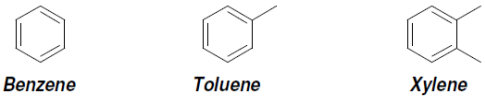
18.1 Introduction to Aromatic Compounds

- AROMATIC compounds or ARENES include benzene and benzene derivatives.



Benzene ***Toluene*** ***Xylene***

- Many aromatic compounds were originally isolated from fragrant oils.
- However, many aromatic compounds are odorless.
- Aromatic compounds are quite common.

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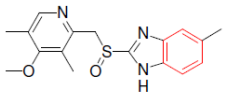
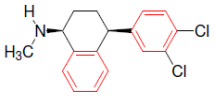
18.1 Introduction to Aromatic Compounds

- 8 of the 10 best-selling drugs have aromatic moieties.



Nexium™ (Omeprazole)
A proton-pump inhibitor used in the treatment of ulcers and acid reflux



Zoloft™ (Sertraline)
Used in the treatment of depression

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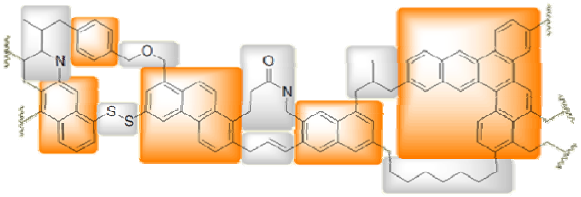
18.1 Introduction to Aromatic Compounds

- Coal contains aromatic rings fused together and joined by nonromantic moieties.



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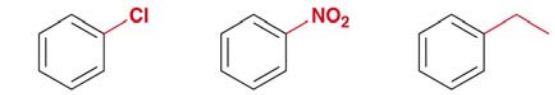
18.2 Nomenclature of Benzene Derivatives

- Benzene is generally the parent name for monosubstituted derivatives.



Chlorobenzene **Nitrobenzene** **Ethylbenzene**

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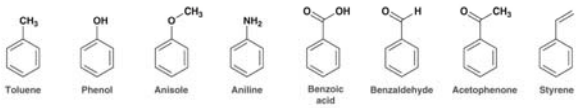
18.2 Nomenclature of Benzene Derivatives

- Many benzene derivatives have common names.
- For some compounds, the common name becomes the parent name.



Toluene Phenol Anisole Aniline Benzoic acid Benzaldehyde Acetophenone Styrene

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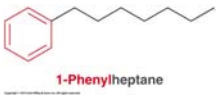
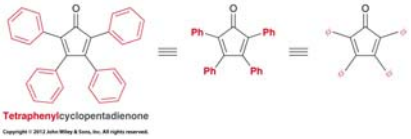
18.2 Nomenclature of Benzene Derivatives

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



1-Phenylheptane

- Aromatic rings are often represented with a Ph (for phenyl) or with a ϕ (phi) symbol.



Tetraphenylcyclopentadienone

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18.2 Nomenclature of Benzene Derivatives

- The common name for dimethyl benzene derivatives is XYLENE.

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- What do ORTHO, META, and PARA mean?

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18.2 Nomenclature of Benzene Derivatives

1. Identify the parent chain (the longest consecutive chain of carbons).
2. Identify and name the substituents.
3. Number the parent chain and assign a locant (and prefix if necessary) 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.

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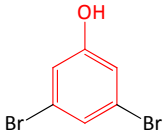
18.2 Nomenclature of Benzene Derivatives

- Locants are required for rings with more than 2 substituents.

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



2. Identify and name the substituents.

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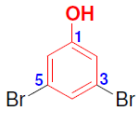
18.2 Nomenclature of Benzene Derivatives

3. Number the parent chain and assign a locant (and prefix if necessary) 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.
   - Complete the name for the molecule above.

- Practice with SKILLBUILDER 18.1.

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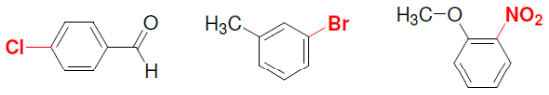
18.2 Nomenclature of Benzene Derivatives

- Name the following molecules.



