Chapter 12
Conjugated and Aromatic Molecules

from
Organic Chemistry
by

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Chapter Outline of the Book

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**Note: Chapters marked with an (*) are not yet posted.*

12: Conjugated and Aromatic Molecules

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12: Conjugated and Aromatic Molecules

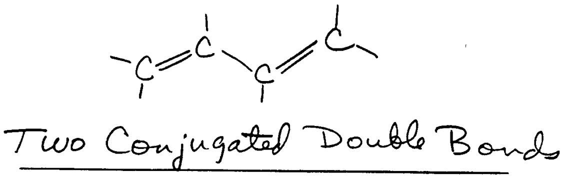
12.1 Conjugated Molecules

Conjugated molecules have π electrons that are not localized in individual double or triple bonds. Rather their π electrons are delocalized throughout an extended π system. We will see later that aromatic molecules are a special class of conjgated molecules.

1,3-Butadiene (12.1A)

We show the simplest arrangement of multiple bonds that leads to π electron delocalization and conjugation in Figure 12.001 where two C=C bonds are separated by a C-C single bond.

Figure 12.001

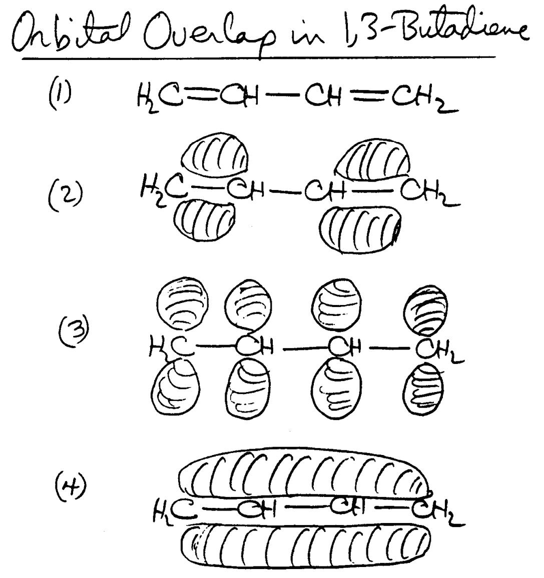


The simplest example of a molecule with that arrangement of C=C bonds is *1,3-butadiene.* with the structure CH_2=CH-CH=CH_2.

Atomic Orbital Overlap in 1,3-Butadiene. We focus on different aspects of the atomic orbitals in *1,3-butadiene* in Figure 12.002 [next page] in order to show why its π electrons are delocalized. The first structure shows 1,3-butadiene as we normally write it. The two C=C bonds appear to be localized between C1 and C2 and between C3 and C4. Without further expanation that formula implies the localized π MO's that we show in the second structure.

The first structure shows 1,3-butadiene as we normally write it. The two C=C bonds appear

Figure 12.002



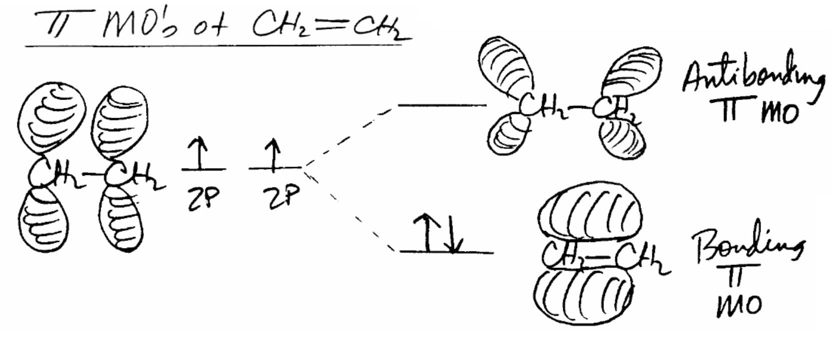
to be localized between C1 and C2 and between C3 and C4. Without further expanation that formula implies the localized π MO's that we show in the second structure.

We learned in Chapter 8 that localized π MO's of C=C bonds result from overlap of the individual 2p atomic orbitals on sp^2 C's that we show in the third structure. However, this third structure reveals that not only can we overlap the 2p orbitals on C1 and C2, and on C3 and C4, but we can also overlap those on C2 and C3.

This possibility for extended overlap of all four 2p orbitals leads to delocalization of π electron density across all four carbons as we represent in the fourth structure of Figure 12.002. Because all four 2p orbitals can overlap, the resultant π molecular orbitals in 1,3-butadiene are more complex than those arising from overlap of two 2p AO's on adjacent C's.

Molecular Orbitals. We learned in Chapter 8 that overlap of two 2p AO's in a molecule such as $CH_2=CH_2$ gives one *bonding* and one *antibonding* π MO (Figure 12.003).

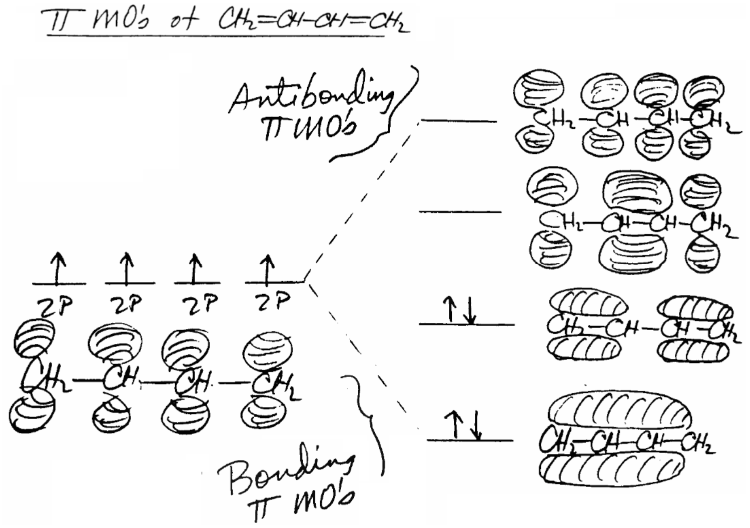
Figure 12.003



The two electrons in the π bond are normally in the lowest energy bonding MO.

Since the number of molecular orbitals that form as the result of atomic orbital overlap is always equal to the number of overlapping AO's, overlap of the four 2p AO's in 1,3-butadiene leads to the formation of four molecular orbitals (Figure 12.004).

Figure 12.004



We show these 4 MO's here without explaining their mathematical origins. Since the two MO's of lowest energy contain the 4 π electrons, we call them *bonding MO's*. The two higher energy MO's without electrons are called *antibonding MO's*.

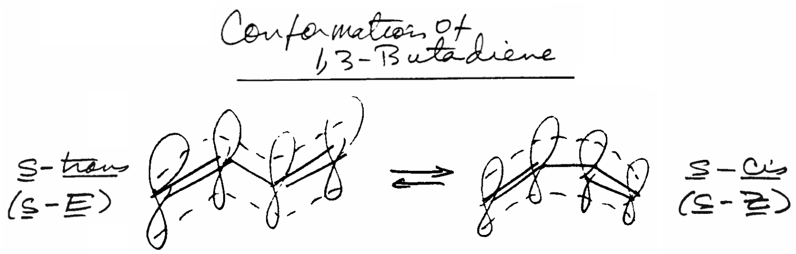
The Bonding M.O.'s. The lowest energy π MO has two lobes that lie above and below a plane containing the carbon skeleton. This single MO with two lobes extends over all four carbon atoms of the molecule and contains two π electrons. The remaining two π electrons are in the next higher energy bonding MO that consists of four lobes as we show in Figure 12.004.

Although this second bonding π MO looks like the second structure in Figure 12.002, it has a very different meaning. We drew the structure in Figure 12.002 to represent the localized bonding π MO's of the two C=C bonds. In contrast, the second bonding π MO in Figure 12.004 is a single MO that is made up of four lobes.

The lowest energy π MO (Figure 12.004) includes all four C atoms of the two double bonds. As a result, the 2 electrons in that MO are delocalized over four carbons rather than just localized between two C's of a single C=C. We will see shortly that this delocalization has important effects on both the stability and chemical reactions of this conjugated molecule.

Conformations. Conjugated dienes such as 1,3-butadiene have two different planar conformations like those we show in Figure 12.005.

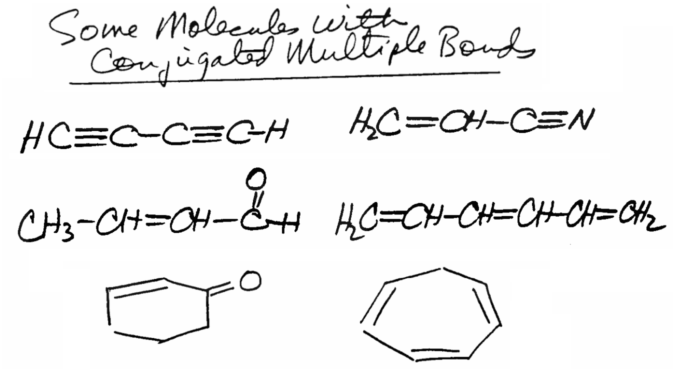
Figure 12.005



We designate them as the *s-trans* and *s-cis* conformations (or *s-E* and *s-Z* conformations) where the terms *cis* (*Z*) and *trans* (*E*) refer to the orientations of the two C=C bonds with respect to the intervening C2-C3 single bond. While the *s-trans* conformation of 1,3-butadiene is more stable than the *s-cis* conformation by 10 to 13 kJ/mol, both conformations have delocalized π electrons.

Other Alternating Multiple Bonds. Conjugation like we have just described is not limited to the interaction of just two C=C bonds, nor is it limited only to C=C bonds. Whenever two or more multiple bonds of any type (eg. C=C, C=O, C=N, C≡C, C≡N, etc.) alternate with single bonds in a pattern such as "*single-multiple-single-multiple-single-multiple*" etc., those multiple bonds are usually conjugated and have delocalized π electrons. We show examples of various conjugated molecules in Figure 12.006.

Figure 12.006

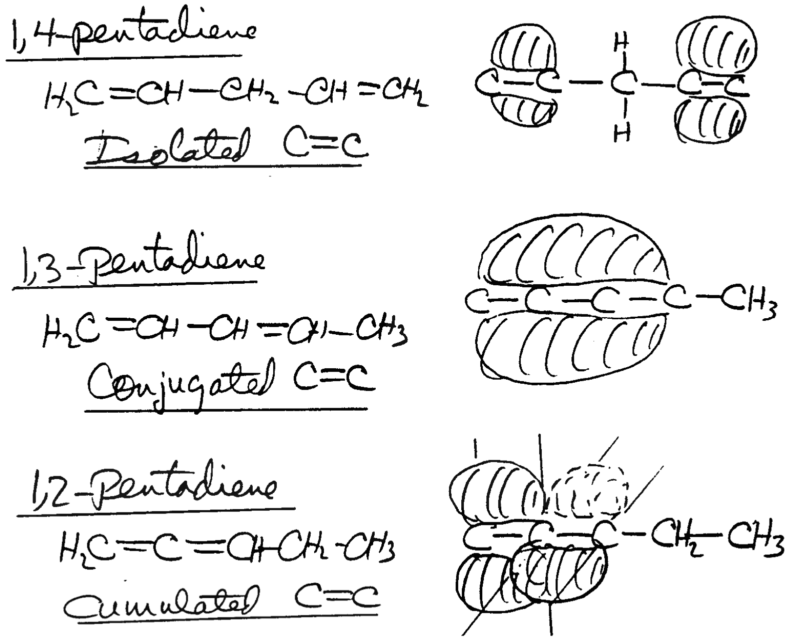


Pentadienes (12.1B)

In order to emphasize the structural requirements for conjugation, we compare three isomeric pentadienes in Figure 12.007 [next page]. Each of these pentadienes has two C=C bonds, but you can see that the relative positions of the two C=C bonds are different in each molecule.

1,3-Pentadiene. Of these three pentadienes, *1,3-pentadiene* is the only molecule that is conjugated. Since its two C=C bonds are separated by just one single bond, all four 2p orbitals can simultaneously interact. As a result, it has four π MO's that are completely equivalent to those that we showed in Figure 12.004 for 1,3-butadiene.

Figure 12.007



The C=C bond between C3 and C4 can be either *cis* or *trans*. In fact, *cis*-1,3-pentadiene and *trans*-1,3-pentadiene are discrete isomers, but both are conjugated. We will discuss differences between them below. (Each of these *cis* and *trans* isomers can also have *s-trans* and *s-cis* conformations).

1,4-Pentadiene. In contrast to *cis* and *trans*-1,3-pentadiene, the two C=C bonds in 1,4-pentadiene are separated by two C-C single bonds (and an intervening CH_2 group) (Figure 12.007). As a result, the two sets of 2p orbitals that overlap to form the two C=C bonds cannot interact with each other so we say that these C=C bonds are **isolated**. Each C=C bond has a localized bonding π MO that contains the two π electrons of that C=C (Figure 12.007).

1,2-Pentadiene. Even though the two C=C bonds in 1,2-pentadiene share the same C, they cannot interact with each other. The C that is common to each of these C=C bonds is sp hybridized so it has two 2p orbitals that are perpendicular (orthogonal) to each other as we described for molecules of this type in Chapter 8.

As a result, the two π bonds in this compound are also orthogonal (perpendicular) to each other and do not overlap. The π electrons in each C=C bond are localized in their respective

C=C bonding MO's. Two such orthogonal double bonds attached to the same carbon are said to be **cumulated** and *cumulated* systems are <u>not</u> *conjugated. Cumulated* dienes like 1,2-pentadiene are commonly called *allenes.*

Stability of Conjugated Systems (12.1C)

Conjugation affects the chemical and physical properties of the molecules containing those conjugated bonds. Molecules with conjugated multiple bonds are generally more stable than comparable molecules with unconjugated multiple bonds. We can see this extra stability due to conjugation when we compare heats of hydrogenation of related conjugated and unconjugated systems as we show in the next section.

Heats of Hydrogenation of Pentadienes. We show heats of hydrogenation for three of the pentadienes that we just discussed in the reactions below:

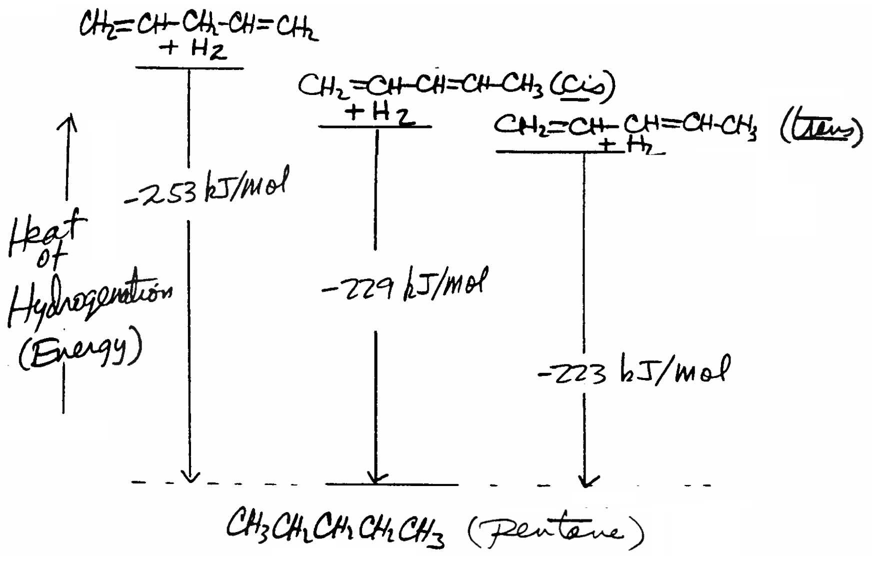
$CH_2=CH-CH_2-CH=CH_2 + 2H_2 \rightarrow CH_3CH_2CH_2CH_2CH_3 +$ 253 kJ/mol
1,4-pentadiene pentane

$CH_2=CH-CH=CH-CH_3 + 2H_2 \rightarrow CH_3CH_2CH_2CH_2CH_3 +$ 223 kJ/mol
trans-1,3-pentadiene pentane

$CH_2=CH-CH=CH-CH_3 + 2H_2 \rightarrow CH_3CH_2CH_2CH_2CH_3 +$ 229 kJ/mol
cis-1,3-pentadiene pentane

You can see that more heat is given off when we hydrogenate the *unconjugated diene* 1,4-pentadiene than when we hydrogenate either of the two *conjugated* 1,3-pentadienes. This is a quantitative demonstration that *conjugated cis* and *trans*-1,3-pentadiene are more stable than *unconjugated* 1,4-pentadiene (Figure 12.008).

Figure 12.008



You can also see in Figure 12.008 that the *trans* isomer is slightly more stable than the cis isomer reflecting the general situation that *trans* C=C bonds are more stable than *cis* C=C bonds (Chapter 8).

The Sign Convention. We prefer to think of a heat of hydrogenation as the quantity of heat evolved during a hydrogenation reaction, so we describe them as positive quantities. An example is hydrogenation of *1,4-pentadiene* that leads to *pentane* and the evolution of +253 kJ of heat.

Generally, however, you will see heats of hydrogenation reported as negative numbers. When you see the heat of hydrogenation for *1,4-pentadiene* reported as -253 kJ/mol, this reflects that the energy content of a mol of *pentane* is 253 kJ *lower* than the energy content of a mol of *1,4-pentadiene* and the 2 mols of H_2 required to completely hydrogenate that diene. We show those negative values in Figure 12.008.

Heats of Hydrogenation of Butadienes. The heats of hydrogenation for two isomeric butadienes similarly show the stabilizing effects of conjugation.

$$\underset{\text{1,2-butadiene}}{CH_2{=}C{=}CH{-}CH_3} + 2H_2 \rightarrow \underset{\text{butane}}{CH_3CH_2CH_2CH_3} + 288\ \text{kJ/mol}$$

$$\underset{\text{1,3-butadiene}}{CH_2{=}CH{-}CH{=}CH_2} + 2H_2 \rightarrow \underset{\text{butane}}{CH_3CH_2CH_2CH_3} + 236\ \text{kJ/mol}$$

The heat of hydrogenation of the conjugated diene 1,3-butadiene is much lower than that of its unconjugated (but cumulated) isomer 1,2-butadiene.

Additional Details. Conjugation is responsible for most, but not all, of the greater stability of the 1,3-pentadienes compared to 1,4-pentadiene. Note that each 1,3-pentadiene has one *terminal* and one *internal* C=C bond, while 1,4-pentadiene has two *terminal* C=C bonds. We learned in Chapter 8 that an internal C=C bond is more stable than a terminal C=C bond by 5 to 10 kJ/mol. As a result, conjugation actually accounts for about two-thirds of the energy differences that we showed above.

Similarly, in the case of the butadienes, part of the difference in stablity of these two isomers is because cumulated C=C bonds have higher energy (lower stability) than isolated C=C bonds.

An Alternate Analysis. We can also estimate the stability resulting from conjugation by comparing the heats of hydrogenation of conjugated or nonconjugated dienes with those of comparable alkenes with only one C=C (monoenes). In this comparison we use the heat of hydrogenation of the alkene as a measure of the heat of hydrogenation of one unconjugated C=C.

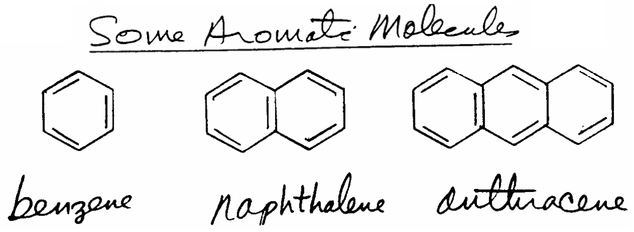
For example, the heat given off when we hydrogenate 1,4-pentadiene (254 kJ/mol) (two nonconjugated C=C bonds) is essentially twice that given off in hydrogenation of 1-pentene (2 x 126 kJ/mol = 252 kJ/mol). In contrast, the heat given off in hydrogenation of *trans*-1,3-pentadiene (226 kJ/mol) (two conjugated C=C bonds) is significantly less than twice that given off during hydrogenation of 1-pentene (252 kJ/mol).

Similarly, the heat given off during hydrogenation of 1,3-butadiene (239 kJ/mol) (two conjugated C=C bonds) is significantly less than twice that given off during hydrogenation of 1-butene (2 x 127 kJ/mol = 254 kJ/mol). We attribute these lower than expected values for *trans*-1,3-pentadiene, and for 1,3-butadiene, to the C=C conjugation.

Aromatic Molecules (12.1D)

We have seen that heats of hydrogenation are lower for *conjugated* dienes than for their *unconjugated* isomers. However, later in the chapter we will see that these energy differences are relatively small compared to the large stabilities of **aromatic molecules**. These particularly stable *aromatic molecules* are cyclic, and often have six-membered rings that show a pattern of three alternating single and double bonds (Figure 12.009).

Figure 12.009



Originally, the term *aromatic* was given to compounds of this type because of their distinctive fragrance. Now, chemists use the term "*aromatic*" to designate specific classes of *conjugated* molecules that exhibit extraordinary stability, special chemical reactivity, and distinctive ^{1}H NMR signals when compared to other molecules either conjugated or unconjugated. We will describe *aromatic molecules*, later in the chapter.

