

## Review Guide #2

Lectures: 1/31/05 –2/6/05 Chapters 15 and 16

### I. Aromatic compounds

- A. Benzene has a special stability that is termed aromaticity and can be depicted as the hybrid of two equally contributing resonance structures. Since the molecule is planar, and the axes of all six  $p$  orbitals are parallel, the  $p$  orbitals can overlap to form a continuous  $\pi$  molecular orbital system that provides additional bonding and additional stability.
- B. Criteria for aromaticity:
1. Aromatic compounds contain rings with a cyclic arrangement of  $p$  orbitals.
  2. Every atom of an aromatic ring has a  $p$  orbital.
  3. Aromatic rings are planar.
  4. The cyclic arrangement of  $p$  orbitals in an aromatic compound must contain  $4n + 2$   $\pi$  electrons (Huckel's rule). So, an aromatic ring must contain 2, 6, 10 ...  $\pi$  electrons.

### II. Nomenclature of Benzene Derivatives

Refer to the textbook for details. You should learn the common names that are often used to describe the substituted benzene derivatives mentioned in lecture. Also know the ortho, meta and para positions for disubstituted benzene derivatives.

### III. Spectroscopy of Benzene Derivatives

Aromatic protons typically resonate between  $\delta$  7 and 8 in  $^1\text{H}$  NMR spectroscopy, farther downfield than vinylic protons (between  $\delta$  4.5 and 6). The applied magnetic field ( $H_{\text{applied}}$ ) causes the  $\pi$  electrons to circulate around the ring, which induces a magnetic field ( $H_{\text{induced}}$ ).  $H_{\text{induced}}$  opposes  $H_{\text{applied}}$  inside the ring, but reinforces it outside the ring where the aromatic protons are located. As a consequence, the aromatic protons are deshielded, from the external field and have greater chemical shifts than other protons. Please check the text and your class notes for  $^{13}\text{C}$  NMR, IR and UV spectroscopy.

### IV. Electrophilic Aromatic Substitution Reactions (the most characteristic reaction of benzene)

- A. The general mechanism of electrophilic aromatic substitution consists of three steps:
1. A strong electrophile is generated. A strong electrophile is required to react with benzene, a poor nucleophile.
  2. Benzene reacts with the electrophile generated in the first step, to form a resonance stabilized carbocation intermediate.
    - a. The positive charge density is always located on the C atoms ortho and para to the C atom attacked by the electrophile. You should be able to write all of the contributing resonance structures for this carbocation intermediate.
    - b. Because it is a resonance hybrid, with delocalized positive charge, this intermediate is considerably more stable than a typical secondary carbocation.
  3. Loss of  $\text{H}^+$  from the carbocation intermediate restores the aromatic  $\pi$  system and leads to the final substitution product.
- B. You should know the reagent conditions used, the overall transformation, and the reaction mechanism for the following electrophilic aromatic substitution reactions: bromination, chlorination, nitration, sulfonation, Friedel-Crafts acylation (used to prepare aryl ketones), and Friedel-Crafts alkylation (used to prepare alkylbenzenes).

**V. Substituent Effects of Electrophilic Aromatic Substitution Reactions**

## A. Directing effects

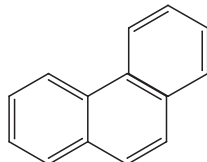
1. Ortho, para directors can stabilize a positive charge. As a result, the intermediates formed when the electrophile reacts at the ortho or para position are relatively more stable than the intermediates formed when the electrophile reacts at the meta position. The more stable intermediates form at a faster rate (recall Hammond's postulate).
  - a. Alkyl groups are ortho, para directors because they can stabilize a positive charge through hyperconjugation.
  - b. Groups in which the atom directly attached to the ring has a lone pair, are ortho, para directors because they can stabilize a positive charge through resonance.
2. Meta directors typically cannot stabilize a positive charge very well. The intermediates formed from ortho or para attack (with a meta director) are very unstable, whereas the intermediate formed from a meta attack is relatively more stable, so it forms faster. Meta directors typically have a polar bond adjacent to the benzene ring, in which the partial positive charge resides on the atom that is directly attached to the ring.

B. Activating and deactivating effects

1. A substituent is said to be activating if its presence leads to an electrophilic aromatic substitution reaction that is faster than that of unsubstituted benzene. All of the ortho, para directors EXCEPT THE HALOGENS are activating groups. Activating groups have a net electron-donating effect to the ring.
2. A substituent is said to be deactivating if its presence leads to an electrophilic aromatic substitution reaction that is slower than that of unsubstituted benzene. The reaction is slower because the intermediate is less stable than that formed in the reaction of unsubstituted benzene. Deactivating groups have a net electron-withdrawing effect from the ring.
  - a. All meta directing groups are also deactivating, for the reasons described above.
  - b. The halogens are deactivating, because of a polar effect. Because the halogens are more electronegative than carbon, they tend to pull electron density away from the aromatic ring making the ring less reactive towards an electrophile. For the halogens, this polar effect is relatively more important than the resonance effect responsible for the halogens being ortho, para directors.

**Supplemental Problems**

1. Some suggested problems are: 16.13, 16.17, 16.18, 16.21, 16.25, 16.26, 16.40, 16.54.
2. There are five resonance structures for Phenanthrene (one is shown). Draw the other four. Which carbon-carbon bond is the shortest? (from McMurry, Organic Chemistry)



3. There are also five resonance structures for Aniline (one is shown). Draw the other four. Why do you suppose that arylamines, such as Aniline, are weaker bases than alkylamines?

