Nuggets of Knowledge for Chapter 17 – Dienes and Aromaticity Chem 2320

I. Isolated, cumulated, and conjugated dienes

- A diene is any compound with two or C=C's is a diene. Compounds containing more than two C=C's can be understood by understanding dienes.
- A diene may be cumulated, conjugated, or isolated.

Isolated dienes

• Isolated dienes have two (or more) C=C's that are separated by at least on sp³ carbon. They undergo the same reactions that alkenes do.

Cumulated dienes

- Cumulated dienes have two C=C's right next to each other, sharing a carbon.
- The center carbon has sp hybridization and linear geometry, while the other two have sp² hybridization and trigonal planar geometry.
- The smallest cumulated diene has a condensed structure of H₂C=C=CH₂, and is called allene. More substituted cumulated dienes are sometimes referred to as allenes.
- The substituents on a cumulated diene are oriented at 90° to each other. One set is in the plane of the page, the other is forward and back.
- A cumulated diene may be chiral if the substituents on both ends are different. If this is so, then there will be no plane of symmetry, and both end carbons will be stereocenters. Two enantiomers will exist.

Conjugated dienes

- Conjugated dienes have two or more C=C's connected by a single bond.
- Conjugated dienes have the lowest energy when all of the pi bonds are in the same plane. If the diene is free to rotate, it will have two conformations that fulfill this requirement; these are called the s-cis and s-trans conformations.
 - S-cis and s-trans conformation are not the same as cis and trans stereoisomers. Conformations can change by a simple rotation of a bond, while stereoisomers are different compounds, and can only be changed by a chemical reaction.

• Dienes may be unable to achieve both conformations because of being in a ring, or because of steric hindrance of the substituents.

Energies of dienes

- The relative energies of the different kinds of dienes has been determined using heats of hydrogenation.
- Cumulated dienes are highest in energy; conjugated dienes are lowest in energy.

II. Reactions Involving Allylic Intermediates

Molecular orbitals of compounds with multiple p orbitals

- When two p orbitals are combined in a C=C, two pi orbitals are formed one is bonding, and the other antibonding. Normally, the electrons from the p orbitals both go into the bonding orbital, while the antibonding orbital is empty.
 - The bonding orbital has electron density between the atoms, holding them together, while the antibonding orbital has electron density outside the two atoms.
 - The bonding orbital has lower energy than the antibonding orbital, which makes it more stable for the atoms to be bonded.
- When more than 2 p orbitals are on neighboring carbons, all of the p orbitals combine into a set of pi orbitals.
 - For example, in 1,3-butadiene, all four p orbitals combine to form four pi orbitals. Two have lower energy than the original p orbitals, and are bonding; two have higher energy than the original p orbitals, and are antibonding. The four electrons go into the two bonding orbitals.
 - The first pi orbital has no nodes, with electron density across all 4 carbons. The second pi orbital has one node, with electron density between C1 and C2, and C3 and C4. The third pi orbital has two nodes, and the fourth has three nodes.
 - The lowest pi orbital is lower than an ordinary pi orbital, which explains why conjugated dienes are lower in energy than isolated dienes.
 - The distance between the middle carbons of 1,3-butadiene is consistent with this molecular orbital picture. The distance is 148 pm, which is shorter than a single bond (153 pm) but longer than a double bond (134 pm).

Allylic carbocations, radicals, and anions

- An allyl group is three carbons, the second and third having a C=C.
 - Allyl is used in common names, for example allyl alcohol, allyl chloride, and allylbenzene.
 - Allyl carbocations have three carbon atoms in a row, with a + on the first carbon, and a C=C on the second and third carbons. Allyl radicals and allyl carbanions are similar.
 - These structures are particularly stable because they have a resonance structure.
 - The resonance structures may be equal contributors to the overall structure, or one may be a greater resonance contributor because it is more stable (C+ on a 3° vs. 2° carbon, for example).
- If a compound has an allyl carbocation with substituents on it, it is called an allylic carbocation; likewise with allylic radicals and allylic anions.
- Allyl cations (with no substituents) are about as stable as 2° carbocations; allylic cations with one substituent are about as stable as 3° carbocations; allylic cations with more than one substituent are more stable than 3° carbocations.
- Allyl radicals (with no substituents) are more stable than 3° radicals; allylic cations with any substituents are even more stable.
- The molecular orbitals of an allylic pi system are made from the 3 p orbitals of the carbon atoms. They form 3 pi orbitals, one bonding, one nonbonding, and one antibonding.
 - The bonding orbital has 0 nodes, the nonbonding orbital has 1 node, and the antibonding orbital has 2 nodes.
 - The second, nonbonding orbital has electron density on only the end carbons.
 - Although all 3 allylic intermediates have the same orbitals, they don't have the same number of electrons, so they aren't all equally filled.
 - In all 3 allylic intermediates, the lowest, bonding orbital is filled, with 2 electrons.
 - In the allylic cation, the nonbonding orbital is empty; in the allylic radical, the nonbonding orbital has one electron; in the allylic anion, the nonbonding orbital has two electrons.