12.2 Reactivity of Conjugated Systems

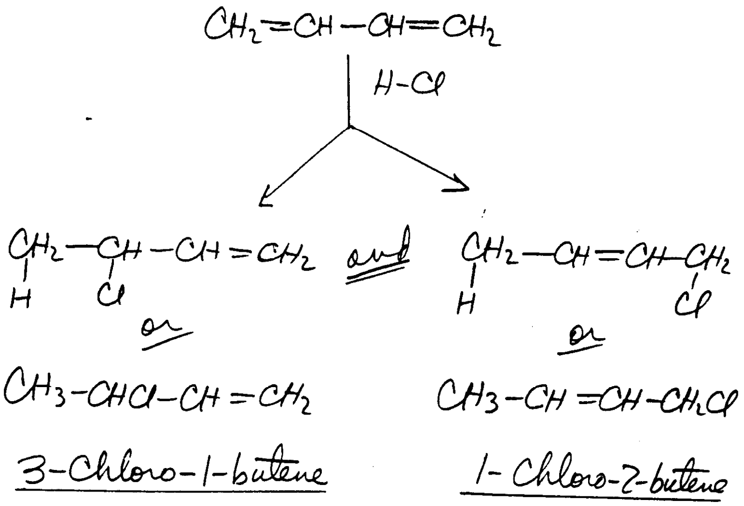
Conjugated dienes such as *1,3-butadiene* or *1,3-pentadiene* undergo chemical reactions that are mechanistically similar to those of unconjugated alkenes. However their conjugation leads to significant differences in reaction products.

Addition of H-Cl to 1,3-Butadiene (12.2A)

We will use the addition of H-Cl to 1,3-butadiene to illustrate how conjugation affects reaction products and mechanisms.

Products. Reaction of 1,3-butadiene with one mole of H-Cl gives two isomeric chlorobutene products (Figure 12.010).

Figure 12.010

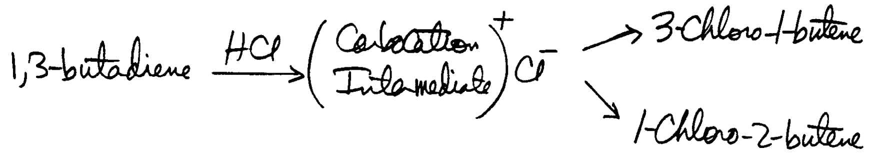


3-Chloro-1-butene is the product we might predict for Markovnikov addition of H-Cl across either of the two equivalent C=C bonds. However, based on what we learned in Chapter 10, we do not expect the other product 1-chloro-2-butene.

This latter product has a C=C bond between C2 and C3 where no C=C bond is present in the reactant, and Cl is bonded to a "least substituted" terminal C in apparent contradiction to Markovnikov's rule. We must account for both of these products in our mechanisms.

Mechanism. In its general features, H-Cl addition to 1,3-butadiene is mechanistically analogous to H-Cl addition to any alkene. H-Cl protonates 1,3-butadiene to give the "most stable carbocation", and that carbocation subsequently reacts with Cl:$^-$ (Figure 12.011).

Figure 12.011

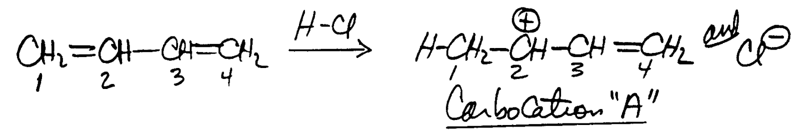


Where the mechanism differs from H-Cl addition to a simple alkene is that the single carbocation formed in Figure 12.011 gives rise to the two different isomeric choloroalkenes shown above. The reason that two products form from a single carbocation is because the positive charge on the intermediate carbocation is not *localized* on a single carbon, but rather is *delocalized*. This delocalization of the carbocation is a direct result of conjugation in the original diene.

Delocalized Carbocation. In order to picture the single delocalized carbocation that forms, let's imagine (INCORRECTLY) that H-Cl protonates C1 to give the hypothetical localized carbocation "A" (Figure 12.012).

Figure 12.012

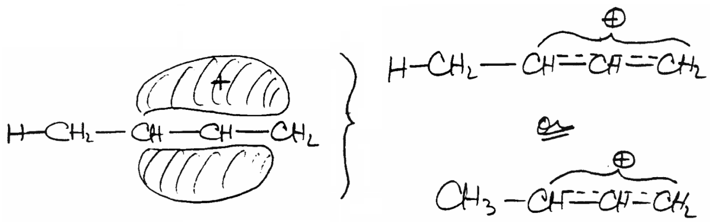
Hypothetical Localized C+ Formation



Although <u>THIS DOES NOT HAPPEN</u>, we can see that if it did that the C+ center would be directly attached to the C=C bond. As a result, the π electrons in the C=C bond could interact with (delocalize into) the empty 2p orbital on the C+ center.

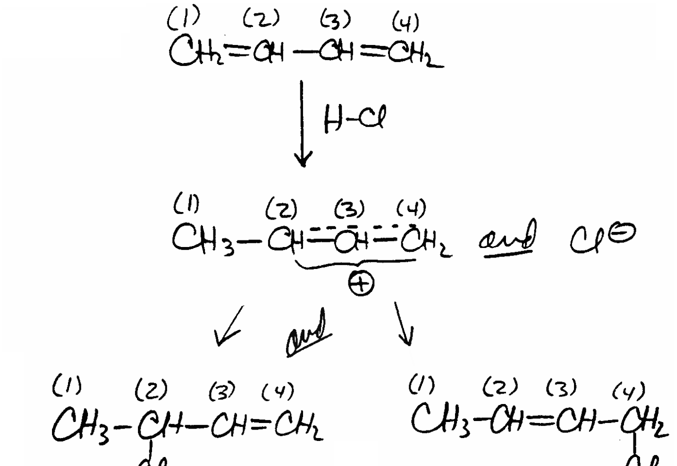
We can picture the "real" resultant delocalized carbocation as we show in Figure 12.013.

Figure 12.013



Carbocation "A" (Figure 12.012) never exists, but the delocalized carbocation (Figure 12.013) forms directly from protonation of C1 on 1.3-butadiene (Figure 12.014).

Figure 12.014

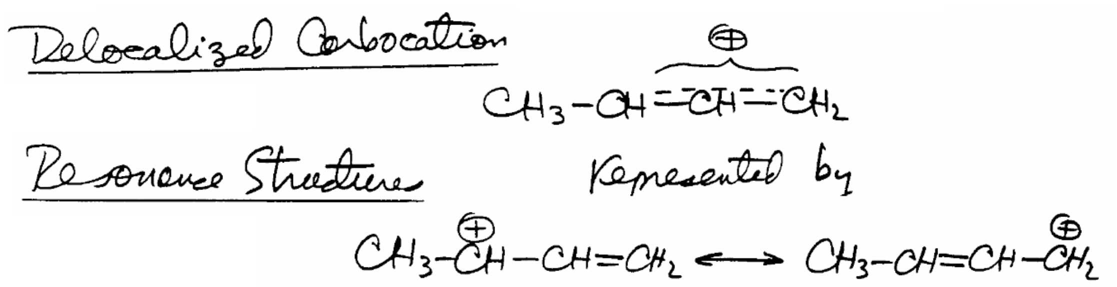


The problem with this vague description of the delocalized carbocation is that it does not show us that $Cl:^-$ can react at C2 and C4, but not at C3. We can see this by depicting the delocalized carbocation intermediate using resonance structures that we describe in the next section.

Resonance Structures (12.2B)

Organic chemists represent the single delocalized carbocation (Figures 12.013 and 12.014) using the *resonance structures* that we show in Figure 12.015.

Figure 12.015

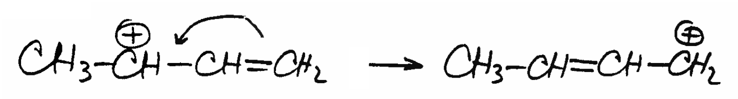


These resonance structures are the two different carbocation structures that we connect with a **double-headed arrow**.

Carbocation Resonance Structures. Both resonance structures in Figure 12.015 look like normal carbocations. In fact the structure on your left is the one that we previously called carbocation "A". You can see that if it was present in the reaction mixture it would serve as the carbocation precursor to *3-chloro-1-butene*.

Similarly, the other resonance structure looks like it could serve as a precursor for the isomeric product *1-chloro-2-butene*. Moreover, we can make that second carbocation structure by simply moving the π electron pair in the C=C bond of carbocation "A" toward the C+ center so that it is localized between C2 and C3 rather than C3 and C4 (Figure 12.016).

Figure 12.016



While it would be nice if we could say that protonation of 1,3-butadiene led to a mixture of these two carbocations that reacted with Cl:⁻ to give the isomeric chlorobutenes, this is NOT the case. <u>The double headed arrow between them signifies that neither of these two carbocations actually exists</u>. Each of these two carbocation structures represents just a part of the "nature" of the *<u>real</u> delocalized carbocation*. Neither of them by themselves represents a complete description of that *single delocalized carbocation*.

Meaning of Resonance Structures. The following non-chemical examples help illustrate the meaning of resonance stuctures. In the first example, we describe the color *green* in terms of the colors *blue* and *yellow* because those colors give *green* when blended together. In this case using "resonance structure terminology" we might say that:

Green
is
Blue ↔ Yellow

Our second example represents a *mule* in terms of its biological parents that are a *horse* and a *donkey*. In this case we might write:

Mule
is
Horse ↔ Donkey

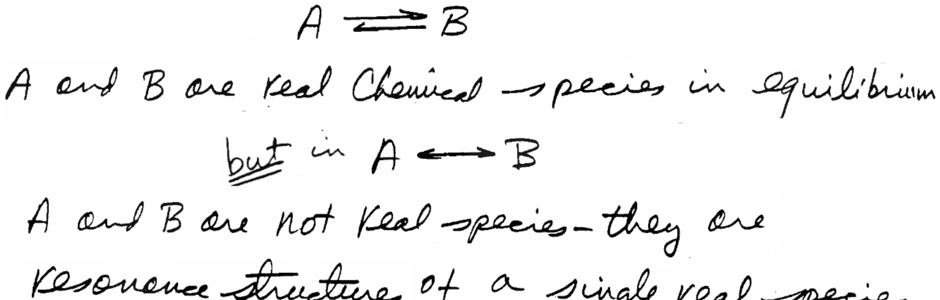
We know that *green* is neither *blue* nor *yellow*, but it has aspects of both. Similarly, a *mule* is not a *horse* or a *donkey*, but is a result of the pooling of the genes of both a horse and a donkey.

Meaning of The Double Headed Arrow. These two examples also emphasize an important feature of resonance structures. Resonance structures are NOT in equilibrium with each other.

Mules are not an equilibrium mixture of horses and donkeys. Similarly, green ping pong balls are not an equilibrium mixture of blue ping pong balls and yellow ping pong balls.

The double headed arrow ↔ is NOT a shorthand way to represent forward and reverse equilibrium arrows as we emphasize in Figure 12.017.

Figure 12.017



$A \rightleftharpoons B$

A and B are real Chemical species in equilibrium

but in $A \longleftrightarrow B$

A and B are not real species - they are resonance structures of a single real species.

When we separate the species A and B, by the *double headed arrow* in that figure, that means that A and B do not really exist! The structures separated by the *double-headed arrow* are *resonance structures* that attempt to portray the multiple properties of a single chemical species for which we cannot draw a unique single chemical structure.

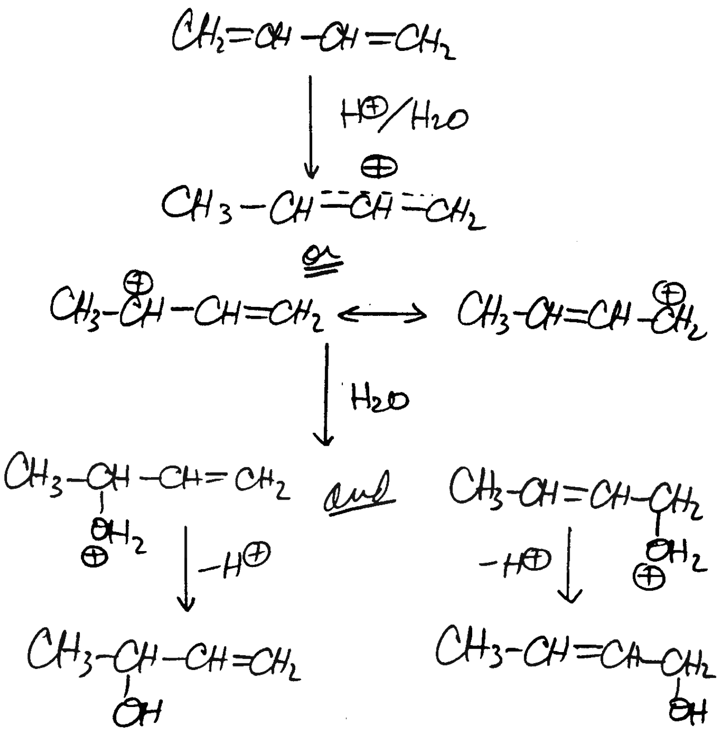
Resonance is a difficult concept but it will become less difficult as you become more familiar with it. Drawing resonance structures is one of the major challenges that we face in terms of understanding and using the concept of resonance. We have introduced this topic already in terms of the two resonance structures that we illustrated in H-Cl addition to 1,3-butadiene. Before we describe a stepwise approach to drawing resonance structures, lets look at some more examples of reactions where we use resonance structures.

Other Reactions with Delocalized Intermediates (12.2C)

Other addition reactions to conjugated systems give delocalized intermediates that we can represent with resonance structures. These delocalized intermediates include not only cations, but also radicals, and anions. We will show two more resonance stabilized cation intermediates, and then a radical intermediate. We defer examples of resonance stabilized anions until later chapters.

Acid Catalyzed Hydration. Acid catalyzed hydration of 1,3-butadiene gives the same delocalized carbocation and corresponding resonance structures that we showed for H-Cl addition (Figure 12.018).

Figure 12.018

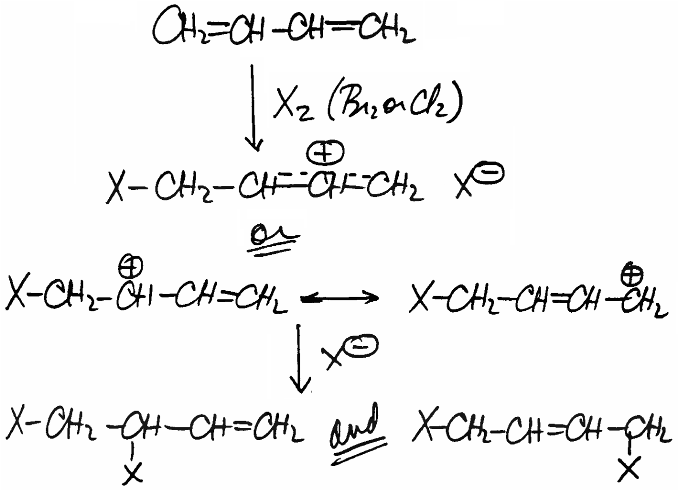


The two isomeric alcohol products are analogous to the two isomeric chloroalkenes from H-Cl addition. They look like they came from attack of H_2O on each of the two respective resonance structures.

Although this is a convenient way to predict the products formed in these reactions, the actual reactions that lead to all the products begin with the single real delocalized carbocation. The products do not originate from the hypothetical resonance structures since those structures do not exist.

Electrophilic Halogenation. Electrophilic bromination (or chlorination) of 1,3-butadiene also takes place by way of a single delocalized carbocation intermediate (Figure 12.019).

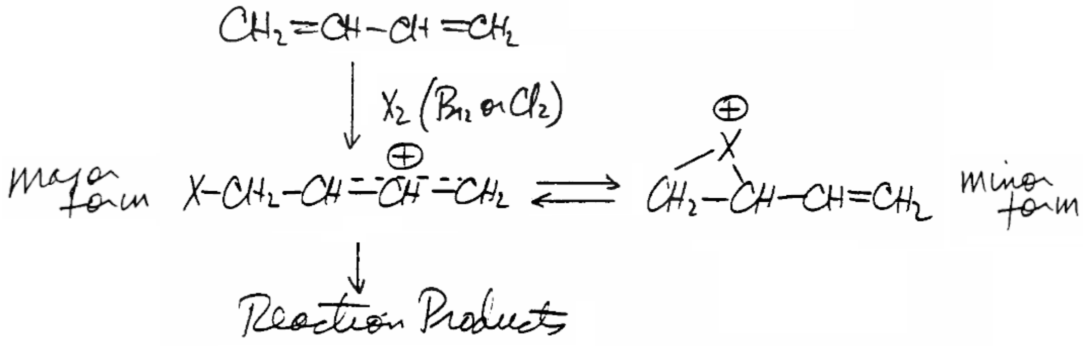
Figure 12.019



Two products simultaneously form in those reactions, but we emphasize again that they arise by reaction of the halide ion X:$^-$ with a single delocalized cabocation that we can represent with the two resonance structures that we show in Figure 12.019.

These halogenation reactions of 1,3-butadiene are more complicated than either H-Cl addition, or acid catalyzed hydration, because a localized bridged halonium ion can conceivably form in competition with the delocalized ion (Figure 12.020).

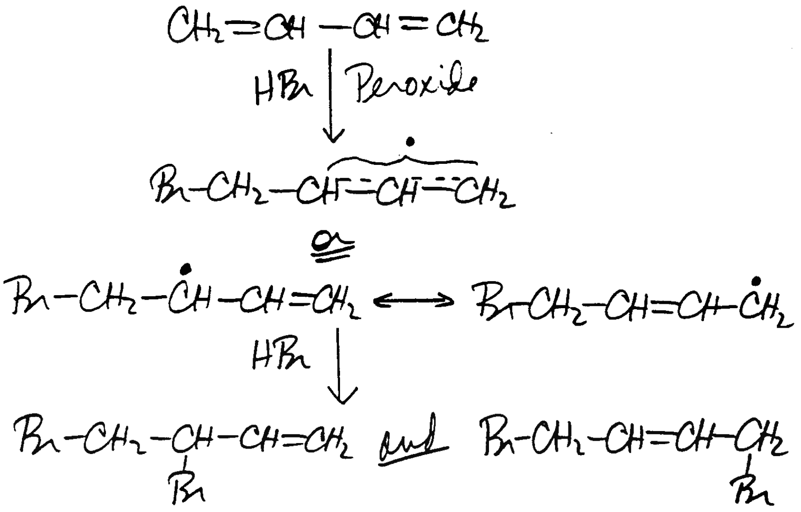
Figure 12.020



Organic chemists believe, however, that this bridged ion is less stable than the delocalized ion and that it does not contribute signifcantly in the reaction.

***Free Radical Addition of H-Br*.** Delocalized intermediates also form in radical reactions. For example, H-Br adds to 1,3-butadiene in the presence of peroxide by a radical mechanism that has the intermediate delocalized radical we show in Figure 12.021.

Figure 12.021



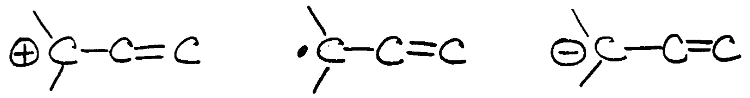
We can represent that delocalized radical by the two resonance structures in the figure. It subsequently abstracts H from H-Br to give the final products that we show above.

***Summary*.** We have seen that resonance structures help describe the delocalized intermediate in several different types of reactions. They also provide a useful way to account for the reaction products. We have briefly illustrated how to draw them for one cationic intermediate. The following section outlines stepwise procedures for drawing resonance structures for delocalized cations, radicals, and anions.

12.3 Writing Resonance Structures

When a carbocation (C+), a carbon radical (C·), or a carbanion (C:-) center is directly attached to a double bond (Figure 12.022), the cation, radical, or anion is delocalized.

Figure 12.022



Each of these species has
another resonance structure
because the ⊕, ⊙ or ⊖ center
is <u>directly</u> attached to C=C

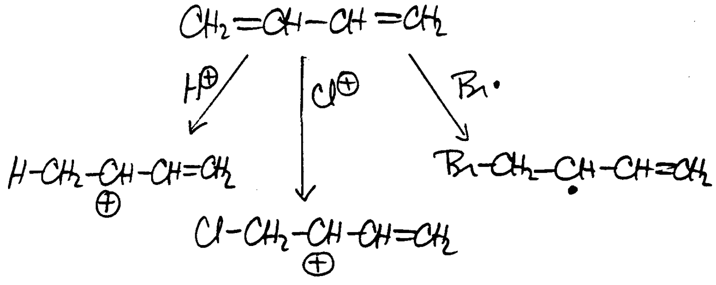
We can write two or more resonance structures that represent the true delocalized intermediate.

A General Procedure (12.3A)

For any delocalized ionic or radical intermediate:

(1) Draw one chemical structure for the ion or radical. In the case of the addition reactions that we described above, this structure normally is the one that we can pretend arises "first" from addition of the H^+, or Cl^+, or Br· to one of the double bonds of the diene to give the ionic or radical center attached to another multiple bond (Figure 12.023).

Figure 12.023

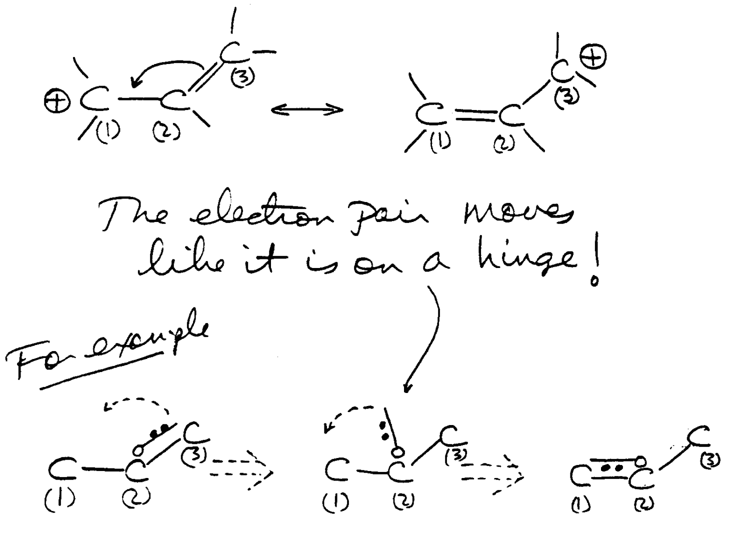


(2) Write the next resonance structure by moving electrons into or out of the double bond depending on whether the intermediate is C+, C-, or C· as we describe below.

