

## STUDY GUIDE FOR CHAPTER 5

### 1. Structure of Alkenes.

- A.  $\sigma$ - and  $\pi$ -bonds – the hybridization of carbon, bond strengths, reasons. Electronegativity of  $sp^2$ -carbon vs.  $sp^3$ -carbon. The double bond, because of the weakness of the  $\pi$ -bond, is quite reactive. It is the alkenes' functional group.

### 2. Nomenclature – the central theme is the double bond.

- A. The longest chain CONTAINING the double bond is selected. The numbering begins from the end closest to the double bond. If the latter is equidistant from the termini, then numbering is done so that branches get lower numbers.
- B. The double bond takes preference over branches or halogens, when numbering is concerned.
- C. The double bond has lower rank in comparison to the hydroxyl group.
- D. In cycloalkenes, it is assumed that the double bond starts at the 1-position.
- E. Some simple groups containing double bonds are often considered as substituents: methylene, vinyl, allyl.
- F. Common names: ethylene, propylene, styrene.

### 3. Nomenclature of geometrical isomers:

- A. *Cis-trans nomenclature* – the double bond is rigid and defines an imaginary plane. If the two substituents are on the same side of the double bond – *cis-isomer*. If they are on opposite sides – *trans-isomer*. Both for alkenes and cycloalkenes.
- B. *E – Z nomenclature*: In certain cases (such as three or four different groups around the double bond) the *cis-trans* notation loses its meaning. A more comprehensive approach is the *E – Z* nomenclature. At each double bonded carbon one has to determine the priorities of the two groups, and this is done according to the following rules:
- 1) First compare the atoms immediately bonded to the chiral center. The atom with highest atomic weight is highest in priority and therefore # 1, the atom with lowest atomic weight is #4.
  - 2) If two or more atoms of the immediate environment are identical, compare the next set of atoms along the chains, applying the criteria from (a).
- REMEMBER:** One atom of higher priority is more important than any number of lower priority atoms.
- 3) Treat double- and triple-bonded atoms as an equivalent number of single-bonded atoms, i.e. imagine that the  $\pi$ -bonds are broken and the atoms at both ends of the bond are duplicated (if it is a double bond) or triplicated (if it is a triple bond).

If the two highest in priority groups (one at each double bond C) are on the same side of the double bond – Z-isomer. If they are on opposite sides – E-isomer.

### 4. Stability of alkenes – this evaluation is done based on the same principles, as was earlier with cycloalkanes. Namely, one has to convert the compared materials to the same end product and compare the energy changes. Combustion is one way to go, but it is accompanied with a huge energy change, so that small energy differences (as it is with the present case) might not be easily detected. Another method, specific for this case, is hydrogenation. Alkenes, which are positional isomers (i.e. differ by the position of the double bond), are converted to alkanes through hydrogenation, and it is invariably an exothermic process. In this process, all positional isomers are of course converted to the same alkane, allowing for stability comparisons, based on the resultant energy differences from the heats of hydrogenation. Several important conclusions:

- A. If one compares any two positional isomers, one finds that invariably a monosubstituted alkene is less stable than disubstituted, or disubstituted is less stable than trisubstituted, etc.

