

## SYNTHESIS OF ALKENES

Alkenes, sometimes also called olefins, are hydrocarbons with one C=C double bond, and fit the general formula  $C_nH_{2n}$ . Ethylene is the first representative of the alkenes. The two carbon atoms in ethylene are in the  $sp^2$ -hybridization state (Figure 1), which means that the three  $sp^2$ -bonds of each carbon atom are in the same plane.

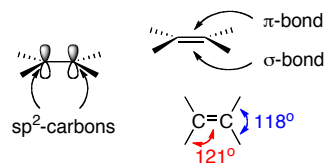


Figure 1

### Nomenclature of alkenes

According to IUPAC, the alkenes are named after their alkane analogues, but the ending **-ene**, instead of **-ane** (Figure 2). Trivial names are often used. Unless there is a functional

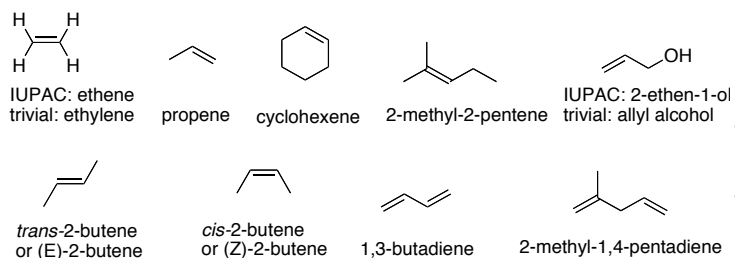


Figure 2

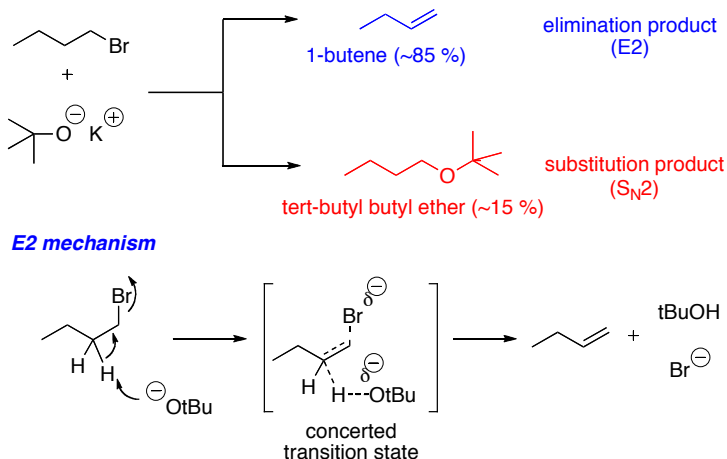
group that has a higher priority, the chain numbering begins from the end that gives the lower number to the double bond. (Figure 2). In addition, the p-bond prevents the free rotation around the C=C double bond, and therefore alkenes can exhibit geometric isomerism, known as *cis/trans* (or *Z/E*). This isomerism should be reflected in the name (Figure 2). In addition, a hydrocarbon with two C=C bonds is called **diene** (to name it one needs to have the ending **-diene**, instead of **-ene**), and with three C=C bonds is called **triene** (so the ending is going to be **-triene**), etc (Figure 2). The positions of the double bonds are indicated by the prefix.

### Synthesis of alkenes

In general, alkenes could be synthesized either by elimination reactions of alcohols (usually under strongly acidic conditions) or alkyl halides (usually accomplished under strongly basic conditions). Unless simple substrates are involved, one can anticipate the formation of several products, which originate from elimination and substitution pathways.

Primary alkyl halides in the presence of a base yield terminal alkenes, as the major products (which follows an elimination route via E2 mechanism) and a small amount of ether (which originates from the substitution pathway, *i.e.*,  $S_N2$  mechanism) as shown in Scheme 1.

From the mechanistic point of view, the elimination reaction proceeds by an attack of the base on the  $\beta$ -hydrogen (*i.e.*, hydrogen that is on  $\beta$ -carbon), which simultaneously leads to



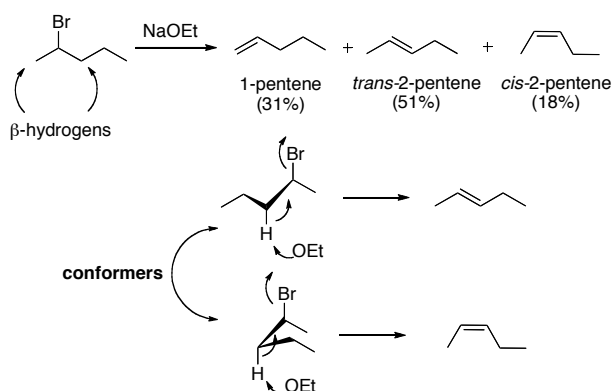
Scheme 1

the formation of C=C bond and elimination of the halogen anion. Thus, it is a concerted process,

that is bimolecular (rate depends on both the concentration of the substrate and the base) in its rate-determining step, *i.e.*, E2 mechanism.

