WILEY

Organic Chemistry

Third Edition

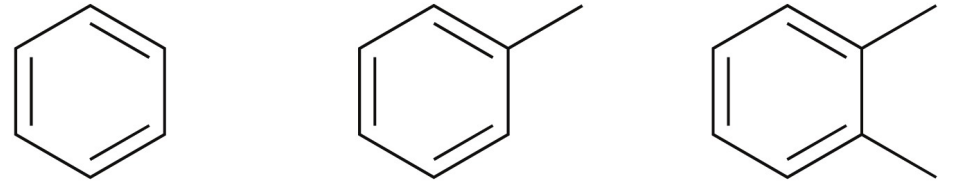
David Klein

Chapter 17

Aromatic Compounds

17.1 Introduction to Aromatic Compounds

- **Aromatic** compounds or **arenes** include benzene and benzene derivatives

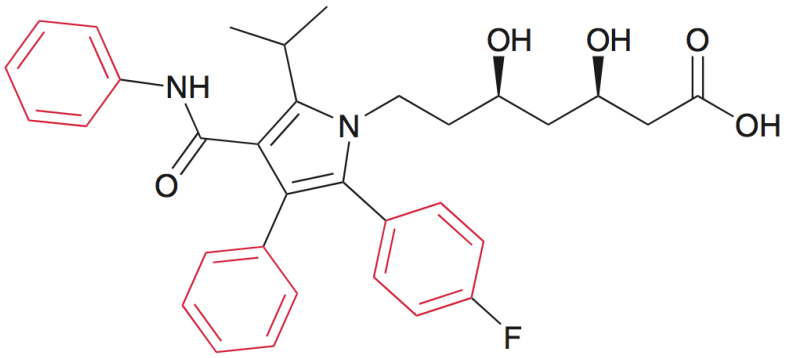


Benzene Toluene *ortho*-Xylene

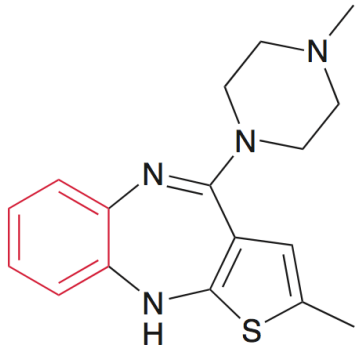
- Benzene derivatives were originally isolated from fragrant oils
- Most aromatic compounds are odorless

17.1 Introduction to Aromatic Compounds

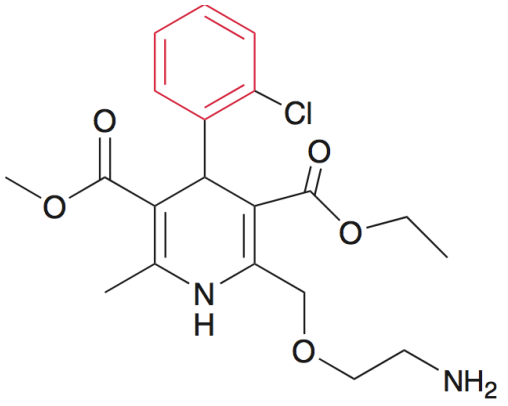
- **Aromatic** rings are a common feature in drugs



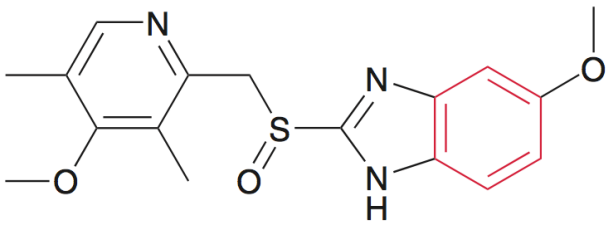
Lipitor
(atorvastatin)



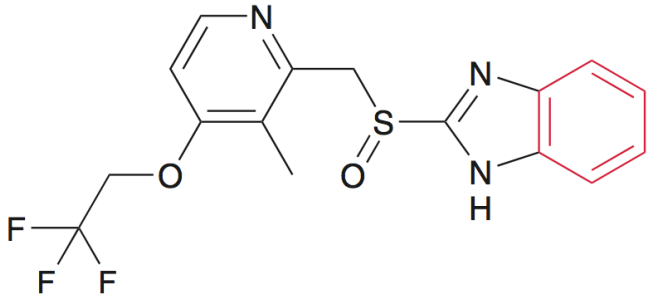
Zyprexa
(olanzapine)



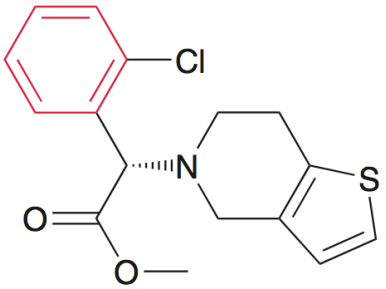
Norvasc
(amlodipine)



Prilosec
(omeprazole)



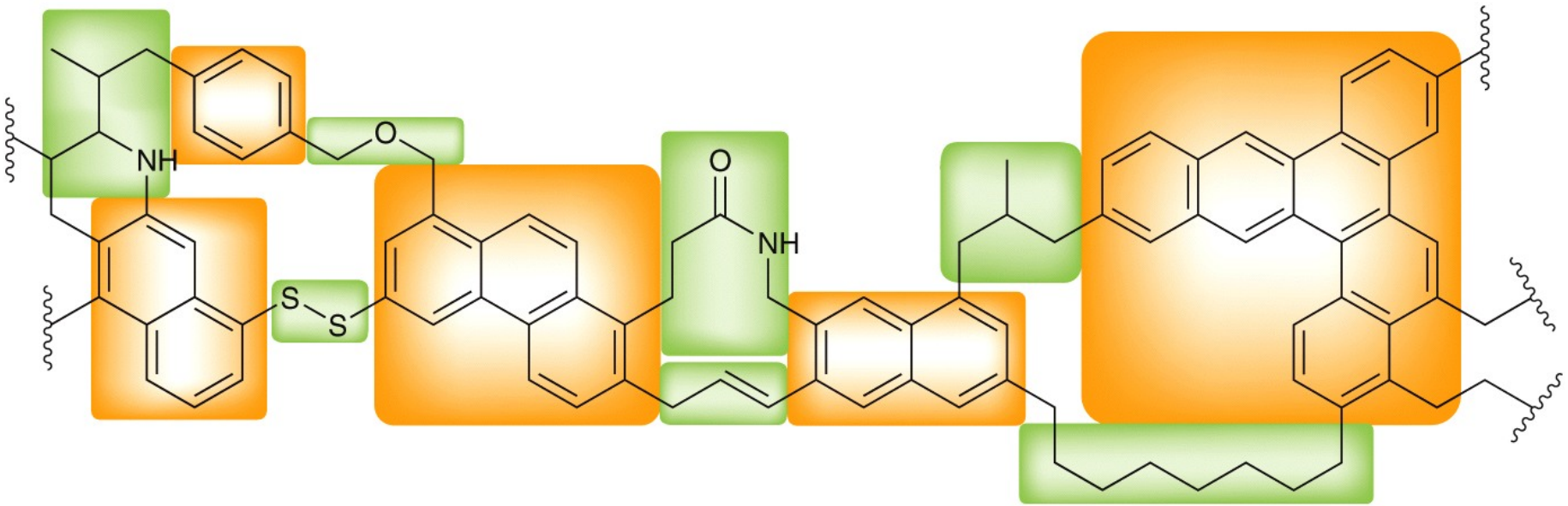
Prevacid
(lansoprazole)



Plavix
(clopidogrel)

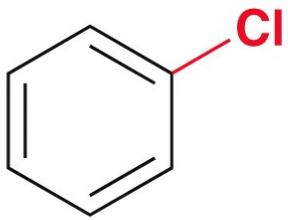
17.1 Introduction to Aromatic Compounds

- Coal contains aromatic rings fused together and joined by nonaromatic functional groups

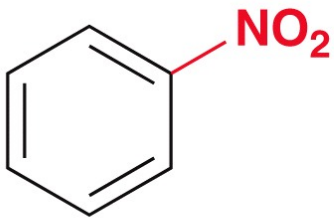


17.2 Nomenclature of Benzene Deriv.

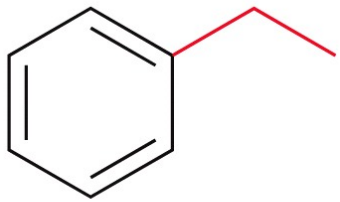
- Benzene is generally the parent name for monosubstituted derivatives



Chlorobenzene



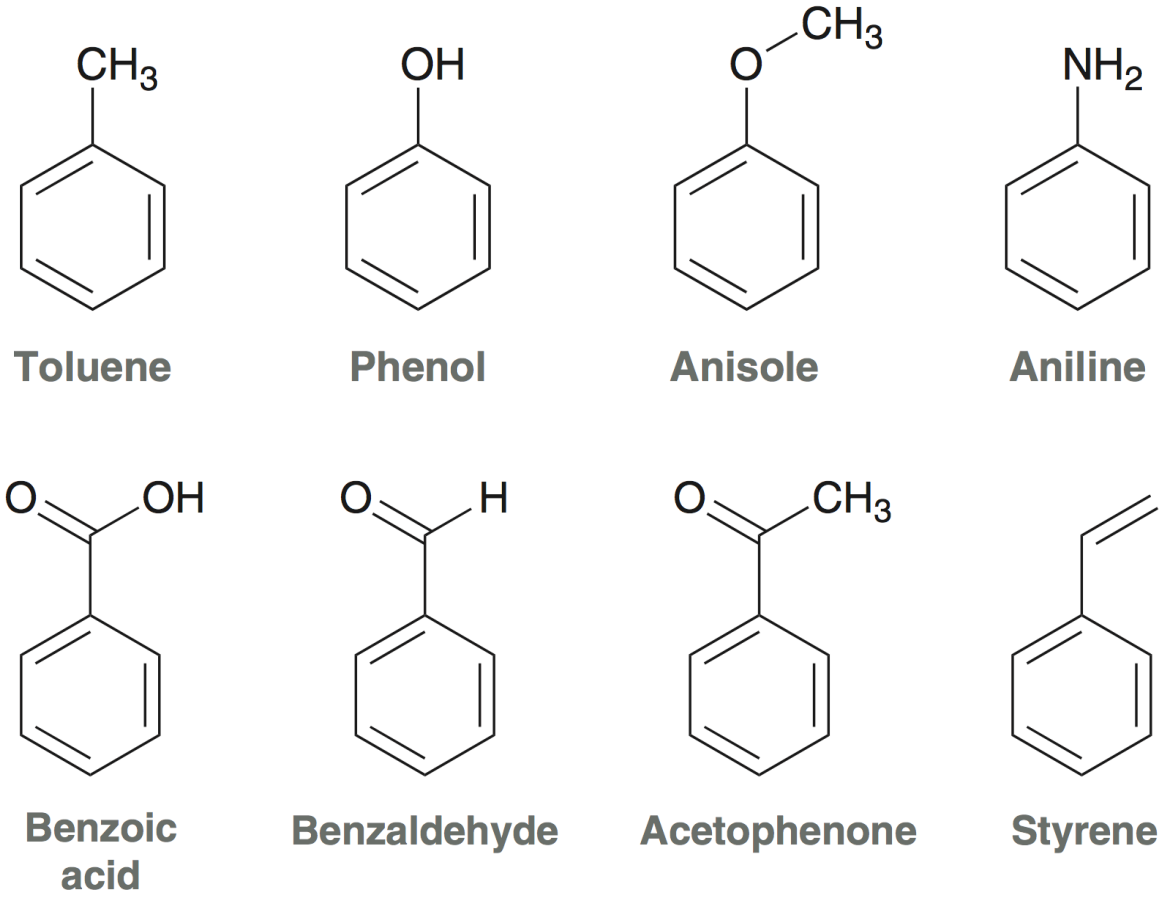
Nitrobenzene



Ethylbenzene

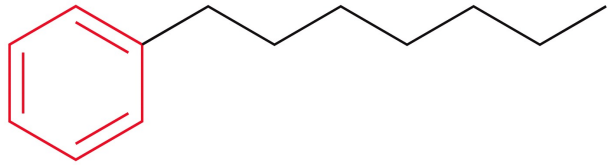
17.2 Nomenclature of Benzene Deriv.

- The following common names are accepted by IUPAC as parent names, and are frequently used:



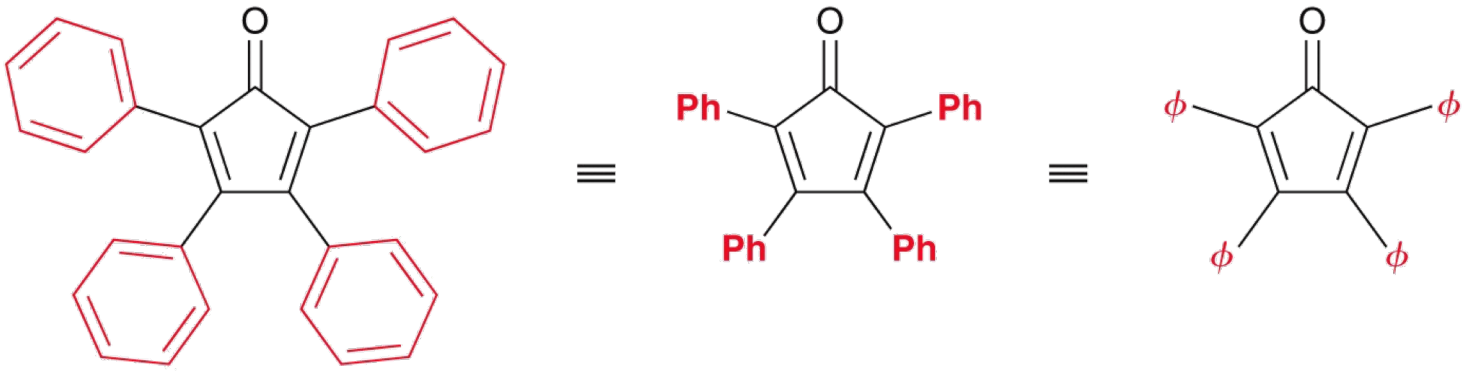
17.2 Nomenclature of Benzene Deriv.

