

CHEM 322 Organic Chemistry II - Professor Kathleen V. Kilway

"Organic Chemistry" by Maitland Jones, 3rd edition

Chapter 13 Homework: 7, 8, 9, 10, 13, 16, 17, 20, 21, 25, 28, 29, 31, 32, 33, 37, 38, 42, 43, 44, 48.

CHAPTER 13 Conjugation and Aromaticity

Section 13.1

I. Preview

A- 1,3,5-cyclohexatriene versus benzene

1- Benzene is a compound where the six $2p$ orbitals overlap, which results in different reactivity than other trienes.

B- Essential Skills

- 1- It is important to understand the relevance of aromaticity.
- 2- Initial reactions with aromatic compounds are introduced.

Section 13.2

II. The Structure of Benzene

A- First Approximation: 1,3,5-cyclohexatriene

- 1- It has a molecular formula of C_6H_6 .
- 2- There are four possible structures.
- 3- One would be 1,3,5-cyclohexatriene with alternating single and double bonds.

B- Physical Properties

- 1- The actual structure is a hexagon with identical C-C bond lengths.
- 2- Therefore, the double bonds are not static in the C_6H_6 structure.

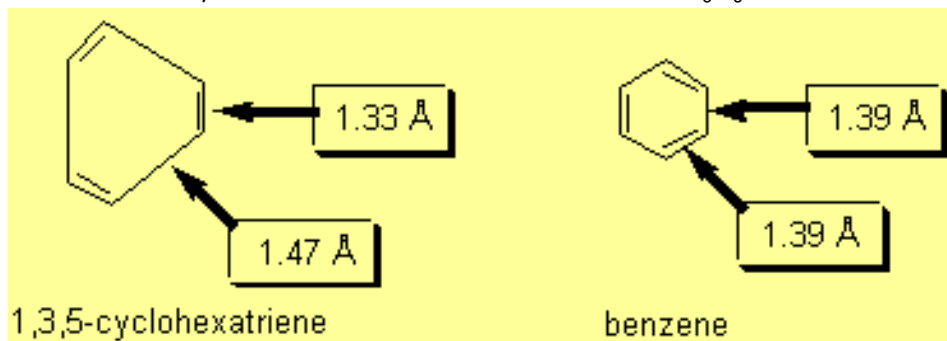


Fig 1

Section 13.3

III. A Resonance Picture of Benzene

A- Kekulé Forms For Benzene.

- 1- Each carbon is sp^2 hybridized with an extra $2p$ orbital on each carbon.

2- Each Kekulé form shows isolated double bonds but in reality there is complete $2p$ - $2p$ overlap.

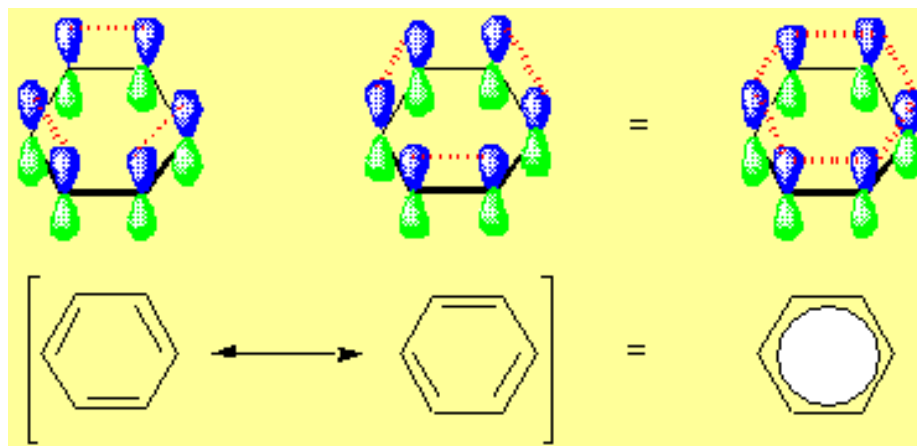


Fig 2

Section 13.4

IV. Molecular Orbital Picture of Benzene

A- Molecular Orbitals arise from the linear combination of the six atomic orbitals.

- 1- Three of the molecular orbitals are bonding and three are antibonding.
- 2- There are six π electrons which go into the bonding molecular orbitals.
- 3- Therefore, the antibonding orbitals are empty.
- 4- The energy stability is on the order of 18 kcal/mol.