Carbocations (C+) (12.3B)

(3)(a) If the first resonance structure is a carbocation, we draw the second resonance structure by moving one of the electron pairs in the double bond toward the C^+ carbon (C1) as if to "neutralize" it (Figure 12.024).

Figure 12.024

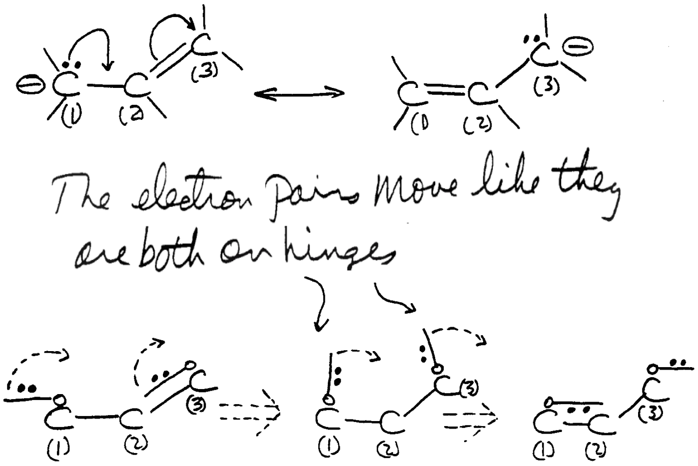


You can think of the central carbon (C2) as the point of attachment of a "hinge" that represents the electron pair. Moving the electron pair (the hinge) toward C1 causes the carbon C3 to become electron deficient and develop a positive charge while the electron pair forms a new π bond between C1 and C2.

Carbanions (C-) (12.3C)

(3)(b) When the intermediate is an anion, we move the electron pair centered on C1 in the first resonance structure toward the central carbon C2 as we show in Figure 12.025.

Figure 12.025

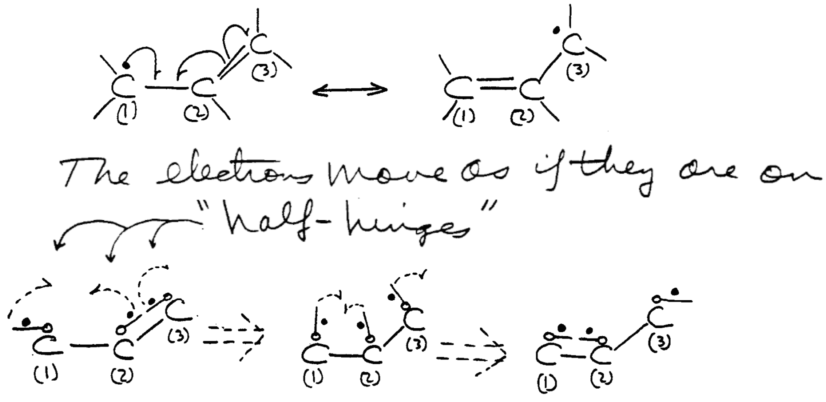


This electron pair becomes the π bond between C1 and C2 in the second resonance structure. The electron pair in the original π bond moves to C3 where it causes C3 to become an anion. You can also imagine this process in terms of "electron hinges", with the points of attachment of the hinges on C1 and C3 respectively.

Radicals (C·) (12.3D)

(3)(c) We draw resonance structures for radicals by moving single electrons rather than electron pairs. We move the electron on C1 in the first resonance structure so that it is between C1 and C2. It pairs up with another electron that was originally in the C=C π bond that we have moved to a position between C1 and C2 (Figure 12.026).

Figure 12.026



We place the remaining electron, from the original C=C π bond, on C3 giving us the second resonance structure shown in the figure. In the case of radicals, we can think of the electrons as "half-hinges" with their points of attachment on each of the carbons C1, C2, and C3.

12.4 More on Delocalized Systems

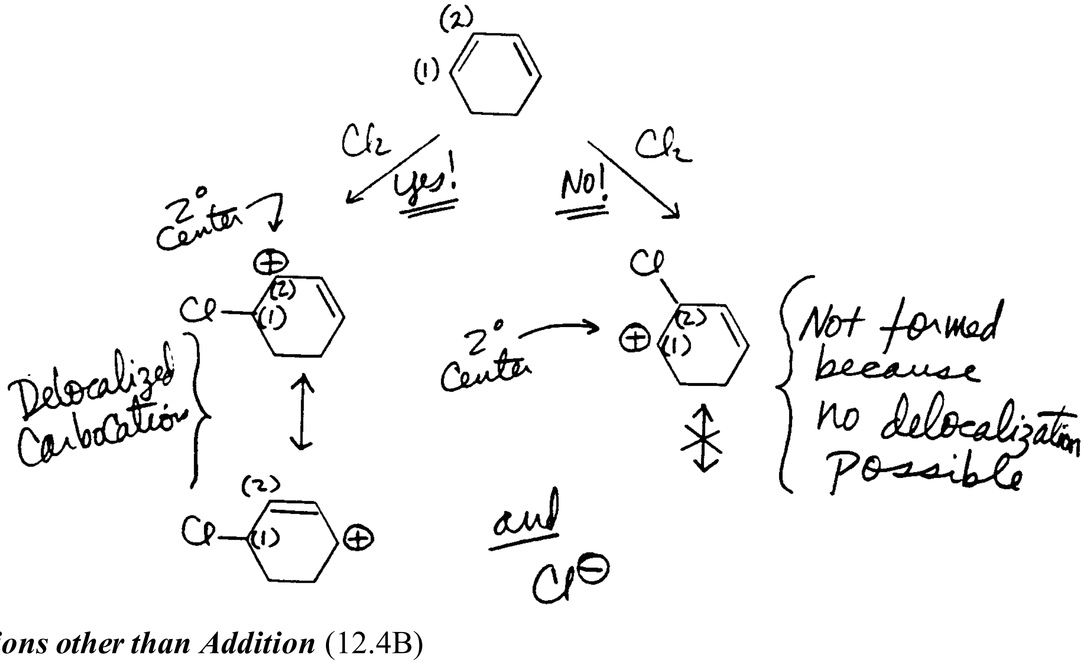
Addition reactions of 1,3-butadiene illustrate *delocalized intermediates*, and the use of *resonance structures* to represent them. There are many other conjugated reactants that undergo a variety of other reactions to give delocalized intermediates. We discuss some of these here and also describe some additional features of conjugated systems and delocalized intermediates.

Localized vs. Delocalized Intermediates (12.4A)

We have seen that when 1,3-butadiene reacts with H-Cl, or aqueous acid, or Cl_2, or H-Br, the intermediate ion or radical (Figure 12.023) is delocalized. But in each of these cases, the first addition step also gives the most highly substituted ion or radical independent of the fact that it is delocalized. What happens when an addition reaction can give <u>either</u> a *delocalized intermediate*, or a *localized intermediate that is more highly substituted*?

Generally speaking, when there is a choice of forming a delocalized intermediate in competition with one that is localized, the delocalized ion is preferentially formed. For example, Cl_2 adds to 1,3-cyclohexadiene, so that the delocalized carbocation forms as shown in Figure 12.027 even though both carbocations are on 2° C's.

Figure 12.027

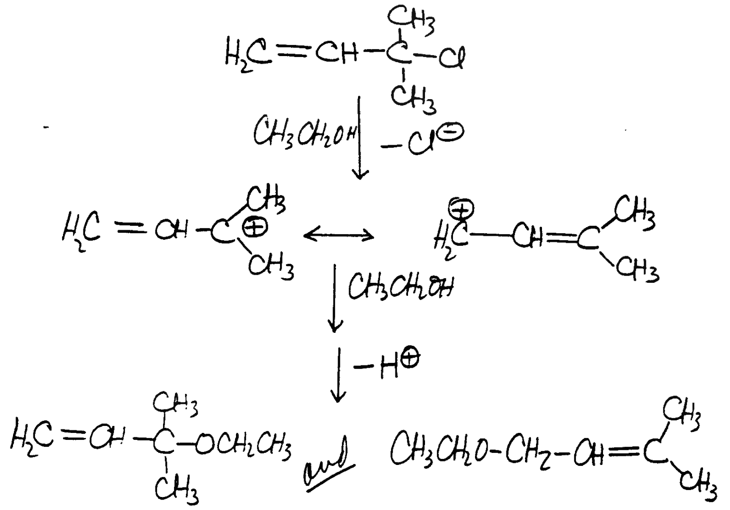


Reactions other than Addition (12.4B)

While the delocalized ions or radicals in all of our examples have come from addition reactions, they can form in other ways.

Solvolysis of Haloalkenes. One example is the solvolysis reaction of a haloalkene in aqueous alcohol by an S_N1 mechanism (Figure 12.028).

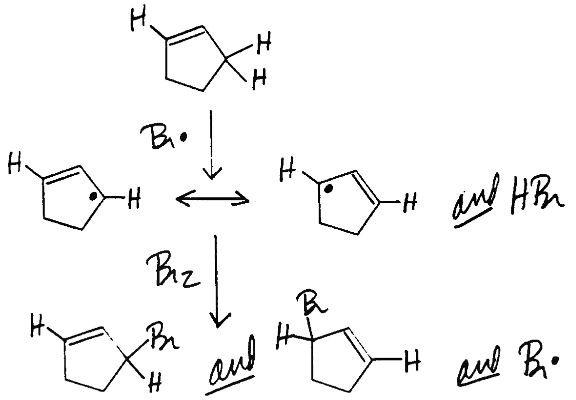
Figure 12.028



The resultant intermediate carbocation is delocalized, has the two resonance stuctures shown, and serves as the single cationic precursor to both of the products shown.

Radical Halogenation. We saw in an earlier chapter that radical halogenation of alkenes gives products where a C=C-C-H group becomes C=C-C-X. This *allylic halogenation* occurs by a mechanism where a radical abstracts the H from the Cα giving a delocalized radical (Figure 12.029).

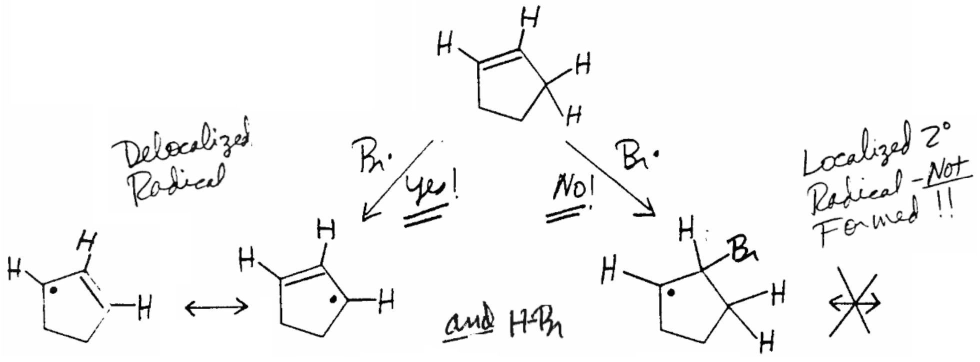
Figure 12.029



This delocalized radical (shown as 2 resonance structures) reacts with a halogen such as Br_2 to give the substitution product that still contains the double bond.

The initial radical abstracts H rather than adding to the C=C because the resultant delocalized radical is more stable than the localized radical formed in C=C addition (Figure 12.030)[next page].

Figure 12.030



Allyl or Allylic Intermediates. The delocalized radical shown in Figure 12.029 is called an **allyl or allylic** radical and the H that is abstracted to give that radical is called an *allylic* hydrogen. This is why the halogenation reaction shown above is called **allylic** halogenation.

In fact, all of the delocalized intermediates that we have seen are called *allyl* or *allylic* intermediates whether they contain C+, C·, or C:- because any C that is directly attached to a C=C is referred to as an *allyl* carbon or *allylic* carbon.

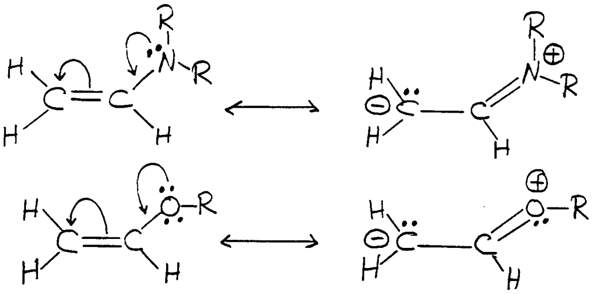
We first saw the term *allyl* in Chapter 8 in the nomenclature of substituted alkenes (see Table 8.1). It is an historic term so deeply imbedded in the nomenclature of organic chemistry that it we will encounter it frequently.

Conjugated Systems with Heteroatoms (12.4C)

When a heteroatom such as O or N is attached to a double bond, electron density is also delocalized in such molecules or intermediates, and we can show that using resonance forms.

Resonance Forms with Heteroatoms. We show some simple molecules with O or N bonded to C=C bonds, and resonance structures illustrating their electron delocalization, in Figure 12.031.

Figure 12.031



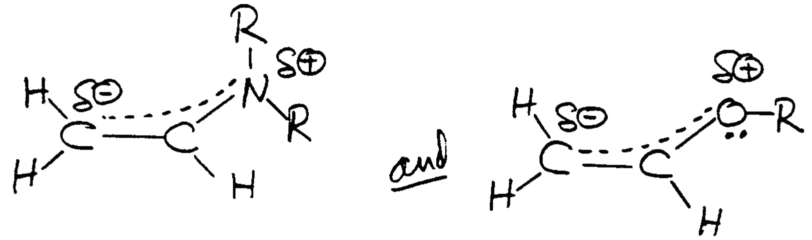
We use rules for drawing these resonance structures that are similar to those we used to draw resonance structures for an allyl carbanion (C:-) (Figure 12.025).

However, there is a significant difference between resonance structures for an allyl carbanion (Figure 12.025) and those for the compounds in Figure 12.031. Both resonance forms for the carbanion are negatively charged, but the resonance forms for the compounds in Figure 12.031 show electrical charges in only one resonance structure. In addition, that structure has charges both on the C, and on the N or O. This happens because we always move an unshared electron pair from O or N toward the C=C.

We must emphasize here that both the forms with charges, and the first uncharged structures in Figure 12.031, are "resonance structures". This may seem confusing because those forms without charges are the ones you would write if you were simply asked to draw the structures of the amine or the ether that we show.

The charge separated resonance form in each case shows that the true character of both of these compounds is more polar than expected based on drawing only the forms without charges. The charge separated resonance forms show that the character and properties of each of these molecules can also be represented using the dotted line drawings shown in Figure 12.032.

Figure 12.032

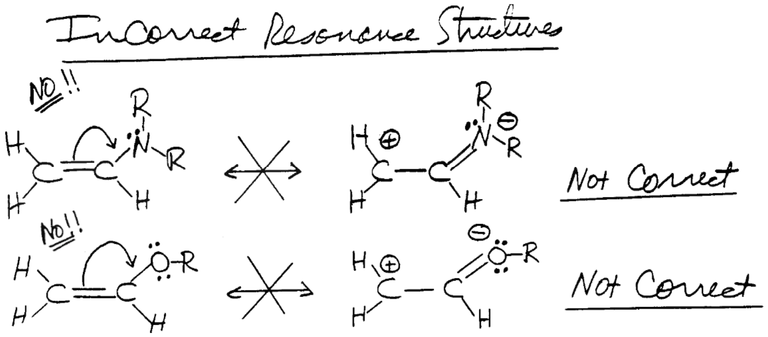


Relative Importance of Resonance Forms. In the allyl carbanion system, both resonance forms are equally important. We say that they contribute equally to our description of the real delocalized carbanion where half of the negative charge is on each of the terminal C's in the true structure. However, for the alcohol and the amine in Figure 12.031, the resonance forms without charge separation are much more important than the forms with charge separation. This means that there is only a small fraction of negative charge on C, and of positive charge on either O or N in the true structures of the compounds shown in Figure 12.032. We represent that "partial charge" using the designations $\delta+$ and $\delta-$ that mean "part of a (full) charge".

Incorrect Resonance Forms. It is important for you to understand that we cannot write resonance forms for these compounds where the C=C donates electron density to either the O or the N.

The resonance forms shown in Figure 12.033 are completely incorrect.

Figure 12.033



Such forms require that O or N expand their outer shell of electrons beyond an octet electron configuration and this cannot occur.

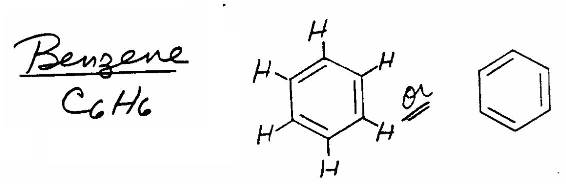
12.5 Benzenoid Aromatic Molecules

Early in this chapter we mentioned a class of conjugated molecules with unusual stability and reactivity that we call *aromatic molecules*. Many *aromatic molecules* contain one or more six-membered rings that we can write with three double bonds alternating with three single bonds (Figure 12.009). These are more specifically named **benzenoid aromatic molecules** and we describe them in this section.

Benzene (12.5A)

The simplest member of this class of *benzenoid aromatic molecules* has the formula C_6H_6 (Figure 12.034).

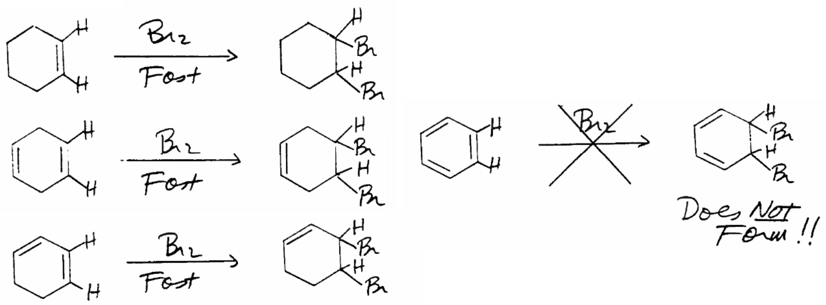
Figure 12.034



The chemical structure that we show here makes it seem that C_6H_6 should be named 1,3,5-cyclohexatriene following the systematic nomenclature rules we learned in Chapter 8. However, that name is never used for this molecule. Its correct *systematic name* is its historical name **benzene**. *Benzene* has been retained as the only systematic name of C_6H_6 in order to emphasize its unusual chemical and physical properties that include the three we describe below.

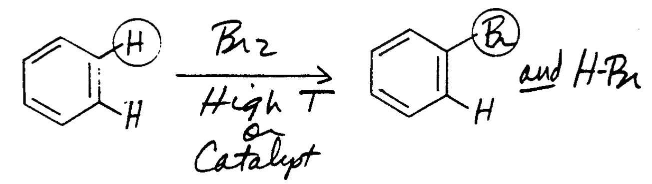
Reactivity. Although we can write a structure for *benzene* that shows three double bonds, *benzene* does not readily undergo addition reactions that we expect for molecules with C=C bonds. For example, Br_2 rapidly adds to cyclohexene, or 1,4-cyclohexadiene, or even the conjugated molecule 1,3-cyclohexadiene at room temperature to give addition products (Figure 12.035) where two Br atoms have added and a C=C bond has disappeared.

Figure 12.035



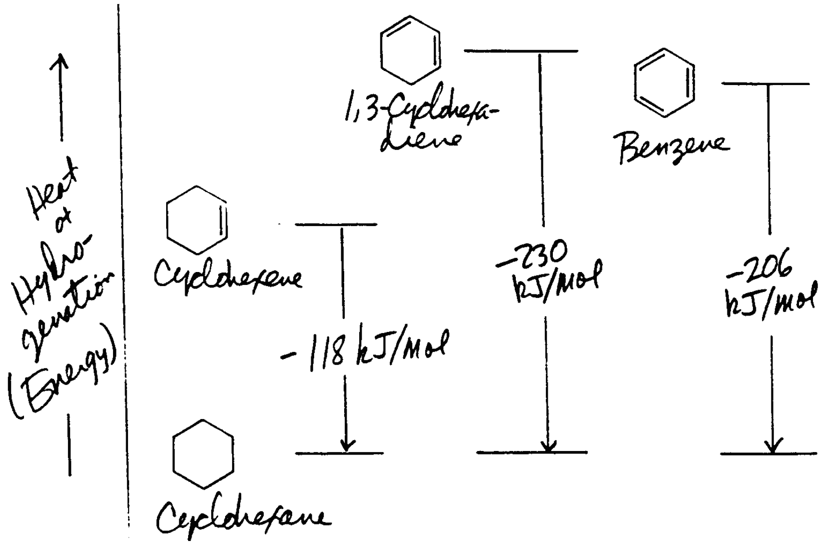
In contrast, Br_2 reacts very slowly with benzene at room temperature and the reaction product loses none of its double bonds. Instead, when we force benzene to react with Br_2 using a catalyst or high temperature, we find that one of the C-H hydrogens is replaced by a bromine atom giving a substitution product and H-Br (Figure 12.036).

Figure 12.036



Stability. The thermodyamic stability of *benzene* is much greater than we would predict based on a comparison of its heat of hydrogenation with those of *cyclohexene* and *1,3-cyclohexadiene*. Complete hydrogenation of each of these molecules gives *cyclohexane*, so we can compare the results on the same energy diagram (Figure 12.037).