- If the substituent is larger than the ring, the substituent becomes the parent chain



1-Phenylheptane

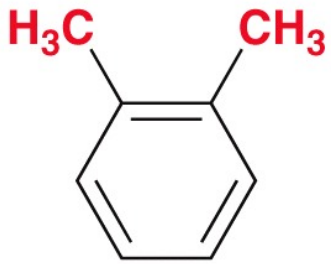
- Benzene rings are represented with "Ph" (for phenyl) or with a "ϕ" (phi) symbol



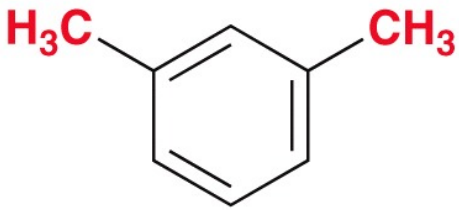
Tetraphenylcyclopentadienone

17.2 Nomenclature of Benzene Deriv.

- The common name for **dimethyl benzene** derivatives is **xylene**



***ortho*-Xylene**
(1,2-dimethylbenzene)



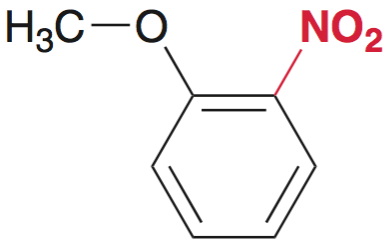
***meta*-Xylene**
(1,3-dimethylbenzene)

***para*-Xylene**
(1,4-dimethylbenzene)

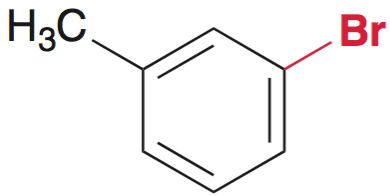
- ***ortho***, ***meta***, and ***para*** are used for the location of substituents on disubstituted benzene rings

17.2 Nomenclature of Benzene Deriv.

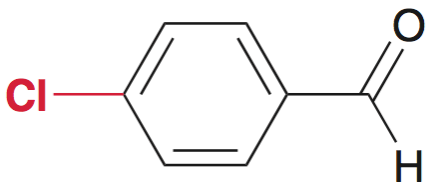
- ***ortho***, ***meta***, and ***para*** are used for the location of substituents on disubstituted benzene rings



***ortho*-Nitroanisole**
(2-Nitroanisole)



***meta*-Bromotoluene**
(3-Bromotoluene)



***para*-Chlorobenzaldehyde**
(4-Chlorobenzaldehyde)

17.2 Nomenclature of Benzene Deriv.

1. Identify the parent

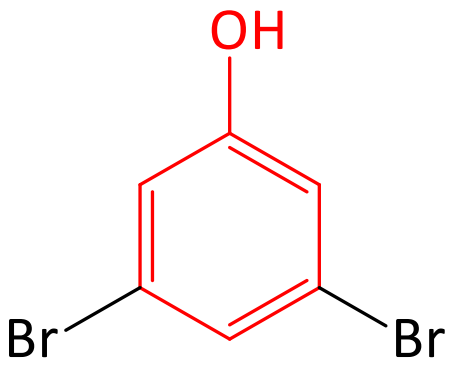
2. Identify and Name the substituents

3. Number the parent chain and assign a locant to each substituent
   - Give the first substituent the lowest number possible

4. List the numbered substituents before the parent name in alphabetical order
   - Ignore prefixes (except iso) when ordering alphabetically

17.2 Nomenclature of Benzene Deriv.

1. Identify the parent chain (generally the aromatic ring)
   - Often a common name can be the parent chain

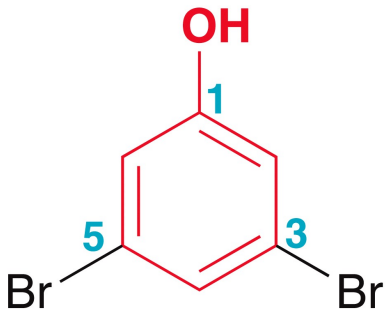


Parent = phenol

2. Identify and Name the substituents

17.2 Nomenclature of Benzene Deriv.

3. Number the parent chain and assign a locant to each substituent
   - A substituent that is part of the parent name must be assigned locant NUMBER 1



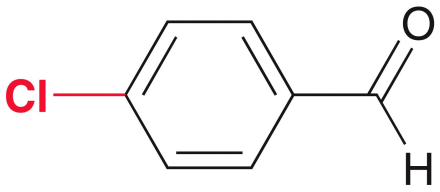
4. List the numbered substituents before the parent name in alphabetical order
   - Ignore prefixes (except iso) when ordering alphabetically

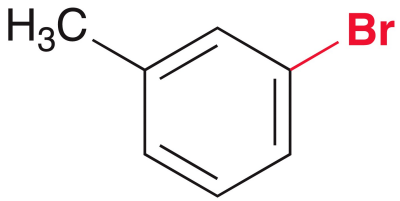
3,5-dibromophenol

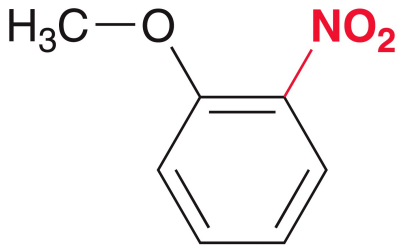
- **Practice with SkillBuilder 17.1**

17.2 Nomenclature of Benzene Deriv.

- Name the following molecules







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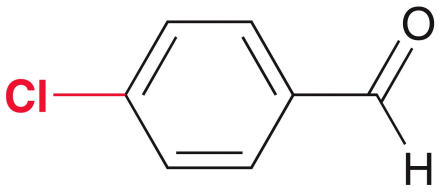
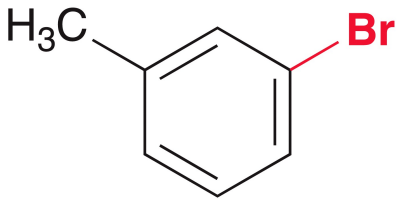
- Name the following molecules



4-chlorobenzaldehyde

or

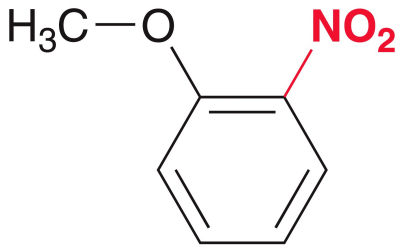
***p*-chlorobenzaldehyde**



3-bromotoluene

or

***m*-bromotoluene**



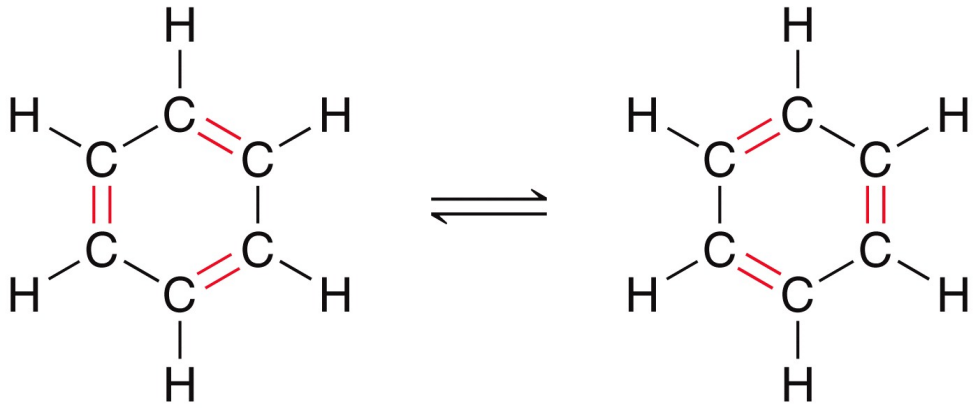
2-nitroanisole

or

***o*-nitroanisole**

17.3 Structure of Benzene

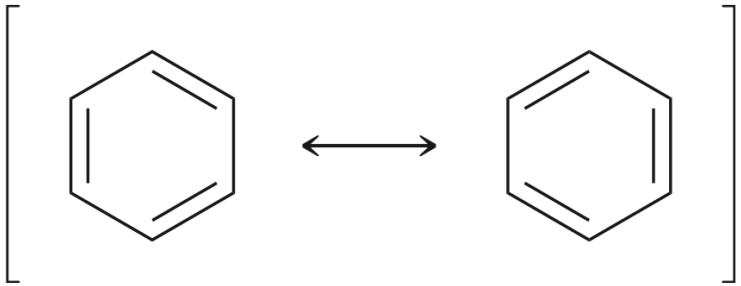
- In 1866, August Kekulé proposed that benzene is a ring comprised of alternating double and single bonds



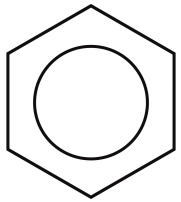
- Kekulé suggested that the exchange of double and single bonds was an equilibrium process

17.3 Structure of Benzene

- We now know that the two drawings are resonance contributors rather than in equilibrium

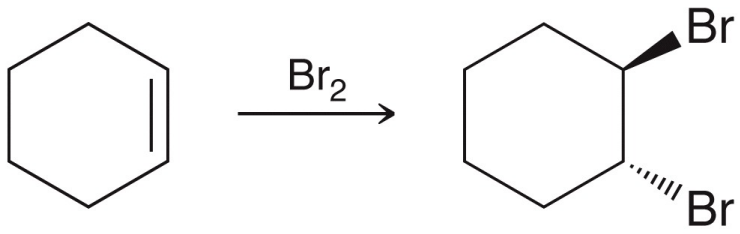


- Sometimes the ring is represented with a circle in it to avoid drawing resonance structures

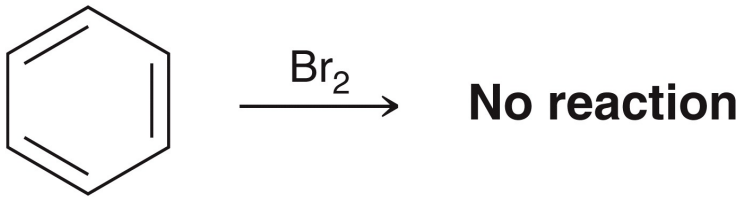


17.4 Stability of Benzene

- Aromatic rings are remarkably stable
- Recall alkenes readily undergo addition reactions

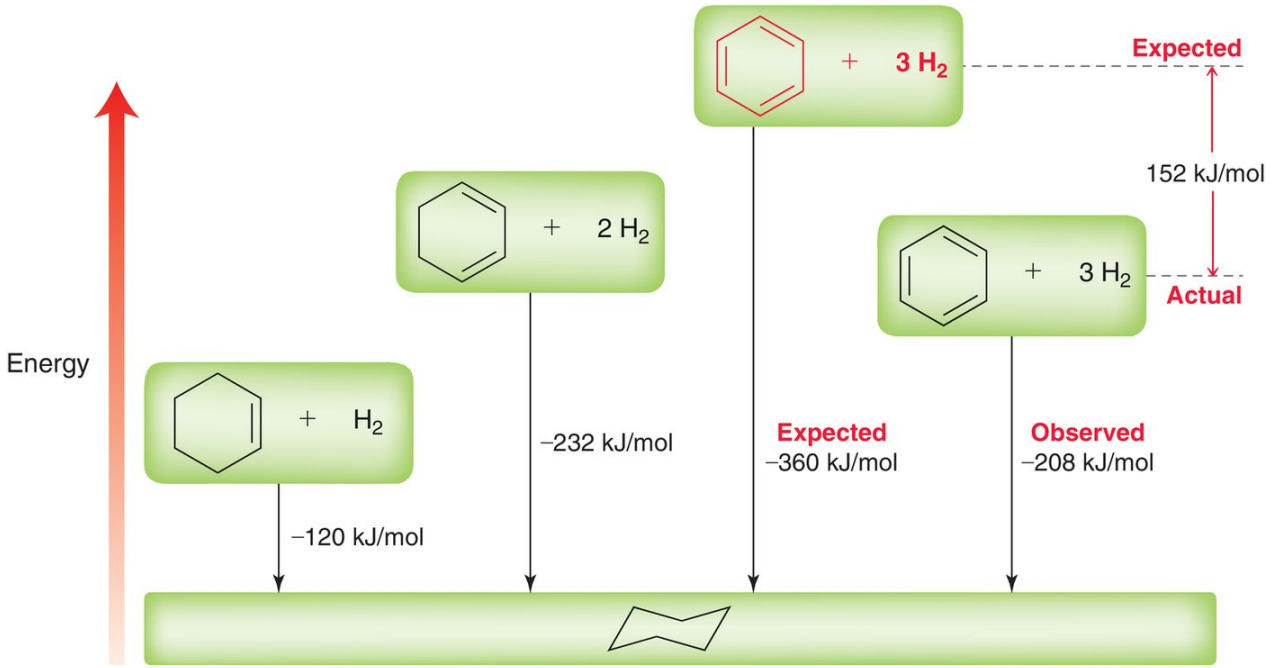


- Aromatic rings are stable enough that they do not undergo such reactions



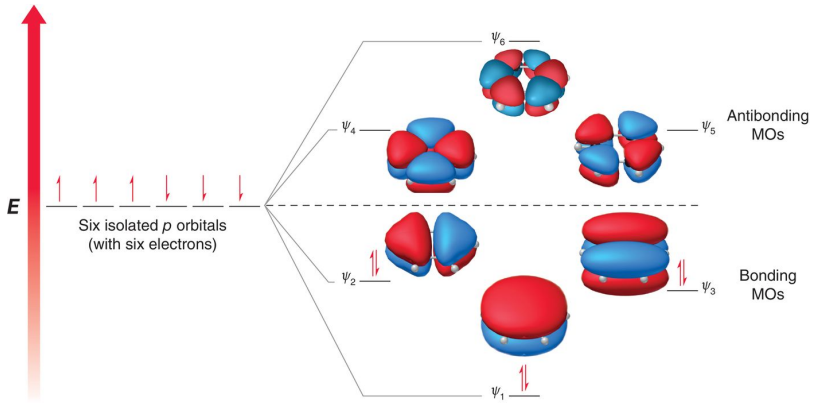
17.4 Stability of Benzene

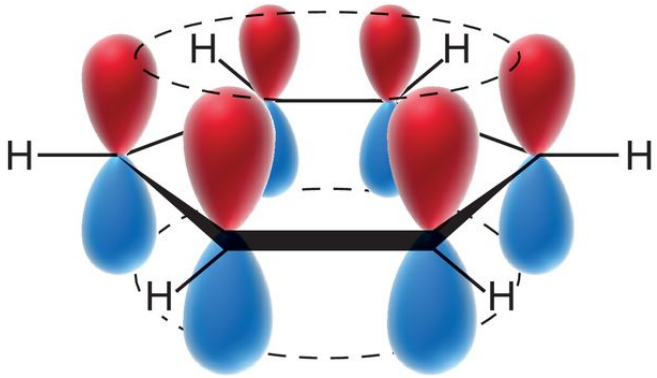
- Heats of hydrogenation can be used to quantify aromatic stability.