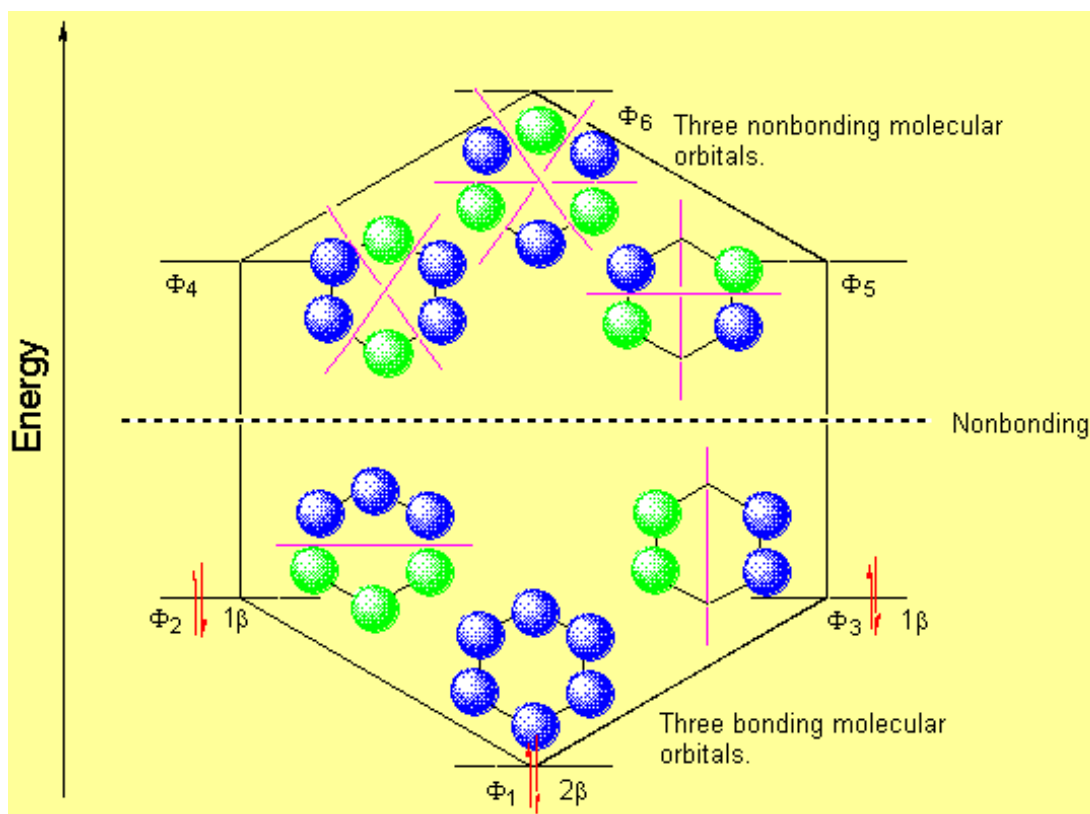


Fig 3

Section 13.5

V. Quantitative Evaluations of Resonance Stabilization (Delocalization Energy) in Benzene

A- Heats of Hydrogenation.

- 1- There is no stabilization of an alkene in a ring vs. an internal alkene.
- 2- Both have a Heat of Hydrogenation of -28.6 kcal/mol.
- 3- For 1,3-cyclohexadiene, there is some stability due to conjugation. (Theoretical $\Delta H = -57.2$ kcal/mol; experimental $\Delta H = -55.4$ kcal/mol).
- 4- For 1,3,5-cyclohexadiene (three isolated double bonds), the ΔH would be -82.2 kcal/mol.
- 5- Benzene has ΔH of -49.3 kcal/mol which is -32.9 kcal/mol lower in energy than the predicted value for 1,3,5-cyclohexatriene.
- 6- **Delocalization or resonance energy** is the energy lowering conferred by the delocalization electrons. For benzene, it is the amount by which benzene is more stable than the hypothetical 1,3,5-cyclohexatriene containing three isolated double bonds.

B- Heats of Formation

- 1- The heats of formation can also be used to estimate the delocalization energy of benzene.
- 2- The ΔH for cyclooctatetraene is 71.23 kcal/mol or 8.9 kcal/mol per each CH unit.
- 3- The ΔH for benzene is 19.82 kcal/mol or 3.3 kcal/mol per each CH unit.
- 4- Therefore, the CH units of benzene are 5.6 kcal/mol and 33.6 kcal/mol more stable than another cyclic polyene.
- 5- Both independent measurements of the resonance or delocalization energy are essentially the same.
- 6- This special stability is known as benzene's **aromatic character** or **aromaticity**.