Figure 12.037

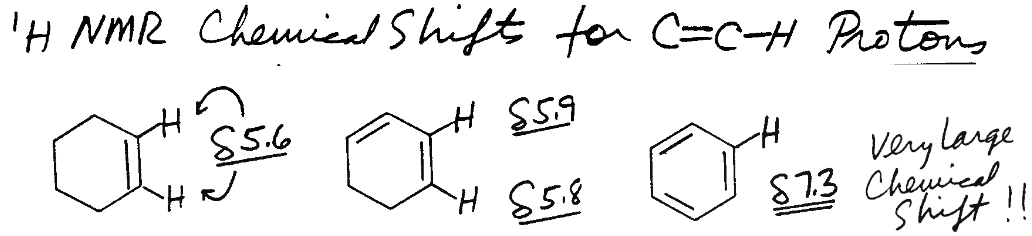


The heat of hydrogenation of cyclohexene is 118 kJ/mol. We can use that value to estimate that 2 isolated C=C bonds in a six-membered ring would have a combined heat of hydrogenation of 236 kJ/mol (2 x 118 kJ/mol), and that 3 hypothetical "isolated C=C bonds" in a six-membered ring would have a heat of hydrogenation of 354 kJ/mol.

We find that the experimental heat of hydrogenation for 1.3-cyclohexadiene (230 kJ/mol) is close to that predicted value, but 6 kJ/mol lower due to 1,3-diene conjugation. In marked contrast, the experimental heat of hydrogenation of benzene (206 kJ/mol) is a whopping 148 kJ/mol lower than we would predict using the data for cyclohexene. In fact the heat of hydrogenation for benzene is even lower than that for 1,3-cyclohexadiene (Figure 12.037). Benzene is dramatically more stable (has dramatically lower energy) than predicted based on the simple chemical structure in Figure 12.034 showing three double bonds.

^{1}H NMR Spectra. The third unusual property of benzene is its ^{1}H NMR spectrum. The ^{1}H NMR chemical shift of δ7.3 for the H's in benzene is substantially larger than the chemical shift values for the C=C-H hydrogens in either cyclohexene or 1,3-cyclohexadiene (Figure 12.038).

Figure 12.038



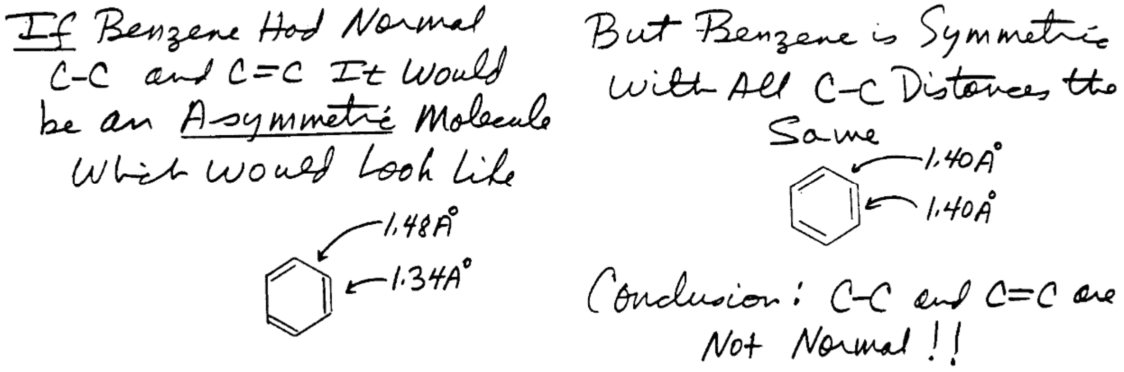
We will see that this unusually large downfield chemical shift is very characteristic of all *aromatic* compounds.

The Real Structure of Benzene (12.5B)

These unusual properties of benzene indicate that the structure we have drawn in Figure 12.034 does not adequately represent the real molecule.

Benzene Geometry. When we look at the structure in Figure 12.034 a second time, we need to recognize that it would represent an asymmetric molecule since C=C bond lengths are typically 1.34 Å, while C-C bond lengths are typically 1.48 Å (Figure 12.039)[next page]. But chemists have determined that benzene has 6 identical carbon-carbon bonds that are 1.40 Å in length. This bond length is almost equal to the average of the normal C-C and C=C bond lengths that we gave above.

Figure 12.039



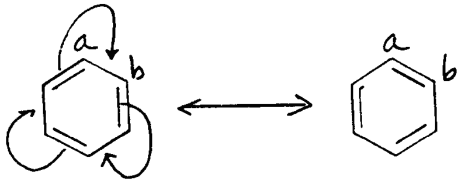
If Benzene Had Normal C-C and C=C It Would be an Asymmetric Molecule Which would Look Like

But Benzene is Symmetric with All C-C Distances the Same

Conclusion: C-C and C=C are Not Normal !!

Benzene Resonance Structures. In fact the structure in Figure 12.034 is just one of two completely equivalent *resonance structures* that we can write for benzene as we show in Figure 12.040.

Figure 12.040



Benzene Resonance Structures

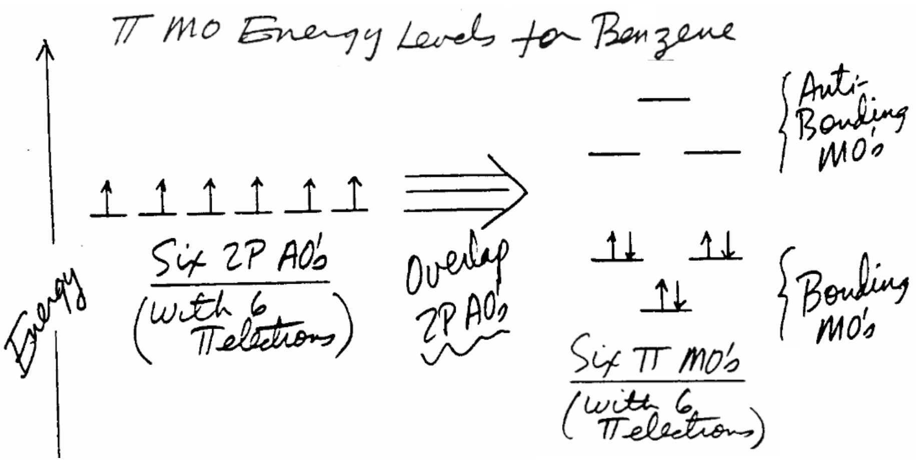
We can shift the set of three double bonds from their positions in the first resonance structure to their positions in the second resonance structure. <u>It is important that you understand that we do not obtain this second structure by rotating the first structure in space</u>. The bond that we show between C_a and C_b in the first structure is a single bond, but it is a double bond in the second structure.

Because we can draw these two different, but completely equivalent, structures for *benzene*, the concept of *resonance* says that neither of them is benzene. Taken together, these two resonance structures imply that the real structure of benzene does not have single or double bonded carbons. Instead, each bond between adjacent carbons has a character that is intermediate between that of a C-C bond and a C=C bond. This is consistent with the experimentally determined intermediate carbon-carbon distances of 1.40 Å in benzene.

Benzene Molecular Orbitals. Since localized C=C bonds do not exist in benzene, the π electrons that would be in these C=C bonds must be delocalized. The act of writing resonance structures implies this delocalization because resonance structures cause you to think of the π electrons as moving freely around the molecule.

While chemists talk about delocalized π electrons in benzene, we must be careful not to misinterpret this concept. We can see the nature of this π electron delocalization from the six molecular orbitals that arise from overlap of the 2p orbitals on each of benzene's six sp^2 carbons. We show these six π MOs and their relative energies in Figure 12.041.

Figure 12.041



Three are *bonding molecular orbitals*, and the other three MO's are *antibonding*. We can place all six of the π electrons in the 3 bonding molecular orbitals (Figure 12.041).

We show the shapes of these three bonding MO's in Figure 12.042.

Figure 12.042

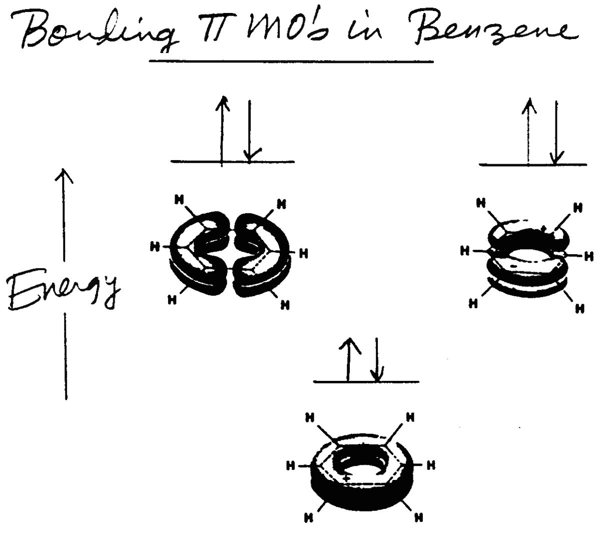
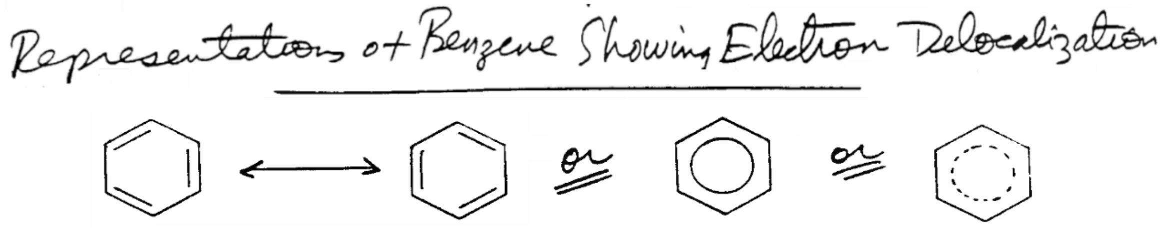


Figure 2.1 Taken from "Advanced Org Chem," March, 4th Ed, Wiley, 1992

Each of them encompasses more than two carbon atoms indicating that the π electrons are delocalized. However, only the lowest energy π MO covers all six of the carbon atoms. As a result, only the two electrons in the lowest energy MO are delocalized completely around the six-carbon ring.

Because of this electron delocalization, and because the benzene representation with three C=C bonds is an inaccurate picture, benzene is sometimes represented using the convention of a solid or even a dotted circle inside of the six-sided ring as we show in Figure 12.043.

Figure 12.043



When we write benzene with 3 C=C bonds as in Figure 12.039, we must understand that the C=C π electrons are not localized and we write it with C=C bonds simply for convenience.

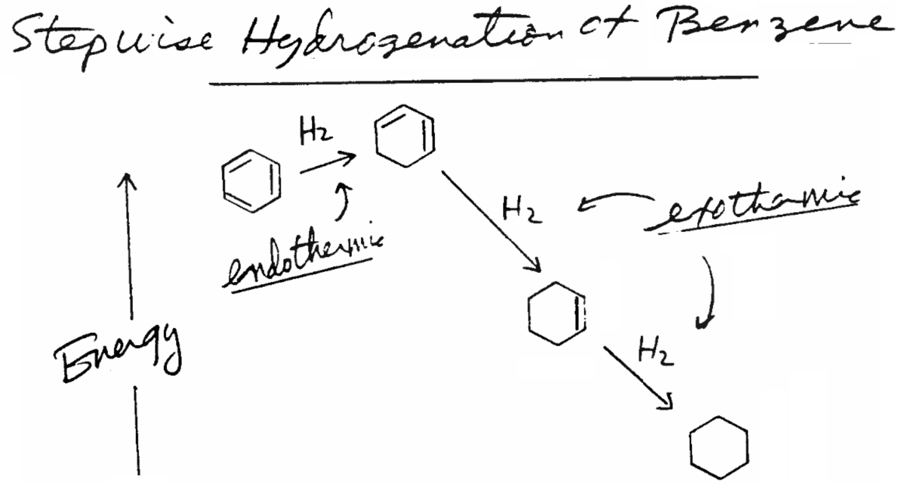
Benzene MO's, Resonance, and Unusual Properties (12.5C)

The circular and fully delocalized π MO is the major source of the three special characteristics of benzene that we described in Section 12.5A. We review those again here with explantions for each observation.

Chemical Reactivity. Any chemical reaction that causes one of the C=C bonds to disappear eliminates the fully delocalized molecular orbital that provides particular stability to the molecule. For this reason, reagents that add to isolated C=C bonds, or even conjugated, C=C bonds that are not aromatic, often do not give addition products with benzene. If they react at all, they frequently form substitution products (Figure 12.036) so that the aromatic π system remains intact.

Stability. Hydrogenation is an addition reaction that disrupts the fully delocalized molecular orbital. We can explain the very small heat of hydrogenation that we observe (Figure 12.037) by proposing that the addition of the first H_2 to benzene that gives 1,3-cyclohexadiene is actually an endothermic reaction. It is thermodynamically unfavorable as are all addition reactions to benzene. In contrast, the heats of hydrogenation for the subsequent additions of the second and third H_2 are exothermic as we show in Figure 12.044 [next page].

Figure 12.044



^{1}H NMR Chemical Shifts. The large value of the ^{1}H NMR chemical shift (δ) for the ring hydrogen atoms of benzene is also due to the fully delocalized bonding MO. The magnetic field applied by the NMR spectrometer causes the "circulating" electrons in the lowest energy fully delocalized MO (Figure 12.042) to set up their own opposing magnetic field in a direction opposite to that of the applied field of the spectrometer. Principles of electricity and magnetism dictate that the lines of force of this opposing field behave as shown in the drawing in Figure 12.045.

Figure 12.045

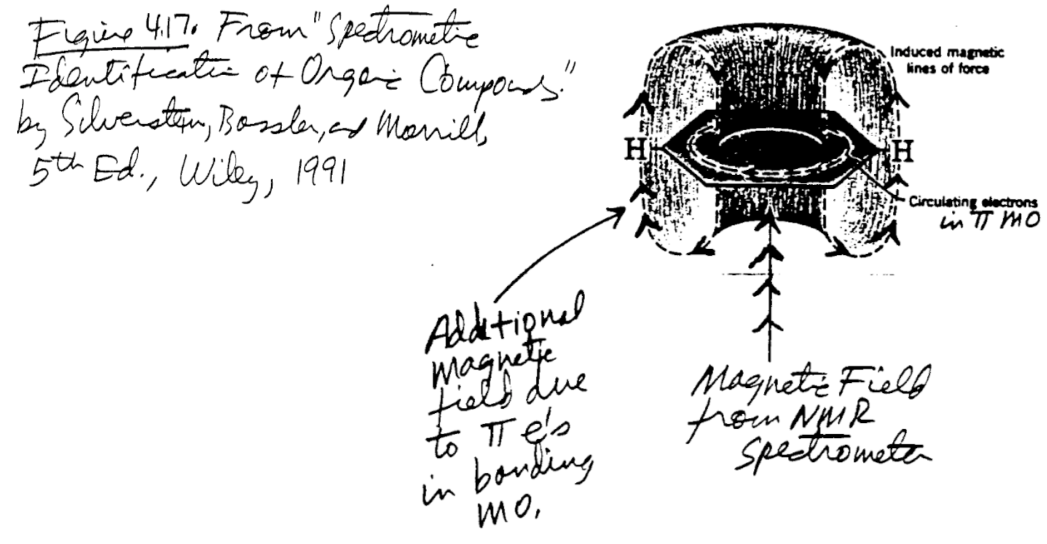


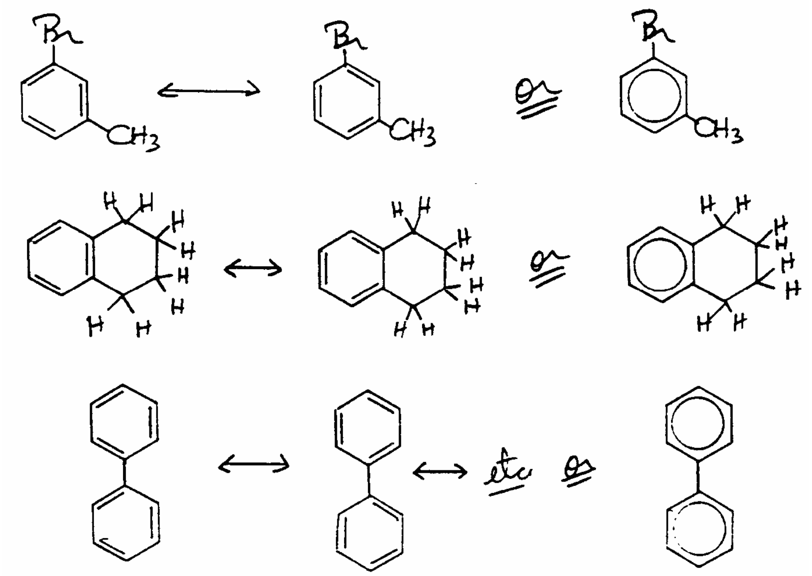
Figure 4.17. From "Spectrometric Identification of Organic Compounds" by Silverstein, Bassler, and Morrill, 5th Ed., Wiley, 1991

These induced magnetic field lines add to the applied magnetic field in the region of the ring hydrogen atoms and this augmented magnetic field leads to the unusually large δ values for these H atoms. More details on NMR spectra of aromatic systems are presented in the spectrometry section at the end of this chapter.

Substituted Benzenes (12.5D)

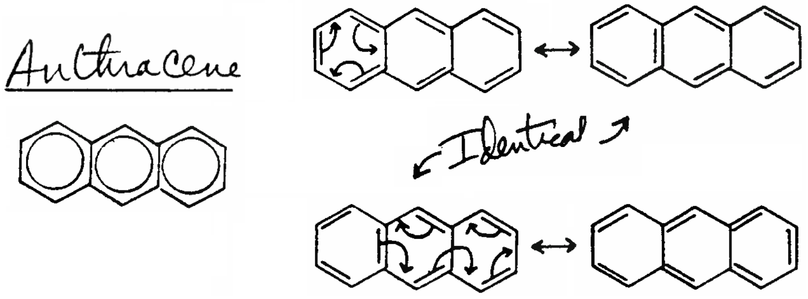
The aromaticity of a benzene ring is preserved even if one or more of its H's are substituted by other functional groups, or it is joined together with one or more additional benzene rings by single bonds, or it is **fused** into polycyclic aromatic molecules. We give examples of these types of molecules in Figure 12.046.

Figure 12.046



In each case, we can write normal benzene resonance structures for each of the benzene rings in the molecules shown above. In the polycyclic aromatic systems, we can write additional resonance structures as we show in Figure 12.047 for the fused benzene ring system named **anthracene**.

Figure 12.047



We describe the nomencalture for substituted benzenes and polycyclic aromatic molecules in the next section.

12.6 Nomenclature of Benzenoid Aromatic Molecules

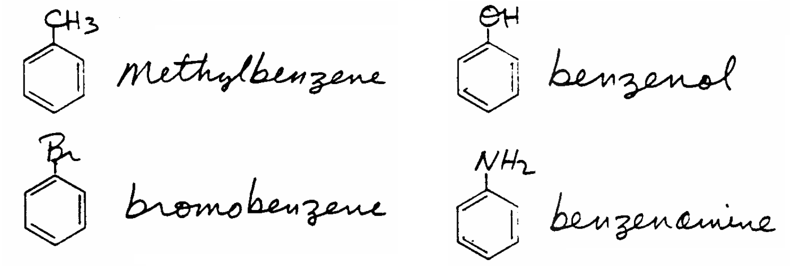
Benzenoid aromatic molecules also have an unusual and diverse set of common names that are accepted as systematic. These names arose historically because of uncertainty of the structures of these compounds with such unusual physical and chemical properties. We present them here along with the alternate systematic names of these compounds.

Monocyclic Arenes (12.6A)

Molecules containing benzene rings are called **arenes** and those with one benzene ring are officially designated as **monocyclic arenes**.

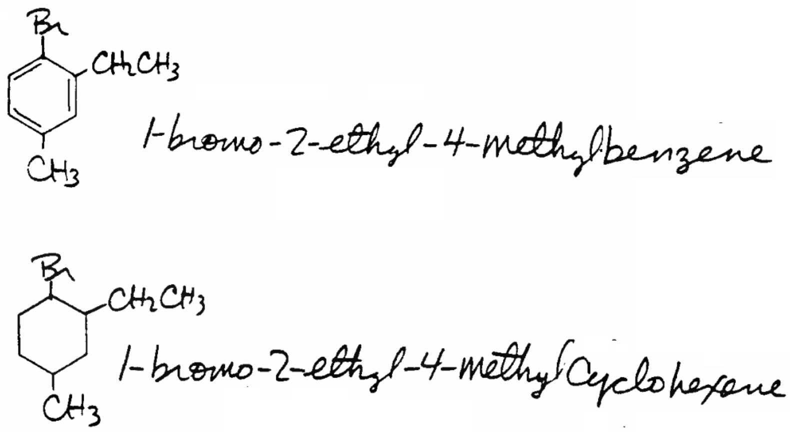
Systematic Nomenclature. A systematic method of naming monocyclic arenes is like that for alkanes except we use *benzene* as the name of the parent hydrocarbon (Figure 12.048).

Figure 12.048



Numbers identify the relative positions of substituents. The rules for assigning these numbers, and placing the substituents in the proper order in the name, are identical to those for naming substituted cyclohexane rings. We see this when we compare 1-bromo-2-ethyl-4-methyl*benzene* and 1-bromo-2-ethyl-4-methyl*cyclohexane* (Figure 12.049).

Figure 12.049



Common Nomenclature. While this systematic nomenclature is straightforward, many simple substituted benzenes have common names that are accepted as alternate systematic names. We show some examples in Figures 12.050 and 12.051 along with their structures.