17.4 Stability of Benzene

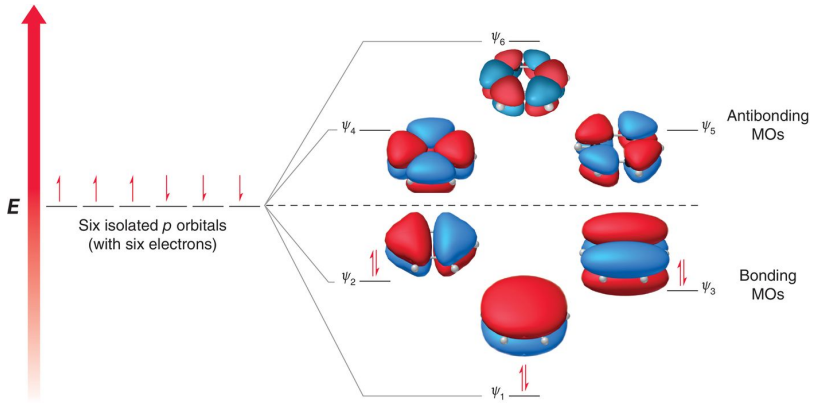
- MO theory can help us explain aromatic stability
- The 6 atomic p-orbitals of benzene overlap to make 6 MOs

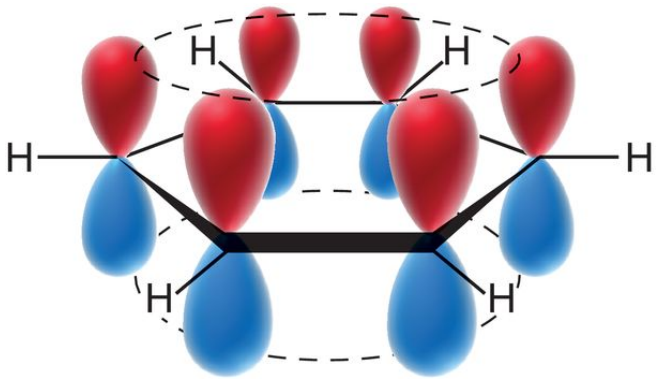




17.4 Stability of Benzene

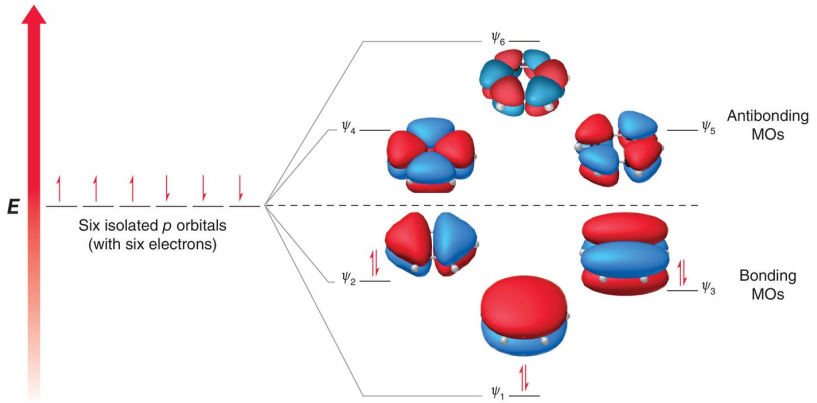
- The locations of nodes in the MOs determines their shapes based on high-level mathematical calculations

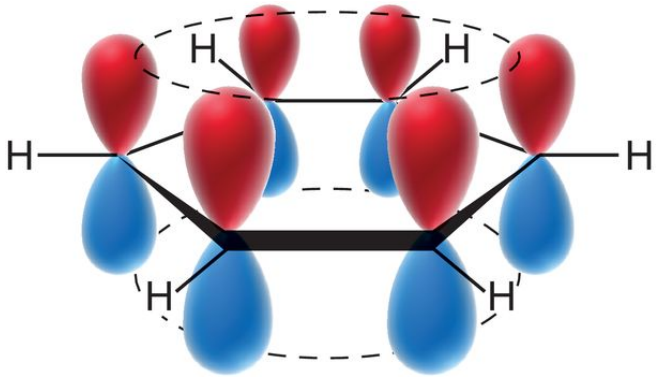




17.4 Stability of Benzene

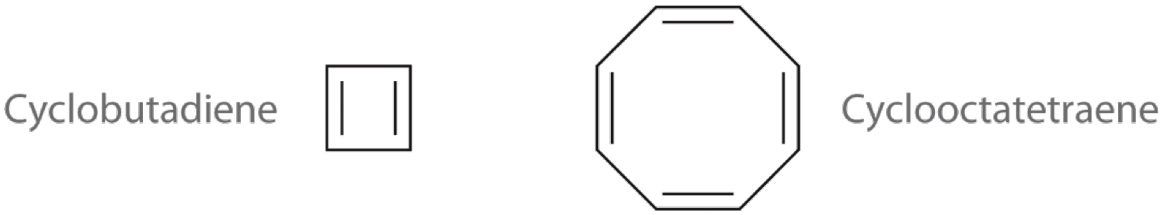
- The delocalization of the 6 pi electrons in the three bonding molecular orbitals accounts for the stability of benzene



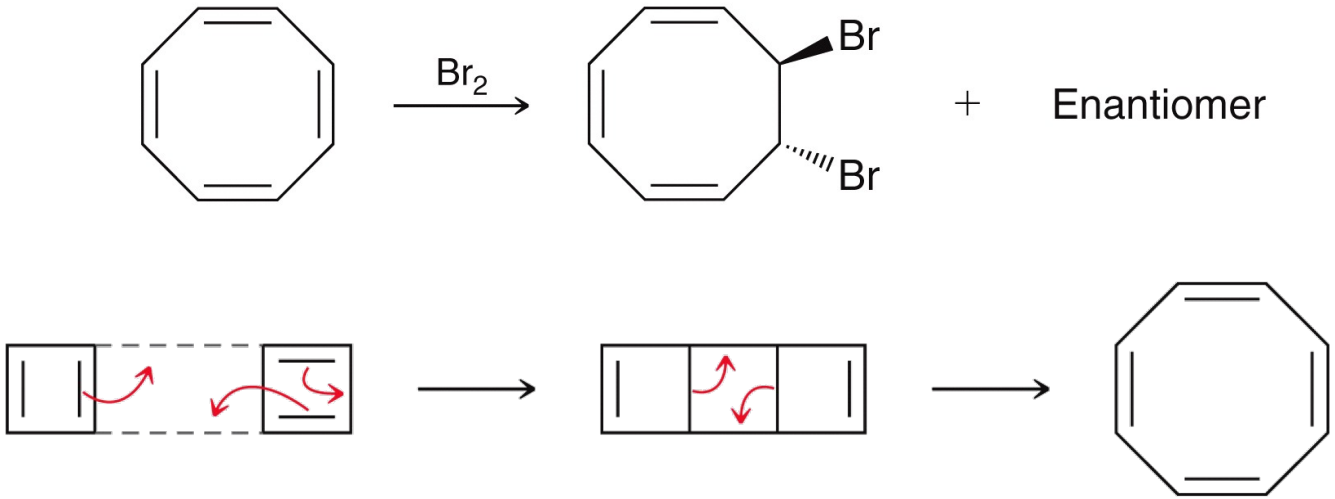


17.4 Stability of Benzene

- Not all fully conjugated rings have aromatic stability



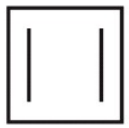
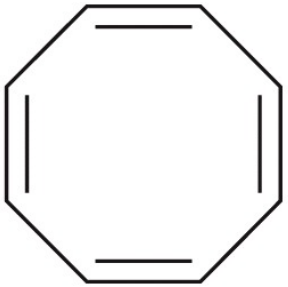
- Some fully conjugated cyclic compounds react like normal alkenes



17.4 Stability of Benzene

- aromatic compounds must meet two criteria:
  1. A fully conjugated ring with overlapping p-orbitals
  2. Meets **Hückel's rule**: an ODD number of e^- pairs or 4n+2 total π electrons where n=0, 1, 2, 3, 4, etc.

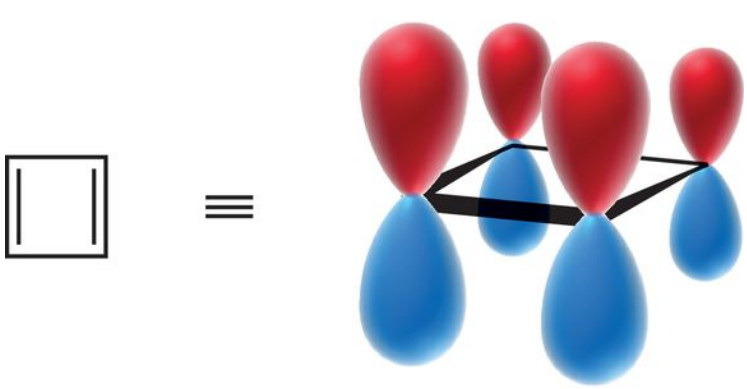
- The following compounds do not meet Huckel's rule:

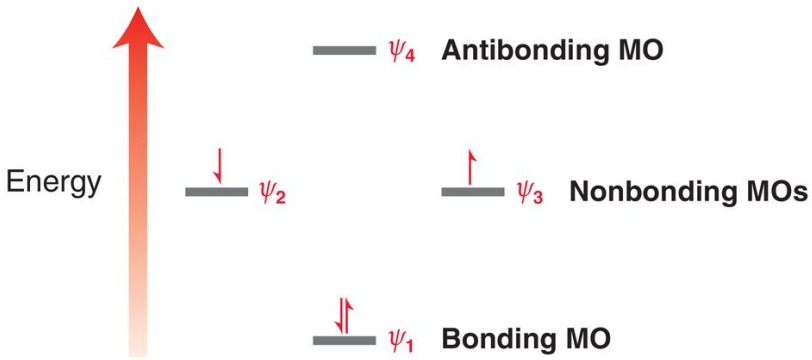
Cyclobutadiene   Cyclooctatetraene

- **Practice with Conceptual Checkpoint 17.8**

17.4 Stability of Benzene

- We can explain Hückel's rule using MO theory
- consider the MOs for cyclobutadiene, which has 4 π electrons:

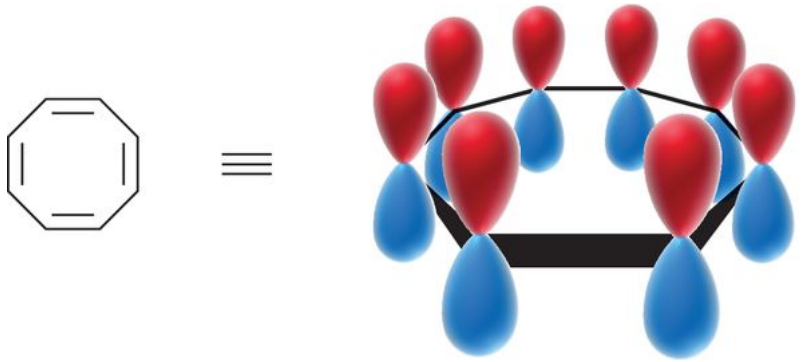


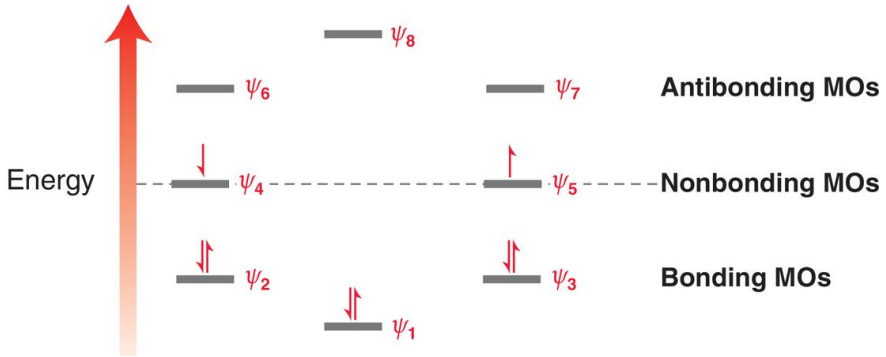


- Lacks a closed-shell electron configuration, and unstable. It is **antiaromatic**

17.4 Stability of Benzene

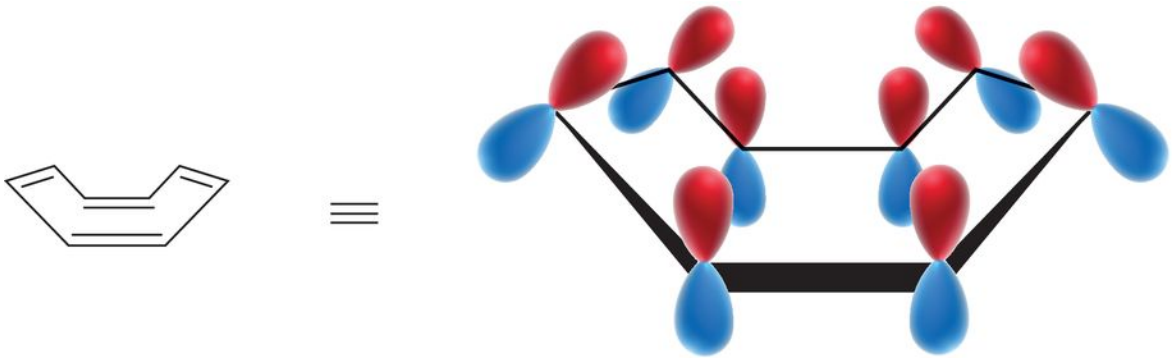
- A similar MO analysis for cyclooctatetraene suggests that it is also **antiaromatic**





