Chapter 11

Arenes and Aromaticity

Chapter 11 suggested problems: 23, 30, 31, 33, 38, 39, 44, 46, 47, 48

Class Notes

I. Introduction

   A. Conjugated systems continued: benzene and aromatic hydrocarbons

   B. Arenes (or, aromatic hydrocarbons): hydrocarbons based on benzene ring as a fundamental structural unit

      1. Originally derived from fragrant gums and oils

      2. "All compounds that contain a benzene ring are aromatic" (Carey: 406)

   C. Aliphatic hydrocarbons - straight and branched chain molecules

      1. Originally derived from chemical treatment of animal fats

II. Benzene's history, Kekulè, and the structure of benzene

   A. History

      1. Discovered in 1825 by Michael Faraday

      2. Early discoveries and research based on research on benzoic acid

      3. Benzene isolated from coal tar in 1845, continued as principal source in until petrochemical industries developed in 1950s

      4. (From "Organic Chemistry," Ray Q. Brewster: Prentice-Hall, 1948. - p. 478) Coal as a source of benzene: one ton of coked coal yields

         a. 1500 pounds coke

         b. 10,000 - 12,000 cubic feet of gas

         c. 8-9 gallons of water

i. ammonia dissolved in the water yields 25 pounds of ammonium sulfate

d. 100 pounds of coal tar: fractional distillation yields

i. 1-2 pounds of benzene

ii. 0.3 - 0.5 pounds of toluene

iii. 0.1 - 0.2 pounds of xylenes

iv. 4 - 6 pounds of naphthalene

v. traces of other compounds (creosote oil: phenol, cresol, anthracene)

vi. 50-60 pounds of pitch (asphalt) remain for use in roofing and road paving

B. Early research demonstrated a perplexing stability in benzene and toluene

1. Halogens, hydrogen halides, water, and sulfuric acid did not add to the double bonds of the ring under any condition
   a. Addition to the ring can occur with appropriate catalysts

2. Substitution of functionalities for ring hydrogens can occur (electrophilic aromatic substitution)

C. Kekulè's proposals (1866)

1. Benzene is C_6H_6

2. All of the hydrogens are equivalent

3. There four bonds to each carbon atom

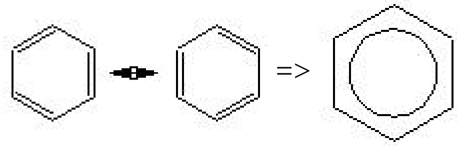
4. Benzene is a cyclic triene

5. Shortcomings
   a. Resonance was not understood in Kekulè's times; 1,2- and 1,6 disubstituted benzenes should have been isomeric rather than the same compound

   b. The bond distances are intermediate between those of sp^2 - sp^2 single and sp^2 - sp^2 double bonds

III. Bonding, resonance, and stability in benzene

A. When comparing benzene to non-aromatic alkenes and dienes, the heat of hydrogenation of benzene is about 152 kJ/mol less than that of 1,3,5-cyclohexatriene (if it actually existed)