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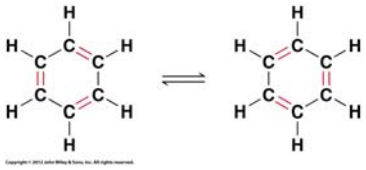
18.3 Structure of Benzene

- 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.

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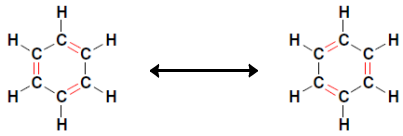
18.3 Structure of Benzene

- We now know that the aromatic structures are resonance contributors rather than in equilibrium.



- HOW is resonance different from equilibrium?
- Sometimes the ring is represented with a circle in it
- WHY?

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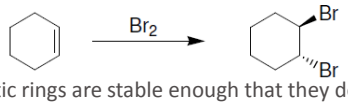
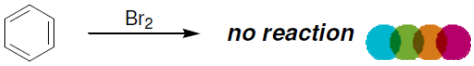
18.4 Stability of Benzene

- The stability that results from a ring being aromatic is striking.
- Recall that in general, alkenes readily undergo addition reactions.



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



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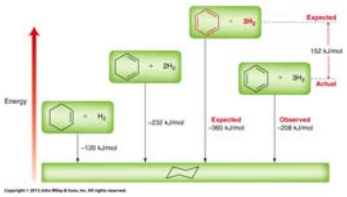
18.4 Stability of Benzene

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



- Practice with CONCEPTUAL CHECKPOINTs 18.6 and 18.7.

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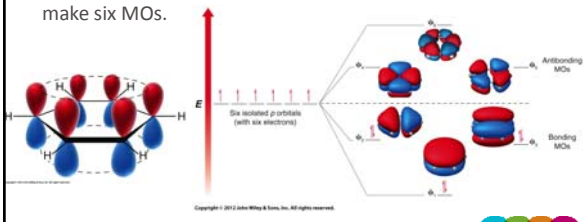
18.4 Stability of Benzene

- Molecular orbital (MO) theory can help us explain aromatic stability.
- The six atomic p-orbitals of benzene overlap to make six MOs.



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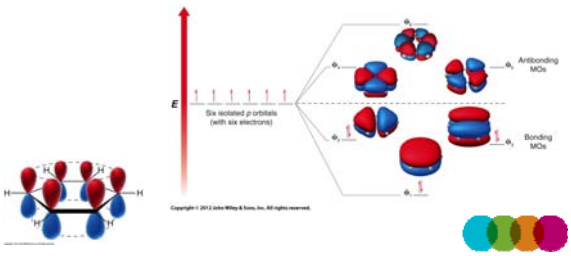
18.4 Stability of Benzene

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



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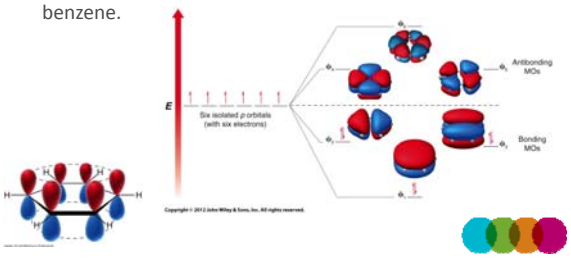
18.4 Stability of Benzene

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



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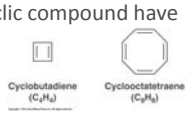
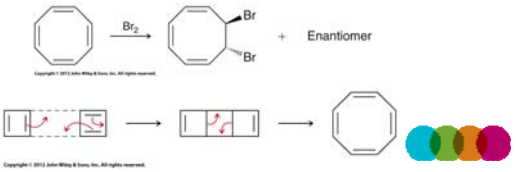
18.4 Stability of Benzene

- Does every fully conjugated cyclic compound have aromatic stability? NO.



- Some fully conjugated cyclic compounds are reactive rather than being stable like benzene.



