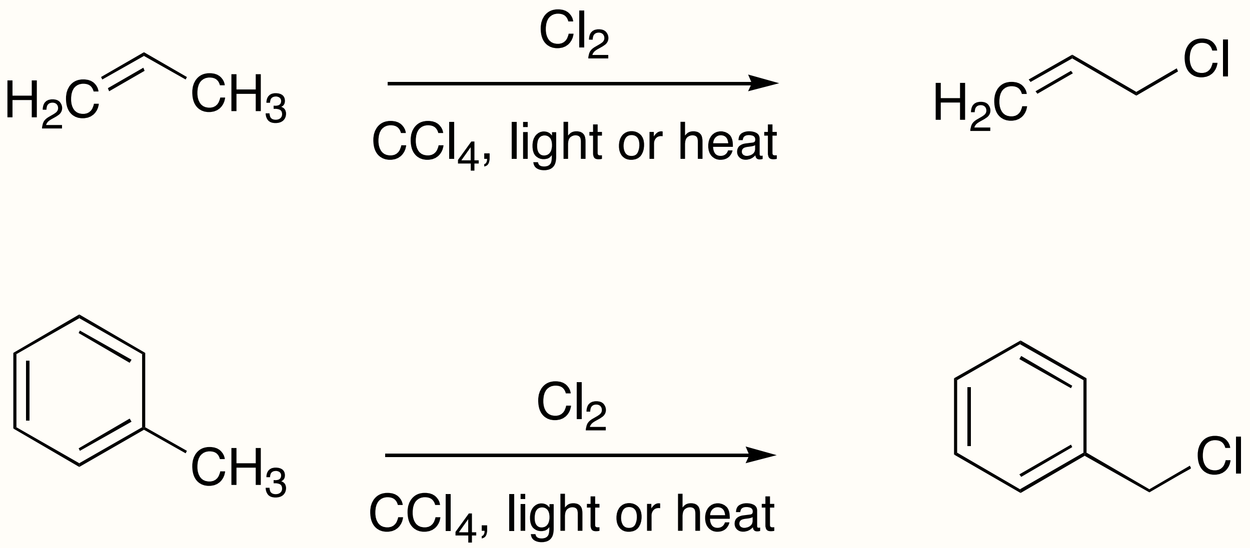
Resonance in a benzyl radical



unpaired electron is delocalized over benzylic carbon as well as the ortho & para carbon ataoms