17.4 Stability of Benzene

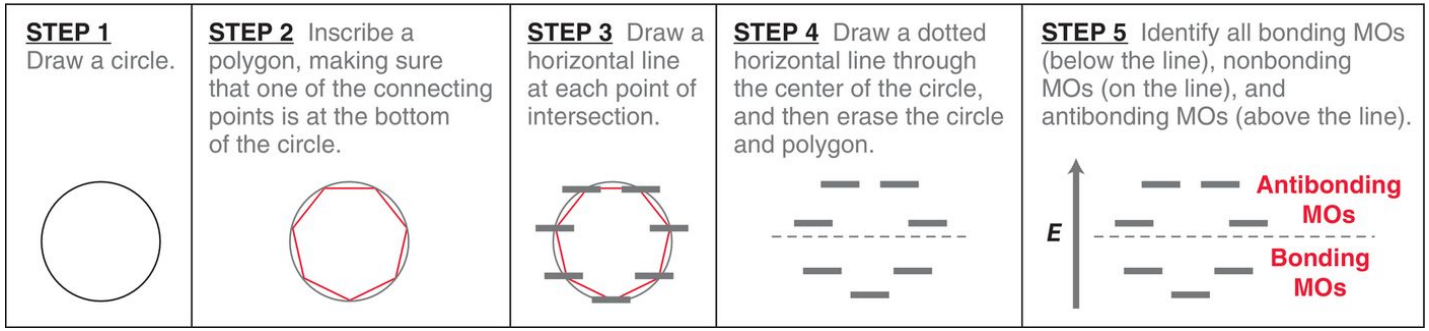
- However, if the structure adopts a tub-shaped conformation, it can avoid being antiaromatic:



- The conjugation does not extend around the entire ring, so the system is neither aromatic nor antiaromatic. It is nonaromatic

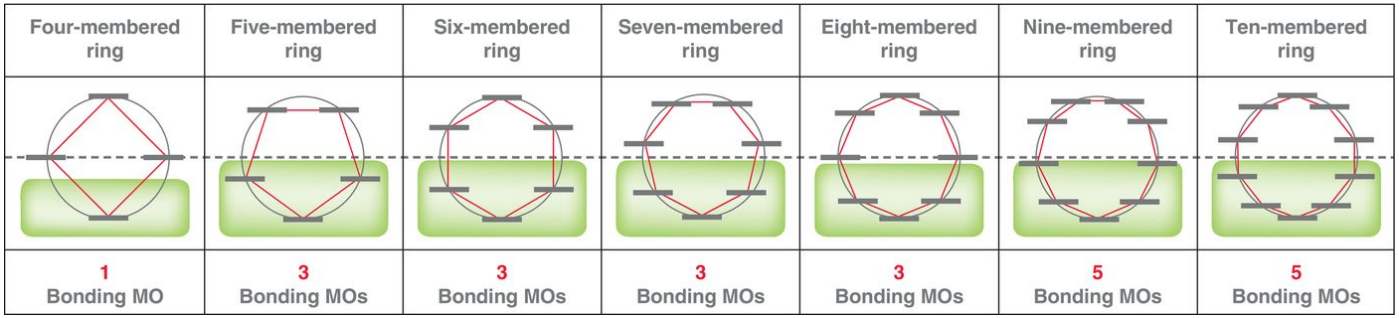
17.4 Stability of Benzene

- Predicting the shapes and energies of MOs can be simplified by drawing **Frost circles** to predict the relative MO energies



17.4 Stability of Benzene

- **Frost circles** help to explain the 4*n*+2 rule:



- Note that the number of bonding orbitals is always an odd number - aromatic compounds will always have an odd number of electron pairs

- **Practice with Conceptual Checkpoint 17.9**

17.5 Other Aromatic Compounds

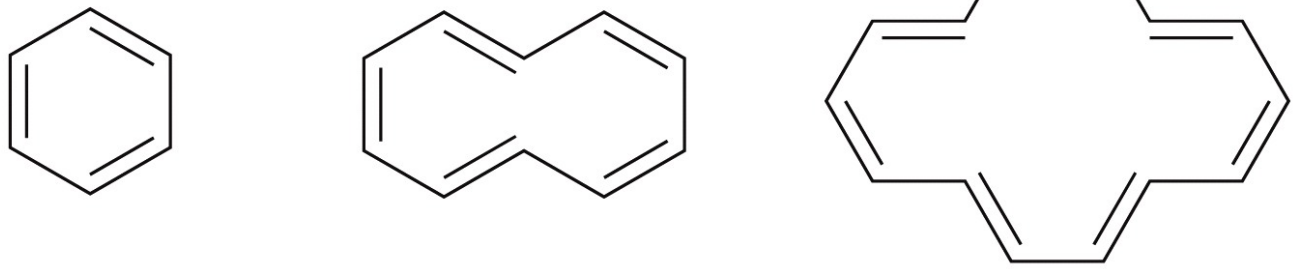
- **Aromatic** compounds fulfill two criteria
  1. A fully conjugated ring with overlapping *p*-orbitals
  2. Meets **Hückel's rule**: an ODD number of e^- pairs or $4n+2$ total π electrons where n=0, 1, 2, 3, 4, etc.

- **Antiaromatic** compounds fulfill two criteria
  1. A fully conjugated ring with overlapping *p*-orbitals
  2. An EVEN number of electron pairs or $4n$ total π electrons where n=0, 1, 2, 3, 4, etc.

- When a compound fails criteria #1, it is **nonaromatic**

17.5 Other Aromatic Compounds

- Annulenes are rings that are fully conjugated



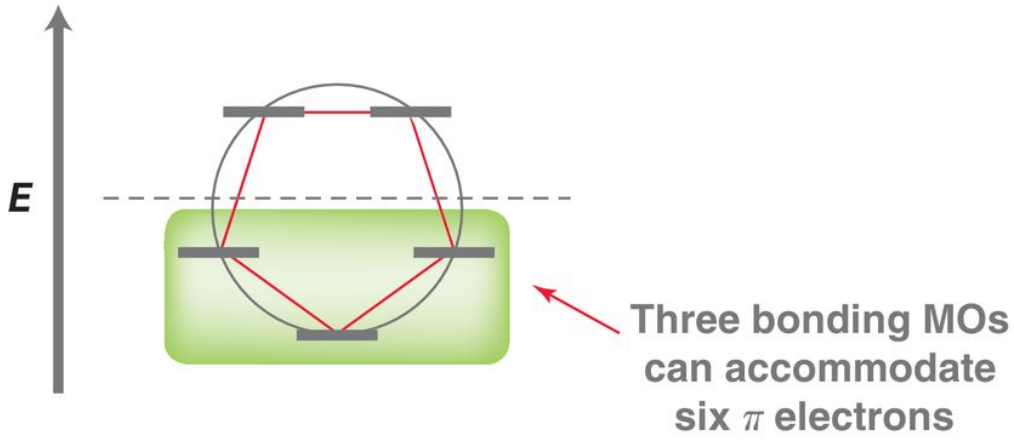
[6]Annulene [10]Annulene [14]Annulene

- Annulenes can aromatic, antiaromatic or nonaromatic

- **Practice with Conceptual Checkpoint 17.10**

17.5 Other Aromatic Compounds

- Aromatic rings can contain carbanions or carbocations
- Consider a 5-membered ring

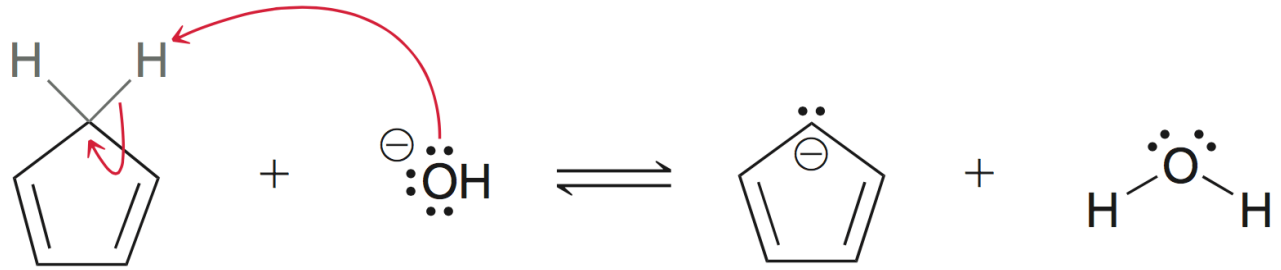


- 6 π electrons must be present in order to be aromatic

17.5 Other Aromatic Compounds

- The **cyclopentadienyl anion** has a lone pair delocalized over each of the 5 carbon atoms, and is an **aromatic anion**

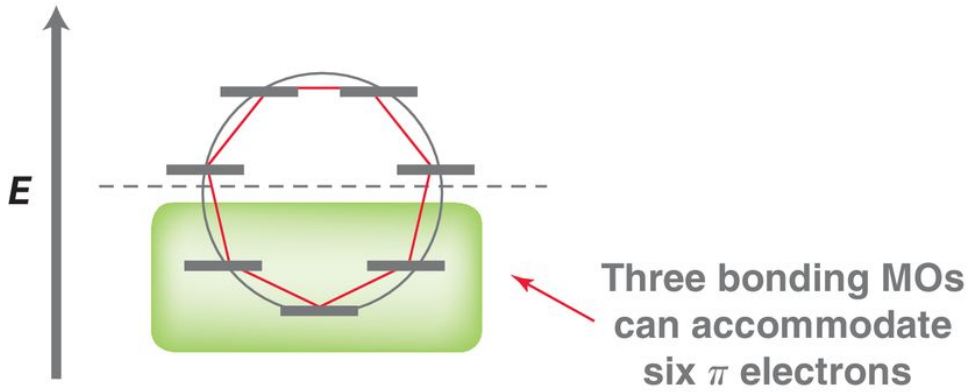
- The acidity of cyclopentadiene is attributed to the aromatic stability of its conjugate base



$pK_a = 16$ $pK_a = 15.7$

17.5 Other Aromatic Compounds

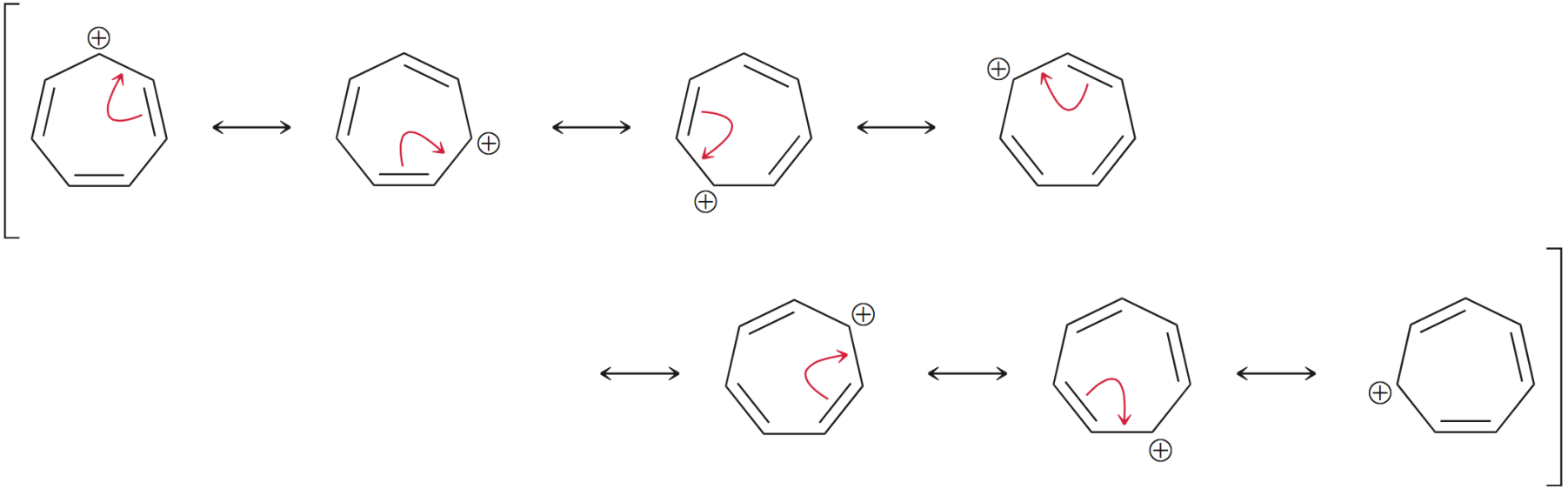
- Consider a 7-membered ring



- With 6 π electrons, one of the carbon atoms has an empty p orbital, and the compound is cationic.

