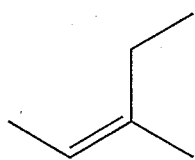


Key

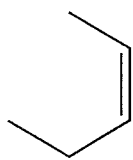
**Chem 51A - SSI 2014**  
**Discussion 9 Worksheet**  
Dr. Renee Link

This worksheet will focus on concepts to be discussed or already discussed, in Chapter 8. Those concepts being 1) Elimination Reactions.

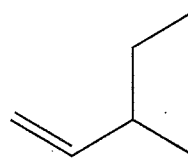
Rate the below alkenes 1-4 in order of increasing stability, with 1 being the least stable and assign each as *cis* or *trans*.



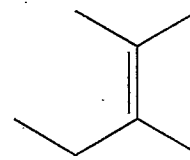
cis  
3



cis  
2



1



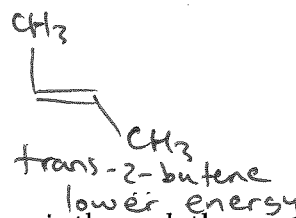
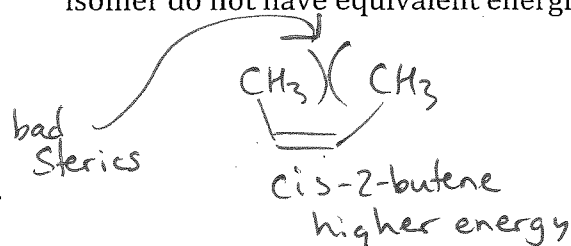
4

*Cis* and *trans* alkenes are **stereoisomers**, meaning they are entirely different compounds (For tri- and tetra-substituted alkenes, the *cis/trans* nomenclature is replaced with the E/Z nomenclature.)

Is it possible to rotate the double bond in an alkene to interconvert between the *cis* and *trans* isomers? Why?

No because  $\pi$  bonds are rigid.

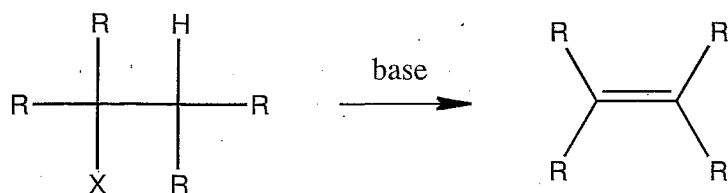
Not all di-substituted alkenes are created equal. The *cis*-isomer and the *trans*-isomer do not have equivalent energies. Which one is higher in energy? Why?



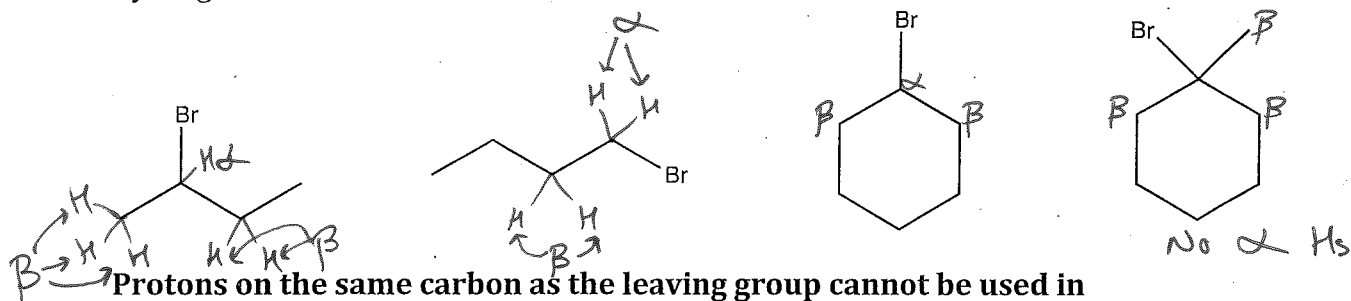
The most common method to synthesize alkenes is through the use of **elimination reactions**. As with nucleophilic substitution reactions, there are two mechanisms for elimination: E1 and E2.