Since the  $\alpha$ -carbon of the alkyl halide has a partial positive charge (due to the electronegative effect of the halogen), it can also undergo an attack by a nucleophile, and lead to a substitution product. Because bases can often be viewed as nucleophiles, the presence of substitution products in elimination reactions is common. It should be kept in mind that the structure of the base could be determining whether it will have more of the character of the base or nucleophile. In order to eliminate the formation of the substitution product, bulky bases, such as *tert*-butoxide (KO*t*-Bu) are used.

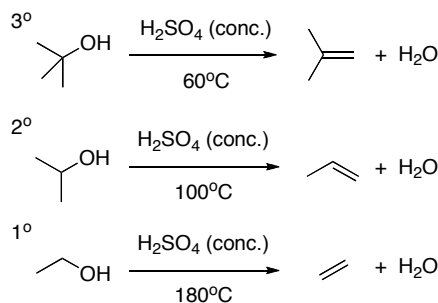
Elimination of secondary alkyl halides gives a mixture of products, if the halogen is unsymmetrically located in the alkyl halides, although the more highly substituted *trans*-alkene is usually the major product (Scheme 2). Due to the presence of two  $\beta$ -positions, terminal and internal alkenes are formed. The formation of *cis*-/*trans*-alkenes is explained by the presence of conformers: more energetically favored staggered conformation leads to the *trans*-alkene, whereas the *cis*-product results from less energetically favored, hence less populated, eclipsed conformation.



In addition, it is important to remember that alkanes that contain an acidic hydrogen in addition to the halogen, such as halogen-containing alcohols, might not yield the expected elimination products under basic conditions (Scheme 3). Acid-base reaction between the base and the OH-group, would lead to the formation of the anion, which could act as a nucleophile. If the length of the alkyl chain permits, an intramolecular process can take place to yield cyclic ethers (Scheme 3).

Scheme 3

Alcohols can also undergo elimination, yet acidic conditions are required. Elimination of water from primary alcohols is very slow, in hot acid (usually H<sub>2</sub>SO<sub>4</sub>), a mixture of the products is formed. Thus, primary alcohols are not useful materials for alkene synthesis. Secondary or tertiary alcohols are much more suitable substrates (Scheme 4), as the elimination can proceed under reasonable conditions. The reaction is believed to proceed predominately *via* an E1 mechanism. A protonation of the OH-group of the alcohol would lead to the elimination of H<sub>2</sub>O, and the formation of a carbocation. The carbocation could then loose H<sup>+</sup> to either H<sub>2</sub>O, conjugated base of the acid, *i.e.*, HSO<sub>4</sub><sup>-</sup>, if H<sub>2</sub>SO<sub>4</sub> was used as an acid or another molecule of alcohol to yield the corresponding alkene. It is important that the conjugate base would be non-nucleophilic, which should eliminate the possibility of the reaction with the carbocation. This might produce a substituted product (via S<sub>N</sub>1 mechanism) that is cannot undergo an elimination under the acidic condition.



Scheme 4

Furthermore, since carbocation can rearrangement, in order to form more stable (more substituted) carbocation via hydride ( $\text{H}^-$ ) or alkyl ( $\text{R}^-$ ) shift, a rearranged product might be observed (Scheme 5). Due to the rearrangement, even primary alcohols could undergo elimination and produce a single product. However, for more practical approaches, often primary alcohols are transformed into halides and subsequent elimination produces alkenes in a much more controlled manner. However, in case of symmetrical, non-substituted alcohols, such as cyclohexanol, elimination proceeds smoothly, and gives only one product.