B. Two Kekulè structures: 

1. Two resonance structures of equal energy

2. Resonance stabilization is greatest when contributing structures are of equivalent energy

C. The six carbon atoms in benzene are sp^2 hybridized

1. The molecule is planar (6 x trigonal planar atoms)

2. The shape is of a regular hexagon (120 bond angles)

3. 6 x unhybridized p electrons to participate in pi bonds

4. The resonance stabilization of benzene is due to the delocalization of the pi electrons

IV. Substituted derivatives of benzene and their nomenclature

A. Monosubstituted benzenes

1. Many are named by placing the substituent name in front of "benzene"

a. Chlorobenzene, bromobenzene, iodobenzene

b. Nitrobenzene

2. Common names and systematic names

a. Toluene - methylbenzene

b. Phenol - benzenol

c. Aniline - benzenamine

d. Benzoic acid - benzenecarboxylic acid

e. Styrene - vinyl benzene

f. Anisole - methoxybenzene

g. Benzaldehyde - benzenecarbaldehyde

h. Acetophenone - methyl phenyl ketone

B. Disubstituted benzenes

1. The constitutional isomers of xylene (dimethyl benzene)
    a. 1,2-xylene or o-xylene
    b. 1,3-xylene or m-xylene
    c. 1,4-xylene or p-xylene
2. The o, m, p prefixes may be used in two circumstances
    a. When a disubstituted substance is named as a benzene derivative
        i. o-dichlorobenzene
    b. When there are two substituents and one of them is responsible for giving benzene a common name
        i. m-nitrotoluene
        ii. p-chloroanisole

C. Trisubstituted benzenes and beyond

1. Numbers must be used for trisubstituted and beyond (substituents are named alphabetically)
2. If all the groups are the same each is given a number such that the sequence gives the lowest possible combination of numbers
3. If the groups are different then the last named group is understood to be in position number 1
    a. 2,4,6-trinitrotoluene
    b. 2,4-dichloronitrobenzene
    c. 3-ethyl-2-methylaniline

D. Benzene as a substituent

1. Benzene rings as substituents are called phenyl groups
    a. 2-phenylethanol
    b. 1-phenylnonane
    c. 1-phenyl-2-propanone

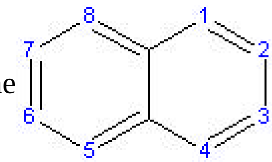
E. Biphenyls

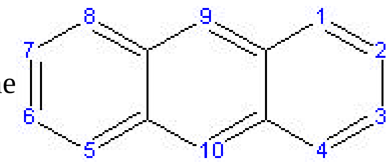
1. Two phenyl groups joined by a sigma bond are called biphenyl

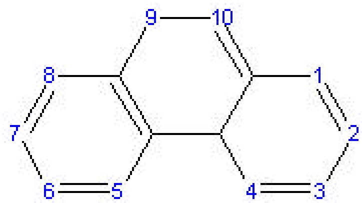
a. polychlorinated biphenyls

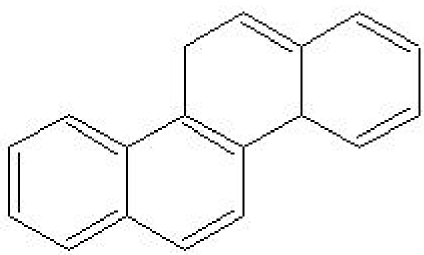
V. Polycyclic aromatic hydrocarbons: systems of fused benzene rings

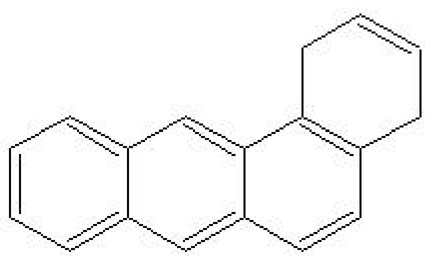
A. Two or more fused benzene rings are called polyaromatic hydrocarbons

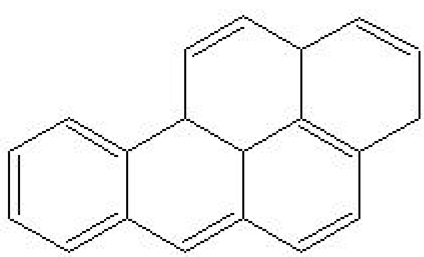
1. Naphthalene 

2. Anthracene 

3. Phenanthrene 

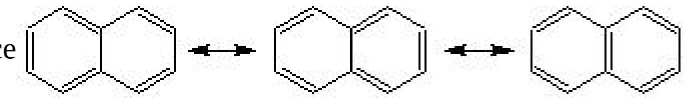
4. Chrysene 

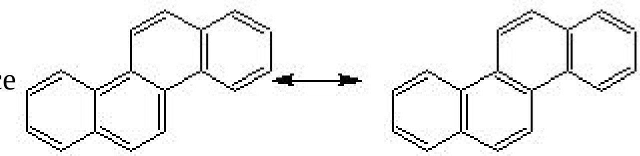
5. 1,2-benzanthracene 

6. Benzo[a]pyrene (BAP) 

7. Chrysene, 1,2-benzanthracene, and benzo[a]pyrene are carcinogens

B. As a general rule the most stable resonance structure for a PAH is the one in which the greatest number of rings correspond to Kekulè structures of benzene