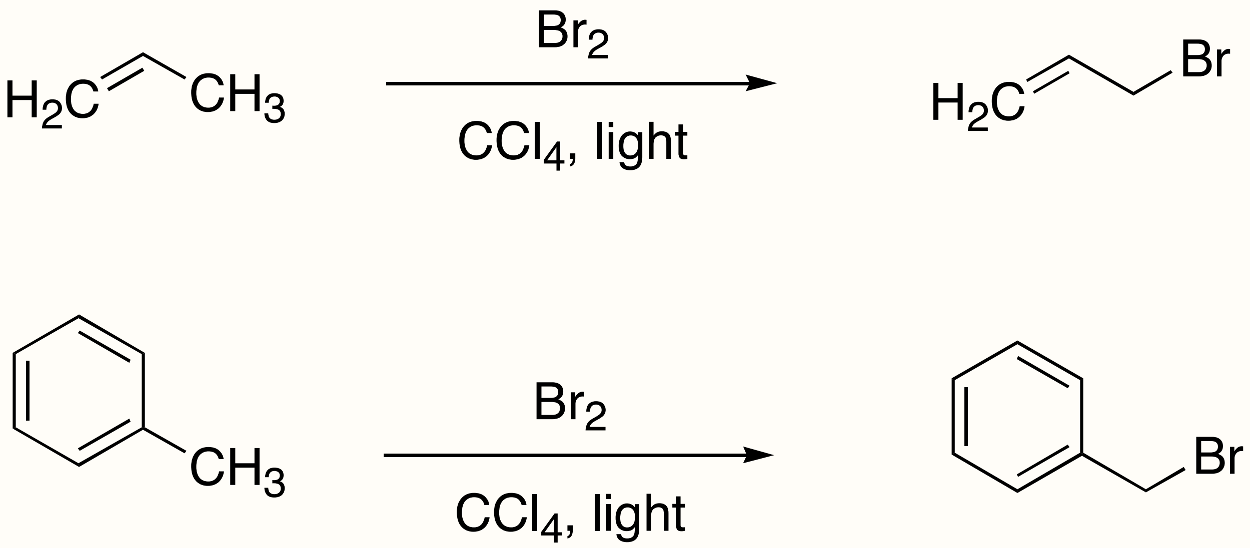
Free Radical Halogenation

Free radical halogenation at the benzylic position is analogous to the same reaction at the allylic position (see lecture 23 for reactivity pattern and mechanism)



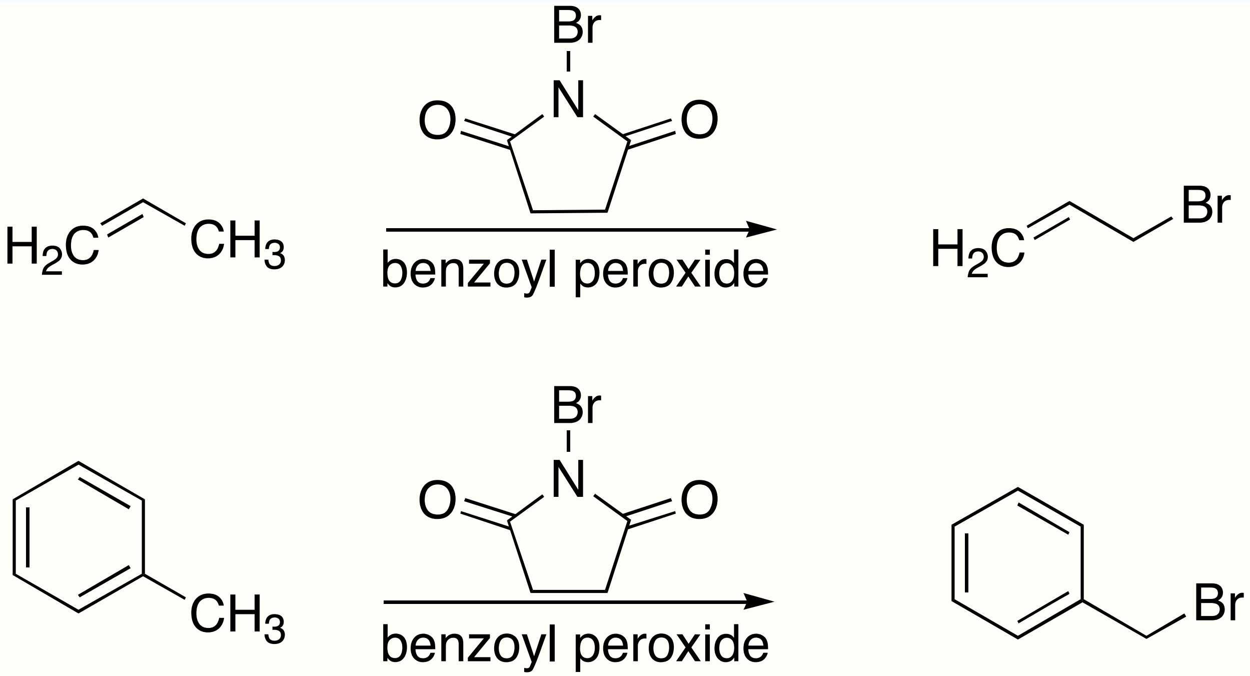
Free Radical Halogenation

Free radical halogenation at the benzylic position is analogous to the same reaction at the allylic position (see lecture 23 for reactivity pattern and mechanism)



