

STUDY GUIDE FOR CHAPTER 10

- Allylic Systems – it is a unique formation of three C-atoms, two double bonded. The third carbon could potentially (and in reality) bear a positive charge (allylic carbocation), odd electron (allylic radical) or lone pair (allylic carbanion).
 - Allylic carbocations – stabilized via resonance. Enhanced S_N1 reactivity. Two products possible if the carbocation is not symmetrical.
 - Allylic radicals – stabilized via resonance. Allylic position is selectively substituted in radical halogenation reactions – allylic halogenation. Bromination is usually done with a special reagent – NBS.
 - Enhanced S_N2 reactivity of allylic systems – in S_N2 reactions the TS is composed of both the substrate and the nucleophile. The carbon bearing the leaving group is temporarily re-hybridized (sp^2) and in the case of allylic substrate there is very efficient overlap within the conjugated system and dispersal of the excess electron density, which leads to stabilization of the TS and higher reaction rate.
- Dienes.
 - Classification.
 - Dienes, in which the double bonds are separated by two or more single bonds, are known as dienes with *isolated double bonds*.
 - Dienes, in which the double bonds are separated by one single bond, are known as conjugated dienes (and the corresponding double bonds as conjugated double bonds).
 - Dienes, in which the double bonds are adjacent, are known as cumulenes (or allenes), and the corresponding double bonds are termed cumulated double bonds.
 - Stability of Dienes. Heats of hydrogenation.
 - Heats of hydrogenation (See Chapter 7, Section 7-7) clearly demonstrate that the stability of alkenes varies in a systematic order, increasing with increased degree of substitution of the double bond.
 - For dienes with isolated double bonds, the effect is strictly additive, i.e. sum of the effects of the corresponding isolated double bonds.
 - For conjugated dienes, the heats of hydrogenation are smaller (by some 3 – 4 kcal/mol) than anticipated by the additivity rule.
 - For cumulated dienes, the heats of formation are considerably larger (by more than 12 kcal/mol), compared to the expected values, based on the additivity rule.
- Bonding in conjugated dienes.
 - In 1,3-butadiene the four C atoms are all sp^2 hybridized and have their p -orbitals aligned in such a fashion that an overlap of all p -orbitals is possible, leading to the formation of a conjugated π -system.
 - Due to such overlap, one would expect a partial double-bond character for the C2 – C3 bond, which is evidenced by the existence of distinct (albeit interconvertible) forms – the *s-cis* (the two double bonds eclipsed) and *s-trans* (the two double bonds *anti*). They are separated by a barrier of about 3.9 kcal/mol, with a TS that has the two double bonds perpendicular.
- Bonding in allenes – the two π -bonds are perpendicular and do not interact.
- Reactions of Conjugated Dienes.
 - Addition of HX.
 - 1,2- and 1,4-addition products – polar addition reactions to conjugated dienes, such as addition of HBr, result in the formation of a mixture of both 1,2- and 1,4-addition product. The reason is the intermediate formation of an allyl cation, so the subsequent attack of the nucleophile can occur at either terminus of the conjugated allyl system.

- b. Kinetic versus Thermodynamic Control – it turns out that the composition of the mixture depends on the temperature at which the reaction is conducted. At lower temperature the 1,2-product predominates, while at higher temperatures it is the 1,4-product. Reason: The 1,2-product results from an attack of the nucleophile on the secondary C-atom, which has a greater positive charge. Thus, this reaction would be expected to occur with lower activation energy. At low T this product will predominate. It is the product of *kinetic control*. The 1,4-product is, however, more stable, since it has a more substituted double bond. At high T, as the process becomes entirely reversible, the outcome will be determined by the equilibrium, which is in favor of the more substituted, thermodynamically more stable alkene, namely the 1,4-product. It will be the predominant product at high T. It is the product of *thermodynamic control*.
- B. Addition of X₂ – also forms 1,2- and 1,4-addition products. The 1,4-addition product predominates and it is mostly *E*.
6. The *Diels-Alder* Reaction.
- The Diels-Alder reaction is the most typical case of the so-called *[4+2] cycloaddition reactions*, since it consists of the interaction of a conjugated *diene* (4π electrons) and an alkene or alkyne (2π electrons). The system with 2π electrons is known as *dienophile*. It is also known as conjugate addition.
 - The diene must be an electron-rich system. Even the most ordinary dienes, such as 1,3-butadiene fulfill this requirement. But additional groups, which enhance electron density via resonance interaction, such as alkoxy groups, can further promote reactivity. The dienophile is supposed to be electron-poor, and ordinary alkenes or alkynes, such as ethylene or acetylene are not good dienophiles. Reactivity is enhanced considerably upon introduction of electron-withdrawing groups, such as carbonyl or nitrile.
 - The mechanism of the Diels-Alder reaction involves the overlap of orbitals of the diene and dienophile and the reaction proceeds in one step, without any distinct intermediates. So it is a concerted process.
 - This overlap is possible only when the two ends of the diene system are close together, in the so-called **s-cis conformation**. The latter is somewhat less stable than the *s-trans* conformation, but the energy difference is not great.
 - If a diene cannot adopt the s-cis conformation, it cannot undergo a Diels-Alder reaction.
 - If a diene is fixed in an s-cis conformation, its reactivity in Diels-Alder reactions is enhanced.
 - The Diels-Alder reaction is highly stereospecific – the addition of diene to dienophile is ALWAYS *syn*. The geometry at both the diene and dienophile is maintained in the product.