- B. If one compares two structural isomers, which have the same pattern of substitution of the double bond, but slight variations in the side chain(s), one finds that there is no detectable difference in the corresponding heats of hydrogenation. This allows to further compare monosubstituted with disubstituted with trisubstituted, etc. in general. The conclusion: More highly substituted double bonds are more stable. Reason: Both *electronic effect (inductive effect + hyperconjugation)* and *steric repulsion*.
- C. If one compares cis- and trans-isomers, one finds that the *cis*- is less stable than the *trans*-. Reason: In *trans* the substituents are farther apart, so less steric interactions.
5. Stability of cycloalkenes.
- A. The double bond implies angles close to  $120^\circ$ , which is even more than the tetrahedral angle of  $109.5^\circ$ . Therefore, small cycles should experience even greater ring strain, which is indeed so.
- B. *Cis*- and *trans*-isomers – for small rings the realization of a *trans* isomer requires an incredible twist of the system, leading to the fact that the first, marginally stable, cycloalkene is cycloheptene. For cyclodecene and higher the *trans* form becomes almost as stable as the *cis*, because of a much enhanced flexibility of the system.
6. Physical Properties of Alkenes.
- A. Boiling points – similar trends as with alkanes.
- B. Densities.
- C. Polarity – the double bond creates slight dipoles, because the  $sp^2$ -carbons are more electronegative than the  $sp^3$ -carbons. Depending on symmetry, some molecules have small dipole moments, which raises slightly their bp.
7. Synthesis of Alkenes via Elimination Reactions.
- A. *Dehydration* of Alcohols – it is a reaction of elimination of water from alcohols. The mechanism involves (much like  $S_N$ ) preliminary protonation by acid, to give the protonated alcohol (alkyloxonium ion). In the case of tertiary (and secondary) alcohols, the resultant alkyloxonium ion undergoes *heterolytic* cleavage (in the rate-determining step) to produce the corresponding carbocation. NOTICE: Up to this point, the mechanism is identical to  $S_N1$ . The difference is the lack of suitable nucleophile. In such conditions the carbocation undergoes an acid-base reaction with water, leading to a proton abstraction and generation of an alkene. The rate-determining step is unimolecular, thus the overall mechanism is known as  $E1$ . If the alcohol is primary, then formation of carbocation is highly disfavored. Instead, the abstraction of proton and departure of the water moiety occur in a concerted fashion, in a single elementary step. Thus this mechanism has a bimolecular rate-determining step and is known as  $E2$ .
- B. The most substituted alkene is usually the predominant product of elimination, since it is the most stable one (*Zaitsev rule, Zaitsev product*). The elimination is regioselective!
- C. The elimination is also stereoselective: The more stable stereoisomer is obtained predominantly. In cases of *cis/trans* mixtures, the *trans* isomer predominates.
- D. In cases when the elimination is  $E1$ , carbocations are the intermediates. They can (and do) rearrange, if possible, to more stable ones, thus giving more complex outcome in a lot of cases. The rearrangement can be materialized via the so-called methyl shift (a methyl group shifts with two electrons) or hydride shift (a hydrogen atom shifts, with two electrons).
- E. *Dehydrohalogenation* –  $E1$  or  $E2$  reactions of alkyl halides. Since, formally, one eliminates HX from these molecules, the process is called *dehydrohalogenation*. It can be carried out via  $E1$  or  $E2$  mechanism, depending on the nature of the substrate and base. Strong, bulky bases are best for elimination.
- 1)  $E2$  elimination requires strong bases – methoxide, ethoxide, t-butoxide.
  - 2)  $E2$  is a single-step, concerted process. So all bond breaking and bond making occurs in the rate-determining step. This leads to the following conclusions:

- a. C – X bond breaking will contribute to the activation energy unfavorably. The smaller its value, the smaller the activation energy, the faster the overall reaction. This explains reactivity in the order:  $C - F < C - Cl < C - Br < C - I$ .
  - b.  $\pi$ -bond making will occur partially in the TS. Thus all factors stabilizing the alkene will also partially affect the TS. In other words, transition states leading to more stable alkenes will also be more stable. Thus more stable alkenes are obtained faster and will be the predominant products (Zaitsev!!).
  - c. Because of that partial p-bond formation, a precondition (and restriction) exists, namely that the C – H and C – X bonds in the starting material are coplanar, in order for the appropriate orbitals to overlap. This is known as a *stereoelectronic effect*. The coplanarity can be in two versions: 1) *anti*-coplanar, when the two bonds are anti to each other or 2) *syn*-coplanar, when the two bonds eclipse. The first is preferred for steric reasons. REMEMBER: E2 will not occur if the condition of coplanarity cannot be fulfilled!!
- 3) E1 dehydrohalogenation takes place in alcohol or water, with no other (stronger) base being present. As usual, it requires a heterolytic cleavage of the substrate, to generate an intermediate carbocation.