Figure 12.050 and Figure 12.051

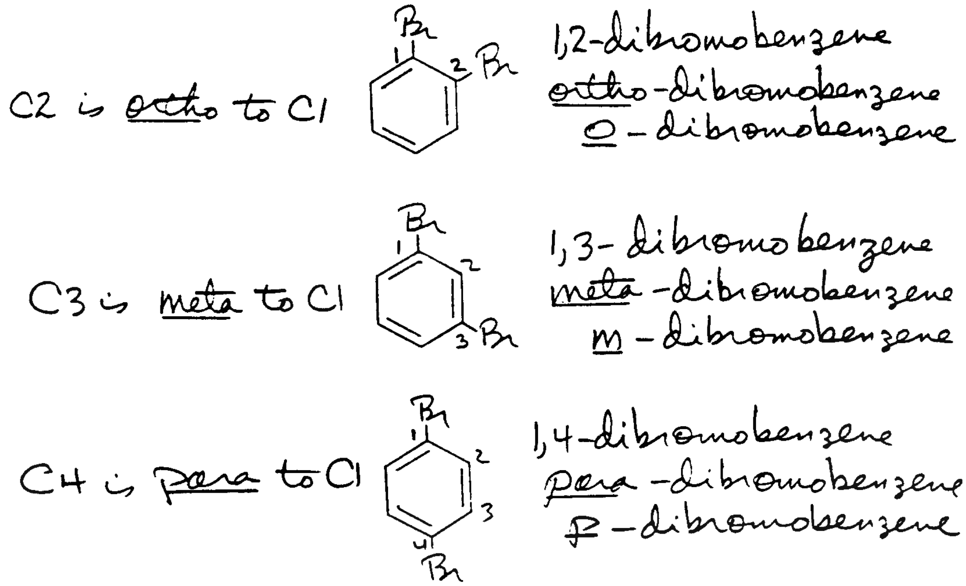
Learn these important common names because they are used more frequently than the alternate systematic names.

ortho, meta, and para (12.6B)

We use the terms ***ortho***, ***meta***, and ***para*** in the common nomenclature of dimethylbenzenes and for other disubstituted benzenes (Figure 12.050 and Figure 12.051). We use them not only in names, but in a broader context to describe the relative positions of any two substitutent groups on a benzene ring. They also describe the relative positions of any two C atoms of the same benzene ring.

You can see in Figure 12.052 that two Br atoms on a benzene ring may be in a *1,2* or a *1,3* or a 1*,4* relationship to each other.

Figure 12.052

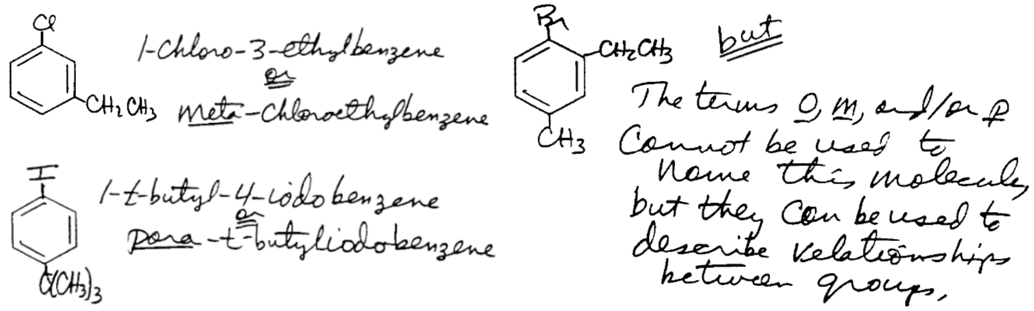


When the two Br atoms are on adjacent carbons (1,2), we say they are *ortho* to each other, and the C bonded to one Br is *ortho* to the C bonded to the other Br. We can even name 1,2-dibromobenzene as *ortho*-dibromobenzene or *o*-dibromobenzene.

Similarly, we say that the relationship between the two Br's in 1,3-dibromobenzene (and their bonded C's) is *meta* , while that between the two Br's and their bonded C's in 1,4-dibromobenzene is *para*. Those compounds are also properly named *meta*-dibromobenzene and *para*-dibromobenzene. We can abbreviate the terms *meta*, and *para* using their first letters *m*, and *p* as we show above for *o*-dibromobenzene.

We can also use these terms to describe the relative relationship of any two substituents on a benzene ring whether these substituents are the same, or are different (Figure 12.051 and Figure 12.053 [next page]).

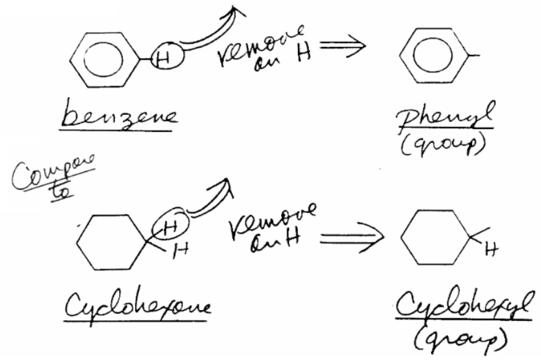
Figure 12.053



However, we can only use them to describe the relationship of two substituents, or two C's on a single benzene ring. For example, we cannot replace the numbers in 1-bromo-2-ethyl-4-methylbenzene with the terms *o*, *m*, and/or *p* because that compound has more than two substituents. However we can properly describe the Br and the CH_3CH_2 group as *ortho*, the Br and the CH_3 as *para*, and the CH_3CH_2 and CH_3 as *meta*.

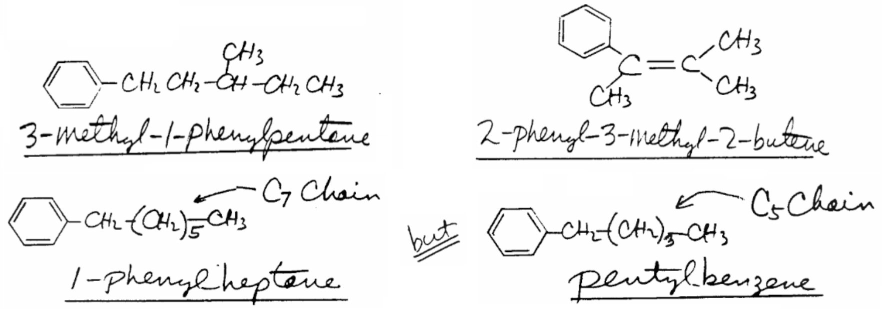
The Phenyl Group. When we need to name a benzene ring as a substituent, we call it the **phenyl group**. This is confusing because, this name bears no connection to the root hydrocarbon name *benzene*. We illustrate the relationship between the group name *phenyl* and the hydrocarbon name *benzene* in Figure 12.054.

Figure 12.054



We often use the term *phenyl* when an alkyl group attached to a benzene ring is complex or large. In such cases, the molecule is named as a *phenyl* substituted alkane (Figure 12.055).

Figure 12.055

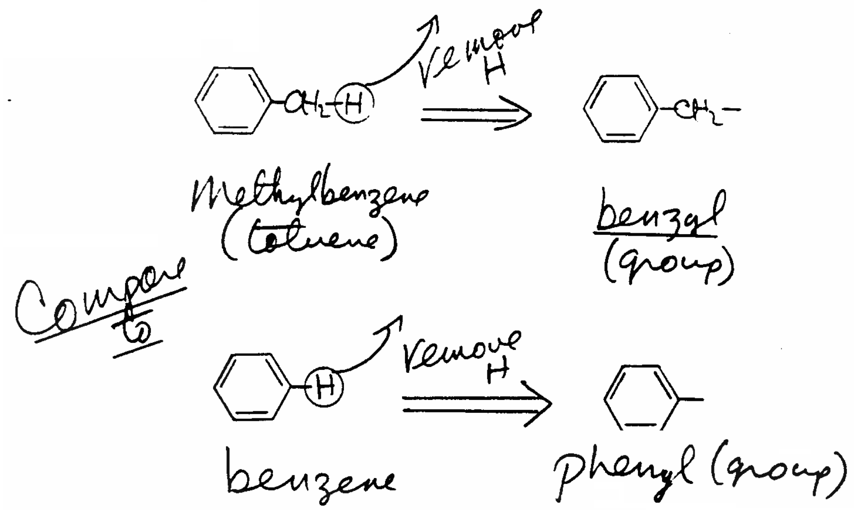


The Benzyl Group. A phenylmethyl substituent is frequently called a **benzyl group** (Figure 12.056).

Figure 12.056

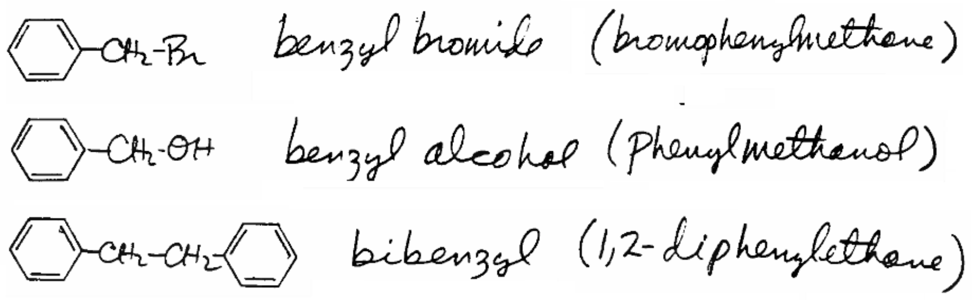
The *benzyl* group is formally derived from *toluene* (*methylbenzene*) by removing an H from its CH_3 group as we show in a comparison with the origin of the *phenyl* group in Figure 12.057.

Figure 12.057



We use the term *benzyl* most often in the common names of compounds as we show in Figure 12.058, or when we wish to simply refer to $PhCH_2$ as a group. We call the H's on CH_2 of the *benzyl* group "benzyl hydrogens".

Figure 12.058



Polycyclic Arenes (12.6C)

Polycyclic arenes are molecules with two or more benzene rings "fused" together (Figure 12.059)[next page]. The names shown are their systematic names. Like the name *benzene* for C_6H_6, these names are the only acceptable names for these compounds. We name substituted polycyclic arenes using the name of the arene as the root name for the compound as in examples shown in Figure 12.060 [next page].

Figure 12.059

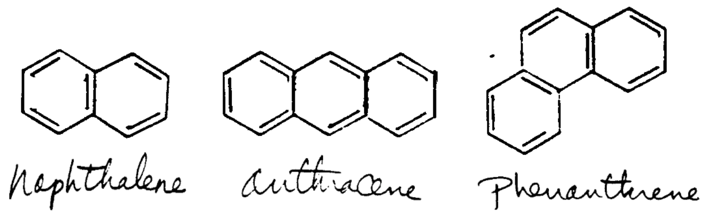
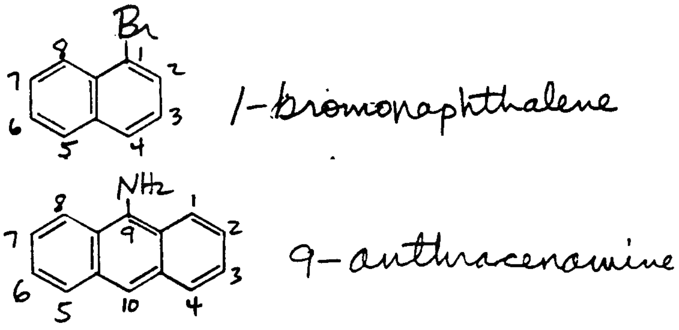


Figure 12.060



12.7 Aromatic Systems without Benzene Rings

We find combination of unusual chemical reactivity, unusually high stability, and large ^{1}H NMR δ values for ring H's in benzenoid aromatic molecules in some other molecules with delocalized π systems but without benzene rings. We call them **nonbenzenoid aromatic molecules** and describe a number of them in this section.

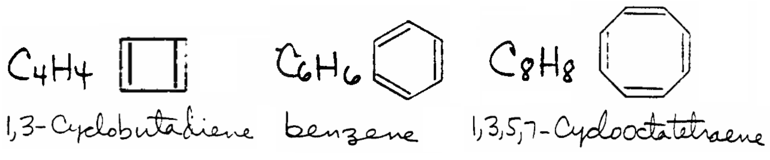
Annulenes (12.7A)

Annulenes are cyclic molecules with alternating C=C and C-C bonds.

Aromatic and Nonaromatic Annulenes. Benzene is an aromatic annulene, and we will see that there are additional aromatic annulenes. However, we will see here that this is not the case for all annulenes.

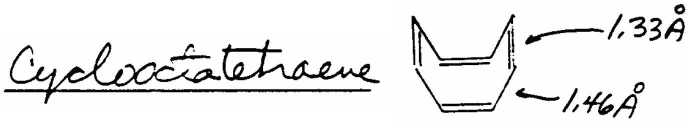
A common structural feature of all *aromatic* molecules, whether *benzenoid* or *nonbenzenoid*, is that they contain a planar ring of sp^2 hybridized atoms whose 2p orbitals overlap to form a "lowest energy" bonding π MO that encompasses all of the overlapping atoms. While it looks like all annulenes should fit this description, we will show that this is not the case by comparing the annulenes **1,3-cyclobutadiene** ("*cyclobutadiene*") and **1,3,5,7-cyclooctatetraene** ("*cyclooctatetraene*") with *benzene* (Figure 12.061).

Figure 12.061



Cyclobutadiene and Cyclooctatetraene. Unlike aromatic molecules, *cyclooctatetraene* readily undergoes addition reactions with reagents such as Br_2. It also has normal thermodynamic stability , and its C-H hydrogens have a normal ^1H δ value (δ 5.8). Moreover, *cyclooctatetraene* is not a planar molecule as we see in Figure 12.062.

Figure 12.062

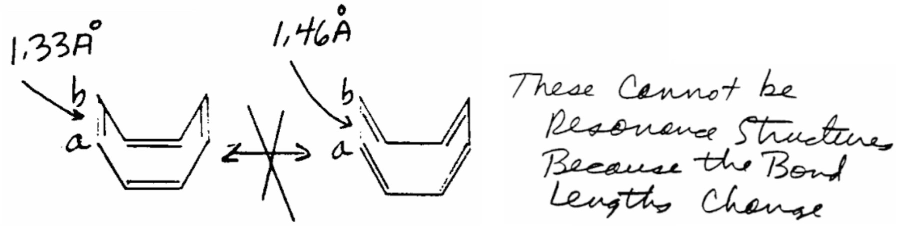


Cyclobutadiene, in contrast with aromatic systems and even *cyclooctatetraene*, is a very unstable molecule that can be formed only with great difficulty at very low temperatures.

Resonance Structures Do Not Tell the Story. It looks like it should be acceptable to draw resonance structures for either *cyclobutadiene* or *cyclooctatetraene* like those we drew for benzene, but this is not the case. Resonance structures of a single compound must differ only in their distribution of π electrons. All bond lengths and positions of atoms must be the same in all resonance structures of a particular compound.

We already know that this would not be the case for *cyclooctatetraene*. Since the molecule is not planar, any movement of π electrons to form the second structure shown in Figure 12.063 requires that we change bond lengths and atom positions.

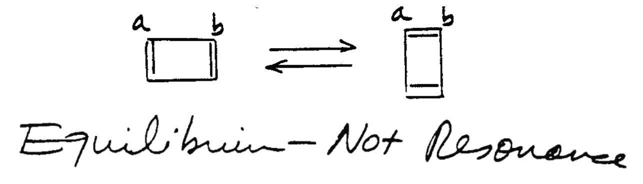
Figure 12.063



These Cannot be Resonance Structures Because the Bond Lengths Change

In the case of *cyclobutadiene*, experiments at very low temperatures show that there is an actual equilibrium between the two asymmetric isomers that we show in Figure 12.064.

Figure 12.064



Equilibrium—Not Resonance

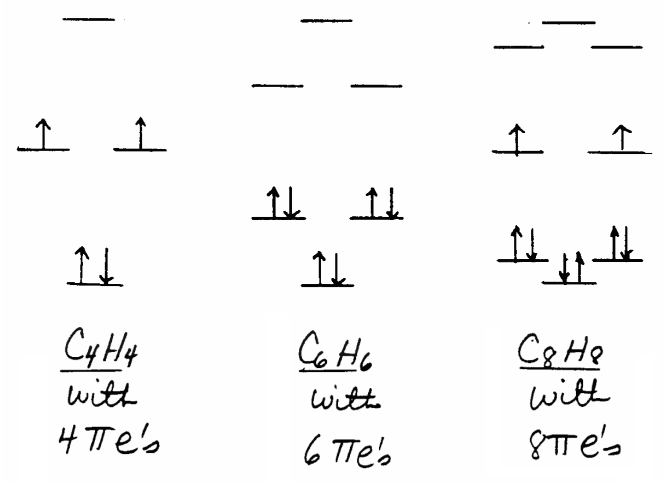
We exaggerate the change in bond lengths and atom positions so that you can clearly see that these are separtate isomers and not resonance structures.

MO Diagrams for C_4H_4, C_6H_6 and C_8H_8 (12.7B)

The reasons that *cyclobutadiene* and *cyclooctatetraene* are not aromatic, although *benzene* is, lies in the electron distribution diagrams for hypothetical planar structures of all these annulenes. We show energy level diagrams for planar structures of cyclobutadiene, benzene, and cyclooctatetraene that result from overlap of the 2p orbitals on each of the ring carbons in Figure 12.065.

Figure 12.065

π Orbital Energy Levels for Planar Annulenes



When we place the 4, or 6, or 8 π electrons, in the π MO energy levels (Figure 12.065) for these molecules, we find that both *cyclobutadiene* and *cyclooctatetraene* have partially filled MO's. This occurs because orbitals at the same energy level must each contain one electron before any of them receives a second electron (Chapter 3). In dramatic contrast, there are no partially filled MO's in benzene. Each bonding MO contains an electron pair.

Cyclooctatetraene. Electron configurations with partially empty orbitals are very unstable. In order to avoid this, cyclooctatetraene distorts its geometry from planarity. As a result, the double bonds become isolated because the 2p orbitals can no longer interact simultaneously with each other. The result for the large cyclooctatetraene molecule is a boat shaped molecule that has separate MO's for each double bond and each contains a localized electron pair (Figure 12.062). The bond angles of this boat shaped molcule are also much more energetically favorable than the 135° angles that a planar octagonal structure requires.

Cyclobutadiene. If cyclobutadiene tried to distort in the same way as cyclooctatetraene, it would have significant strain energy because of its small ring size. In spite of this, that strain is not sufficient to account for the extreme instability of cyclobutadiene. Theoretical considerations beyond the scope of this text indicate that closed loop systems containing four π electrons possess extraordinary instability referred to as **antiaromaticity**.

Aromatic Annulenes Besides Benzene (12.7C)

When we perform analyses of electron configurations in planar closed loop systems with overlapping 2p orbitals on adjacent atoms, we find that there are other annulenes besides benzene that do not have any partially filled bonding MO's. These include 2, 10, 14, and 18 π electron systems and some of those systems are aromatic.

Hückel's Rule. It turns out that you can calculate these particular numbers of π electrons using the simple relationship "number of π electrons" = 4n+2 when n is an integer (e.g. 0, 1, 2, etc.) (Table 12.1).

Table 12.1 Number (n) of π Electrons in an Aromatic Molecule is 4n + 2

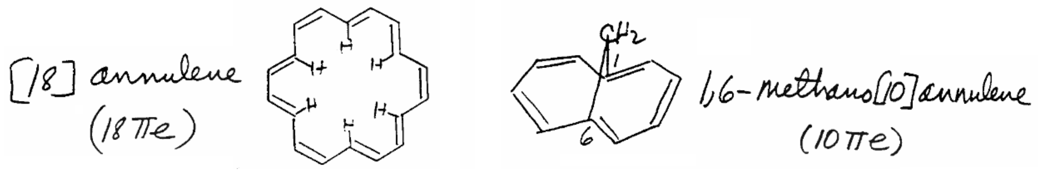
n	4n + 2
0	2
1	6
2	10
3	14
4	18

When a closed loop system as described above has 4n + 2 π electrons, chemists say that it obeys **Hückels rule**.

It is important to be aware that the integer **n** has no physical meaning. It does not correspond to any property of the molecule. The number of π electrons required for an aromatic system simply equals 4n + 2 when n is an integer such as 0, or 1, or 2, etc (Table 12.1).

Other Annulenes. There are many interesting examples of such "4n + 2" π-electron systems and we show two of them in Figure 12.066.

Figure 12.066



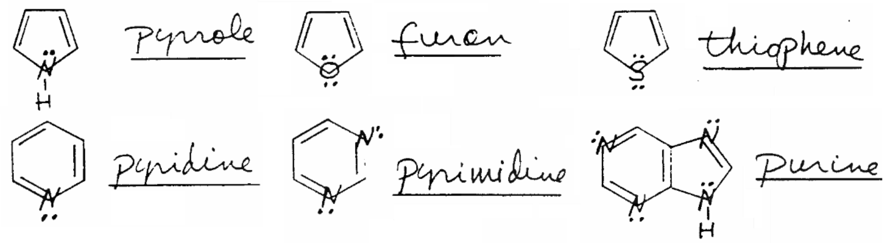
The first compound **[18]annulene** has 18 π electrons (4n + 2 = 18 when n = 4). It has the properties of an aromatic compound and illustrates the alternative nomenclature system for annulenes. The second compound is a [10]annulene with a CH_2 bridge. This bridge eliminates the H's that would otherwise be attached to C1 and C6. Without the bridge, those

H's would point toward the inside of the molecule, sterically interfere with each other, and prevent the ring system from being planar.

Heteroaromatic Systems (12.7D)

Aromatic rings can include atoms other than C. We show some examples in Figure 12.067.

Figure 12.067

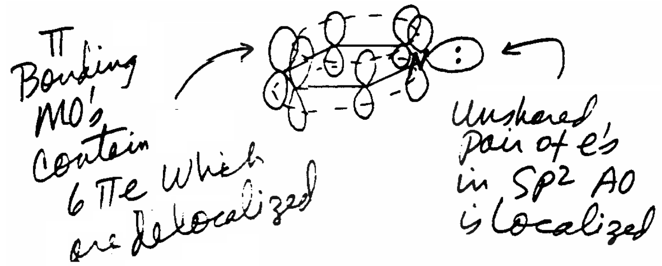


While these molecules have sytematic names, they are always referred to by their common names.