1. Naphthalene resonance 

2. Chrysene resonance 

VI. Physical properties of arenes

A. Unsubstituted arenes are nonpolar, dispersion forces

B. Substituents can impact the intermolecular forces that occur

C. Benzene (10 ppm), toluene (200 ppm), and xylene (100 ppm) as solvents

VII. Reactions of arenes

A. Types of reactivity

1. Reactivity that involves the ring itself

a. Reduction

b. Electrophilic aromatic substitution (Ch. 12)

2. Reactivity in which benzene is a substituent and affects the behavior of the functional group to which it is attached

a. Benzylic carbons - carbon atoms attached to the ring

b. Benzylic hydrogens - attached to benzylic carbons

c. C-H bond dissociation energies [for the reaction R··H -> R· + H·] (B&M inside front cover)

bond type	kcal/mol
CH_3-H	104
C_2H_5-H	98
n-C_3H_7-H	98
i-C_3H_7-H	95
t-C_4H_9-H	91
CH_2=$CHCH_2$-H	88
CH_2=CH-H	104
$C_6H_5CH_2$-H	85

d. Ease of abstraction of hydrogen atoms (M&B:387): benzylic, allylic > 3° > 2° > 1° > methyl, vinylic

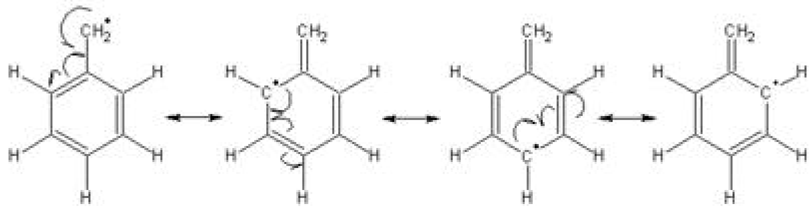
e. Stability of free radicals (M&B:388): allylic, benzylic > 3° > 2° > 1° > methyl, vinylic

f. Ionization potentials [for the reaction R· -> R^+ + e^-] (M&B: 165, 397)

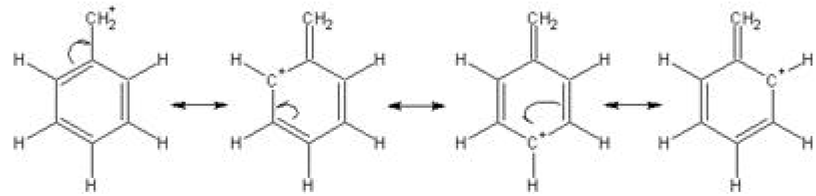
cation	kcal/mol
CH_3·	229
C_2H_5·	202
i-C_3H_7·	182
t-C_4H_9·	171
CH_2=$CHCH_2$·	178
$C_6H_5CH_2$·	160

g. Stability of carbocations (M&B:397): benzylic, 3° > allylic, 2° > 1° > methyl, vinylic

h. Benzylic radicals and resonance



i. Benzylic carbocations and resonance



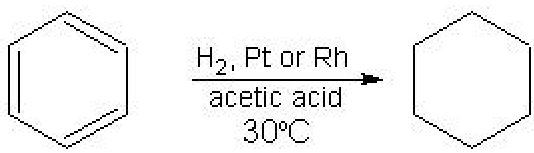
j. Note that while there are multiple resonance structures for both benzylic radical and benzylic carbocation, the most stable structure (and therefore the most significant contributor to the actual structure) is the one in which benzene remains aromatic

k. There is no "benzylic rearrangement" analogous to allylic rearrangement

l. This explains why reactions provide a single substitution product (i.e., substitution of benzylic hydrogens)