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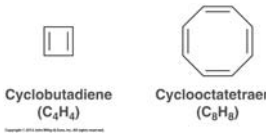
18.4 Stability of Benzene

- AROMATIC compounds fulfill two criteria:
  1. A fully conjugated ring with overlapping p-orbitals
  2. Meets HÜCKEL'S RULE: an ODD number of electron pairs or 4n+2 total π electrons where n = 0, 1, 2, 3, 4, etc.
- Show how the molecules below do NOT meet the criteria.



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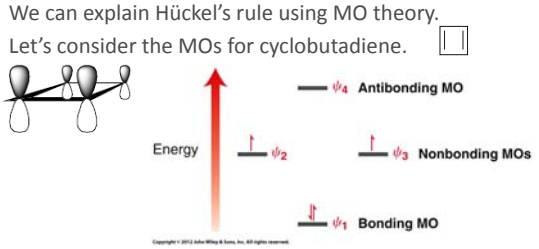
18.4 Stability of Benzene

- We can explain Hückel's rule using MO theory.
- Let's consider the MOs for cyclobutadiene.



- The instability of the unpaired electrons (similar to free radicals) makes this ANTIAROMATIC.

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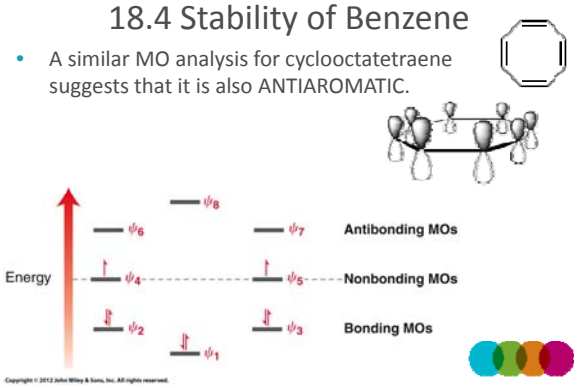
18.4 Stability of Benzene

- A similar MO analysis for cyclooctatetraene suggests that it is also ANTIAROMATIC.



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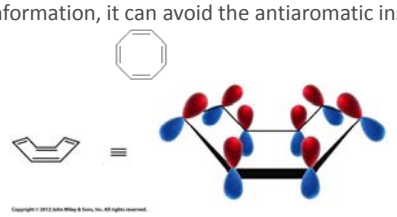
18.4 Stability of Benzene

- However, if the structure adopts a tub-shaped conformation, it can avoid the antiaromatic instability.



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

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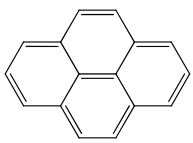
18.4 Stability of Benzene

- Is the compound below aromatic or antiaromatic? HOW?



- Practice with CONCEPTUAL CHECKPOINT 18.8.

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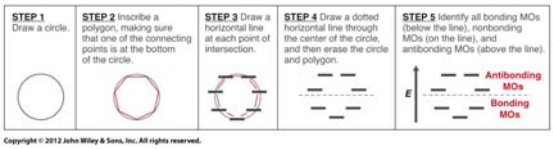
18.4 Stability of Benzene

- Predicting the shapes and energies of MOs requires sophisticated mathematics, but we can use FROST CIRCLES to predict the relative MO energies.



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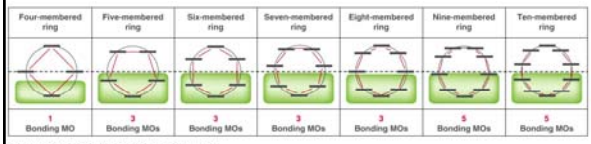
18.4 Stability of Benzene

- Use the FROST CIRCLES below to explain the 4n+2 rule.



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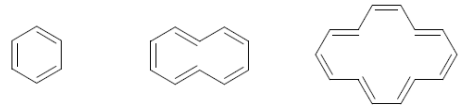
- Note that the number of bonding orbitals is always an odd number; aromatic compounds will always have an odd number of electron pairs.
- Practice with CONCEPTUAL CHECKPOINT 18.9.

18.5 Aromatic Compounds Other Than Benzene

- AROMATIC compounds fulfill two criteria:
  1. A fully conjugated ring with overlapping p-orbitals
  2. Meets HÜCKEL'S RULE: an ODD number of electron 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.