Systematic Names. You can construct systematic names for these molecules using the nomenclature rules for heterocyclic compounds in Chapter 3 and for cycloalkenes in Chapter 8.

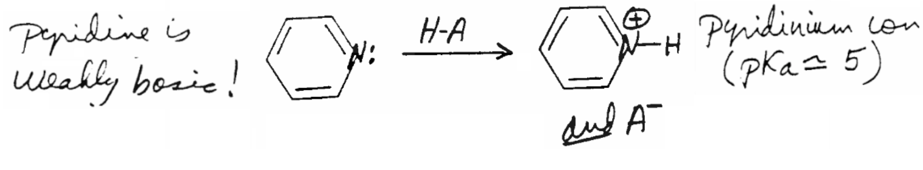
Pyridine. Pyridine looks like benzene except that one of its C-H's has been replaced with an N atom. C's in benzene are hybridized sp^2 so we use that same hybridization for the N that replaces it. The π MO's in pyridine are qualitatively the same as in benzene and arise from overlap of the 2p AO's on each atom including N (Figure 12.068).

Figure 12.068



The unshared electron pair on the sp^2 hybridized N is localized in an sp^2 orbital that is not part of the π electron system. That sp^2 orbital lies in the plane of the ring and is orthogonal to the π system of the ring. As a result the unshared electron pair on N has normal chemical reactivity. For example, pyridine is a weak base because this unshared pair can react with an acid as we show in Figure 12.069.

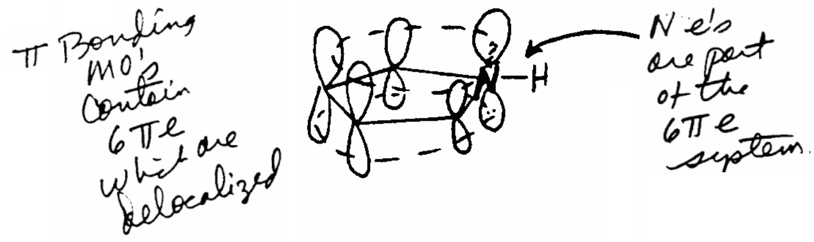
Figure 12.069



The resultant pyridinium ion (Figure 12.069) is also aromatic. The protonation of N does not effect the π electron density because it only involves the unshared electron pair on N that is not part of the π electron system.

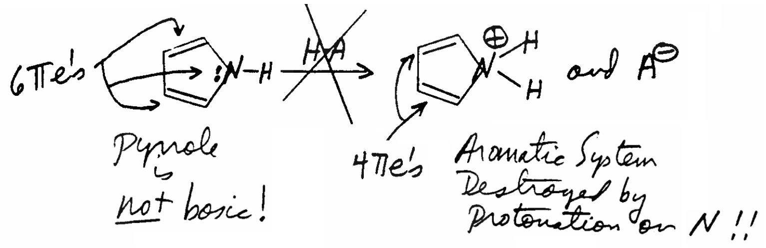
Pyrrole. In contrast with pyridine, the unshared electron pair on the N of pyrrole is part of the π electron system. So pyrrole has 6 π electrons in three bonding π MO's like those for benzene (Figure 12.065). We draw a structure for pyrrole in Figure 12.070 that shows the 2p orbitals that overlap to form the π MO's (Figure 12.070).

Figure 12.070



Since the unshared electron pair on pyrrole is part of the π electron system, it does <u>not</u> have normal chemical reactivity. As a result, pyrrole is not basic because protonation of N would utilize the two electrons on N to form the N-H bond as we show in Figure 12.071.

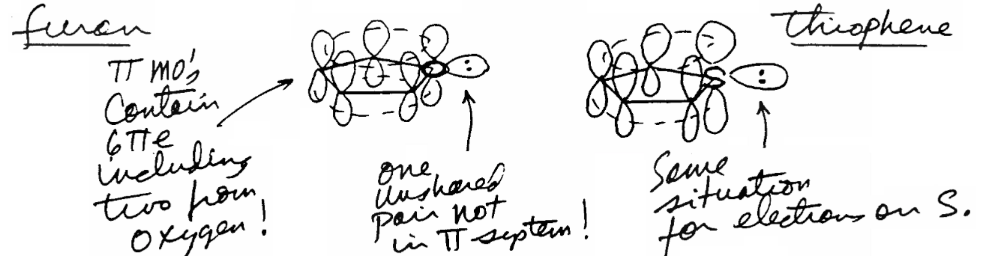
Figure 12.071



These two electrons are part of the aromatic 6π electron system so if they were used to form an N-H bond, pyrrole would lose its aromaticity.

Furan and Thiophene. The heterocyclic molecules with O and S in Figure 12.067 (**furan** and **thiophene**) are analogous to pyrrole. In each case, an unshared electron pair on the O or the S is part of the π electron system as shown in Figure 12.072. Both O and S have an additional unshared pair that is in an sp^2 orbital that is not in the π system.

Figure 12.072



Both *furan* and *thiophene* have six π electrons in a set of bonding MO's analogous to those of *pyrrole* as we show in Figure 12.070.

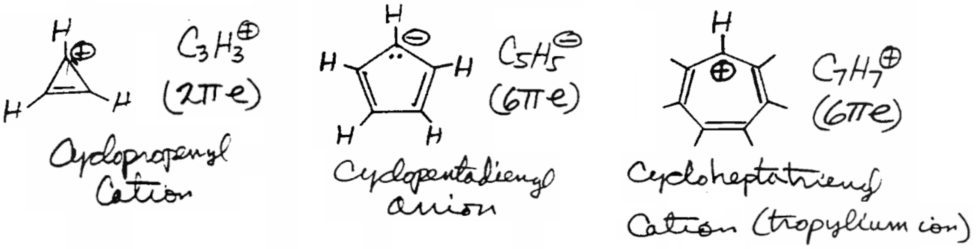
Purine and Pyrimidine. We show the heteroaromatic compounds **purine** and **pyrimidine** because they are related to components of the biologically important nucleic acids that we describe in Chapter 23. The electron distribution in *pyrimidine* is analogous to that of pyridine. Both unshared pairs on the N atoms are in sp^2 orbitals that are not part of the π electron system.

Purine combines the features of *pyrimidine* and *pyrrole*. In the five membered ring, the unshared pair on the NH is part of the π system while that on the other N is not. While the other structures in Figure 12.067 each have 6π electrons, purine has a total of 10 π e's. It is analogous to naphthalene that we showed earlier in Figure 12.009.

Aromatic Ions (12.7E)

Aromatic systems can also be ionic and we show some examples in Figure 12.073.

Figure 12.073



Note that the size of the ring does not need to correspond to the number of π electrons.

Cycloheptatrienyl Cation. The $C_7H_7^+$ cation with 6 π electrons is so stable that 7-bromocycloheptatriene (Figure 12.074a) is actually a salt with the formula $C_7H_7^+$ Br^- commonly named **tropylium bromide**.

Figure 12.074a is in a supplemental appendix at the end of the chapter

This positively charged ring is planar and each C is sp^2 hybridized. The seven 2p AO's overlap with each other to generate seven π MO's with the lowest energy bonding MO delocalized over all 7 C's.

Cyclopentadienyl Anion. Although $C_5H_5^-$ also has 6 π electrons, it only has 5 C's. It is planar and a demonstration of its high stability is the extraordinarily high acidity of its precursor hydrocarbon 1,3-cyclopentadiene (Figure 12.074b).

Figure 12.074b is in a supplemental appendix at the end of the chapter

Its $pK_a = 16$ is comparable to those of H_2O and simple alcohols (R-OH). This ion is isoelectronic with pyrrole (Figure 12.067) and the unshared electron that we show above is part of the 6π electron system just as is the unshared electron pair on the N atom in pyrrole.

Cyclopropenyl Cation. While the preceding aromatic ions have 6π electrons like benzene, the cyclopropenyl cation ($C_3H_3^+$) has only 2π electrons corresponding to 4n + 2 when n = 0 (Figure 12.074c).

Figure 12.074c is in a supplemental appendix at the end of the chapter

This ion has been made by reacting 3-chlorocyclopropene with $SbCl_5$.

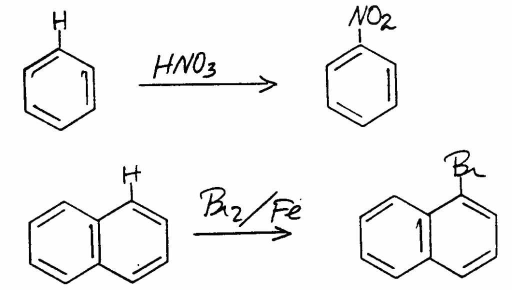
Cyclooctadienyl Dianion. An example of a 10 π electron system (4n + 2 = 10 when n = 2) is the cyclooctatetraenyl dianion ($C_8H_8^{-2}$) that forms when metallic sodium reacts with cyclooctatetraene (Figure 12.074d).

Figure 12.074d is in a supplemental appendix at the end of the chapter

12.8 Making Substituted Benzenes

Many substituted benzenes can be made by reacting benzene with electrophilic reagents in reactions referred to as electrophilic aromatic substitution like the examples in Figure 12.075.

Figure 12.075



We describe the scope and basic mechanism of electrophilic substitution in this section and illustrate the types of substituents that we can add using it. However we must use other reactions to add the important OH and NH_2 groups as we see at the end of this section.

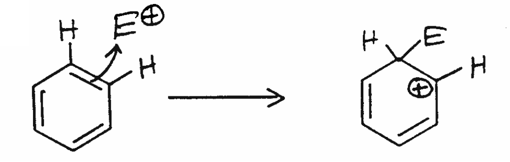
Electrophilic Aromatic Substitution Mechanism (12.8A)

We can divide all of these reactions into 3 distinct mechanistic parts that are (1) formation of the electrophile (E^+), (2) attack of (E^+) on the arene to give a cationic intermediate called an arenium ion, and (3) loss of a proton from the arenium ion to give the substitution product.

Electrophiles. The formation of E^+ occurs by reactions that are unique to the particular E^+. We describe these later after we talk about arenium ion formation and deprotonation using benzene as our grepresentative arene.

Arenium Ion Formation. The electrophile (E^+) reacts with two of the π electrons of benzene to form a C-E bond and the cationic (arenium ion) intermediate (Figure 12.077).

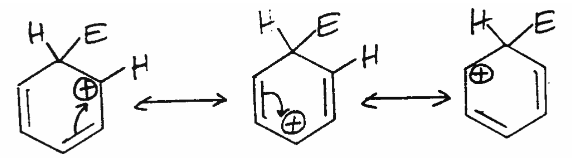
Figure 12.077



Even though the π electrons of benzene are delocalized, it is useful to show this reaction using just one of the benzene resonance structures.

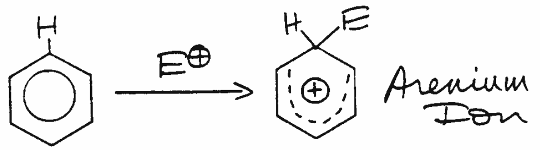
We show the resultant cation as a localized structure, but it is also conjugated like the we cations formed from conjugated polyenes earlier in this chapter. As a result we can represent it using the series of resonance structures in Figure 12.078.

Figure 12.078



These resonance structures represent the delocalized arenium ion that we also represent in a more general representation in Figure 12.079.

Figure 12.079



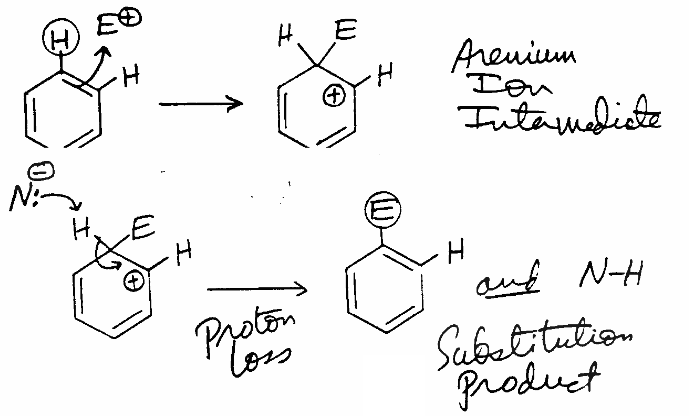
Note that we show the reaction of E^+ at just one of the 6 equivalent C's of benzene. We can draw pictures like those shown in these figures for E^+ reacting at any of the other 5 C's of benzene.

> **Arenium Ion Stability**. Although delocalized, the arenium ion is not aromatic. Unlike its precursor *benzene*, it no longer has 4n+2 π electrons nor is there a continuous loop of carbon atoms with overlapping 2p orbitals. Since aromaticity is such a prized possession, you might wonder why an electrophile would react with an arene such as benzene. The answer is that energetically unfavorable reactions happen all the time if enough energy is available to cause the reactants to react.

> In the case of arenes, the energy required for addition of an electrophile is greater than that required for reaction of the same electrophile with an unconjugated double bond, or even with a normally conjugated double bond as in nonaromatic conjugated polyenes described earlier in this chapter. For example, molecular Br_2 will rapidly react at room temperature with alkenes or conjugated polyenes, but requires elevated temperatures and a catalyst to rapidly react with benzene.

Deprotonation of the Arenium Ion. The loss of aromaticity in the arenium ion explains why it subsequently loses a proton to reform a 6π electron aromatic ring (Figure 12.079a).

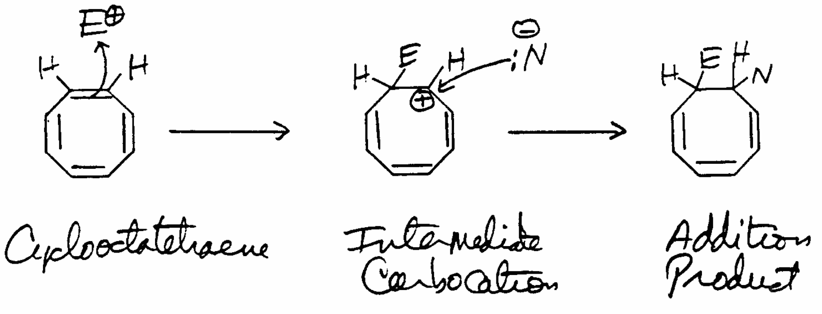
Figure 12.079a



The substituted benzene product that we show in that figure has the same aromatic stability as the reactant benzene. Addition of a nucleophile (N:$^-$) to an arenium ion would lead to overall loss of aromaticity.

While the specific mechanism of proton loss depends on the specific reacting system, proton removal occurs by its transfer to some nucleophilic reagent in the reaction mixture as we indicated in Figure 12.079a. In contrast, after an electrophile adds to a double bond in a nonaromatic system like cyclooctatetraene (Figure 12.080), the intermediate carbocation usually reacts with a nucleophile leading to an overall addition reaction as shown here.

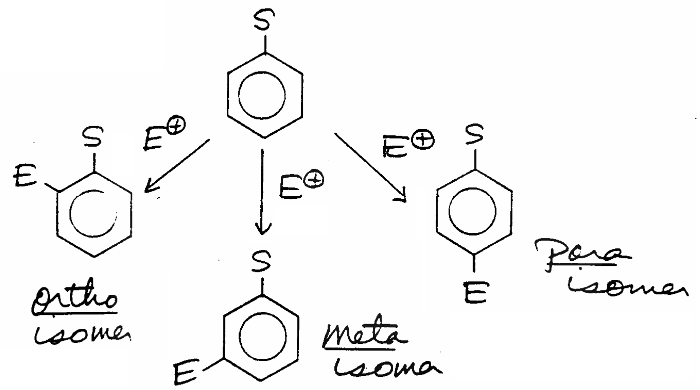
Figure 12.080



We expect the addition product to be more stable that the starting tetraene since we have converted a C=C bond into a C-C bond.

***Reactions with Substituted Benzenes*.** Electrophilic substitution also occurs on substituted benzenes. These reactions share the same three basic mechanistic features that we have described for benzene including (1) electrophile formation, (2) arenium ion formation, and (3) arenium ion deprotonation. In contrast with benzene, the presence of a substituent on the arene ring leads to isomeric products (Figure 12.081).

Figure 12.081

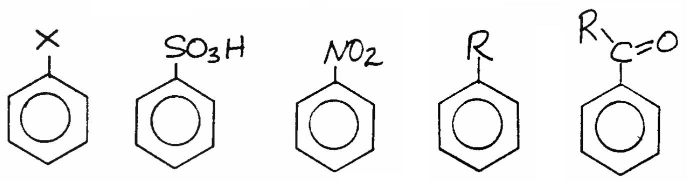


The relative amounts of these different products and their rates of formation depend on the nature of the substituent S, but S does not change the basic features of the reaction mechanism. We refer to the effects of S on product distribution and reaction rates as **substituent effects** and describe them in Chapter 13.

Formation of the Electrophile (12.8B)

We can substitute a variety of different E groups on a benzene ring and show some of these in Figure 12.082.

Figure 12.082

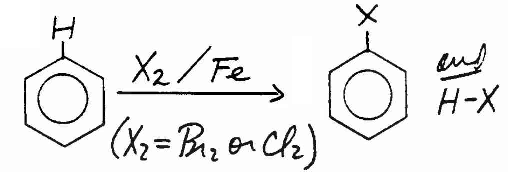


We discuss the nature and formation of the electrophiles leading to each of these substituted benzenes in the following sections.

***Halogenation*.** We chlorinate or brominate arenes using Cl_2 or Br_2 and a catalyst. Iodination is more difficult because I_2 is relatively unreactive in this type of reaction, while F_2 is so reactive that fluorination of arenes using it is not a useful reaction.

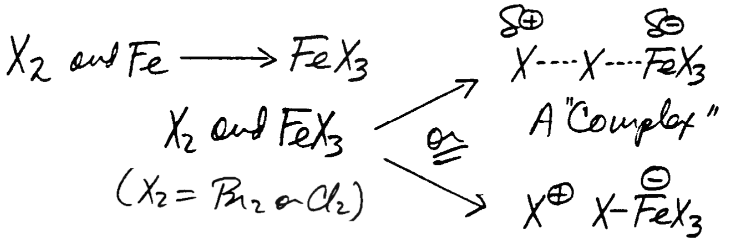
A common method for chlorination or bromination of arenes involves reaction of the arene with Br_2 or Cl_2 in the presence of a trace amount of iron (Figure 12.083)[next page].

Figure 12.083



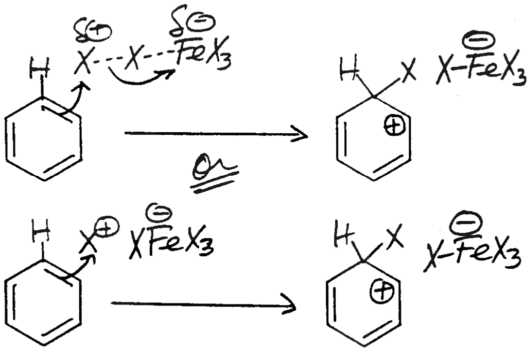
Fe reacts with Br_2 or Cl_2 to form $FeBr_3$ or $FeCl_3$ that serve as the catalysts (Figure 12.084).

Figure 12.084



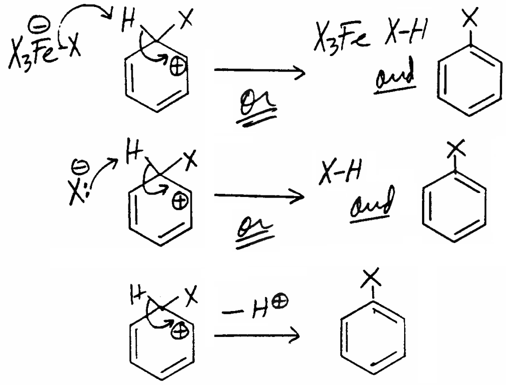
The FeX_3 species activates the reactant X_2 by forming a complex that donates X^+ to benzene or that serves as a source of X^+ as we show in Figure 12.085.

Figure 12.085



There are a variety of basic/nucleophilic species present such as FeX_4^- or X^- (from FeX_4^- or HX) that will serve as the species (see Figure 12.079a) to remove the proton (Figure 12.086).

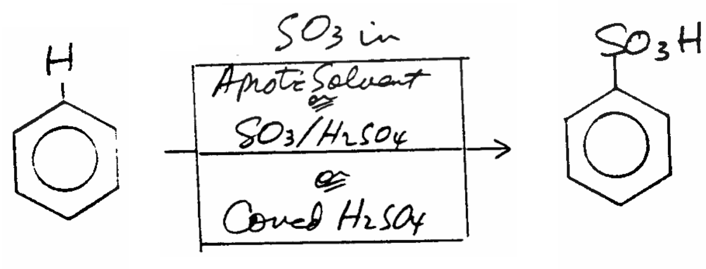
Figure 12.086



Although we know that H^+ cannot simply "fall off" of the intermediate arenium ion, we often write loss of the proton as the third reaction shown in Figure 12.086 since we do not know the specific species that removes it.

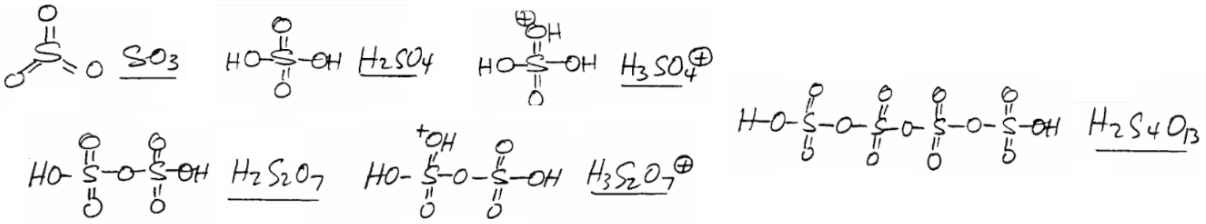
Sulfonation. We can replace H on an arene with the sulfonic acid group -SO_3H using one of three sets of reagents that we show in Figure 12.087 for conversion of *benzene* to *benzenesulfonic acid*.