Section 13.6

VI. A Generalization of Aromaticity: Hückel's $4n + 2$ Rule

A- Rules for Aromaticity

- 1- The molecule must be cyclic.
- 2- The molecule must be fully conjugated; there is a $2p$ orbital on every atom of the ring.
- 3- The molecule is planar or at least close to planar.
- 4- The molecule must follow the $4n + 2$ p electron where n is an integer, $0, 1, 2, 3, \dots$ (i.e., $0, 2, 6, 10, 14, \dots$)
- 5- Antiaromatic molecules follow rules 1-3 and have $4n$ π electrons.

B- Frost Circle is a device to find the molecular orbitals of a cyclic compound.

- 1- Inscribe the cyclic structure inside a circle with its vertex down.
- 2- The nonbonding line is in the center and divides the bonding and antibonding molecular orbitals.
- 3- The intersections of the ring with the circle will mark the positions of the molecular orbitals.
- 4- The orbitals that are of equal energy are said to be **degenerate**.
- 5- Then, the electrons are put into the orbitals unpaired, lowest energy first.
- 6- See figure 13.3 in this outline.

C- Exceptions.

- 1- Planar cyclodecapentaenes are destabilized by an amount greater than the aromaticity can overcome.
- 2- Even though molecules follow the $4n + 2$ rule, severe angle strain is too high of a cost to pay.

Section 13.7

VII. Annulenes

A- Annulene is a generic term for monocyclic, fully conjugated molecules.

Section 13.8

IIX. Substituted Benzenes

A- Monosubstitution

- 1- Phenyl - Ph - stands for a benzene ring.
- 2- Benzyl - Bz - stands for a Ph-CH₂ ring.
- 3- Compounds to know:
 - a- toluene - methylbenzene
 - b- aniline - aminobenzene
 - c- phenol - hydroxybenzene
 - d- anisole - methoxybenzene
 - e- benzyl chloride, benzyl alcohol

B- Polysubstitution - Disubstitution

- 1- *Ortho*- (*o*, 1,2) is disubstitution in a 1,2-fashion on a benzene ring.
- 2- *Meta*- (*m*, 1,3) is disubstitution in a 1,3-fashion on a benzene ring.
- 3- *Para*- (*p*, 1,4) is disubstitution in a 1,4-fashion on a benzene ring.

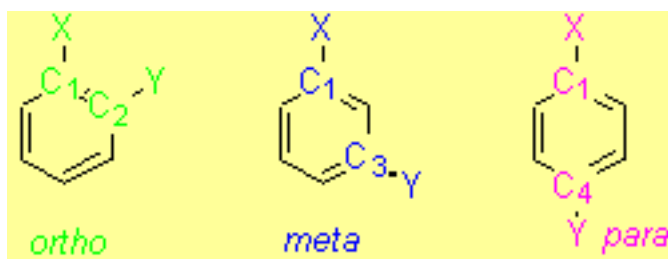


Fig 4

4- Examples:

- a- *o*-bromotoluene or 1-bromo-2-methylbenzene
- b- 1,3-dichlorobenzene
- c- 4-nitrophenol.

5- Common Names:

- a- Xylene is dimethylbenzene.
- b- Cresol is methylphenol.
- c- Hydroquinone.

C- Polysubstitution - Trisubstitution and More...

- 1- These compounds are numbered and named alphabetically.

Section 13.9

IX. Physical Properties of Substituted Benzenes

A- Melting Points.

- 1- Symmetry increases overall melting point.
- 2- *Para* substitution increases the melting points because the compound can pack better.

B- Other.

- 1- Aromatic compounds are also called arenes and are abbreviated as Aryl or Ar.

Section 13.10

X. Heterobenzenes and Other Heterocyclic Aromatic Compounds

A- Contrasting Structures of Pyridine and the Five-Membered Rings: Pyrrole, Furan, and Thiophene

- 1- Pyridine is a heteroaromatic compound. There is a lone pair of electrons on the nitrogen that is not utilized in the π system. In fact, the lone pair is perpendicular to the π system.
- 2- Pyrrole is another example of a heteroaromatic compound. In this case, the lone pair of electrons on the nitrogen is included in the p system.
- 3- There is a better overlap for $2p-2p$ orbitals which explains why C-Si overlap is not favored.
- 4- Furan is a five-membered ring with two double bonds and one oxygen.
- 5- Thiophene is the sulfur derivative of furan.