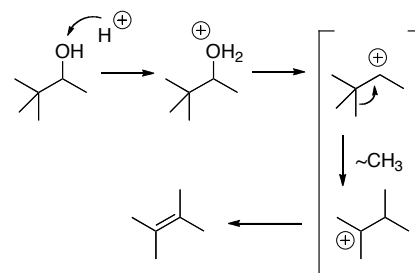


Figure 5

### Practical considerations for dehydration of alcohols

- Alkenes are volatile, flammable materials, hence flameless heating is a must.
- In order to induce the elimination strong acids are used, and therefore, extreme caution is required while handling the acids. Also, the choice of acid is crucial: acids, which have non-nucleophilic type of conjugate bases, are required to produce alkenes from alcohols.
- A number of alkenes form azeotrope mixture with water. This requires a drying step prior to purification of the alkenes.

### Functional group identification: Quantitative determination of alkenes

#### **Bromine test for unsaturation:** addition of halogens to alkenes

This test relies on the addition of  $\text{Br}_2$  to the  $\text{C}=\text{C}$  bond (Scheme 6). Neither  $\text{F}_2$ ,  $\text{Cl}_2$  nor  $\text{I}_2$  is useful for this reaction:  $\text{F}_2$  and  $\text{Cl}_2$  are gases, hence hard to operate with under normal laboratory conditions, besides  $\text{F}_2$  undergoes an explosive reaction with organic compounds;  $\text{I}_2$  does add to the  $\text{C}=\text{C}$  bond, but the reaction is reversible, with equilibrium being shifted towards alkene +  $\text{I}_2$ , therefore visual determination of positive/negative outcome is not possible.

From the mechanistic point of view, the addition of  $\text{Br}_2$  to an alkene could be viewed as an initial nucleophilic attack of the  $\pi$ -bond electrons on the polarized  $\text{Br}_2$  molecules leading to the formation of the bromonium ion (Scheme 6). The repulsion between the electrons of the alkene and electrons of the  $\text{Br}_2$  is a reason for polarization of the  $\text{Br}-\text{Br}$  bond. In the bromonium ion intermediate, the  $\alpha$ -carbons are partially positively charged, and therefore are susceptible to a nucleophilic attack by  $\text{Br}^-$ . Note, the  $\text{Br}^-$  attack is taking place from opposite side of the  $\text{Br}$ -bridge of the bromonium intermediate, which results in *anti-addition* of  $\text{Br}_2$ . In case of unsymmetrical alkenes, the most substituted carbon on the bromonium intermediate is the more positively charged carbon, and, therefore, the attack of the nucleophilic  $\text{Br}^-$  takes place on that particular carbon.

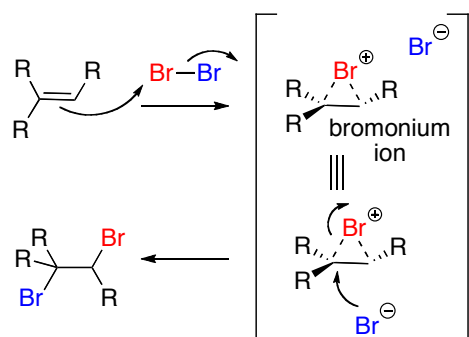
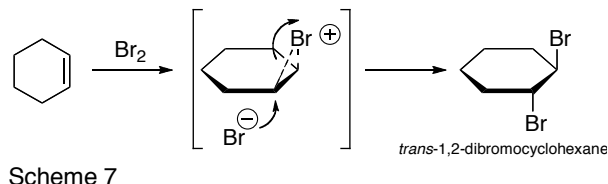


Figure 6

In case of acyclic alkenes the anti-addition is not obvious, due to the free rotation around  $\text{C}-\text{C}$  bond. However, when cyclohexene is brominated with  $\text{Br}_2$ , the product is *trans*-1,2-dibromocyclohexane (Scheme 7). Due to the cyclic structure, the rotation around the formed  $\text{C}-\text{C}$  bond is impossible, hence the bromine atoms are fixed. If the intermediate were a simple carbocation, both *cis* and *trans*-1,2-dibromocyclohexane should be formed, due to the planar

nature of the carbocation that is not stabilized by the neighboring Br, and equal probability of the Br<sup>-</sup> attack either from the top or from the bottom.



**The general procedure for the bromine test** is as follows: an unknown compound (usually ~50mg or 1-2 drops) is dissolved in dichloromethane. About 0.1M bromine solution in dichloromethane, which has a dark brownish color, is added dropwise to the solution of the unknown compound. Rapid disappearance of the bromine color, *i.e.*, the formation of colorless solution, is a positive test for unsaturation. If the color change takes place after an extended period of time (> 20 sec), the test cannot be considered positive. Please keep in mind that the decolorization of Br<sub>2</sub>-solution is indicative of the presence of the double bond, yet it is not definitive, since other unsaturated compounds, such as phenols, ketones and aldehydes, could also decolorize the Br<sub>2</sub>-solution.