Free Radical Halogenation

Free radical halogenation at the benzylic position is analogous to the same reaction at the allylic position (see lecture 23 for reactivity pattern and mechanism)



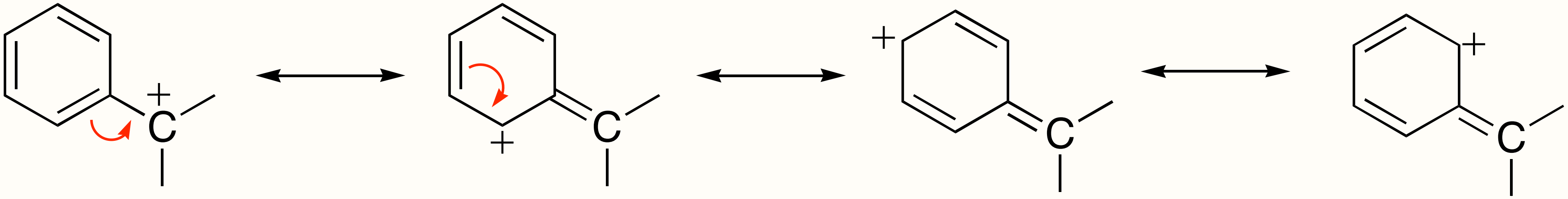
S_N1 Reactions of Benzylic Halides

benzyllic carbon: carbon atom attached to a benzene ring
benzyllic hydrogen: hydrogen attached to a benzyllic carbon

- benzyllic carbocation is analogous to an allylic carbocation
- both are stabilized by resonance
- benzyllic is more stabilized than allylic because more resonance structures
- see lecture 23 (April 7) for reactivity of allylic systems

S_N1 Reactions of Benzylic Halides

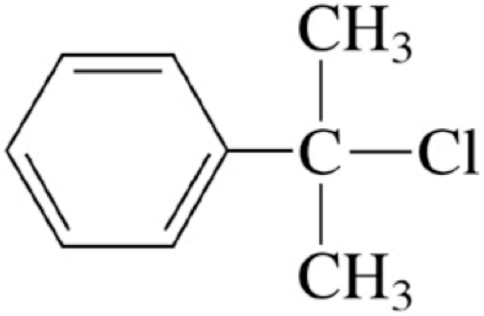
Resonance in a benzylic carbocation



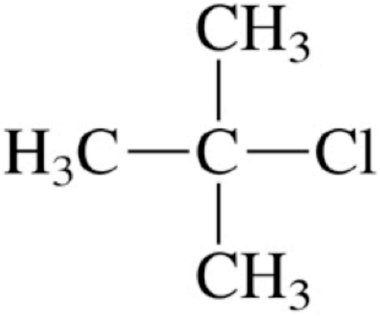
positive charge is delocalized over benzylic carbon as well as the ortho & para carbon ataoms

S_N1 Reactions of Benzylic Halides

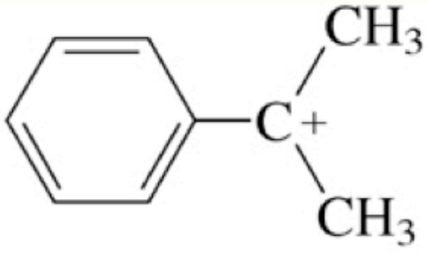
SN1 of benzylic halides is faster since carbocation formed is more stable (lower NRG)



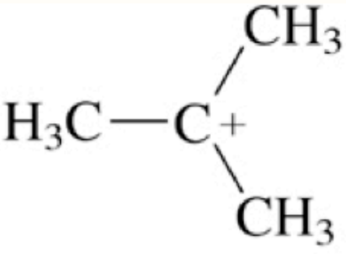
2-Chloro-2-phenylpropane
More reactive: *k*(rel) 620



tert-Butyl chloride
Less reactive: *k*(rel) 1.0



is more stable than



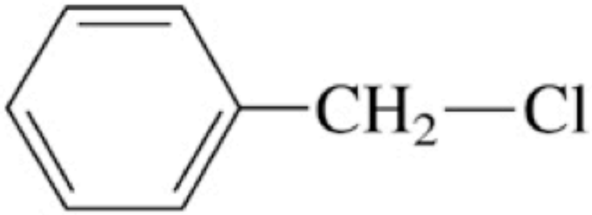
1-Methyl-1-phenylethyl cation

tert-Butyl cation

S_N2 Reactions of Benzylic Halides

S$_N$2 of benzylic halides is faster than allylic halides.