18.5 Aromatic Compounds Other Than Benzene

- Annulenes are rings that are fully conjugated.

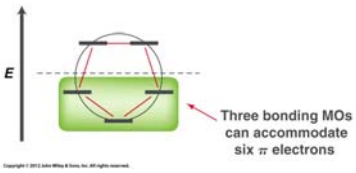


[6]Annulene ***[10]Annulene*** ***[14]Annulene***

- Some annulenes are aromatic, while others are antiaromatic.
- [10]Annulene is neither. WHY?
- Practice with CONCEPTUAL CHECKPOINT 18.10.

18.5 Aromatic Compounds Other Than Benzene

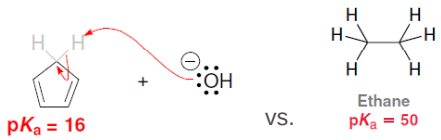
- Some rings must carry a formal charge to be aromatic.
- Consider a 5-membered ring.



- If six pi electrons are present, draw the resonance contributors for the structure.

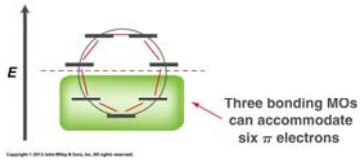
18.5 Aromatic Compounds Other Than Benzene

- The pK_a value for cyclopentadiene is much lower than typical C-H bonds. WHY?



18.5 Aromatic Compounds Other Than Benzene

- Consider a 7-membered ring.



- If six pi electrons are present, what charge will be necessary?
- Draw the resonance contributors for the structure.
- Practice with SKILLBUILDER 18.2.

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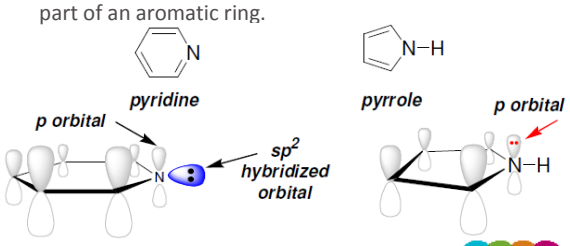
18.5 Aromatic Compounds Other Than Benzene

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



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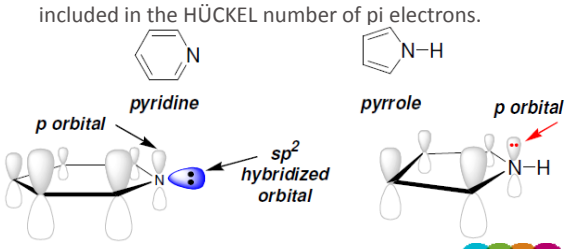
18.5 Aromatic Compounds Other Than Benzene

- If the heteroatom's lone pair is necessary, it will be included in the HÜCKEL number of pi electrons.



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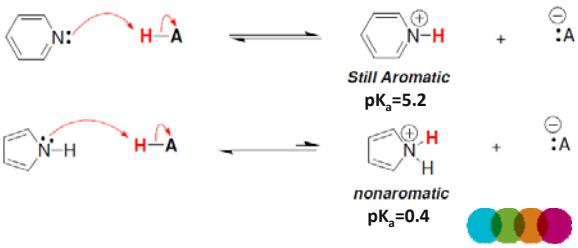
18.5 Aromatic Compounds Other Than Benzene

- If the lone pair is necessary to make it aromatic, the electrons will not be as basic.



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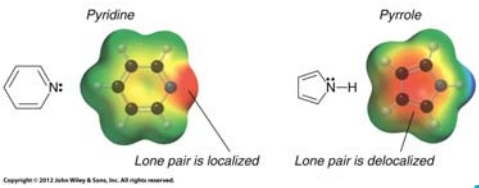
18.5 Aromatic Compounds Other Than Benzene

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



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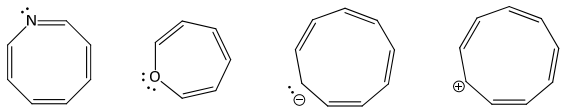
18.5 Aromatic Compounds Other Than Benzene

- Will the compounds below be aromatic, antiaromatic, or non aromatic?