For any elimination to occur, there are several factors that must be considered. The first is the **leaving group**. As with the nucleophilic substitution you learned about last week, a good leaving group is required for an elimination reaction to occur. The second is the **base**. A stronger base makes for an easier elimination reaction.

The third consideration is the need for hydrogens in the correct **position and orientation**. The general scheme of an elimination reaction is shown below.



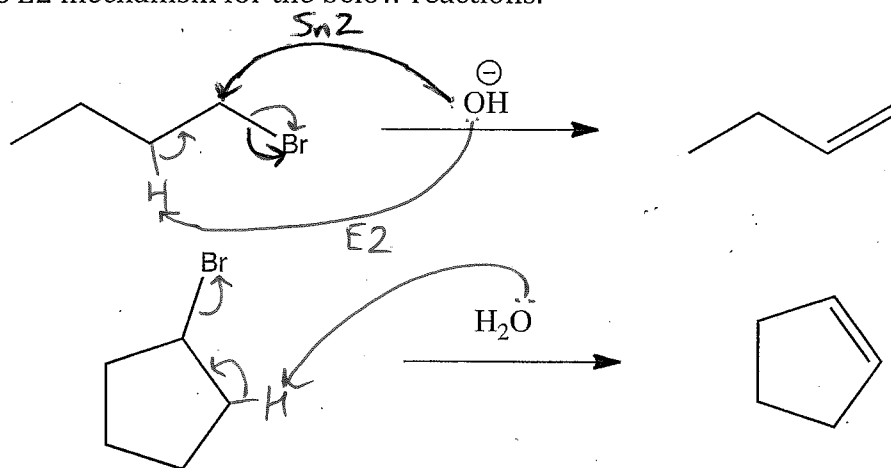
You will notice that a proton on a carbon **directly adjacent** to the carbon the leaving group is attached is **required** for this reaction. These hydrogens are called  **$\beta$ -hydrogens**, because they are on the adjacent, or  $\beta$ , carbon. Identify the  $\alpha$ - and  $\beta$ -hydrogens in the below structures.



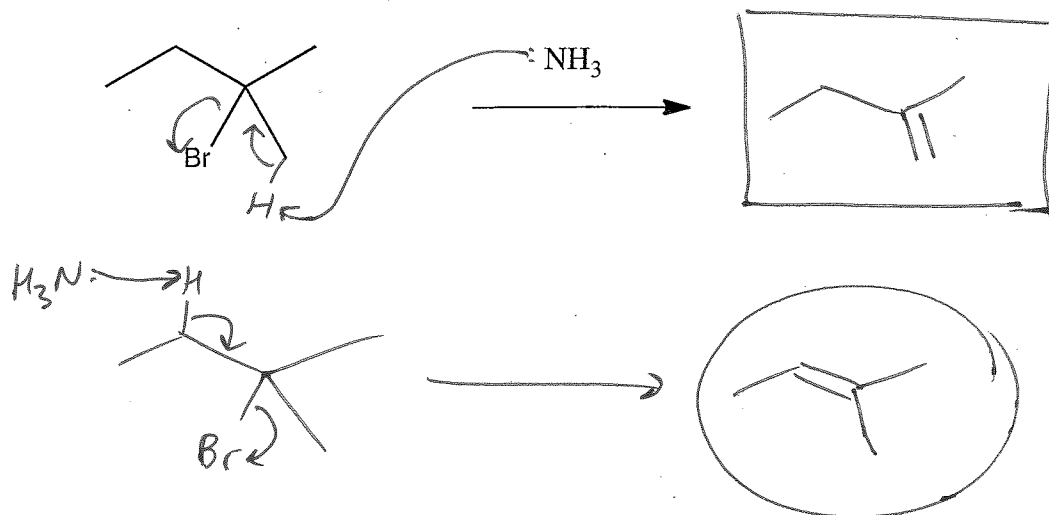
**Protons on the same carbon as the leaving group cannot be used in elimination reactions.** Also be aware that simply having  $\beta$ -hydrogens is not enough to be able to undergo elimination reactions

**E2 mechanisms** are similar to  $\text{S}_{\text{N}}2$  mechanisms in that they are **bimolecular, concerted** reactions. You should be able to write the rate law and draw the reaction coordinate diagram for the E2 mechanism. Apply the same concepts you used for the substitution mechanisms.

