Objectives for Chapter 17 – Dienes and Aromaticity

I. Isolated, cumulated, and conjugated dienes

1. Explain the difference between cumulated, isolated, and conjugated dienes, and be able to draw or recognize examples of these compounds.

2. Give the relative energy of the three types of dienes.

Cumulated dienes

3. Explain the geometry and hybridization of cumulated dienes, as well as the orientation of substituents to each other.

4. Explain why some cumulated dienes are chiral, and be able to draw or recognize chiral and achiral cumulated dienes.

Conjugated dienes

5. Explain why conjugated dienes have two preferred conformations (s-cis and s-trans), and how this is different from cis and trans stereoisomers of alkenes.h

II. Reactions Involving Allylic Intermediates

Molecular orbitals of compounds with multiple p orbitals

1. Explain how the p orbitals from the four carbons of 1,3-butadiene come together for form four pi orbitals, including which are bonding and which are antibonding, how their energy compares, which are occupied, and what they look like.

2. Explain how the molecular orbital picture explains the lower energy of cumulated dienes, and the unusual distance between the middle carbons of 1,3-butadiene.

Allylic carbocations, radicals, and anions

3. Explain how the term “allyl” is used in common names and names of reactive intermediates; draw or recognize allylic carbocations, radicals, or anions.

4. Draw resonance structures for allylic carbocations, radicals, and anions, and determine which is a greater resonance contributor (if any).

5. Rank carbocations and radicals according to their stability.

6. Describe the molecular orbitals of an allylic bonding system, including the number of orbitals, bonding, nonbonding, and antibonding orbitals, number of nodes, and number of electrons occupying each orbital depending on the type of intermediate.

7. Explain how the resonance structures of allylic intermediates are consistent with the molecular

orbital picture.

Reactions involving allylic carbocations as intermediates

1. Identify five reactions which give carbocation intermediates and draw their mechanisms.

2. Draw mechanisms and predict the number and structures of products for reactions involving allylic carbocations as intermediates.

3. Explain why a different ratio of products is formed in the addition of HX to a diene at low temperature vs. higher temperatures.

Reactions using allylic radical as intermediates

1. Draw the mechanism for an alkene reacting with bromine to form an allylic bromide.

2. Predict the number and structure of allylic bromides formed by this reaction.

3. Explain why NBS is often used instead of bromine in this reaction.

S_N2 reactions of allylic halides

1. Explain why allylic halides will react as electrophiles in S_N2 reactions much faster than regular alkyl halides, even though there is no allylic carbocation as an intermediate.

2. Predict products of allylic halides with organometallic reagents, and use this reaction to synthesize alkenes.

III. The Diels-Alder Reaction

1. Explain what starting materials and reagents are needed for a Diels-Alder reaction, including what a dienophile is.

2. Draw the mechanism for a Diels-Alder reaction.

3. Explain what conformation the diene must achieve in order to participate in a Diels-Alder reaction, and what consequences this will have for cyclic and sterically hindered dienes.

4. Explain what kind of substituents are commonly used on dienophiles, and what kind are sometimes used on dienes, and how this affects the mechanism of the reaction.

5. Explain what kinds of starting materials can form two constitutional isomers as products of a Diels-Alder reaction, and how to determine which will be the major product.

6. Explain what kinds of starting materials will give fused or bridged products in a Diels-Alder reaction.

7. Give the correct products of a Diels-Alder reaction when given the starting materials.

Stereochemistry of the Diels-Alder reaction

8. Explain what carbons can become new stereocenters in the Diels-Alder reaction, and what happens to the substitutents on the diene and the dienophile.

9. Give all isomers that will be formed in a Diels-Alder reaction with a given set of starting materials, and identify constitutional isomers, enantiomers, and diastereomers.

Using the Diels-Alder reaction for synthesis

10. Explain what structure must be present in order to use the Diels-Alder reaction for synthesis, how to locate the atoms that made up the diene and dienophile in the product, and how the electrons must flow to reverse the reaction.

11. Give the starting materials needed to make a given set of products in the Diels-Alder reaction.