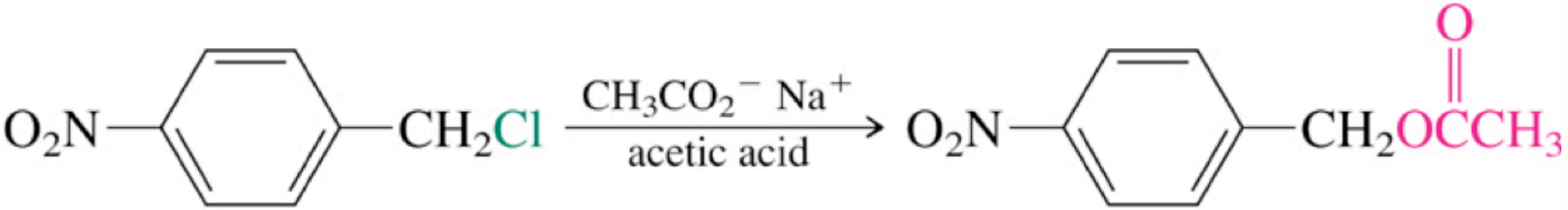
How can this be explained if there is no carbocation intermediate?



$H_2C{=}CHCH_2{-}Cl$

$CH_3CH_2CH_2{-}Cl$

Benzyl chloride	Allyl chloride	1-Chloropropane
Most reactive: *k*(rel) 197	*k*(rel) 80	Least reactive: *k*(rel) 1.0