### **Baeyer test (KMnO<sub>4</sub> test): oxidation of alkenes:**

This test relies on the oxidizing power of KMnO<sub>4</sub> to oxidize the C=C bond to give diols or the C≡C bond to give carboxylic acids (Scheme 8). The oxidation of alkynes takes place via

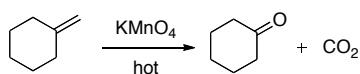
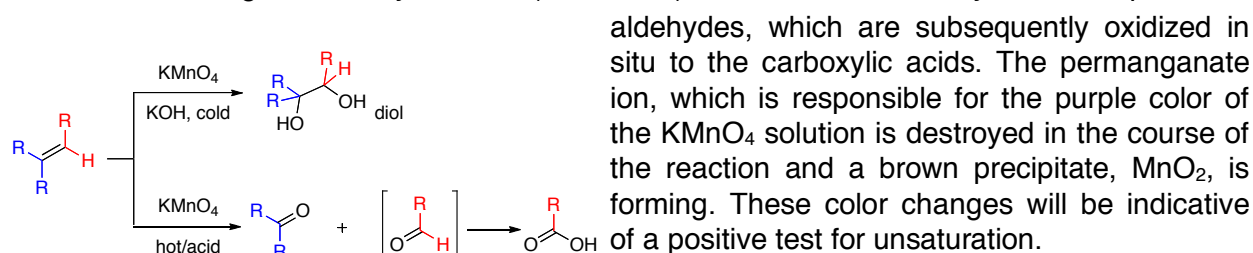


Figure 8

diol, if a cold basic solution of KMnO<sub>4</sub> is used. Carboxylic acids and/or ketones are formed if the alkene is subjected to KMnO<sub>4</sub> treatment at elevated temperatures. Under these conditions, the terminal C=C bond will be oxidized to CO<sub>2</sub>. The formation of CO<sub>2</sub> is due to initial oxidation to formic acid, followed by the formation of carbonic acid, which spontaneously decomposes to CO<sub>2</sub> and H<sub>2</sub>O.

**The general procedure for the Baeyer test** is as follows: an unknown is (usually ~50mg or 1-2 drops) is dissolved in ~ 2ml of ethanol and 0.1M aqueous solution of KMnO<sub>4</sub> solution is added dropwise. Note the number of drops that are required before the purple color persists. Depending on the amounts, the presence of MnO<sub>2</sub> precipitate in the colored mixture might be hard to observe. Therefore, a blank determination might be required: add the 0.1M KMnO<sub>4</sub> solution dropwise to ~2ml of ethanol, and count the number of drops before the color persists. A significant difference in the number of drops required in those two cases (*i.e.*, the unknown and blank) will indicate a positive test for unsaturation.

## PROBLEMS

1. Cyclohexane and cyclohexene differ only by 2H atoms. Yet, the difference in the melting point of cyclohexane is  $\sim 6^{\circ}\text{C}$  and that of cyclohexene is  $-104^{\circ}\text{C}$ . Speculate on the origin of such a big difference.
2. Is it possible for cyclohexene to exist in a trans configuration? If necessary, make a model to answer the question.
3. Based on a general knowledge of alkenes structure would you expect alkenes to act as electrophiles or nucleophiles?
4. Provide the reason for the order of carbocation stability:  $3^{\circ} > 2^{\circ} > 1^{\circ}$ . Where would the methyl carbocation fit in this series and why?
5. Would a diene give a positive bromine test? Provide a general reaction scheme that supports your answer.
6. 2-methylcyclohexanol under acidic conditions undergoes an elimination reaction to yield a mixture of alkenes. Provide the structures of all possible products.
7. Consider that 1-bromo-2-methylcyclohexane undergoes an elimination reaction under basic conditions. Provide the structures of all possible products.
8. Compare the products from questions 6 and 7, and rationalize the differences/similarities.
9. Would you expect benzoic acid to give a positive Baeyer test?
10. Why is it necessary to remove the drying agent from the organic solution prior to distillation?
11. For dehydration of alcohols strong acids, such as  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ , are used. However,  $\text{HCl}$  or  $\text{HBr}$  are also strong acids, and therefore excellent sources of  $\text{H}^+$ . Would it be possible to use  $\text{HBr}$ , for example, for the dehydration of an alcohol to produce an alkene as the major product? Explain your answer (reaction scheme will suffice).