 Having the positive charge, lone electron, or electron pair spread over the two end carbons is consistent in both the molecular orbital model and resonance structures.

Reactions involving allylic carbocations as intermediates

- We have studied 5 reactions which involve carbocations as intermediates.
 - Alkyl halides can form carbocations when in the presence of a weak nucleophile.
 - They dissociate, and then the weak nucleophile attacks and is deprotonated, forming an alcohol (if the nucleophile is water) or an ether (if the nucleophile is an alcohol).
 - Alcohols can form carbocations when reacted with strong acid.
 - The OH is protonated, then the compound dissociates to form water and a carbocation. If sulfuric acid is used, the water removes a H to form an alkene. If HX is used, the halide attacks to form an alkyl halide.
 - Alkenes can form carbocations when reacted with strong acid.
 - When the pi bond attacks the acid, an H is added, and a carbocation is formed. If sulfuric acid and water are used, an alcohol is formed. If HX is used, an alkyl halide is formed.
- Allylic halides, allylic alcohols, and dienes can form two products when they undergo reactions with carbocation intermediates. The positive charge is shared between two different carbons, so the reaction can continue at either site.
 - If the two resonance structures of the carbocation are symmetrical, then only one product will result.
 - Allylic carbocations do not rearrange. Rearrangements take place in order to form a more stable carbocation, and resonance stabilized secondary carbocations are more stable than tertiary carbocations with no resonance.
 - When forming a diene from an allylic alcohol, the H removed by water is always on the side away from the C=C, so that a conjugated diene is formed instead of a cumulated diene.
 - When a diene reacts with acid, the carbocation always forms next to the other C=C, so that the carbocation will be stabilized by resonance.
- When a diene reacts with acid and water or with HX, the two products are labeled 1,2 and 1,4 to show the relationship between the H and OH or the H and X that are added.

- Either C=C may react with the acid. If the diene is not symmetrical, reaction at the two different C=C's will result in two different carbocations which are constitutional isomers to each other, and 4 products will result.
- At different temperatures, the addition of HX to a 1,3-butadiene will give different ratios of products. At very cold temperatures (-80°C) the 1,2 product will be favored, while at warmer temperatures (40°C) the 1,4 product will be favored.
 - The resonance structure that leads to the formation of the 1,2 product is a greater resonance contributor; in other words, the molecular orbital has more density on this carbon. This means that the transition state for the formation of the 1,2 product is lower, so this product forms faster.
 - However, the 1,4 product has a more substituted C=C, so the 1,4 product is more stable than the 1,2 product.
 - At low temperatures, the 1,2 product is formed first, and very few molecules have enough energy to undergo the reverse reaction, so an equilibrium is not established, and the 1,2 product is favored. This is called kinetic control.
 - At higher temperatures, the 1,2 product is still formed first, but many molecules have enough energy to undergo the reverse reaction. The 1,2 product has a lower activation energy going backwards, so as the equilibrium is established, the more stable 1,4 product is favored. This is called thermodynamic control.

Reactions involving allylic radicals as intermediates

- When bromine reacts with an alkene, an allylic halide is formed.
 - The initiation step is the homolytic cleavage of bromine by light, forming two bromine radicals.
 - The bromine radical takes a hydrogen atom from the allylic position of the alkene, forming an allylic radical and HBr.
 - The allylic radical reacts with another molecule of bromine, forming the product and another bromine radical, which continues the chain reaction.
- Unlike reactions of alkanes with bromine, multiple products are avoided because the allylic radical is much more stable than any other radical, so only allylic hydrogens are removed.
- If the two resonance structures of the allylic radical are not symmetrical, two products may be formed.