17.5 Other Aromatic Compounds

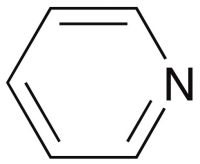
- The **tropylium cation** is an **aromatic cation**:



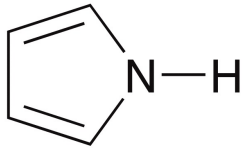
- **Practice with SkillBuilder 17.2**

17.5 Aromatic Heterocycles

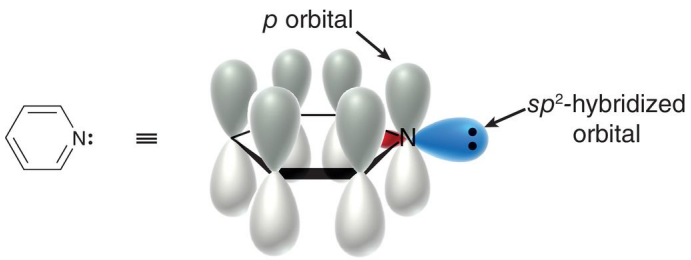
- Heteroatoms (atoms other than C or H) can also be part of an aromatic ring

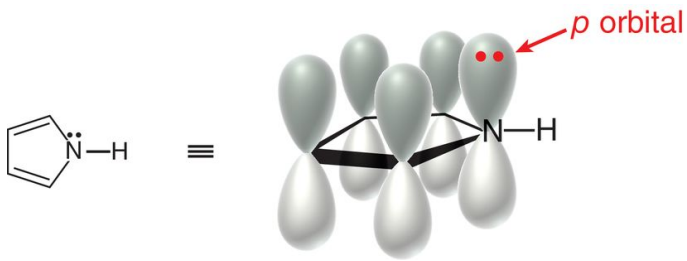


Pyridine



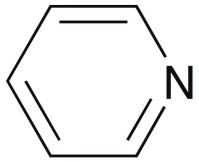
Pyrrole



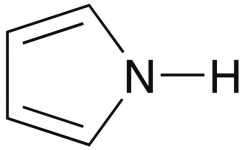


17.5 Aromatic Heterocycles

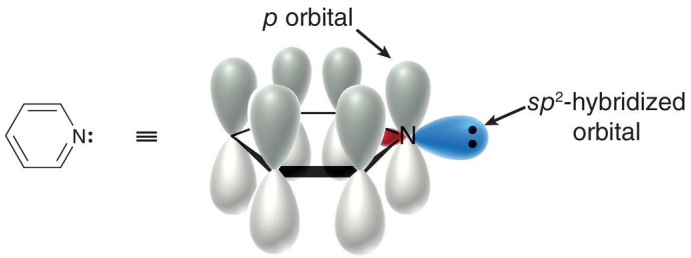
- If the heteroatom's lone pair is necessary for aromaticity, it will be included in the **Hückel** number of π electrons

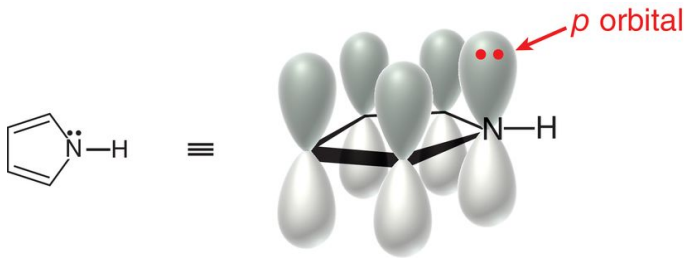


Pyridine



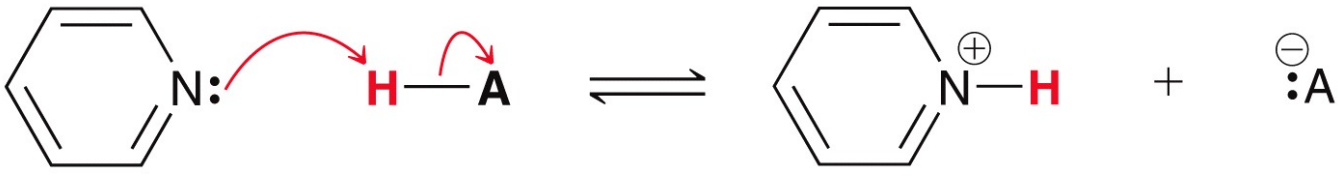
Pyrrole





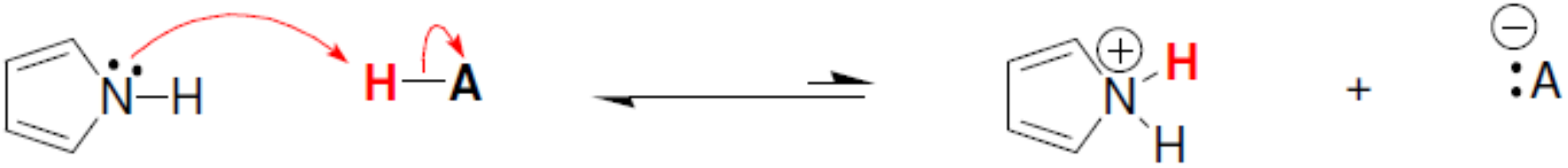
17.5 Aromatic Heterocycles

- If the lone pair is necessary for aromaticity, then the lone pair will not be as basic



Still aromatic

pK_a=5.2

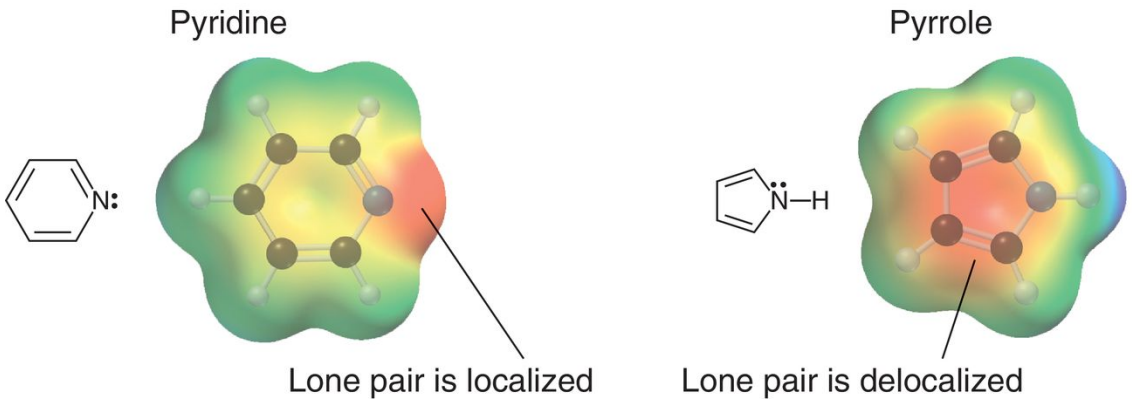


nonaromatic

pK_a=0.4

17.5 Aromatic Heterocycles

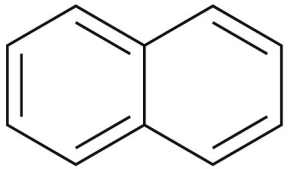
- The difference in electron density can also be observed by viewing the electrostatic potential maps



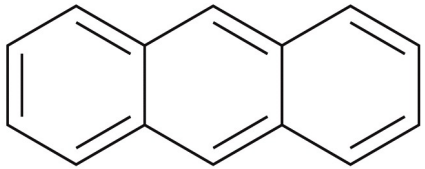
- **Practice with SkillBuilder 17.3**

17.5 Polycyclic Aromatic Compounds

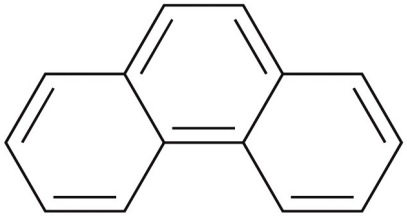
- Many polycyclic compounds are also aromatic



Naphthalene



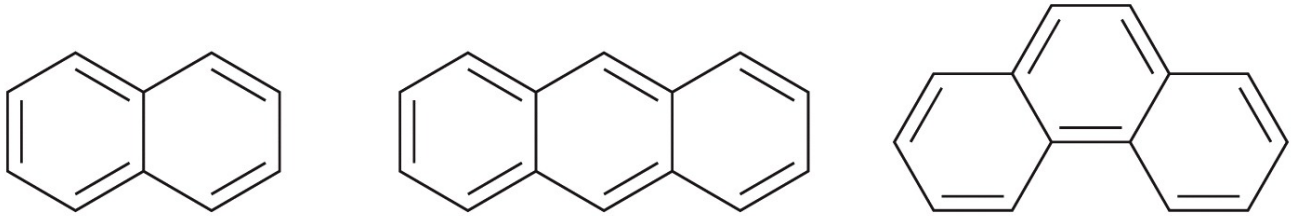
Anthracene



Phenanthrene

17.5 Polycyclic Aromatic Compounds

- The stabilization energy can be measured by comparing heats of hydrogenation:



Naphthalene Anthracene Phenanthrene

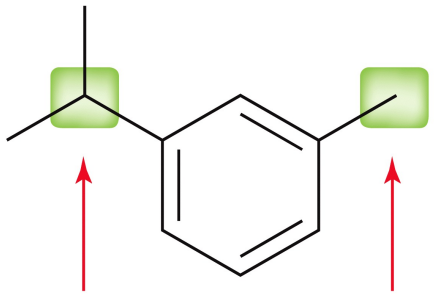
TABLE 17.1 STABILIZATION ENERGY FOR A FEW POLYCYCLIC AROMATIC HYDROCARBONS

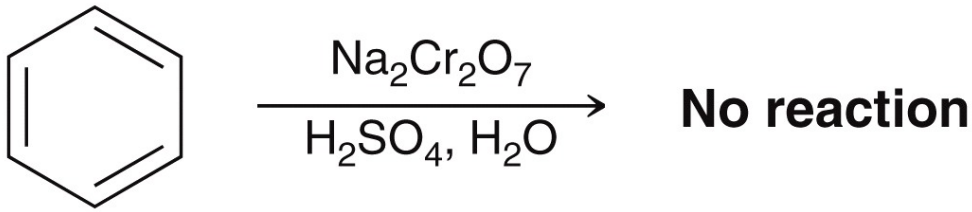
COMPOUND	STABILIZATION ENERGY (KJ/MOL)	AVERAGE STABILIZATION ENERGY PER RING (KJ/MOL)
Benzene	152	152
Naphthalene	255	128
Anthracene	347	116
Phenanthrene	381	127

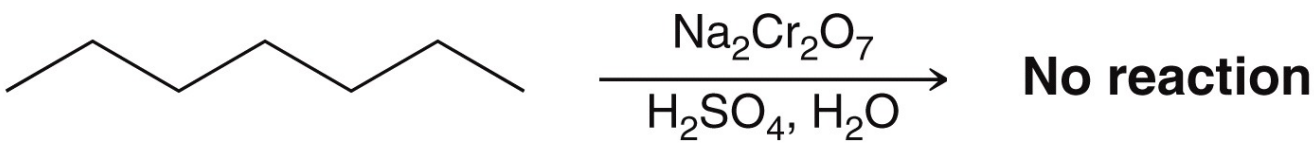
17.6 Reactions at the Benzylic Position

- A carbon directly attached to a benzene ring is called a **benzylic position**

- Recall that aromatic rings and alkyl groups are not easily oxidized

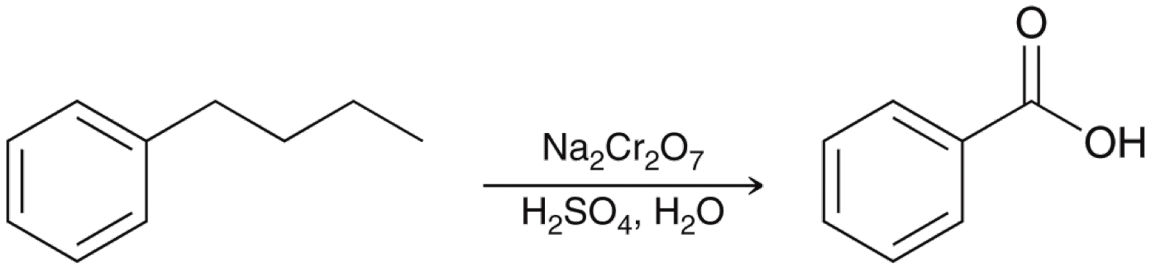




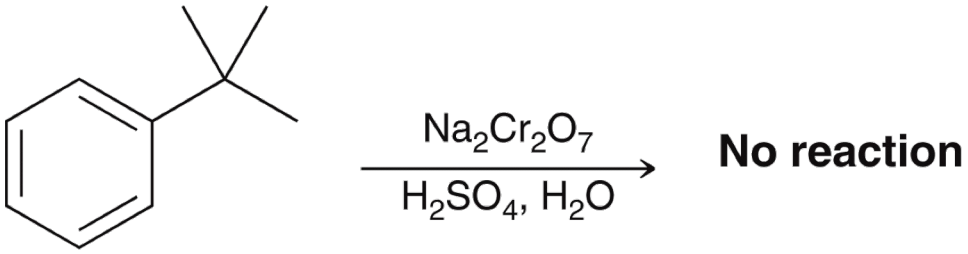


17.6 Reactions at the Benzylic Position

- However, benzylic positions are readily oxidized by chromic acid:

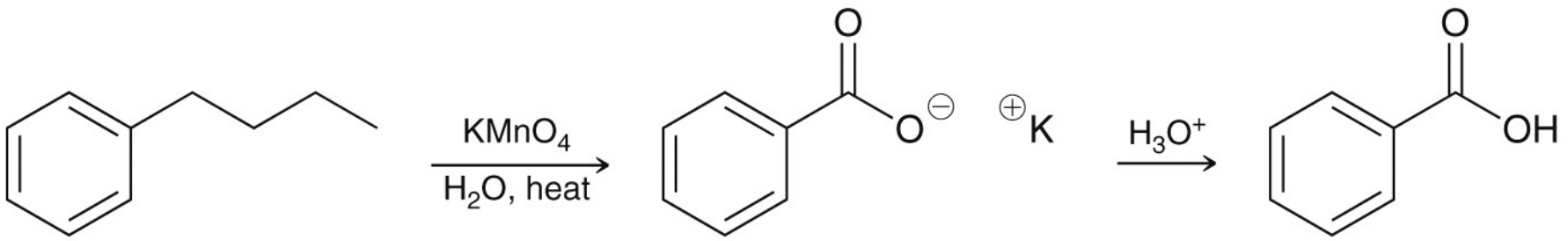


- The benzylic position needs to have at least 1 proton attached to undergo oxidation



17.6 Reactions at the Benzylic Position

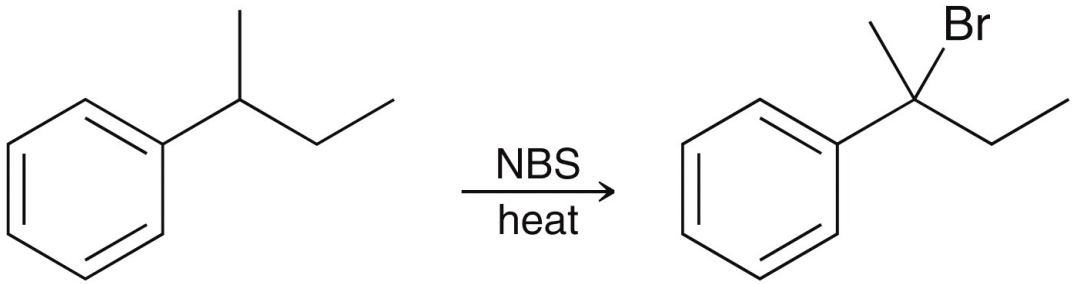
- Permanganate can also be used as an oxidizing reagent