B- Acid and Base Properties

- 1- Pyridine can be protonated in acid but is a weak base.
- 2- The pK_a of the corresponding protonated ammonium ion of pyridine is 5.2 which is much more acidic than a normal ammonium ion like piperidine ($pK_a \sim 11$).
- 3- Whereas, pyrrole is a very weak base (pK_a of corresponding ammonium ion is approximately -4).
- 4- But the pK_a of cyclopentadiene is 15 because the resulting anion is aromatic.

C- Pyridine as a Nucleophile

- 1- Pyridine can be alkylated in an S_N2 reaction (Chapter 7, p. 334) resulting in an alkyl pyridinium ion.
- 2- When these compounds are oxidized (e.g., H_2O_2 , hydrogen peroxide), a pyridine *N*-oxide.

Section 13.11

XI. Polynuclear Aromatic Compounds

A- All-Carbon Polynuclear Aromatic Compounds.

- 1- Naphthalene is the simplest example with two benzene rings sharing an edge.
- 2- In quinoline and isoquinoline, benzene and pyridine share an edge.
- 3- Anthracene and phenanthrene contain three fused benzene rings.
- 4- Graphite is a polymer composed of fused benzene rings in a nearly infinite plane.
- 5- When a carbon rod is vaporized, the major fragment is known as Buckminsterfullerene (C_{60}). It has the structure of a soccer ball of pure carbon and is fully aromatic.
- 6- Hexihelicene and Twistoflex are chiral examples of fused benzene rings.
- 7- Some polynuclear aromatic compounds are carcinogenic; one example is benz[*a*]pyrene.

B- Related Heterocycles: Indole, Benzofuran, and Benzothiophene.

- 1- These are examples of fused aromatic compounds with atoms other than carbon.
- 2- They are important because these structures found in natural products.

Section 13.12

XII. Introduction to the Chemistry of Benzene

A- Aromatic Substitution

- 1- Benzene does not react under normal alkene addition conditions.
- 2- The activation barriers produced by the stabilization of benzene by aromaticity are too high for Br_2 and HBr to react.
- 3- But if deuterated acid is used, the hydrogens in benzene can be exchanged for deuterium. (See Figure 5).

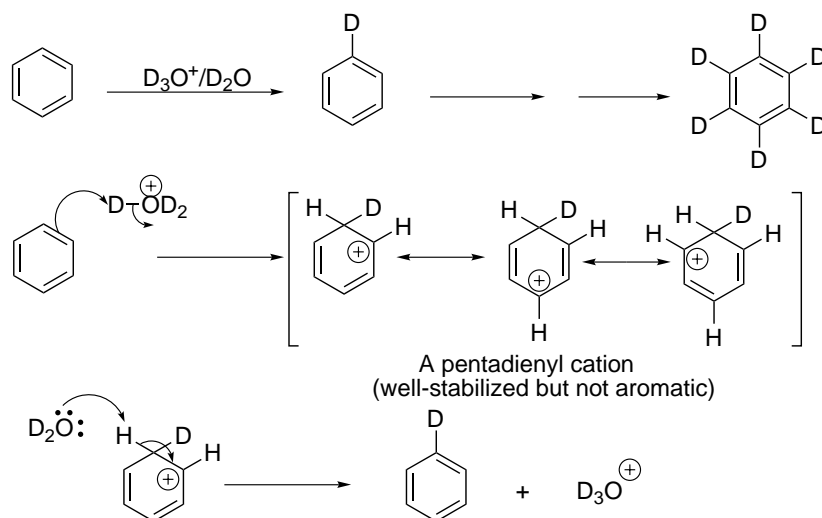


Fig 5

B- Birch Reduction of Aromatic Compounds.

1- A Birch reduction is the treatment of benzene with sodium in liquid ammonia and a little alcohol, which leads to the reduced product: 1,4-cyclohexadiene. (See Figure 6.)