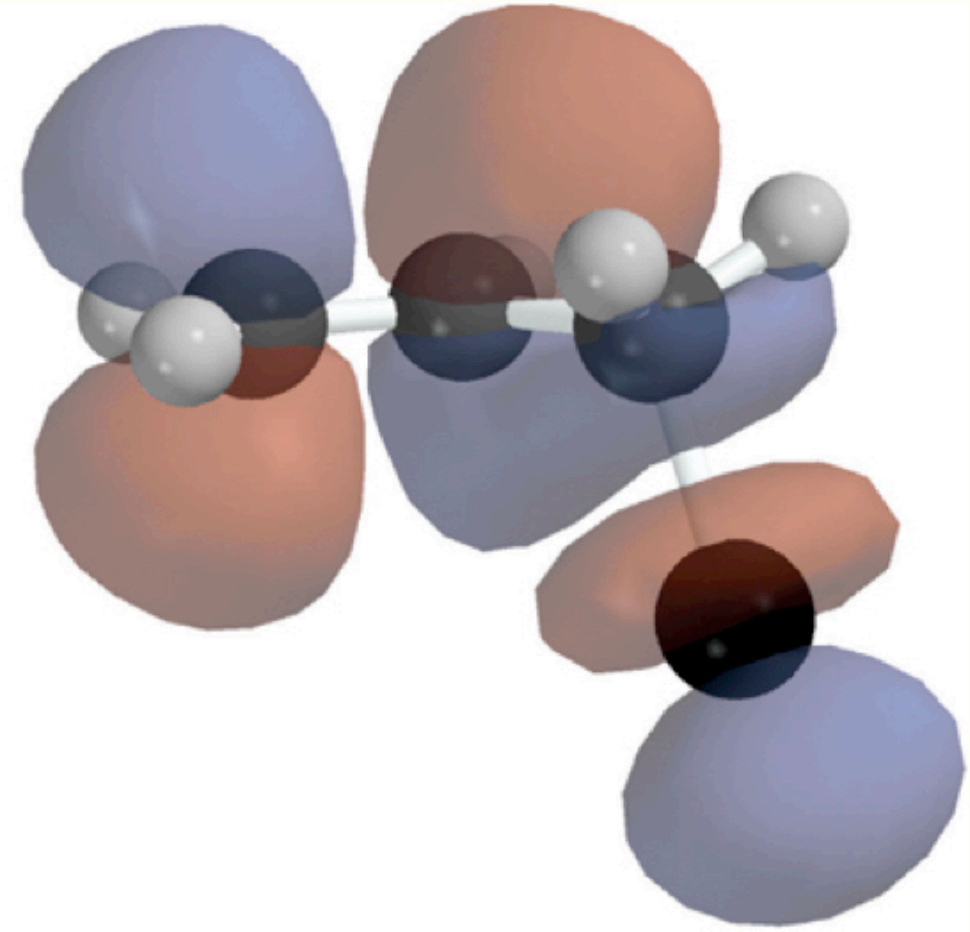


p-Nitrobenzyl chloride

p-Nitrobenzyl acetate (78–82%)

Allylic SN2 Faster: Two Arguments

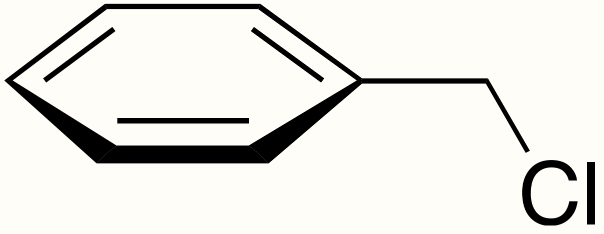
1. steric hinderance (VWF)
2. molecular orbital interactions

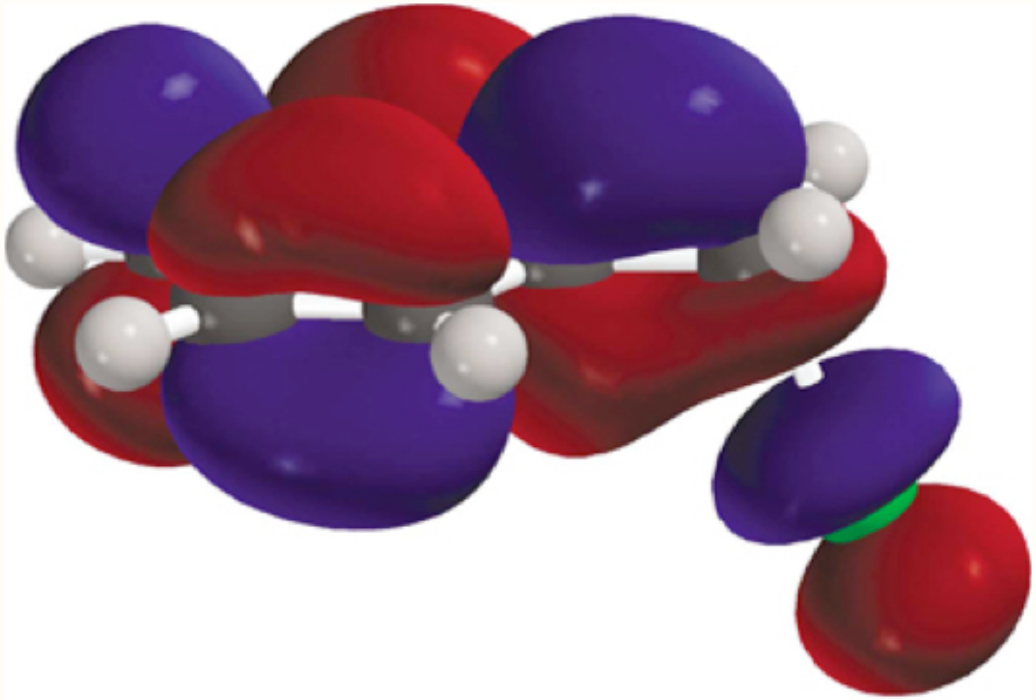


- LUMO of C-X bond can adopt a coplanar arrangement with p-orbitals of p-bond =
- electron delocalization over three orbitals =
- lower energy LUMO =
- lower activation energy =
- faster reaction
- *Why does lower energy LUMO result in lower activation energy?*