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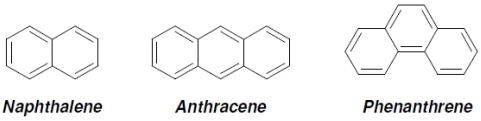
18.5 Aromatic Compounds Other Than Benzene

- Many polycyclic compounds are also aromatic.



Naphthalene *Anthracene* *Phenanthrene*

- Such compounds are shown to be aromatic using heats of hydrogenation. HOW?

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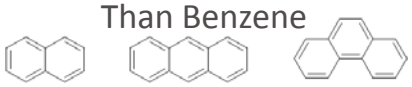
18.5 Aromatic Compounds Other Than Benzene



Naphthalene *Anthracene* *Phenanthrene*

Compound	Stabilization Energy (kJ / mol)	Average Stabilization Energy *per ring* (kJ / mol)
Benzene	152	152
Naphthalene	255	128
Anthracene	347	115
Phenanthrene	381	127

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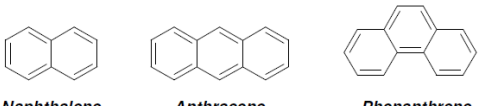
18.5 Aromatic Compounds Other Than Benzene

- Show that the molecules below meet the criteria for aromaticity:
  1. A fully conjugated ring with overlapping p-orbitals
  2. Meets HÜCKEL'S RULE: an ODD number of electron pairs or 4n+2 total π electrons where n = 0, 1, 2, 3, 4, etc.



Naphthalene *Anthracene* *Phenanthrene*

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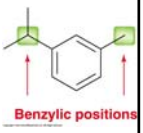
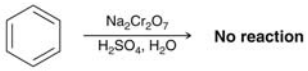
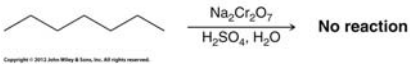
18.6 Reactions at the Benzylic Position

- A carbon that is attached to a benzene ring is BENZYLIC.
- Recall that aromatic rings and alkyl groups are not easily oxidized.







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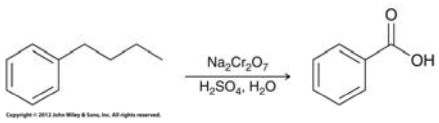
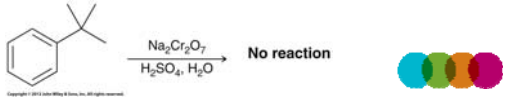
18.6 Reactions at the Benzylic Position

- In general, benzylic positions can readily be fully oxidized.



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



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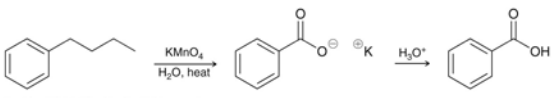
18.6 Reactions at the Benzylic Position

- Permanganate can also be used as an oxidizing reagent.



- Practice with CONCEPTUAL CHECKPOINT 18.19.

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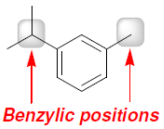
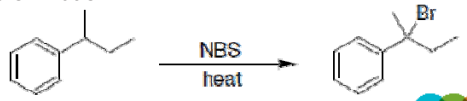
18.6 Reactions at the Benzylic Position

- BENZYLIC positions have similar reactivity to allylic positions. WHY?



- Benzylic positions readily undergo free radical bromination.



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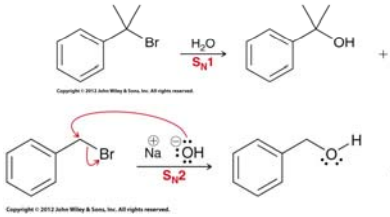
18.6 Reactions at the Benzylic Position

- Once the benzylic position is substituted with a bromine atom, a range of functional group transformations are possible.