- **Practice with Conceptual Checkpoint 17.17**

17.6 Reactions at the Benzylic Position

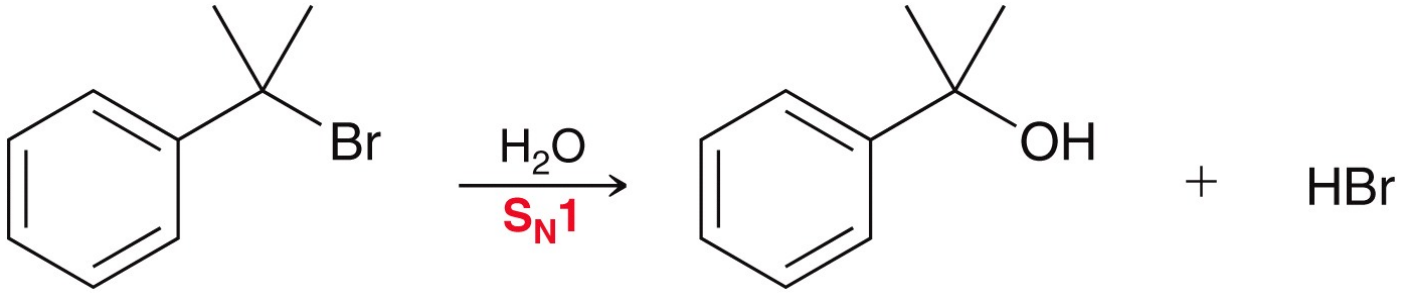
- **Benzylic positions** are similar to allylic positions, and readily **undergo free radical bromination**



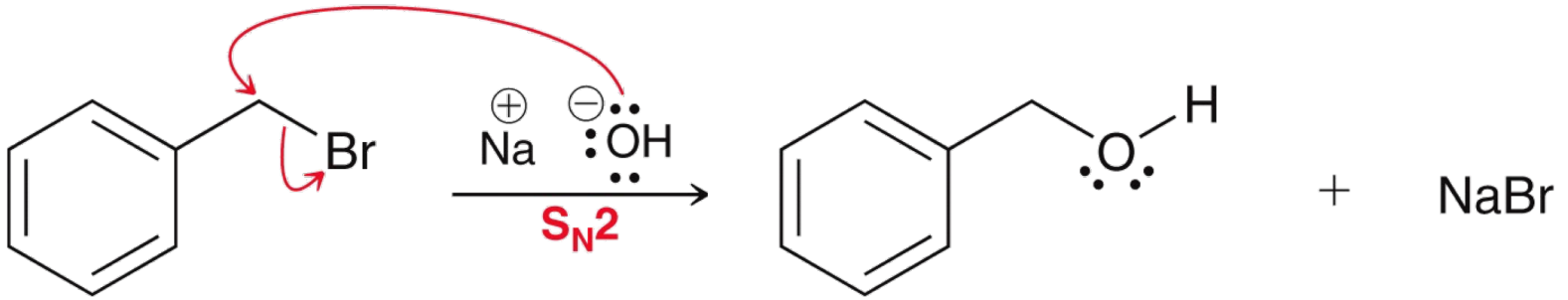
- **Benzylic bromides** are useful synthetic intermediates

17.6 Reactions at the Benzylic Position

- Benzylic bromides readily undergo SN1 substitution:

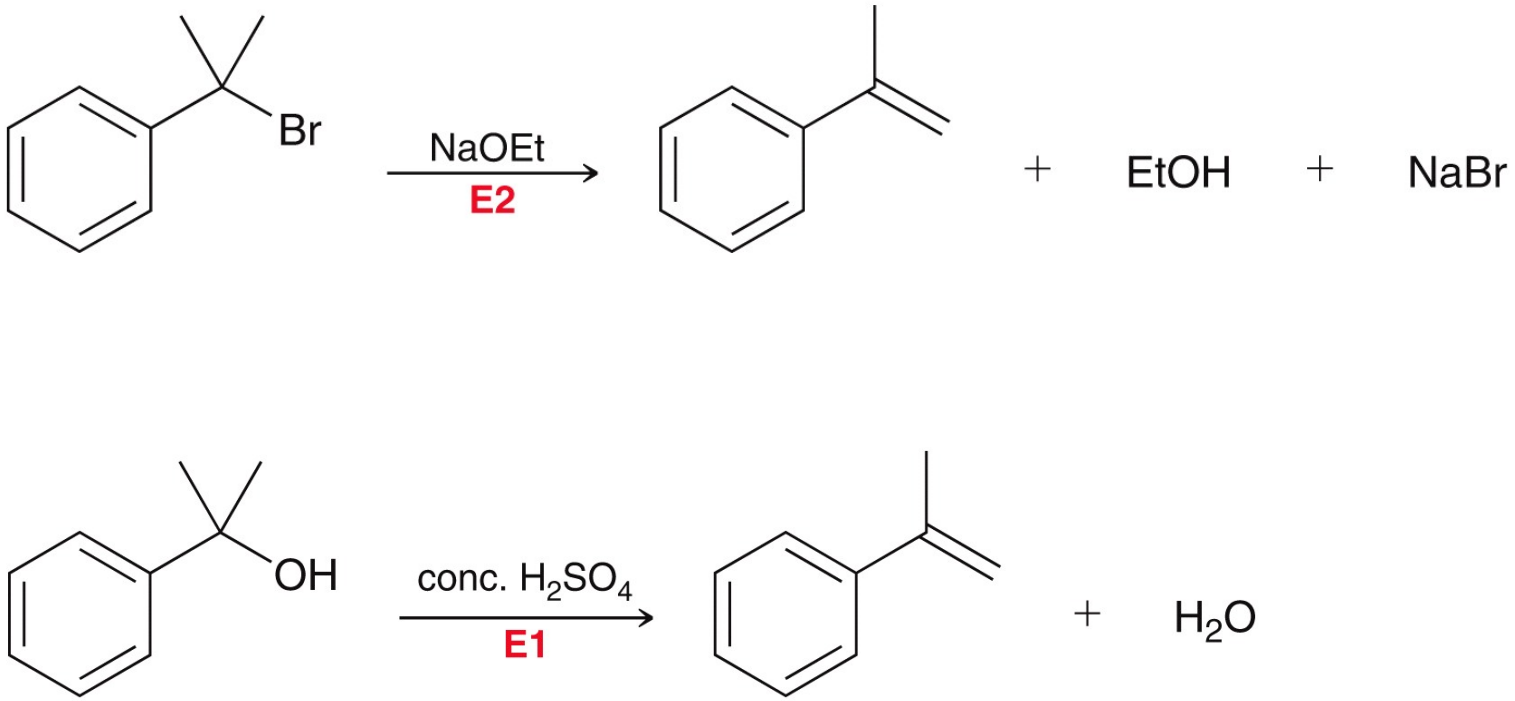


- Unhindered benzylic bromides undergo SN2 substitution as well:

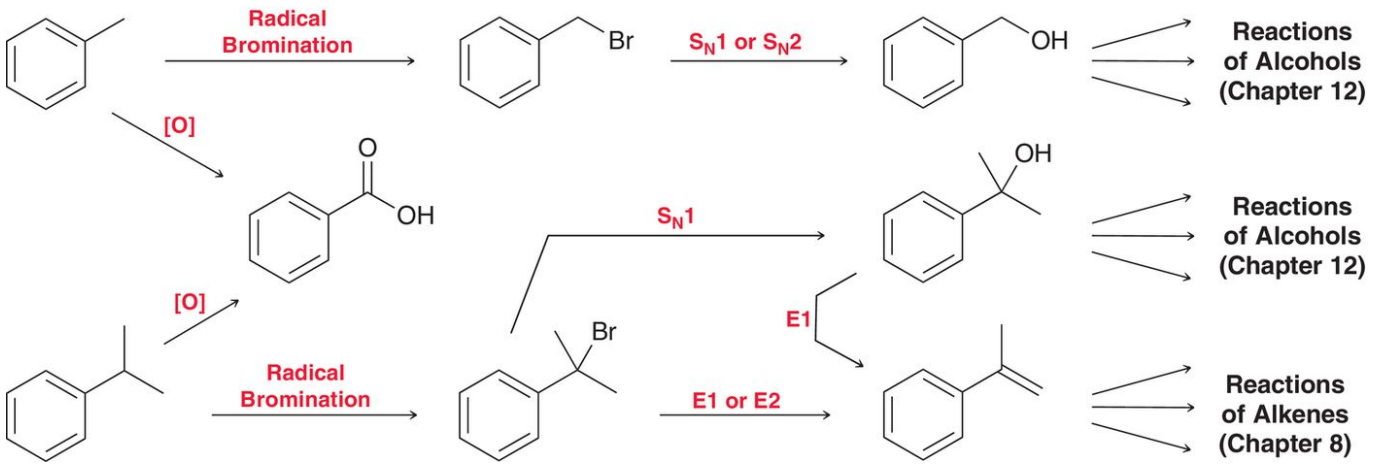


17.6 Reactions at the Benzylic Position

- Benzylic bromides are readily converted to the corresponding alkene(s) via E1 or E2 elimination:



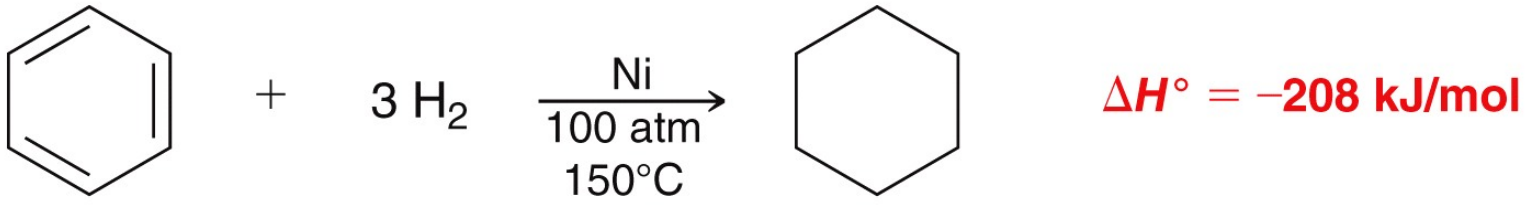
17.6 Reactions at the Benzylic Position



- **Practice with SkillBuilder 17.4**

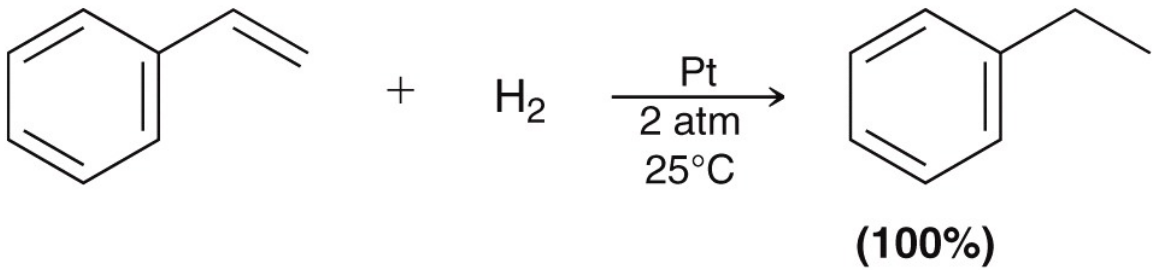
17.7 Reduction of Benzene

- Under forceful conditions, benzene can be reduced to cyclohexane



$\Delta H° = -208$ kJ/mol

- However, alkenes can be selectively hydrogenated in the presence of a benzene ring:

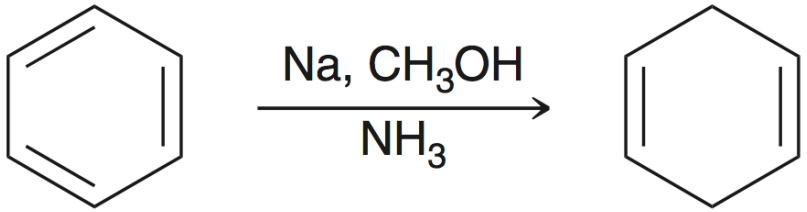


(100%)

$\Delta H° = -117$ kJ/mol

17.7 Reduction of Benzene

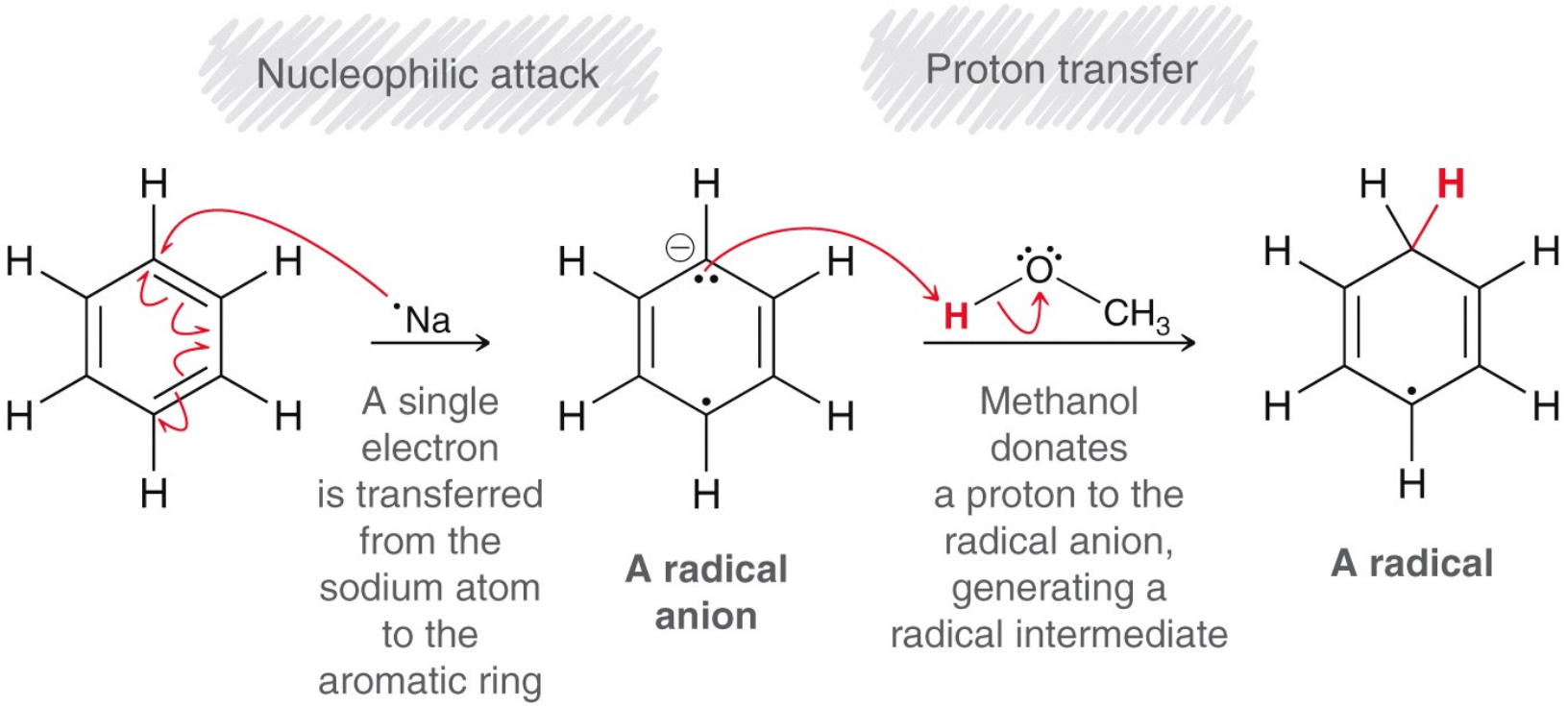
- Benzene can be reduced via **Birch** reduction (chapter 9.5)