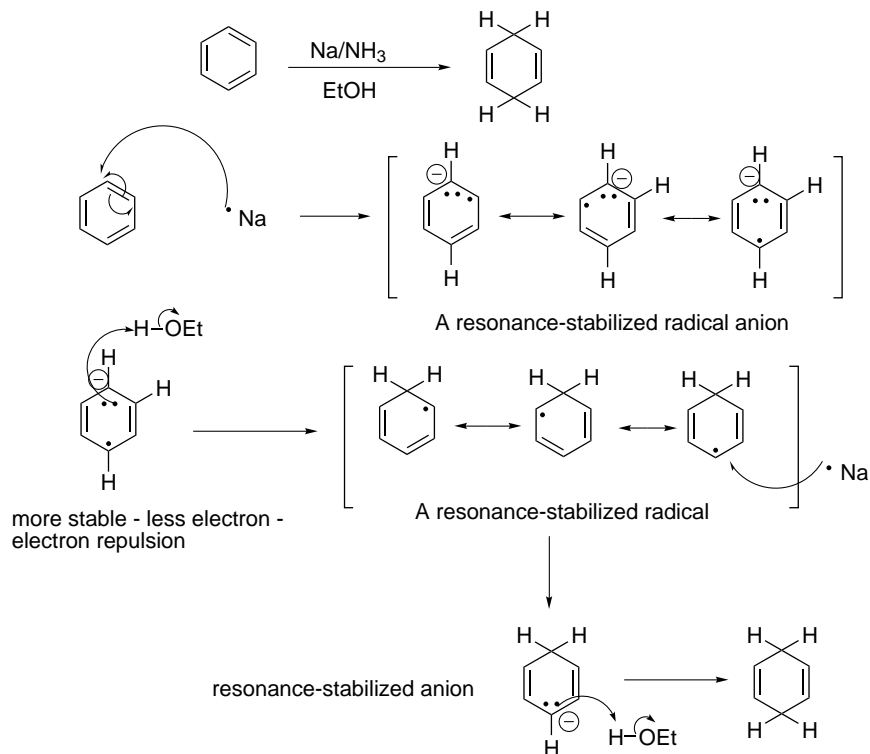


Fig 6

2- The reduction is sensitive to R groups on the benzene ring.

a- If the group is an electron withdrawing group (withdraws electron density), one product is formed (NO_2 , COCH_3 , etc).

b- If the group is an electron donating group (donates electron density), another product is formed (NH_2 , $-\text{OCH}_3$, etc). (See Figure 7)

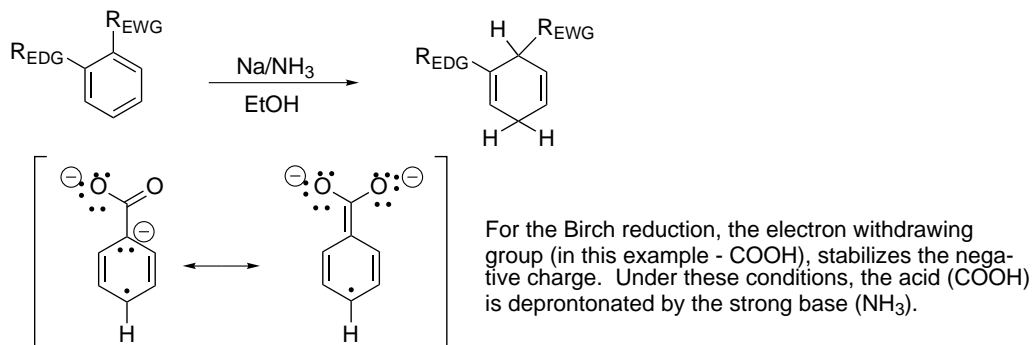


Fig 7

Section 13.13

XIII. The benzyl group and its Reactivity: Activation of the Adjacent (Benzyl) Position by Benzene Rings.

A- Substitution Reactions of Benzyl Compounds.

- 1- Benzyl compounds undergo both S_N1 and S_N2 reactions
- 2- In S_N1 reactions, the carbocation is stabilized due to the resonance stabilization of the benzene ring (i.e., the positive charge can be delocalized into the ring). There is an increase in the reaction rate in comparison to its alkyl counterpart.
- 3- For S_N2 reactions, the benzene or aromatic portion withdraws electron density of the transition state.

B- Radical Reactions at the Benzyl Position

- 1- Again, there is an increase in the rate of reaction because the intermediate radical can be delocalized into the benzene ring.

C- Oxidation at the Benzylic Position

- 1- Benzylic position is easily oxidized to benzoic acid with $KMnO_4$ or H_2CrO_7 .

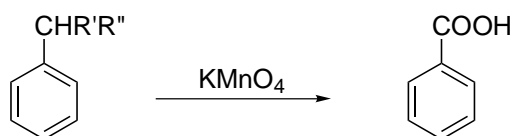


Fig 8

- 2- Tertiary benzylic systems are unreactive.

Section 13.14

XIV. The Mechanism of Carcinogenesis by Polycyclic Aromatic Compounds