B. The reduction of benzene

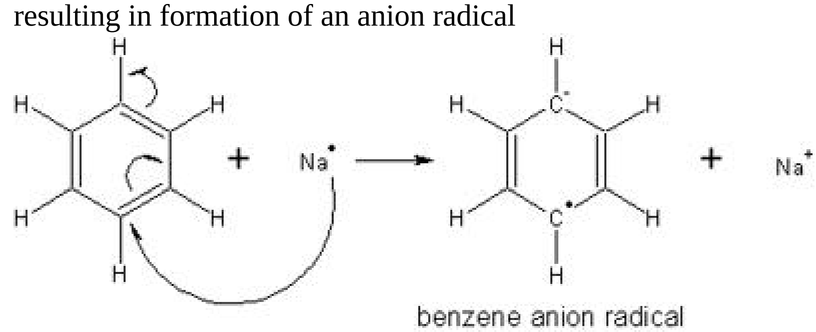
1. The reduction of benzene



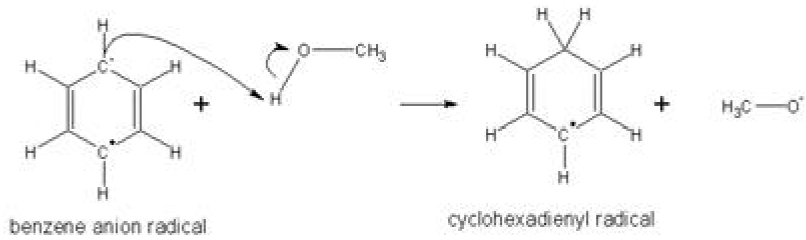
2. The Birch reduction: the 1,4-addition of hydrogen to benzene (but not a hydrogenation reaction, since molecular H_2 is not involved)

a. A metal-ammonia-alcohol reduction (sodium and methanol or ethanol in liquid ammonia for benzene) of aromatic compounds which results in the formation of 1,4 dienes

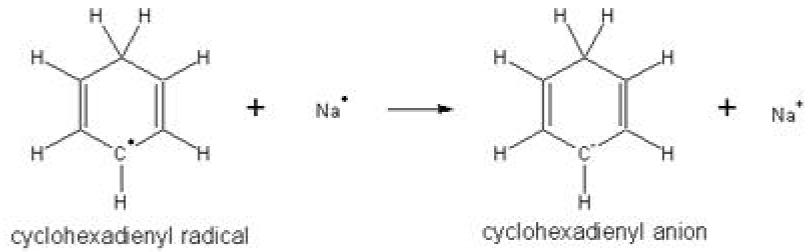
b. Transfer of an electron from sodium to the pi system of the aromatic ring resulting in formation of an anion radical



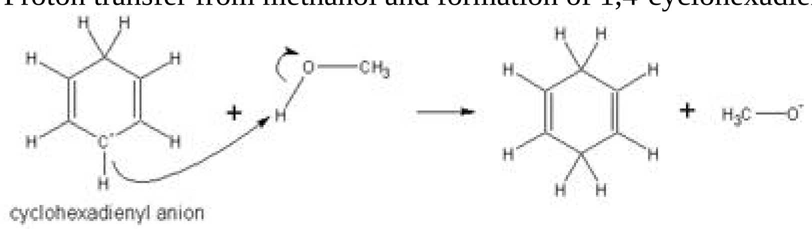
c. Abstraction of a proton from methanol by the anion radical and formation of a cyclohexadienyl radical



d. Conversion of cyclohexadienyl radical to cyclohexadienyl anion by electron transfer from sodium



e. Proton transfer from methanol and formation of 1,4-cyclohexadiene



f. Alkyl-substituted arenes produce a 1,4- substitution product in which the alkyl group is a substituent on a double bond