- The mechanism is similar to dissolving metal reduction of an alkyne

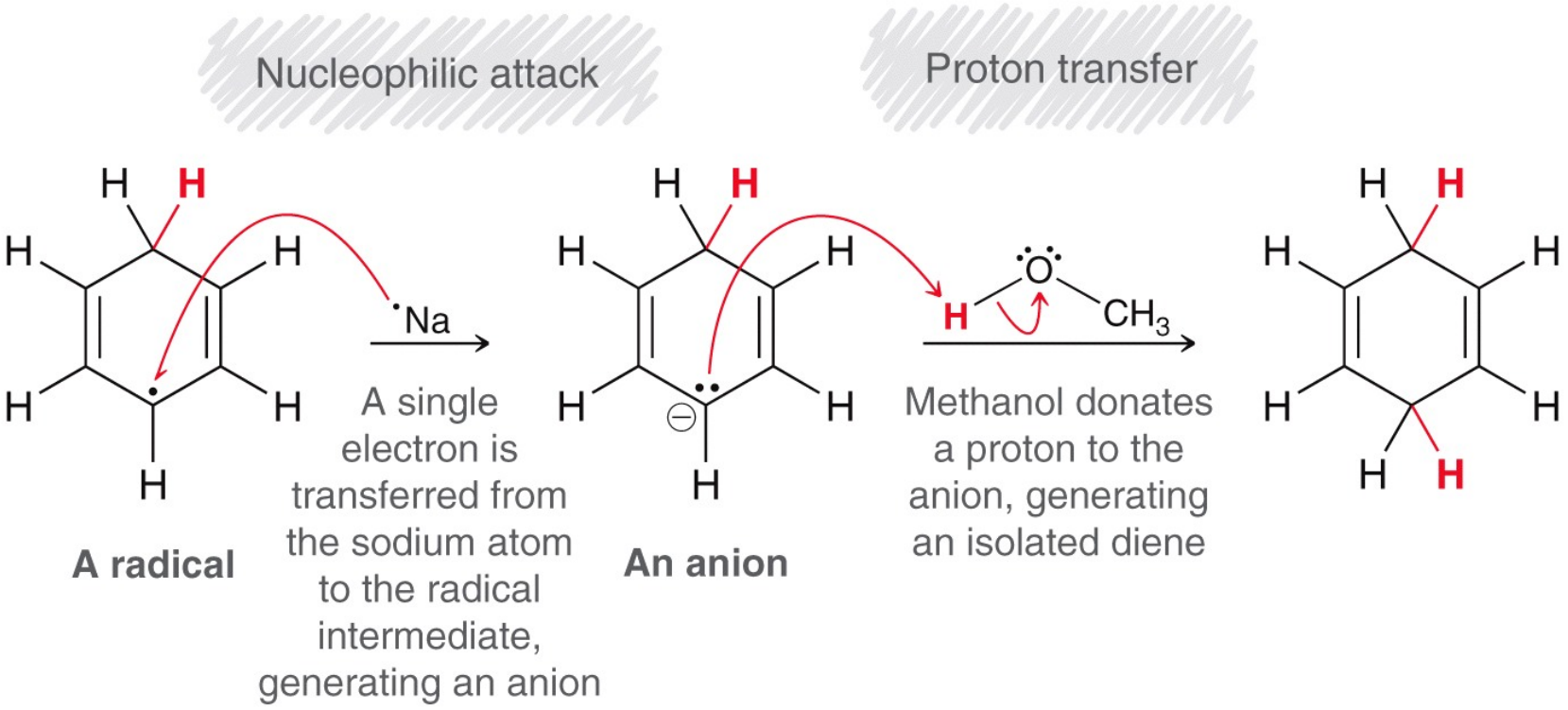
17.7 Reduction of Benzene

- Benzene can be reduced via **Birch** reduction (chapter 9.5)



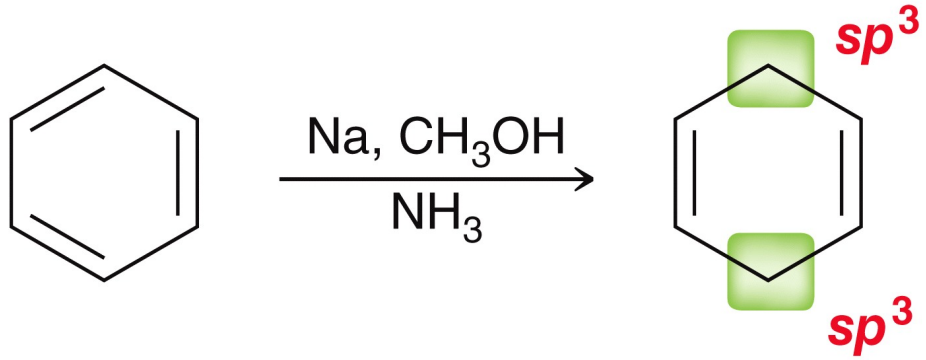
17.7 Reduction of Benzene

- Benzene can be reduced via **Birch** reduction (chapter 9.5)



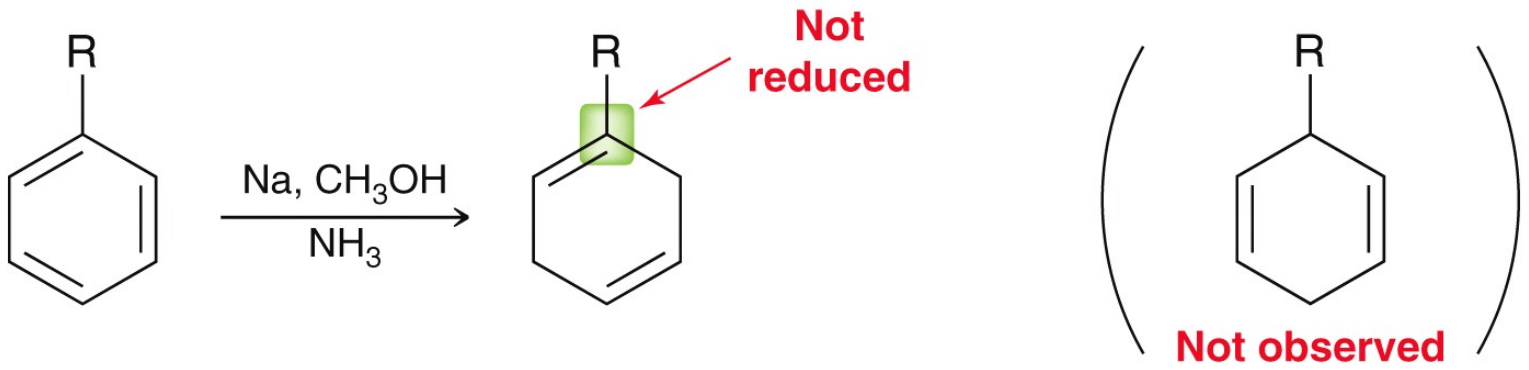
17.7 Reduction of Benzene

- Note that the **Birch** reduction does not completely reduce the benzene ring
- product has sp^3 hybridized carbons on opposite ends of the ring



17.7 Reduction of Benzene

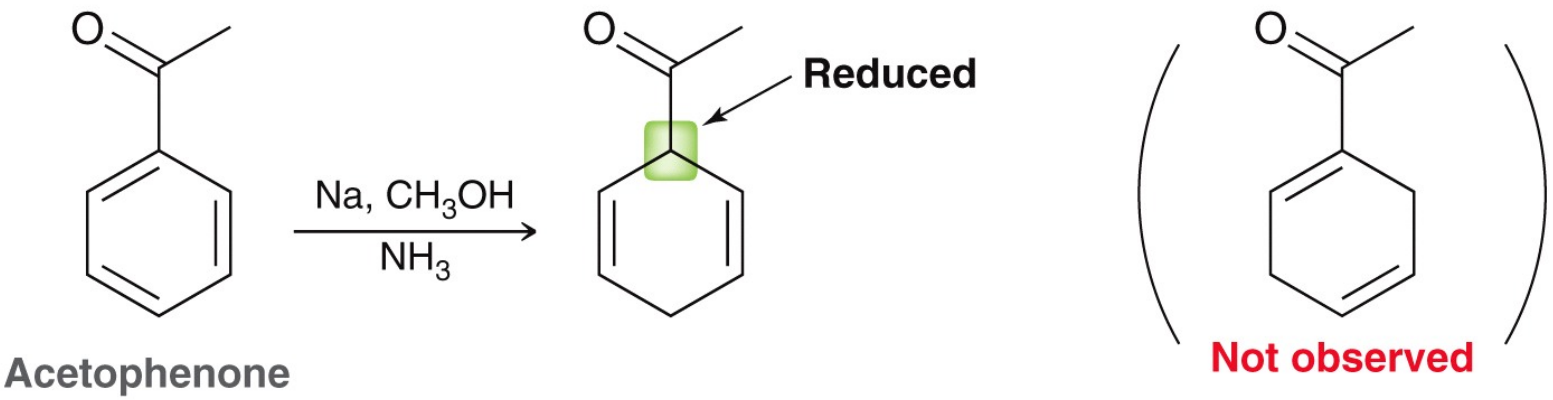
- The presence of an electron donating alkyl side group provides regioselectivity.



- An electron-donating group destabilizes the radical cation, and so reduction does not occur at a carbon possessing an electron-donating group.

17.7 Reduction of Benzene

- The presence of an electron-withdrawing group results in the opposite regioselectivity:



- **Practice with SkillBuilder 17.5**

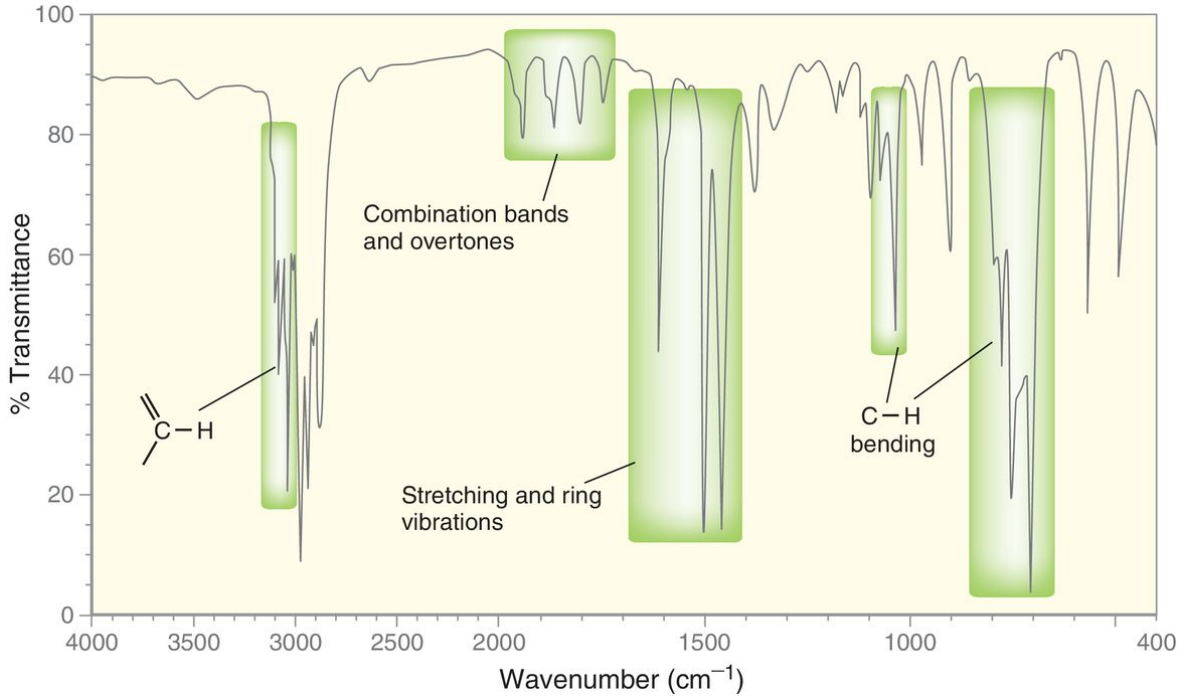
17.8 Spectroscopy of Aromatic Compounds

TABLE 17.2 CHARACTERISTIC SIGNALS IN THE IR SPECTRA OF AROMATIC COMPOUNDS

ABSORPTION	FEATURE	COMMENTS
3000–3100 cm^{-1}	C_{sp^2}—H stretching	One or more signals just above 3000 cm^{-1}. Intensity is generally weak or medium
1700–2000 cm^{-1}	Combination bands and overtones	A group of very weak signals
1450–1650 cm^{-1}	Stretching of carbon-carbon bonds as well as ring vibrations	Generally three signals (medium intensity) at around 1450, 1500, and 1600 cm^{-1}
1000–1275 cm^{-1}	C—H bending (in plane)	Several signals of strong intensity
690–900 cm^{-1}	C—H bending (out of plane)	One or two strong signals