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18.6 Reactions at the Benzylic Position

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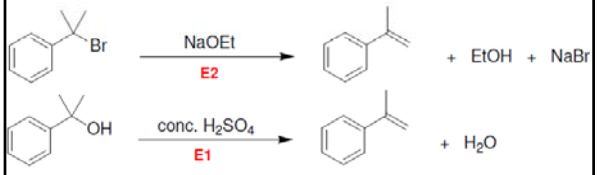

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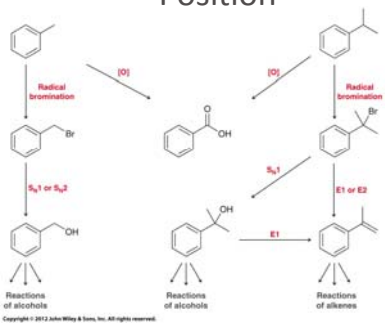
18.6 Reactions at the Benzylic Position



- Practice with SKILLBUILDER 18.4.

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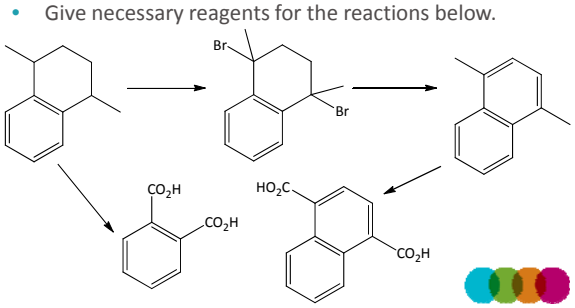
18.6 Reactions at the Benzylic Position

- Give necessary reagents for the reactions below.



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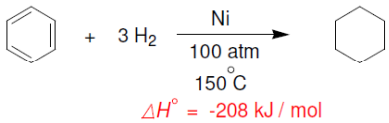
18.7 Reduction of the Aromatic Moiety

- Under forceful conditions, benzene can be reduced to cyclohexane.



ΔH° = -208 kJ / mol

- Is the process endothermic or exothermic? WHY?
- WHY are forceful conditions required?

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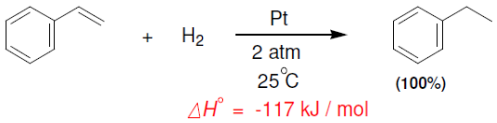
18.7 Reduction of the Aromatic Moiety

- Vinyl side groups can be selectively reduced.



$\triangle H^\circ$ = -117 kJ / mol

- ΔH is just slightly less than the expected –120 kJ/mol expected for a C=C → C–C conversion.
- WHY are less forceful conditions required?

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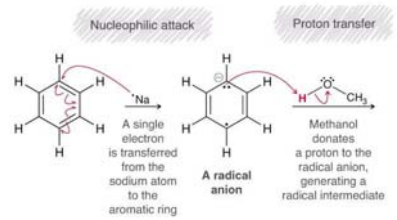
18.7 Reduction of the Aromatic Moiety

- Like alkenes, benzene can undergo the BIRCH reduction.



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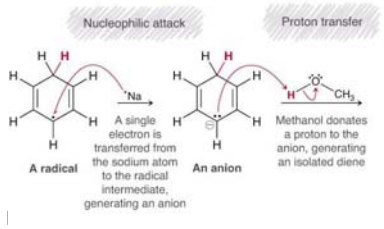
18.7 Reduction of the Aromatic Moiety

- Like alkenes, benzene can undergo the BIRCH reduction.



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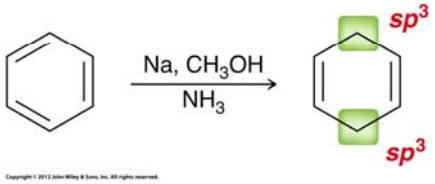
18.7 Reduction of the Aromatic Moiety

- Note that the BIRCH reduction product has sp^3 hybridized carbons on opposite ends of the ring.