C. Free-radical halogenation of alkylbenzenes

1. Alkylbenzenes offer two possible reactions - halogenation of either the ring or the alkyl side chain

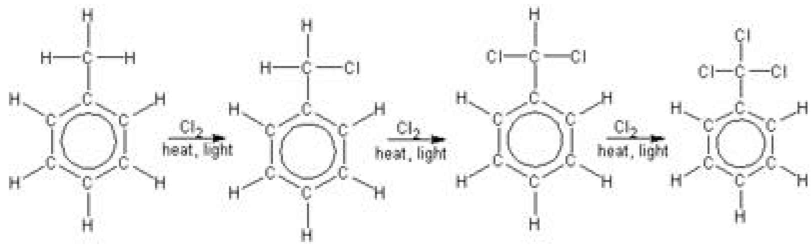
2. Halogenation is controlled very simply by choosing appropriate reaction conditions

3. Halogenation of alkanes requires high temperature and/or light

4. Halogenation of the benzene ring requires transfer of halogen cations, the formation of which is stimulated by Lewis acid catalysts such as ferric chloride

5. Bromination: more common lab procedure, performed with NBS in carbon tetrachloride and produces monobromo product

6. Chlorination: toluene -> benzyl chloride with further chlorination to dichloromethylbenzene (benzal chloride) and trichloromethylbenzene (benzotrichloride) possible



D. Oxidation of alkylbenzenes by sodium (potassium) dichromate

1. Dichromates will not attack either benzene or alkanes

2. Alkyl substituents with one or more benzylic hydrogens result in oxidation of the benzylic carbon to a carboxylic acid

3. This will occur to all alkyl groups on multi-substituted alkyl benzenes, provided the alkyl groups have one or more benzylic hydrogens

E. Nucleophilic substitution in benzylic halides

1. S_N2 and E2 reactions

a. Primary benzylic halides are ideal for S_N2 reactions since they are reactive, cannot rearrange, and cannot undergo elimination

b. Secondary benzylic halides will preferentially undergo E2 elimination unless the nucleophile is only weakly basic

i. Remember that elimination is preferred to substitution unless the conditions are right

ii. Weakly basic nucleophiles include substances less basic than hydroxide ion, e.g.: the conjugate bases of nearly all organic acids

iii. If the acid is a stronger acid than water, its conjugate base will be less basic than hydroxide

iv. Conversely, if the acid is a weaker acid than water its conjugate base will be more basic than hydroxide (e.g. alcohols and alkoxy compounds) and would rather abstract an H atom than participate in substitutions

2. S_N1 reactions

a. Due to the stability of benzylic carbocations, under conditions that favor substitution S_N1 substitution occurs and results in formation of a single (major) substitution product (conditions: weakly basic nucleophile, solvolysis)

VIII. Alkylbenzenes

A. Preparation of alkylbenzenes

  1. Dehydrogenation

     a. Used industrially to convert ethylbenzene to styrene

     b. Not a convenient lab method

  2. Acid-catalyzed dehydration of benzylic alcohols

     a. E2 mechanism

  3. Acid-catalyzed dehydrohalogenation of benzyl halides

     a. E2 mechanism

B. Addition reactions of alkylbenzenes

  1. Hydrogenation of side-chain alkenyl groups

  2. Addition to side-chain alkenyl groups

  3. Effects are most pronounced when double bonds are conjugated with ring, resulting in stabilization of resulting carbocation