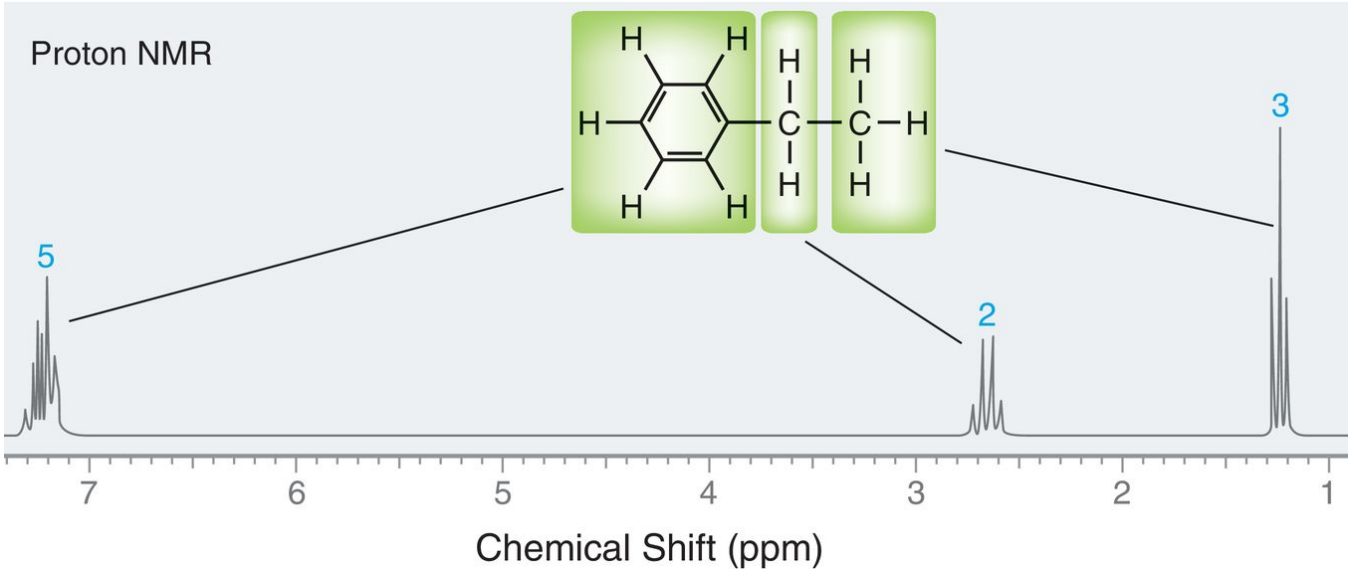
17.8 Spectroscopy of Aromatic Compounds

- IR spectrum for ethylbenzene



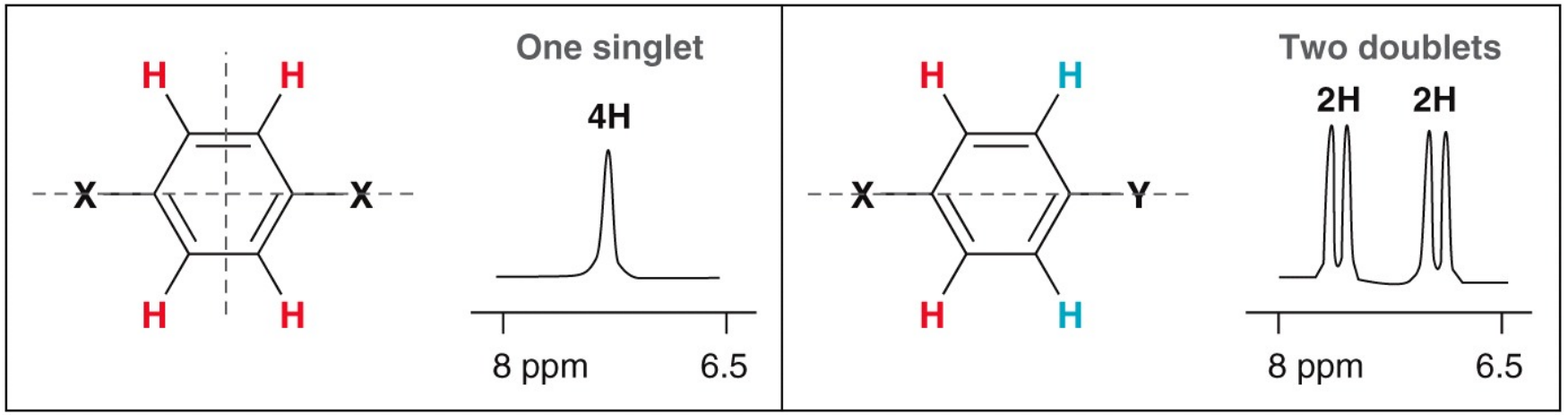
17.8 Spectroscopy of Aromatic Compounds

- Aromatic protons typically appear 6.5 to 8 ppm (chapter 15.5)



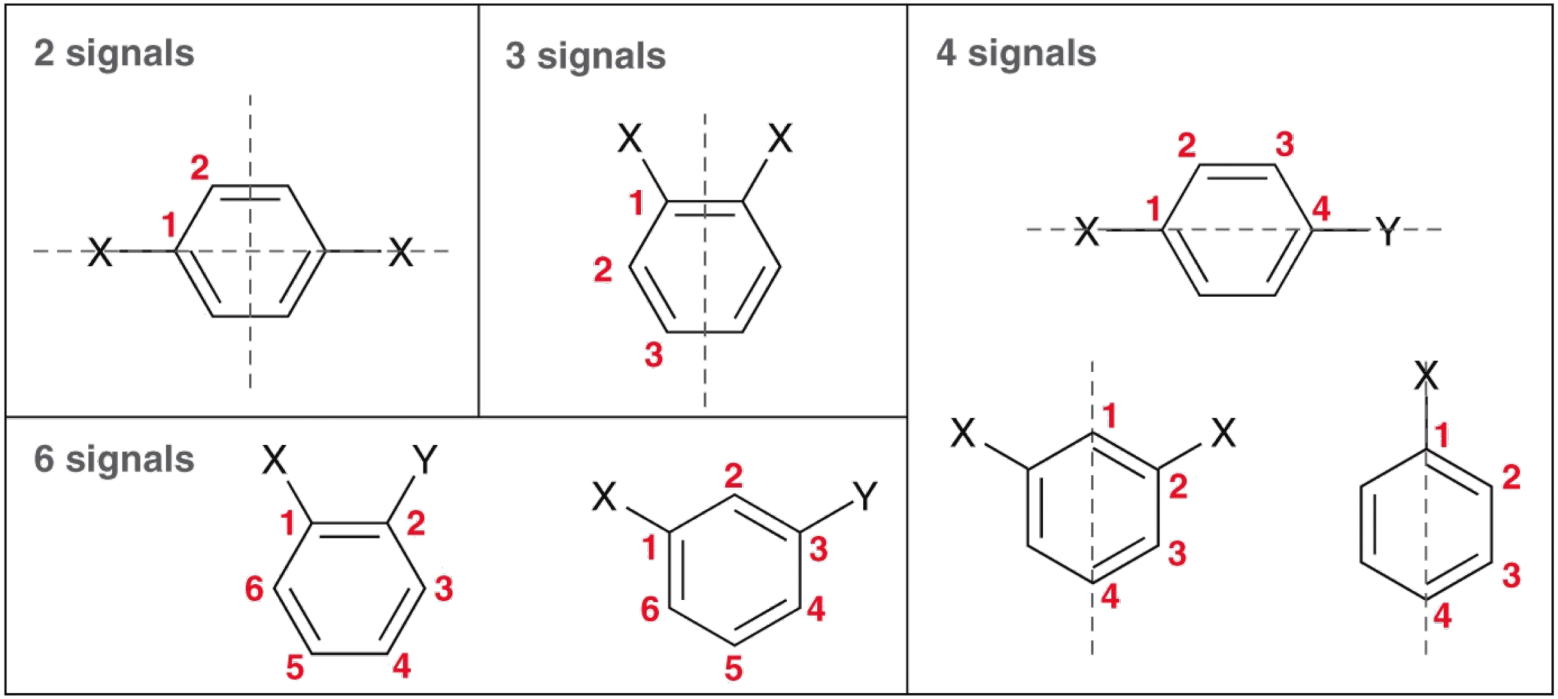
17.8 Spectroscopy of Aromatic Compounds

- The integration and splitting of protons in the aromatic region of the ^1H NMR is useful for rings with multiple substituents:



17.8 Spectroscopy of Aromatic Compounds

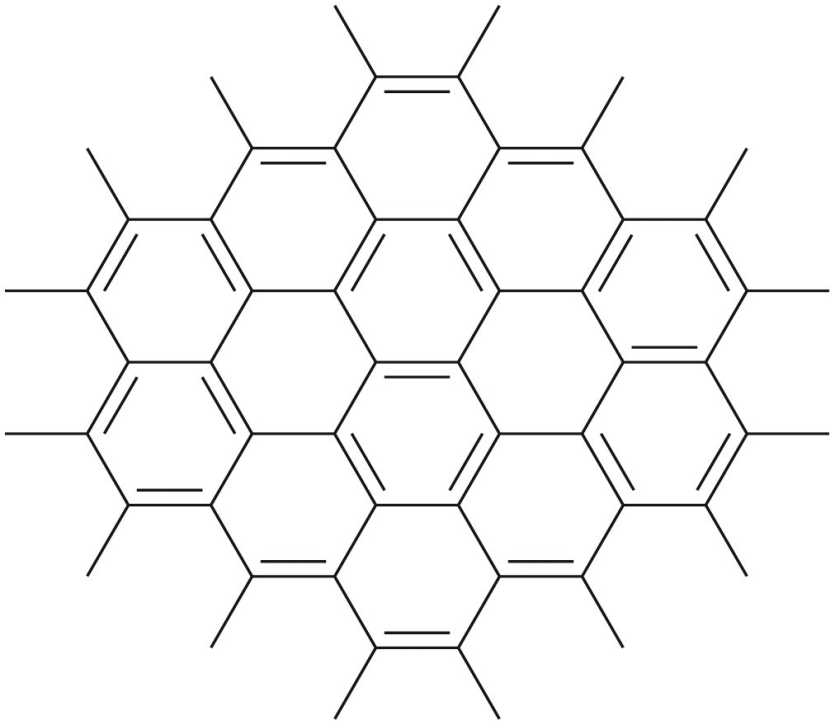
- In ^{13}C NMR, carbon atoms of benzene typically appear from approx. 100 to 150 ppm.



- The # of signals is helpful to determine the substitution pattern.
- **Practice with Conceptual Checkpoint 17.22 – 17.23**

Buckyballs and Nanotubes

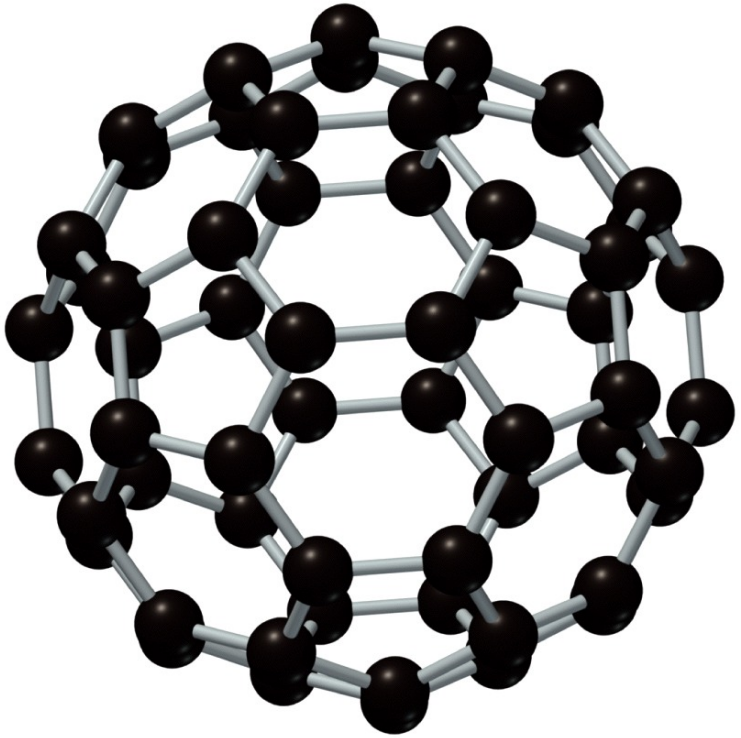
- Graphite consists of layers of sheets of fused aromatic rings

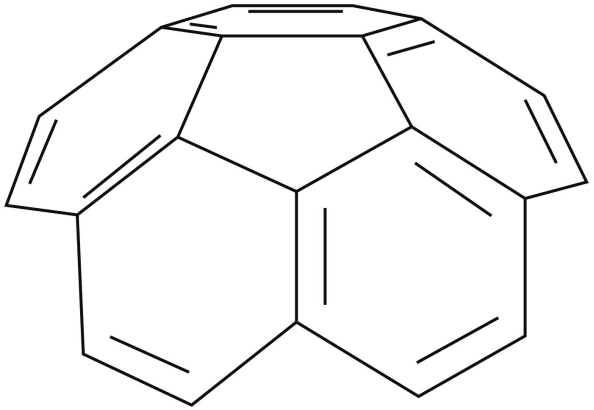


Graphite

Buckyballs and Nanotubes

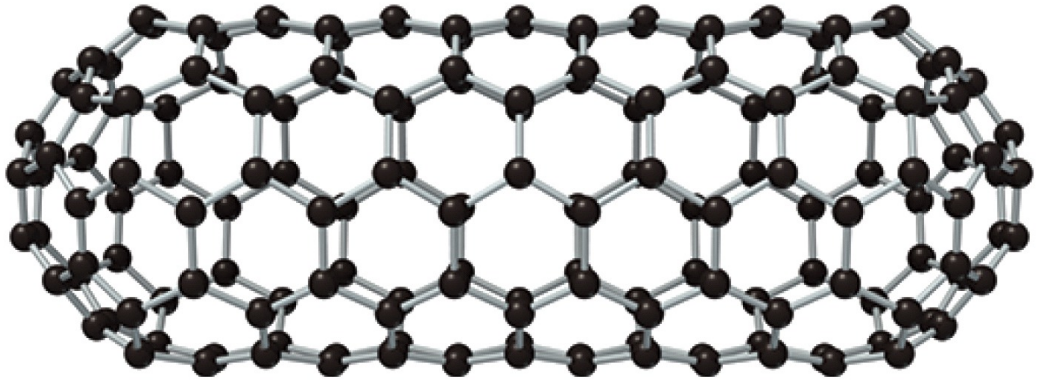
- Buckyballs are C_{60} spheres made of interlocking aromatic rings





Buckyballs and Nanotubes

- Fullerenes can be made into tubes (cylinders) = **nanotubes**



- Single, double, and multi-walled carbon nanotubes have many applications:
  - Conductive Plastics, Energy Storage, Conductive Adhesives, Molecular Electronics, Thermal Materials, Fibres and Fabrics, Catalyst Supports, Biomedical Applications