- If more than one allylic hydrogen is available on different C's, two allylic radicals which are constitutional isomers will be formed, giving four products.
- Bromine can also react with an alkene by adding to the C=C. This reaction competes with the free radical substitution reaction.
 - The addition reaction is favored by a high concentration of bromine, and cold, dark reaction conditions. The substitution reaction is favored by a low concentration of bromine and heat or light.
 - NBS (N-bromosuccinimide) is used instead of bromine to favor the substitution product because it reacts with the HBr created by the reaction to produce low concentrations of bromine.

<u>S_N2 reactions of allylic halides</u>

- Allylic halides undergo SN2 reactions much faster than alkyl halides; for example, allyl bromide reacts 40 times faster than propyl bromide with strong nucleophiles.
- This reaction occurs in one step, so no carbocation is formed. However, the transition state is stabilized by overlap with the pi bond, lowering its energy and making the reaction much faster.
- The fact that allylic halides are much better electrophiles makes it possible for them to react with Grignards and organolithium reagents to form new alkenes; regular alkyl halides do not react with organometallic reagents.

III. The Diels-Alder Reaction

- The Diels-Alder reaction requires to starting materials: 1) a diene and 2) an alkene or alkyne. The alkene or alkyne is called a dienophile.
 - No other reagents are needed, but the reaction must be heated in order to reach the activation energy.
- The product of this reaction is always a 6-membered ring with one C=C. If an alkyne is used as the dienophile, then two C=C's will be present at opposite sides of the ring.
- The reaction takes place in one step. The electrons flow in a circular pattern, making this an electrocyclic reaction. The arrows may be drawn in a clockwise or counterclockwise direction.
- The diene must be in an s-cis conformation in order for the reaction to proceed. An strans compound must rotate before it can react.

- If an s-trans diene is unable to rotate because it is in a ring or because of steric hindrance, then no reaction will occur.
- If an s-cis diene is unable to rotate because it is in a ring, the reaction will be faster than usual, because the diene is always in the correct conformation.
- In order for the reaction to proceed at a reasonable rate, the dienophile usually needs to have electron-withdrawing substituents such as nitriles, esters, ketones, aldehydes, anhydrides, or CF₃ groups. This makes the dienophile behave as the electrophile.
- Dienes are already electron rich, and behave as the nucleophile. However, substituents which are electron-donating, such as alkyl groups or alkoxy groups, make the reaction faster.
- More than one constitutional isomer may be formed if both the diene and the dienophile are unsymmetrical.
 - Constitutional isomers in which there is a 1,2 or 1,4 relationship between electrondonating and electron-withdrawing substituents will be strongly favored, while 1,3 isomers will be disfavored.
- Bicyclic rings may be formed by the Diels-Alder reaction.
 - If the dienophile is cyclic, or if the diene is cyclic but the C=C's are not inside the ring, a fused ring may be formed.
 - If the diene is cyclic, and the C=C's are inside the ring, a bridged ring will be formed.

Stereochemistry of the Diels-Alder reaction

- 4 atoms are involved in the Diels-Alder reaction, and there is the potential for 4 stereoisomers to be formed.
 - If the substituents on the dienophile are trans to each other, they will be trans in the product; if they are cis in the dienophile, they will be cis in the product.
 - If the two substituents on the end of the diene are both "out" or both "in," they will be cis in the product. If one is "out" and one is "in," they will be trans in the product.
 - Another way to look at it is if both C=C's are trans or both are cis, they will be cis in the product, but if one C=C is cis and the other is trans, they will be trans in the product.
 - If any four of these carbons do not have substituents, or the molecule contains a plane of symmetry, fewer than four stereoisomers may form.

- The diastereomers in which the substituents on the diene are in the opposite direction as in the dienophile will usually be favored (especially if there are pi bonds in the substituents on the dienophile). This is called the endo rule.
- When two enantiomers are formed, neither is favored (unless a chiral starting material is used).
- Substituents on the double bond formed by the reaction, or substituents on an alkyne as the dienophile, will be on trigonal planar carbons, and will not be stereocenters.

Using the Diels-Alder reaction for synthesis

- In order for a compound to be synthesized using the Diels-Alder reaction, it must have a cyclohexene ring as part of its structure. It must also have some kind of electron-withdrawing group on the carbon(s) where the dienophile was.
- When analyzing the structure to determine the starting materials, first look for the carbons which came from the diene and the dienophile.
 - The C=C was originally the middle of the diene. If two C=C's are present, then the dienophile was an alkyne, and it should be chosen as the one with electron-withdrawing groups on it.
- To reverse the reaction, the electrons flow in a cyclic direction, similar to the resonance structures of a benzene ring.