Benzylic S_N2 Faster: Two Arguments

1. steric hinderance (VWF)
2. molecular orbital interactions



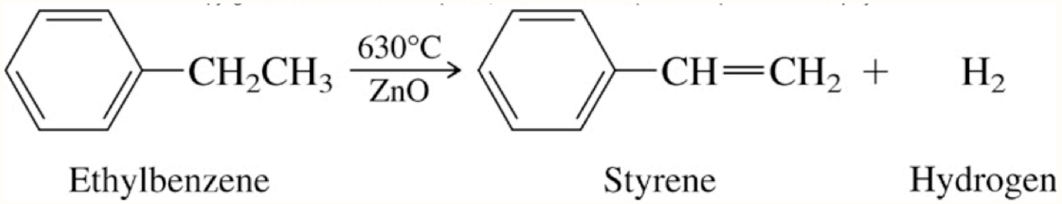


- LUMO of C-X bond can adopt a coplanar arrangement with p-orbitals of p-bond =
- more p-orbitals in benzene than alkene =
- more electron donation into LUMO of C-Cl bond =
- weaker C-X bond =
- *faster reaction*

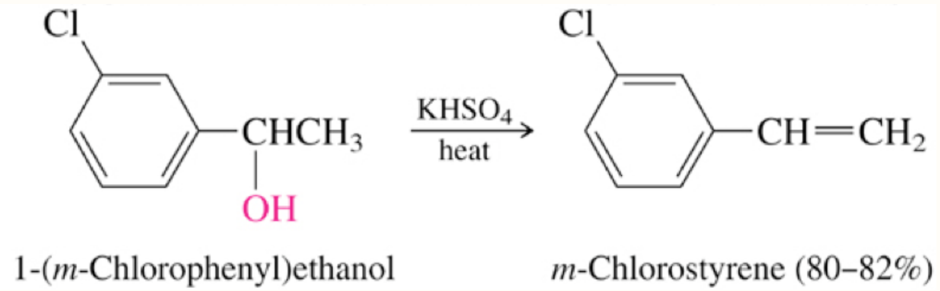
Preparation of Alkenylbenzenes

Same methods used to prepare alkenes can be used to prepare alkenylbenzenes

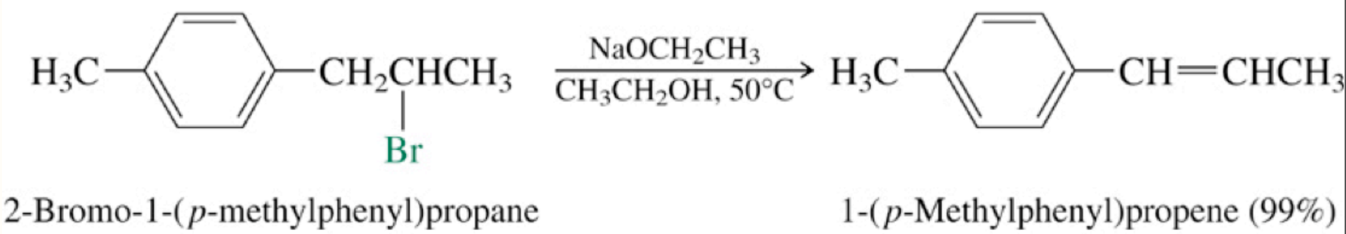
Dehydrogenation



Dehydration



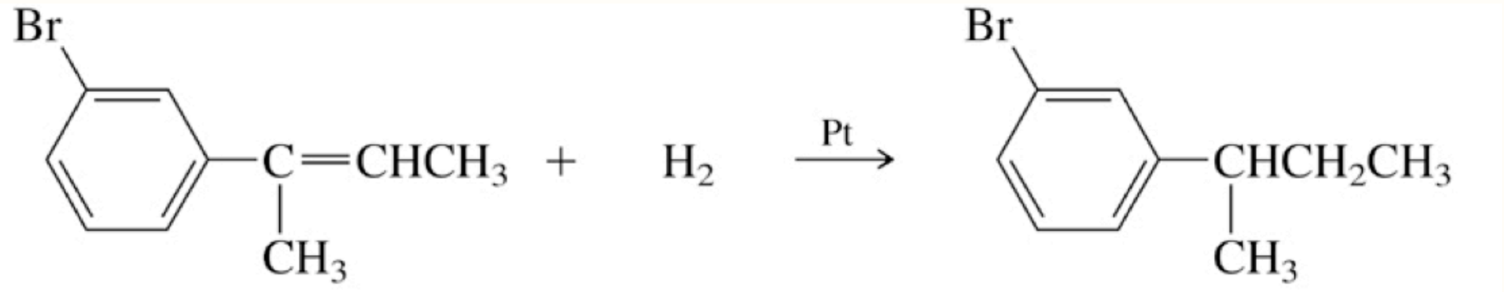
Dehydrohalogenation



Elimination of Benzylic Hydrogens

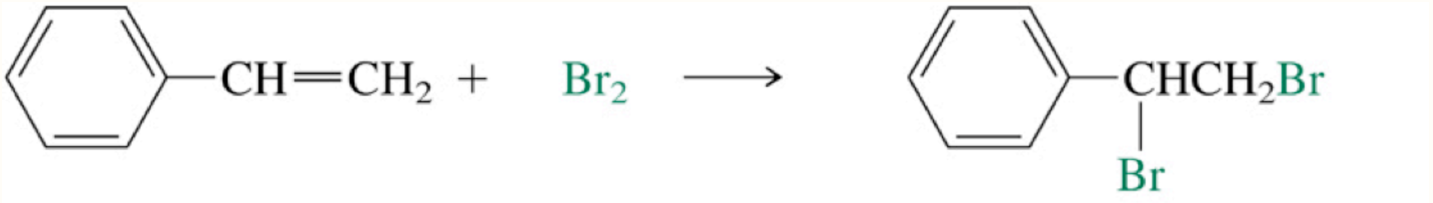
Addition reactions to alkenes can also be applied to addition reactions to alkenylbenzenes

Hydrogenation



2-(*m*-Bromophenyl)-2-butene Hydrogen 2-(*m*-Bromophenyl)butane (92%)