Figure 12.087



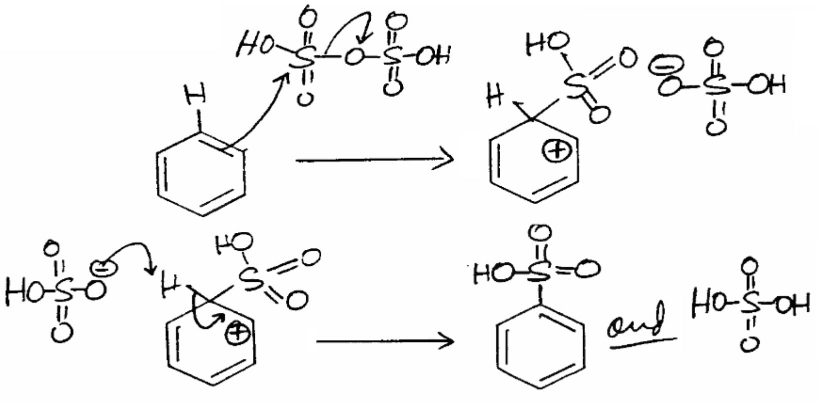
The specific electrophile depends on whcih set of reagents we use for the sulfonation. It can include protonated sulfuric acid ($H_3SO_4^+$) or SO_3 itself, or various inorganic species formed from reaction of SO_3 and H_2SO_4 (Figure 12.088).

Figure 12.088



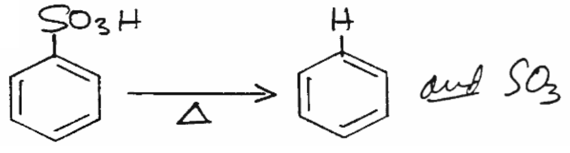
We show a mechanism for sulfonation in highly concentrated sulfuric acid using $H_2S_2O_7$ as the electrophile in Figure 12.089.

Figure 12.089



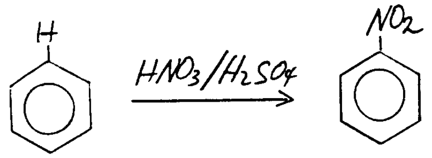
Sulfonation reactions are reversible at high temperatures (Figure 12.090).

Figure 12.090



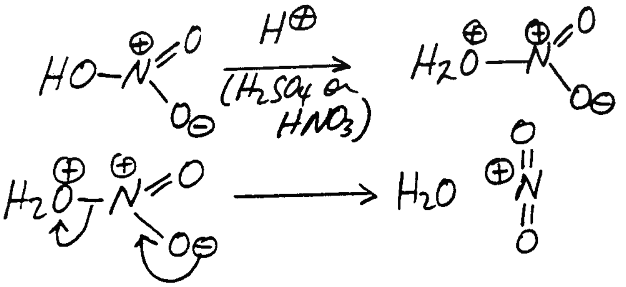
Nitration. We can form nitrobenzene from benzene (Figure 12.091) by reacting it with HNO_3 (nitric acid) in H_2SO_4.

Figure 12.091



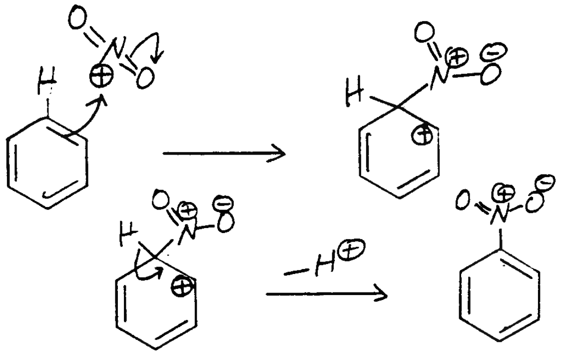
The electrophile NO_2^+ (**nitronium ion**) forms in sulfuric acid or even in pure nitric acid as we show in Figure 12.092.

Figure 12.092



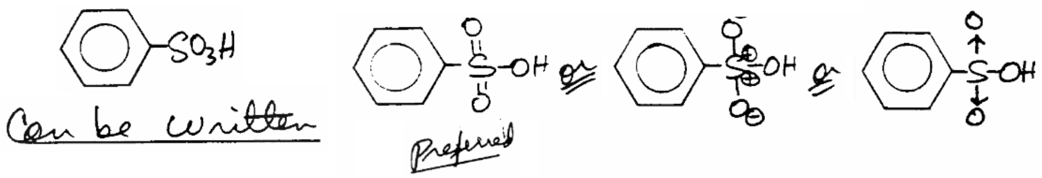
NO_2^+ reacts with benzene to form an arenium ion intermediate (Figure 12.093) that subsequently "loses a proton" (donates a proton to a base/nucleophile in the reaction mixture) to give *nitrobenzene* .

Figure 12.093



Structures with S=O and N=O Bonds. Sometimes "S=O" bonds are written in other ways that we show in Figure 12.094.

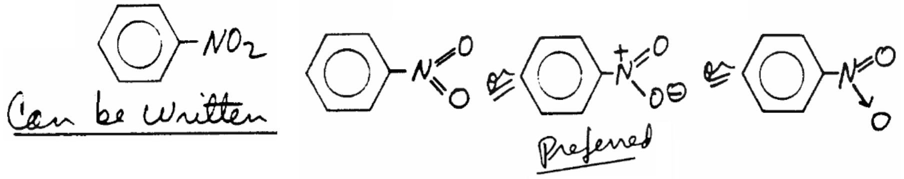
Figure 12.094



Each of these symbolize that S has an expanded octet of outer shell electrons. We will use the S=O convention because it is convenient.

The same choices are possible when writing N=O bonds in NO_2 groups or in nitric acid HNO_3 as we show for the NO_2 group in Figure 12.095.

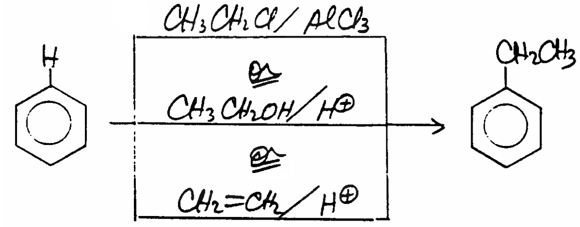
Figure 12.095



We feel that it is more convenient to use N=O rather than N^+-O^-, but the N^+-O^- representation is more accurate because N does not easily expand its outer shell electron octet but this is implied by structures using all N=O bonds. In any case, the most important aspects of these structures are that the benzene ring is directly bonded to the N or to the S of the NO_2 and SO_3H groups, and that the H on SO_3H is attached to one of the oxygens

Alkylation. We can substitute alkyl groups on arenes by an electrophilic substitution reaction known as a **Friedel-Crafts alkylation**. We can generally use different sets of reactants as we show in Figure 12.096 for the formation of ethylbenzene from benzene.

Figure 12.096



In the mechanism, we can imagine that the electrophile is an ethyl carbocation ($CH_3CH_2^+$) (Figure 12.097) that is transferred to an arene to give an intermediate arenium ion that subsequently loses a proton to give an alkyl substituted benzene (Figure 12.098).

Figure 12.097

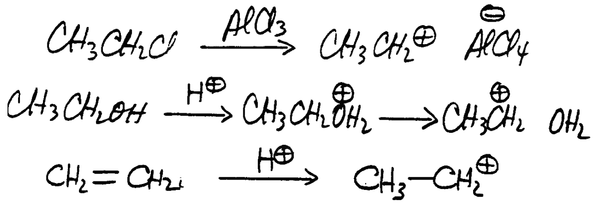
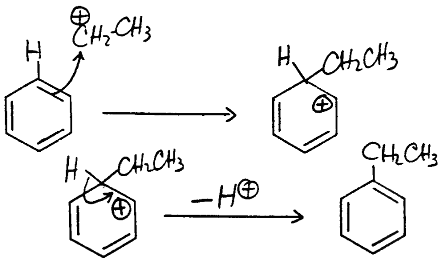


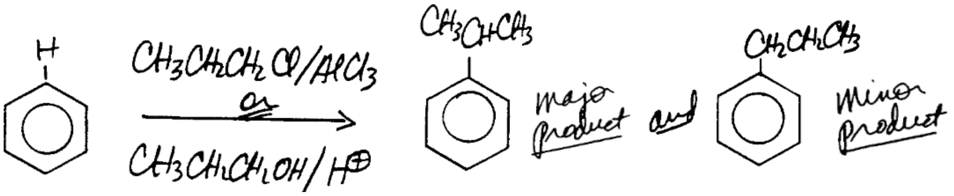
Figure 12.098



A common haloalkane reaction system includes the R-Cl and $AlCl_3$, while sulfuric acid (H_2SO_4) is the usual acid catalyst for either alcohol or alkene reactants.

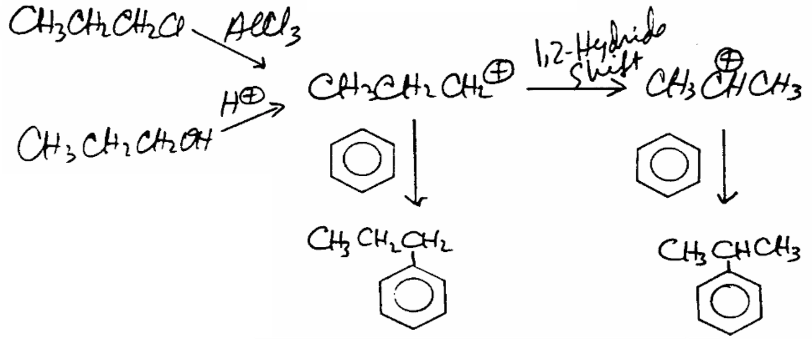
The carbocation intermediates in Friedel-Crafts alkylation reactions rearrange as we described earlier in the text. As a result, reaction between benzene and a haloalkane such as 1-chloropropane, or an alcohol such as 1-propanol, gives primarily isopropylbenzene and only a small amount of propylbenzene (Figure 12.099).

Figure 12.099



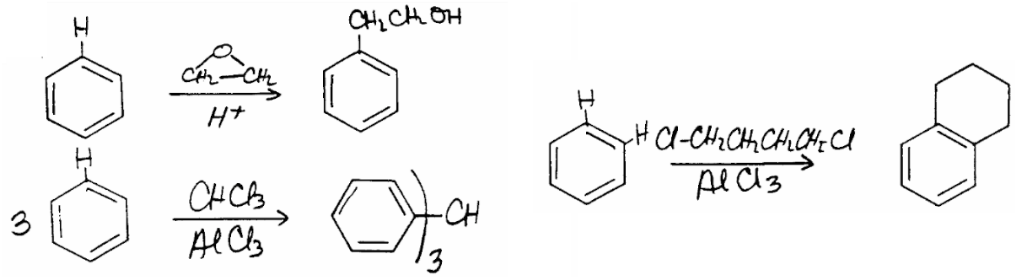
The intermediate 1-propyl carbocation rearranges during its formation to the 1-methylethyl carbocation (isopropyl carbocation) by a hydride shift in competition with its reaction with benzene (Figure 12.100).

Figure 12.100



Because of the wide variety of reactants, there is a great deal of diversity associated with the Friedel-Crafts alkylation reaction (Figure 12.101).

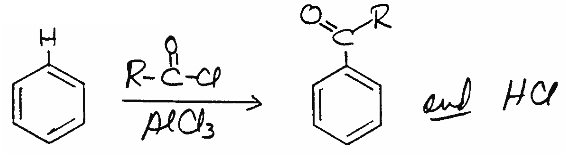
Figure 12.101



We will learn in Chapter 13 that alkyl groups on an arene make it more reactive than the unsubstituted arene so that the alkylbenzene reaction product can easily undergo a second alkylation reaction.

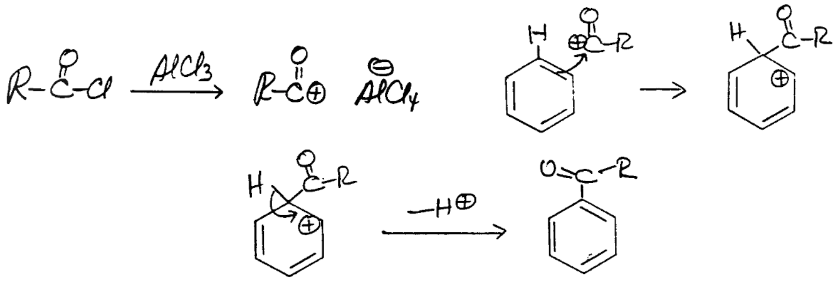
Acylation. Another electrophilic substitution reaction that is important in organic synthesis is the **Friedel-Crafts acylation** reaction (Figure 12.102).

Figure 12.102



This reaction utilizes an **acid halide** (**R-C(=O)-Cl**) reactant, and forms a **ketone** product, that both have C=O functional groups that we have not yet introduced. As a result we will discuss this reaction in more detail later in this text. However, we outline its general mechanism in Figure 12.103 because it is analogous to mechanisms of other electrophilic aromatic substitution reactions already presented.

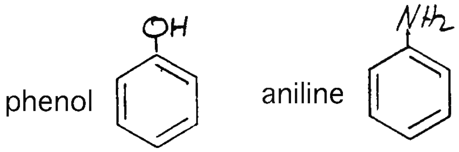
Figure 12.103



NH_2 and OH Groups on Arenes (12.8C)

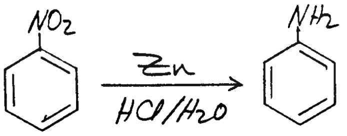
The **OH** and **NH_2** groups are important substituents on aromatic compounds, but they cannot be added to arenes using electrophilic aromatic substitution reactions. We discuss these compounds and their syntheses in greater detail later in the text, but here use **phenol** (**Ph-OH**) and **aniline** (**Ph-NH_2**), the simplest members of these classes, to give a brief preview of their synthetic origins, and how conjugation affects their acid-base properties.

Figure 12.104



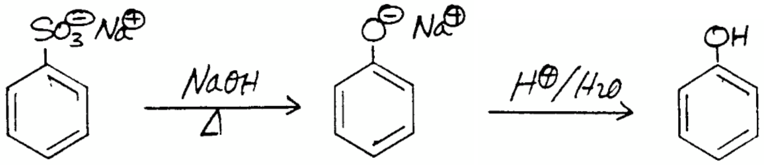
Synthesis of Aniline (Ph-NH_2). We learned how to place NO_2 groups on aromatic rings by electrophilic substitution. Although this is not possible for the NH_2 group, we can convert NO_2 groups on aromatic rings into NH_2 groups by reaction of the corresponding nitroarene with Zn metal in aqueous HCl as we show for the conversion of nitrobenzene (Ph-NO_2) into aniline (Ph-NH_2) in Figure 12.105.

Figure 12.105



Synthesis of Phenol (Ph-OH). There are several different ways to synthesize phenol from benzene. One way is to heat benzenesulfonic acid at high temperature with NaOH (a **fusion reaction**). The sodium salt of benzenesulfonic acid is converted into the sodium salt of phenol (Figure 12.106).

Figure 12.106



We subsequently obtain phenol by neutralization of the reaction product with acid. We prepare benzenesulfonic acid from benzene by electrophilic aromatic substitution as we described above.

Acidity of Arene OH Groups. Most alcohols (R-OH) are not acidic in aqueous solution, but arenes with OH groups are weak acids as we see from acidity constants (K_a values) in Table 12.2 where we compare data for phenol (Ph-OH) with H_2O and typical alcohols (RO-H) such as ethanol.

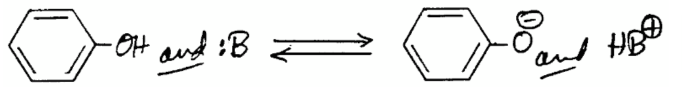
Table 12.2 Some Approximate Acid Dissociation Constants

Compound	**K_a**
H-Cl	10^{+7}
H-F	10^{-3}
Ph-OH	10^{-10}
H-OH	10^{-16}
R-OH	10^{-16}

Phenol is much less acidic than mineral acids (H-X), but it is much more acidic than typical alcohols (RO-H) or water.

We explain the higher acidity of Ph-OH compared to a typical R-OH by the presence of electron delocalization in the phenoxide anion (Ph-O:$^-$) formed when phenol donates a proton to a base (:B) (Figure 12.107), and the absence of such delocalization in the alkoxide ion (R-O:$^-$) formed when R-OH) loses a proton.

Figure 12.107



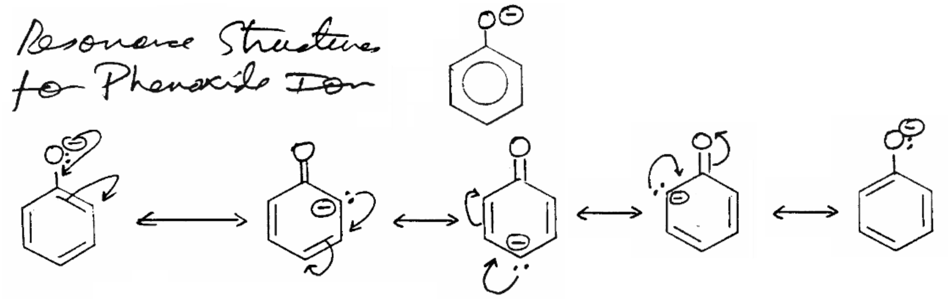
$HB^{\oplus}$ Stabilized by Resonance

Compare to

$R{-}OH$ and $:B \rightleftharpoons R{-}O^{\ominus}$ and $HB^{\oplus}$ No Resonance Stabilization

We illustrate this delocalization using resonance structures for the phenoxide ion (Figure 12.108).

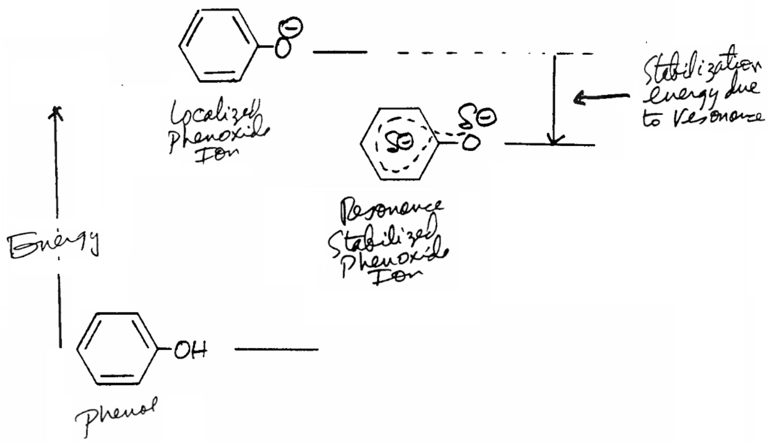
Figure 12.108



In contrast, we cannot draw resonance structures for the alkoxide ion from a typical alcohol such as CH_3CH_2OH because there is no π system in which to delocalize electron density.

Electron delocalization in Ph-O:$^-$ lowers its energy compared to that expected for a hypothetical localized phenoxide ion without resonance stabilization (Figure 12.109).

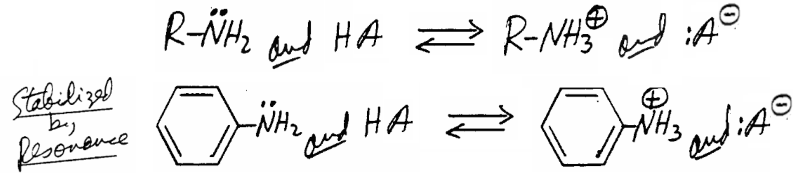
Figure 12.109



This lower energy for the delocalized phenoxide translates into a larger K_a value because the energy difference between PhO-H and PhO$^-$ is smaller with resonance stabilization of PhO:$^-$ than the energy difference between RO-H and RO:$^-$ where there is no resonance stabilization.

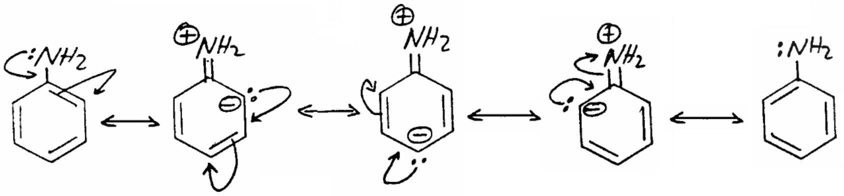
Basicity of Arene NH$_2$ Groups. Electron delocalization in aniline (Ph-NH_2) also makes it a weaker base than normal alkylamines (R-NH_2). Amines are basic because acids donate a proton to the unshared electron pair on their N atoms (Figure 12.110).

Figure 12.110



That unshared pair on N is delocalized into the aromatic ring of aniline as we show using resonance structures (Figure 12.111).

Figure 12.111



This electron delocalization provides extra stabilization for aniline that is lost when the N is protonated. Since the unshared pair on the N of alkylamines is already localized, protonation of alkylamines is not as energetically unfavorable.