Draw the E2 mechanism for the below reactions.



If there are several  $\beta$ -hydrogens available to be removed, which product gets made? Draw all possible products, and then draw the mechanisms to get to those products.



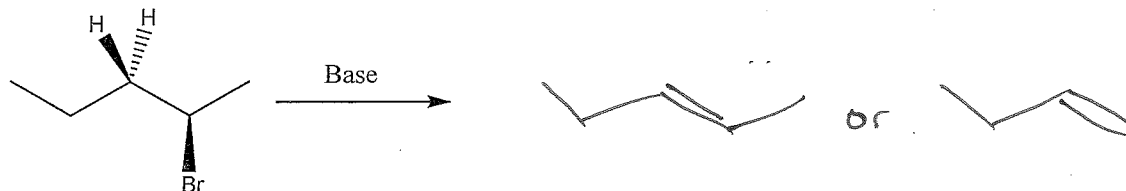
Generally, the major product of an elimination reaction is the most stable product. This is **Zaitsev's rule**. Circle the most stable structure above.

As always, there are caveats to this rule. Draw a box around the product you would expect to be formed when using sodium *tert*-butoxide. Why?

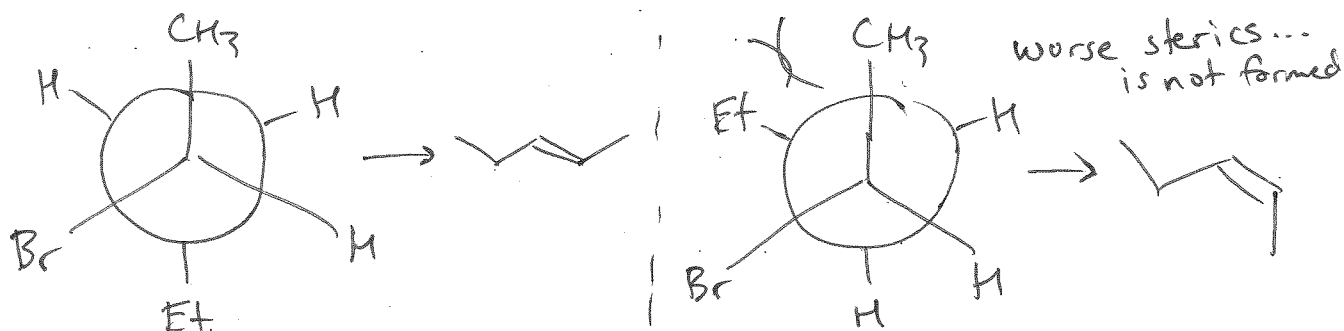
A bulky base will favor the more sterically accessible Hs.

The E2 mechanism has a crucial nuance that you must remember. The proton being removed by the base must be **anti-periplanar** to the leaving group. If this condition cannot be met, then the elimination cannot occur, **even if there are  $\beta$ -hydrogens**. **If the required conformation cannot be met, the reaction cannot occur.**

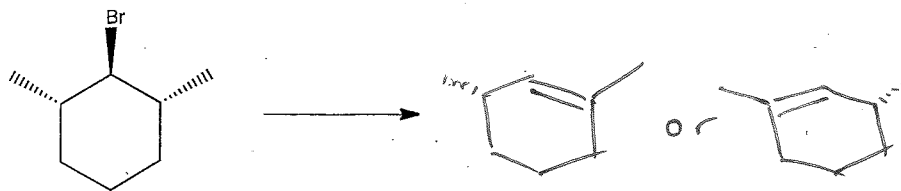
Draw the theoretical products that form with an internal alkene if the compound below did an E2 elimination reaction.