C. Free radical polymerization of styrene - of industrial importance

IX. Hückel's rule and other aromatic compounds

A. Hückel's rule: conditions for aromatic compounds

  1. Planar

  2. Monocyclic

  3. Fully conjugated

  4. Total number of pi electrons = (4n + 2)

B. Examples of surprisingly non-aromatic compounds

  1. Cyclobutadiene

  2. Cyclooctatetraene

C. While the requirement is for monocyclic systems, it also seems to apply to some polycyclic systems but not all

  1. N = 1: benzene

  2. N = 2: naphthalene

3. N = 3: anthracene, phenanthrene

4. N = 4: 1,2-benzanthracene

5. Benzo[a]pyrene N = 4.5 (?)

D. Other aromatic compounds

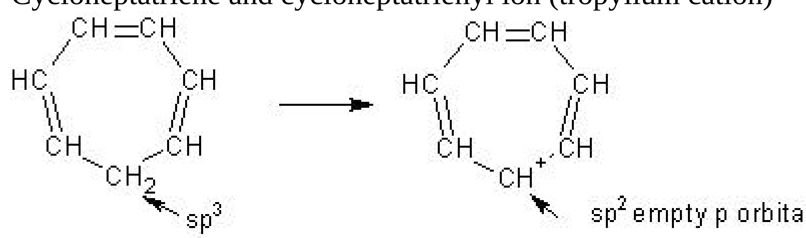
1. Annulenes

2. Aromatic ions - if ions meet the conditions described by Hückel then ions too can be aromatic

   a. Planar, monocyclic, continuous pi system or p orbital system, and 4n + 2 pi electrons

   b. Cations

      i. Cycloheptatriene and cycloheptatrienyl ion (tropylium cation)



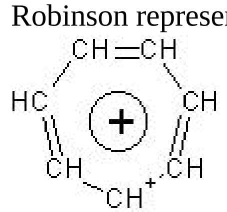
      ii. Note that an aromatic ion is not necessarily more stable than the structure from which it came.

      iii. Cycloheptatriene is a stable hydrocarbon but is not aromatic

      iv. Tropylium is an aromatic cation, and as such is more stable than non-aromatic cations; it forms with greater ease

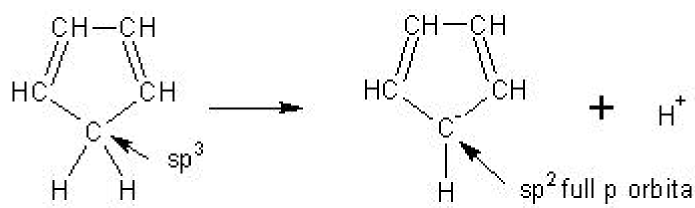
      v. Tropylium salts exist and are stable in water

      vi. Robinson representation: indicate charge within benzene ring



   c. Anions

      i. Cyclopentadiene and cyclopentadienylide



ii. Cyclopentadiene is a stable hydrocarbon but is not aromatic

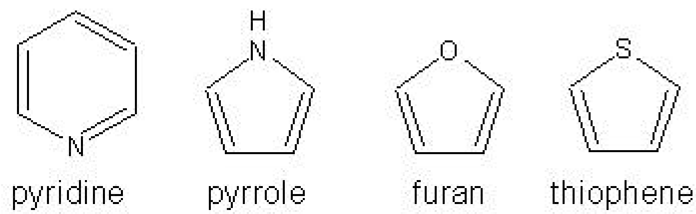
iii. Cyclopentadienylide is an aromatic anion, and as such is more stable than non-aromatic anion; it forms with greater ease

iv. The stability of the cyclopentadienylide ion makes it somewhat acidic

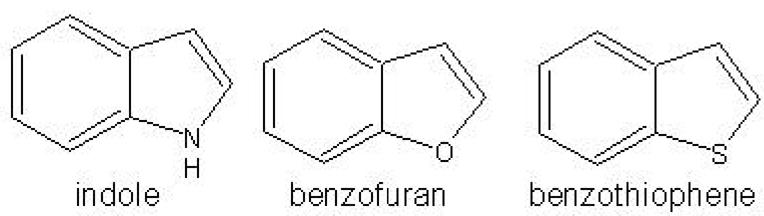
v. Ferrocene and conducting polymers

3. Heterocyclic aromatic compounds and Hückel's rule

   a. Heterocyclic compounds are cyclic compounds that contain one or more nonmetal atoms (heteroatoms)



   b. Can be monocyclic or polycyclic



   c. A single heteroatom can donate either zero or two lone-pair electrons to achieve a 4n + 2 pi electron configuration

   d. The heteroatom is sp2 hybridized and either has an empty p orbital or a full p orbital

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