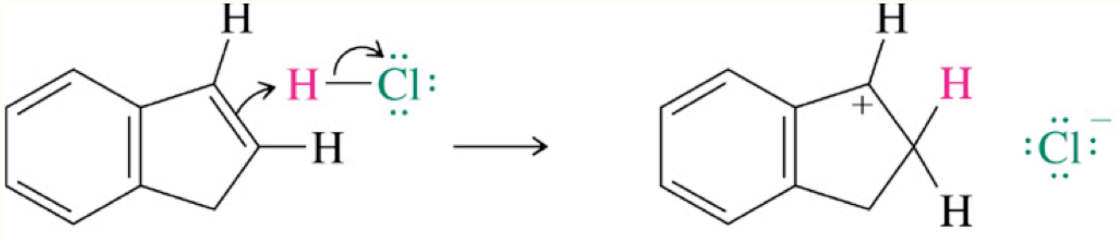
Bromination



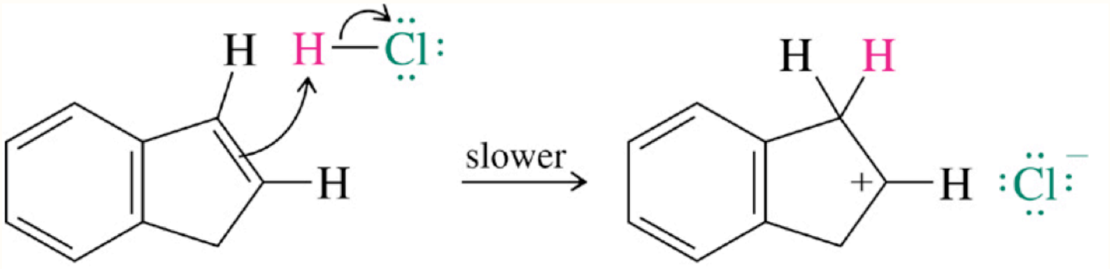
Styrene Bromine 1,2-Dibromo-1-phenylethane (82%)

Regioselective Addition of Electrophiles to Alkenylbenzenes

Addition to alkenylbenzenes favors (faster) formation of the more stable benzylic carbocation



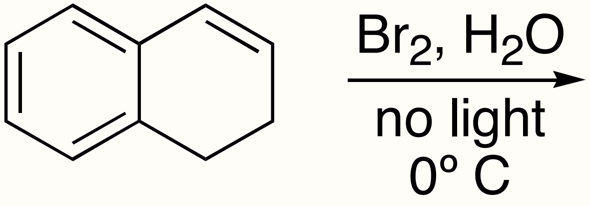
Carbocation is secondary and benzylic and gives the observed product

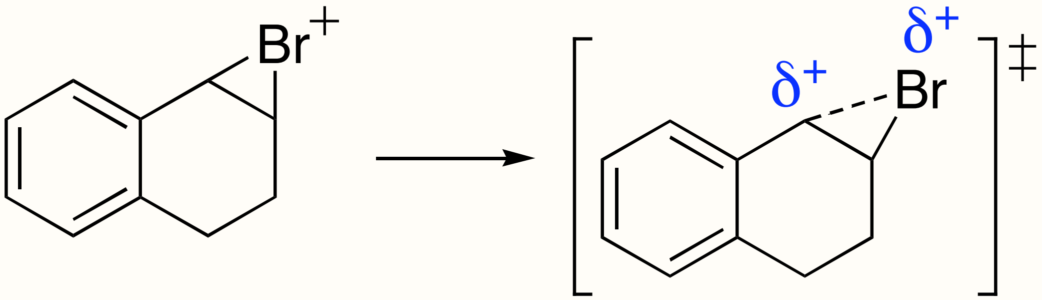


Less stable carbocation is secondary but not benzylic

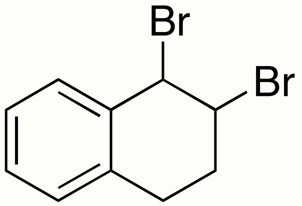
Self Test Question

What is the *major regioisomeric* halohydrin formed by the reaciton below?

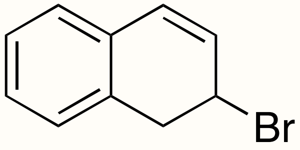




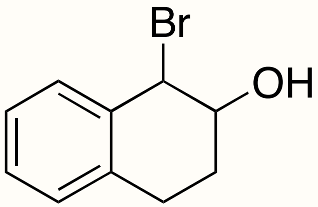
A



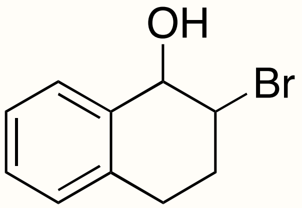
B



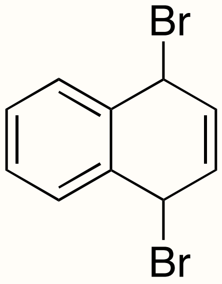
C



[✓ D]



E



Next Lecture...

Chapter 12: Sections 12.1-12.8

No Quiz This Week. . .

Grade Distribution