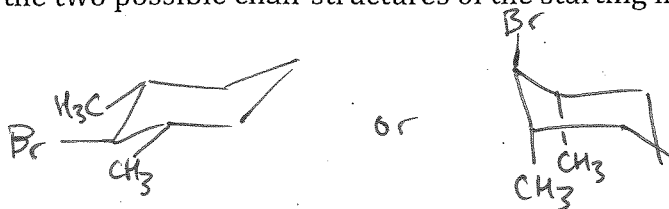
Only one of these products can actually be formed. Draw a Newman Projection of this compound and determine which stereoisomer is the one that is formed.



The same concepts apply to cyclic systems. Again, draw the theoretical products that could be formed from the below compound undergoing an E2 elimination.



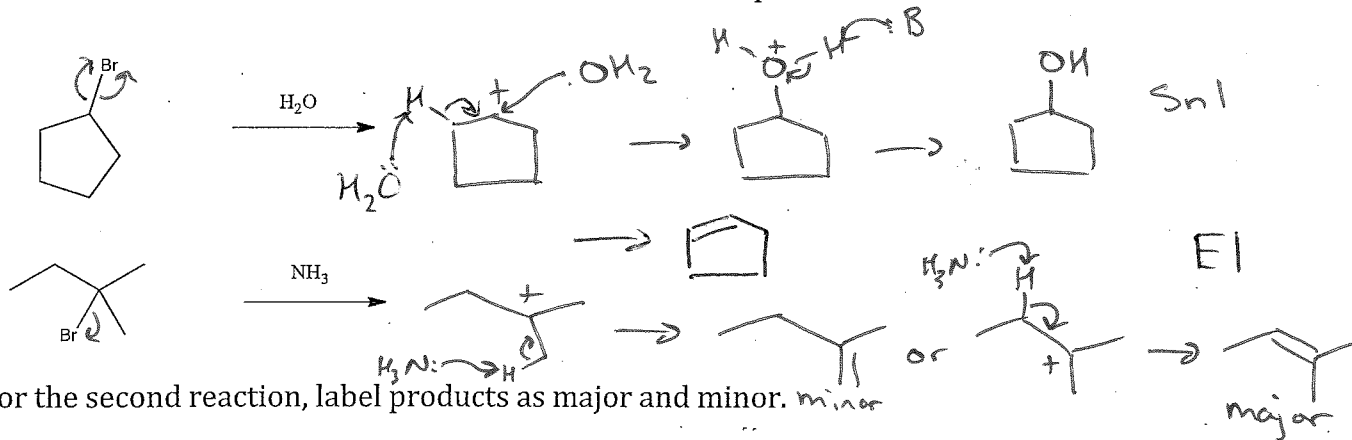
Draw the two possible chair structures of the starting material.



Is there an available  $\beta$ -hydrogen that is anti-periplanar to the leaving group when the leaving group is in the axial position? **No.**

Conditions that favor E2 reactions are the same as those that favor S<sub>N</sub>2. Polar aprotic solvents are preferred because they do not solvate the base. Strong bases are preferred because they deprotonate quickly.

**E1 mechanisms** go through the same carbocation intermediate that S<sub>N</sub>1 mechanism reactions do. Draw the E1 mechanism for the below compounds.



For the second reaction, label products as major and minor. *minor*

*major*

Conditions that favor E1 reactions are the same as those that favor S<sub>N</sub>1. Polar protic solvents are preferred because they solvate the ions that form, stabilizing them. Weak bases are preferred because they do not deprotonate quickly.

So, if the starting materials are all alkyl halides and the conditions are similar, how can you tell whether a reaction will undergo a substitution or an elimination?

*Strong nucleophile is not always the same as strong base.*