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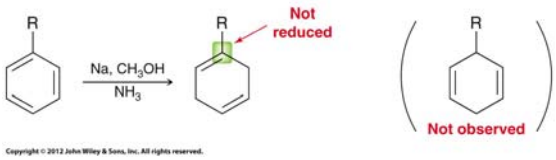
18.7 Reduction of the Aromatic Moiety

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



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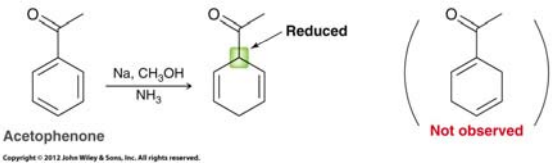
18.7 Reduction of the Aromatic Moiety

- The presence of an electron withdrawing carbonyl side group provides different regioselectivity. HOW?



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- Practice with SKILLBUILDER 18.5.

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18.8 Spectroscopy of Aromatic Compounds

TABLE 18.2 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}	C=C stretching and 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

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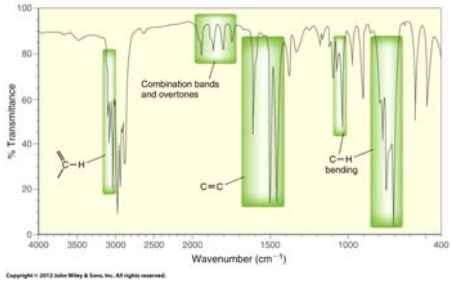
18.8 Spectroscopy of Aromatic Compounds

- IR spectra for ethylbenzene:



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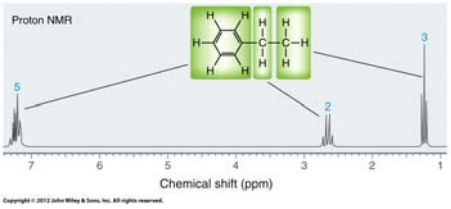
18.8 Spectroscopy of Aromatic Compounds

- Recall from Section 16.5 how the anisotropic effects of an aromatic ring affect NMR shifts.



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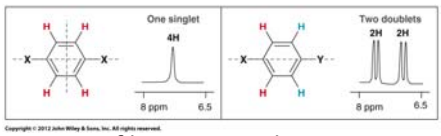
18.8 Spectroscopy of Aromatic Compounds

- The integration and splitting of protons in the aromatic region of the ^1H NMR (≈7 ppm) in often very useful.



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- Be aware of long-range splitting on aromatic rings and the possibility of signal overlap.

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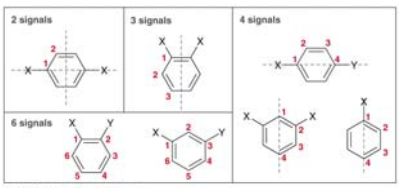
18.8 Spectroscopy of Aromatic Compounds

- Because of possible ring symmetry, the number of signals in the ^{13}C NMR (≈100-150 ppm) generally provides structural information.



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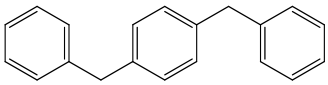
18.8 Spectroscopy of Aromatic Compounds

- For the molecule below, predict the shift for the ^{13}C signals, and predict the shift, integration, and multiplicity for the ^1H NMR signals.



- Practice with CONCEPTUAL CHECKPOINTs 18.26 and 18.27.

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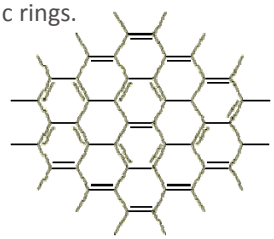
Graphite, Buckyballs, and Nanotubes

- Graphite consists of layers of sheets of fused aromatic rings.



Graphite

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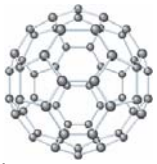
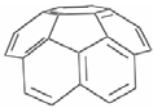
Graphite, Buckyballs, and Nanotubes

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





- Fullerenes come in other sizes such as C_{70}.
- How are Buckyballs aromatic when they are not FLAT?

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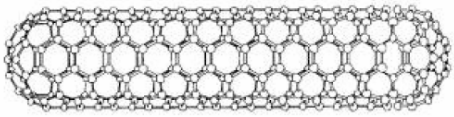
Graphite, Buckyballs, and Nanotubes

- Fullerenes can also be made into tubes (cylinders).



- 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

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