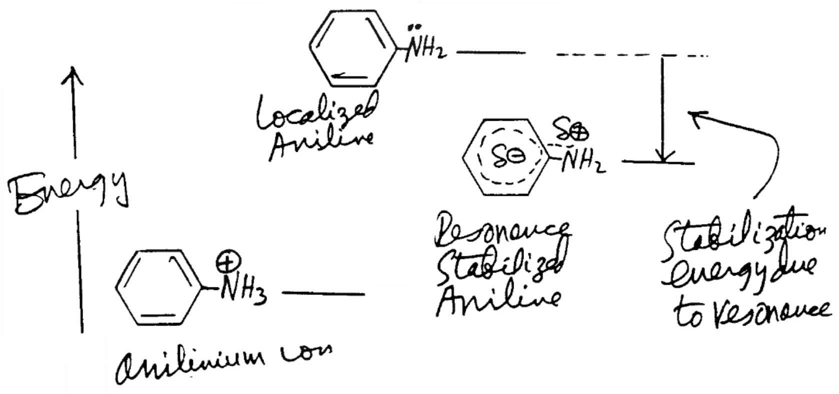
We can analyze this in another way. As we did in Chapter 3, lets view basicity of amines in terms of the acidity of their conjugate aminium ions. From this perspective we see from the data in Table 12.3 that the benzene ring <u>increases</u> the acidity of the anilinium ion (Ph-NH_3^+) compared to the acidity of a "normal" alkylaminium ion (R-NH_3^+).

Table 12.3. Acidity constants for Some Aminium Ions

Compound	**K_a**
Ph-NH_3^+	10^{-5}
R-NH_3^+	10^{-11}

We explain this by noting that electron delocalization of the unshared electron pair on the N of unprotonated aniline stabilizes aniline compared to what we would expect if that electron pair was localized (Figure 12.112).

Figure 12.112



This lower energy for resonance stabilized aniline translates into a larger K_a value for Ph-NH_3^+ because the energy difference between Ph-NH_3^+ and Ph-NH_2 is smaller than that between R-NH_3^+ and R-NH_2. The greater acidity of the anilinium ion (comapred to an alkylaminium ion) means a lesser basicity for aniline (compared to an alkylamine).

12.9 Spectrometry of Conjugated and Aromatic Molecules

The NMR and UV-Visible spectral data of conjugated and aromatic systems have particularly unique aspects that we describe in this section. The material in Chapter 5 provides a basis for the additional spectrometric information that we include here.

NMR Spectral Data (12.9A)

Aromatic compounds give NMR spectra that are particularly useful in identifying them. Some chemists have argued that ^{1}H NMR spectra should be used as the single most important criteria in judging whether a compound possesses the property that we call "aromaticity".

^{1}H Chemical Shifts. The most significant features in NMR spectra of molecules discussed in this chapter are the large ^{1}H chemical shift values for protons on *aromatic rings*. As we mentioned earlier (Section 12.5B), this is the result of a *ring current* induced in the molecule by the fully delocalized electron pair in the lowest energy molecular orbital of an aromatic molecule (Figure 12.113).

Figure 12.113

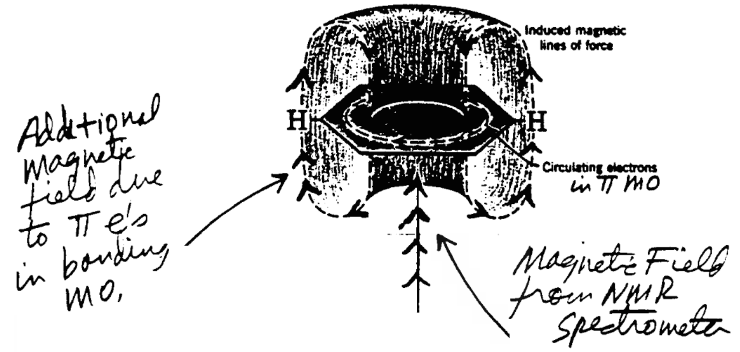
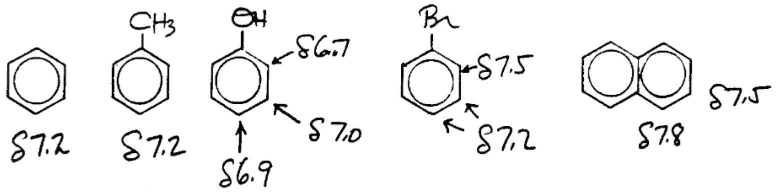


Figure 4.17. From "Spectrometric Identification of Organic Compounds" by Silverstein, Bassler, and Morrill, 5th Ed., Wiley, 1991

We give some examples of the resulting large δ values for various types of aromatic protons in Figure 12.114.

Figure 12.114



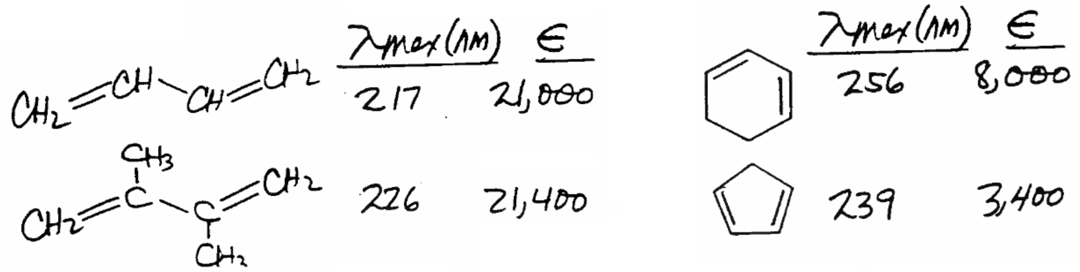
^{13}C Chemical Shifts. In contrast, this induced ring current does not affect the ^{13}C δ values of C's in an aromatic ring. The H's on an aromatic ring are located in a region of space where the magnetic lines of force induced in the molecule augment the applied magnetic field, but this is not the case for the C's in the ring (Figure 12.113). The ^{13}C chemical shift values are slightly greater than, but comparable to those of C's in multiple bonds that are not part of aromatic rings.

UV-Visible Spectral Data (12.9B)

All of the aromatic molecules, and many conjugated molecules that are not aromatic, absorb UV-Visible electromagnetic radiation and give UV-Visible spectra. We give examples of these spectra in this section and also briefly discuss why these molecules absorb UV-Visible radiation.

Conjugated Polyenes. Conjugated polyenes provide dramatic examples of the effects of conjugation on UV-Visible spectral data. An isolated C=C bond does not have UV absorption above 200 nm, but conjugated dienes absorb UV radiation between 215 and 260 nm depending on their structure as we show in Figure 12.115.

Figure 12.115



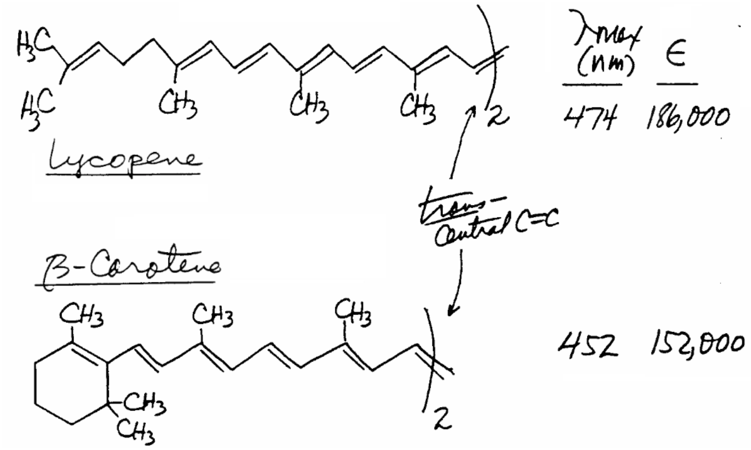
You can see that λ_{max} values steadily increase with an increase in the number of conjugated C=C bonds in compounds of the structure $CH_3(CH=CH)_nCH_3$ with *trans* C=C bonds for n = 3 to 8 (Table 12.4).

Table 12.4. UV-Vis Spectral Data for $CH_3(CH=CH)_nCH_3$ with *trans* Double Bonds

n	λ_{max} (nm)	ε
3	275	30,000
4	310	76,500
5	342	122,000
6	380	146,500
7	401	
8	411	

Moreover, the two polyenes in Figure 12.116 [next page] each have 11 conjugated C=C bonds and you can see that their λ_{max} values are even larger than those in Table 12.4 as you would expect from the trends in Table 12.4. The large values of ε (see Chapter 5) (Table 12.4 and Figures 12.115 and 12.116) show that these UV-Visible absorption bands are very intense.

Figure 12.116

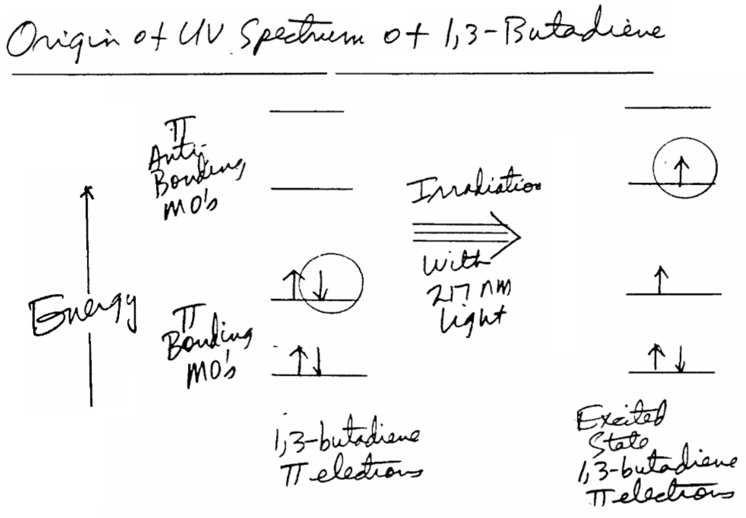


Electromagnetic radiation above 380 nm is in the visible region of the electromagnetic spectrum, so as a result the polyenes in Table 12.4 and Figure 12.116 with 7 or more conjugated C=C are colored compounds. β-Carotene, found in carrots and other vegetables, is orange, while lycopene is a red compound found in tomatos.

Polyene λ_{max} Values. Chemists determined many years ago that quantitative relationships exist between the number of conjugated double bonds, their geometry and substitution, and the observed λ_{max} values for various conjugated polyenes. You can find these relationships in a variety of texts dealing with organic spectrometry. They have led to a series of rules that permit precise prediction of λ_{max} values for conjugated polyene systems.

The Electron Excitation Process. We briefly mentioned in Chapter 5 that UV-Visible absorption spectra result from excitation of π electrons. We illustrate this for 1,3-butadiene using the energy level diagram that shows its π MO's and four π electrons (Figure 12.117).

Figure 12.117



Its UV absorption band that we observe at 217 nm corresponds to the excitation of one π electron from the highest occupied bonding π MO into the lowest energy antibonding π MO (Figure 12.117). The energy required for this excitation corresponds to that of the electromagnetic radiation at $\lambda = 217$ nm. (Remember from Chapter 5 that energy and wavelength of electromagnetic radiation are related to each other by the equation $E = hc/\lambda$).

UV-Visible absorption bands for all conjugated polyenes are due to this excitation of one π electron in the highest occupied bonding π MO into the lowest unoccupied π antibonding MO. We refer to these processes as $\pi \rightarrow \pi^*$ excitations. Since E is inversely proportional to λ, the λ value of this excitation <u>increases</u>, as the number of conjugated C=C bonds increases, because the energy gap between the highest occupied π MO and the lowest unoccupied π MO to <u>decreases</u>.

Arenes. The UV-Visible spectra of benzene, substituted benzenes, and of other benzenoid aromatic systems, are more complex than those of polyenes (Table 12.5).

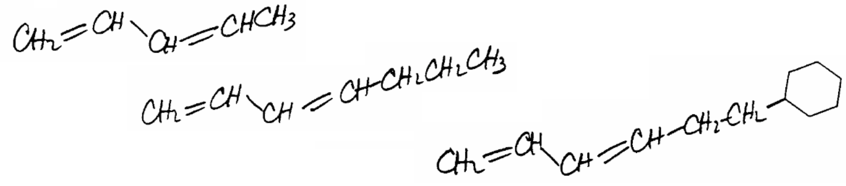
Table 12.5. UV-Visible Spectral Data for Benzenoid Aromatic Systems.

Compound	**λ_{max} (nm)**	**ε**
Benzene	204	7,900
	256	200
Chlorobenzene	210	7,600
	265	240
Phenol	211	6,200
	270	1,450
Aniline	230	8,600
	280	1,430
Naphthalene	221	133,000
	286	9,300
	312	289
Anthracene	221	14,500
	256	180,000
	375	9,000

These absorption bands are primarily due to $\pi \rightarrow \pi^*$ excitations.

The Use of UV-Visible Data. Although different types of conjugated and aromatic systems have different UV-Visible spectra, they are not particularly useful for exact structural identification. For example, we expect the different conjugated dienes we show in Figure 12.118 [next page] to all have essentially the same UV spectrum.

Figure 12.118



As a result, UV-Visible spectra are generally used either to help confirm the structure of a compound already identified by a spectrometric method such as NMR, or as an aid in determining details about the extent of the π system.

A particularly important use of UV-Visible spectral data for a compound is to determine its concentration, or its change in concentration with time. The intensity of most UV-Visible absorption bands is linearly related to the concentration of the species giving rise to that absorption band as we described in Chapter 5. This featrure of UV-Visible absorption bands is extensively used in clinical laboratory instruments and methods for biomedical testing.

Infrared Spectrometry (12.9C)

There are a series of IR absorption bands that specifically characterize benzenoid aromatic systems. The aromatic ring C-H stretching bands occur between 3100 and 3000 cm^{-1} (A), skeletal vibrations associated with the aromatic rings give bands between 1600 and 1400 cm^{-1} (B), and bands due to C-H bending occur between 1300 and 1000 cm^{-1} and 900 and 675 cm^{-1} (C).

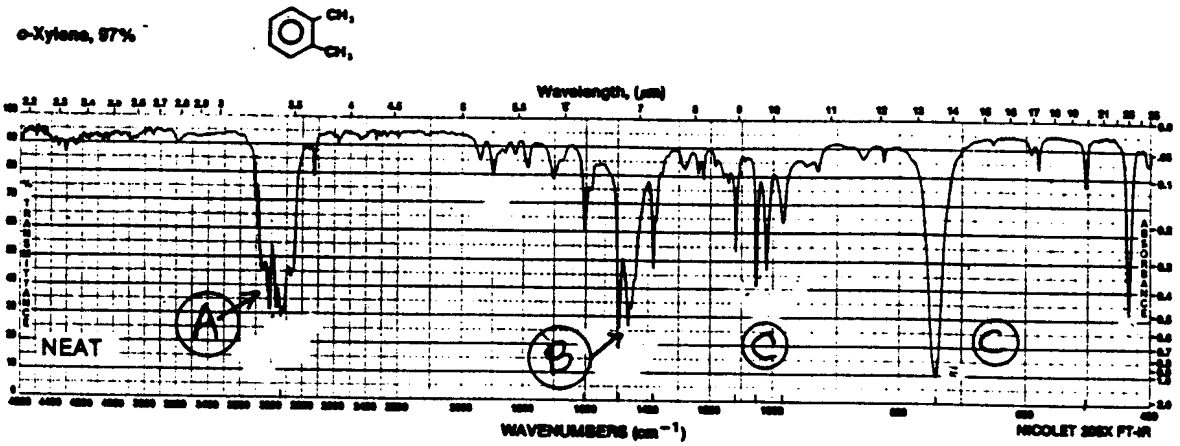
We show these types of bands in the representative IR spectra reproduced in Figure 12.119 [next page]. If you compare these spectra with other IR spectra in Chapter 5, you will see that these bands are not typically present in nonaromatic systems.

Because of their complexity, IR spectra generally cannot be used alone to assign a chemical structure to an unknown compound as we described in Chapter 5. But IR spectra can be used to unambiguously confirm a structure when an authentic sample of an unknown compound is available since no two compounds have exactly the same IR spectra.

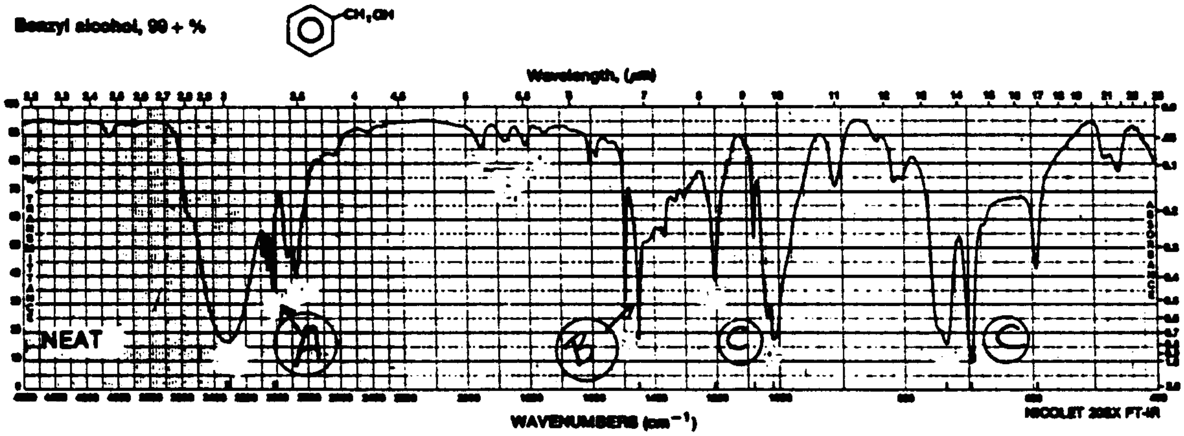
Figure 12.119 [next page]

Figure 12.119

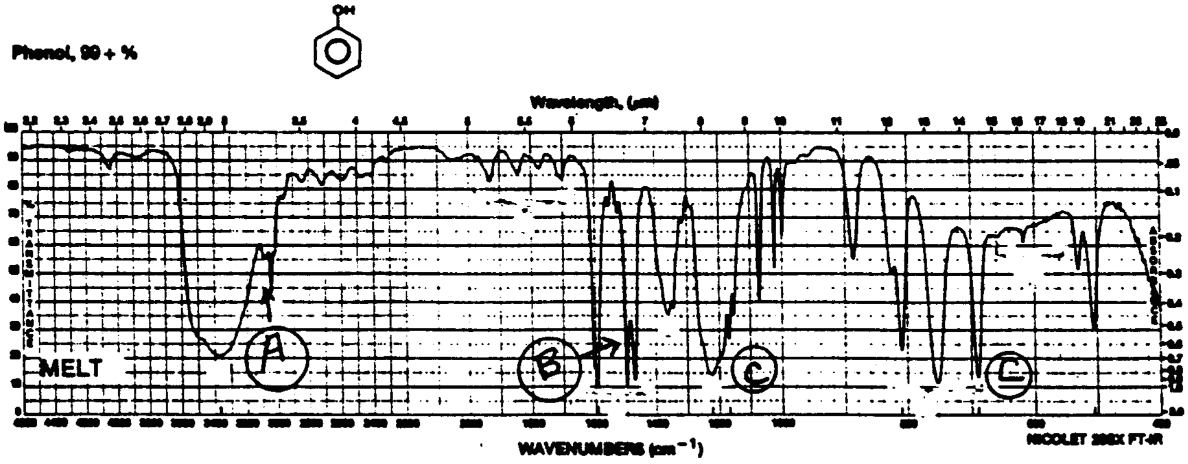
o-Xylene, 97%



Benzyl alcohol, 99+%



Phenol, 99+%

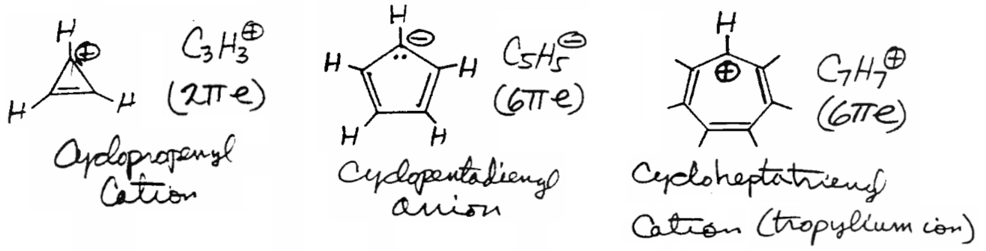


These are Figs 3.13, 3.14 and 3.16 in Silverstein + Bassler

Supplemental Appendix to Aromatic Ions (12.7E)

Aromatic systems can also be ionic and we show some examples in Figure 12.073.

Figure 12.073



Note that the size of the ring does not need to correspond to the number of π electrons.

Cycloheptatrienyl Cation. The $C_7H_7^+$ cation with 6 π electrons is so stable that 7-bromocycloheptatriene (Figure 12.074a) is actually a salt with the formula $C_7H_7^+$ Br^- commonly named **tropylium bromide**.

Figure 12.074a (*To be added*)

This positively charged ring is planar and each C is sp^2 hybridized. The seven 2p AO's overlap with each other to generate seven π MO's with the lowest energy bonding MO delocalized over all 7 C's.

Cyclopentadienyl Anion. Although $C_5H_5^-$ also has 6 π electrons, it only has 5 C's. It is planar and a demonstration of its high stability is the extraordinarily high acidity of its precursor hydrocarbon 1,3-cyclopentadiene (Figure 12.074b).

Figure 12.074b (*To be added*)

Its $pK_a = 16$ is comparable to those of H_2O and simple alcohols (R-OH). This ion is isoelectronic with pyrrole (Figure 12.067) and the unshared electron that we show above is part of the 6π electron system just as is the unshared electron pair on the N atom in pyrrole.

Cyclopropenyl Cation. While the preceding aromatic ions have 6π electrons like benzene, the cyclopropenyl cation ($C_3H_3^+$) has only 2π electrons corresponding to 4n + 2 when n = 0 (Figure 12.074c).

Figure 12.074c (*To be added*)

This ion has been made by reacting 3-chlorocyclopropene with $SbCl_5$.

Cyclooctadienyl Dianion. An example of a 10 π electron system (4n + 2 = 10 when n = 2) is the cyclooctatetraenyl dianion ($C_8H_8^{-2}$) that forms when metallic sodium reacts with cyclooctatetraene (Figure 12.074d).

Figure 12.074d (*To be added*)