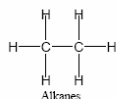
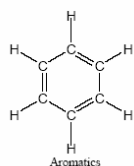
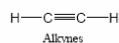


## Unsaturated Hydrocarbons

- **Saturated Hydrocarbons** — contain only carbon-carbon single bonds.



- **Unsaturated Hydrocarbons** — contain carbon-carbon double or triple bonds (more hydrogens can be added).

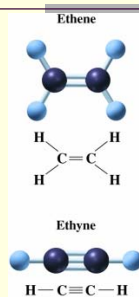


## Alkenes and Alkynes

Saturated compounds (alkanes):  
Have the maximum number of hydrogen atoms attached to each carbon atom.

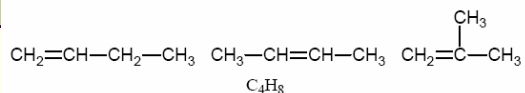
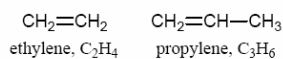
Unsaturated compounds:  
Have fewer hydrogen atoms attached to the carbon chain than alkanes.

- Containing **double bond** are **alkenes**.  
 $C_nH_{2n}$
- Containing **triple bond** are **alkynes**.  
 $C_nH_{2n-2}$

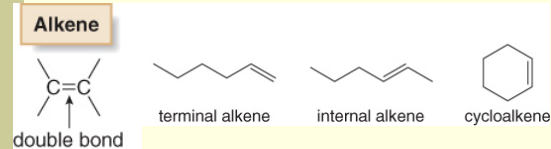


## Alkenes

- **Alkenes** contain **carbon-carbon double bonds**.
  - General formula:  $C_nH_{2n}$  (for one double bond)
  - Suffix = **-ene**
- In the carbon-carbon double bond, two pairs of electrons are being shared, leaving the carbon free to bond to two other things.

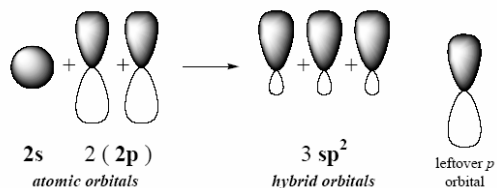


## Classes of Alkenes

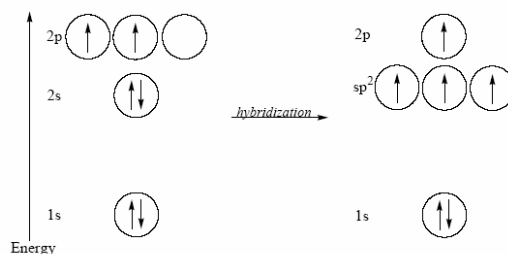


## Hybridization of Alkenes

- When a carbon is connect to three other things (that is, one of the bonds is a double bond), the molecule is modeled by combining the  $2s$  and two of the  $2p$  orbitals to produce **three  $sp^2$  orbitals**.
- Since only two of the  $2p$  orbitals were hybridized, there is **one leftover  $p$  orbital** in an  $sp^2$ -hybridized carbon atom.



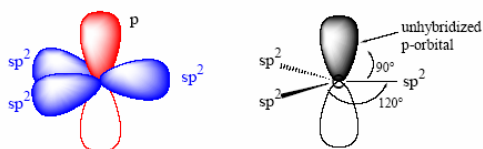
## Hybrid Orbitals



- All three  $sp^2$  orbitals are at the same energy level, with one electron in each hybrid orbital, and one in the slightly higher-energy unhybridized  $2p$  orbital.

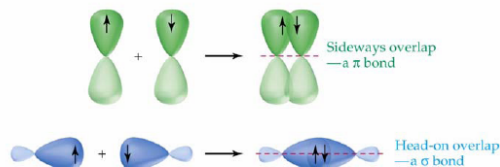
### The Shape of an $sp^2$ Carbon

- The  $sp^2$  orbitals are arranged in a **trigonal planar** shape around the central carbon atom, with bond angles of  $120^\circ$ .
- The unhybridized  $p$  orbital is perpendicular to this plane.



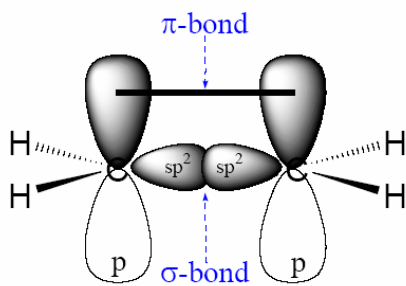
### Sigma and Pi Bonds

- When two  $sp^2$ -hybridized carbons are next to each other, two kinds of orbital overlap take place:
  - end-on-end overlap* of the  $sp^2$  orbitals to make a  **$\sigma$ -bond** (sigma bond).
  - side-to-side overlap* of the unhybridized  $p$  orbitals to make a  **$\pi$ -bond** (pi bond).

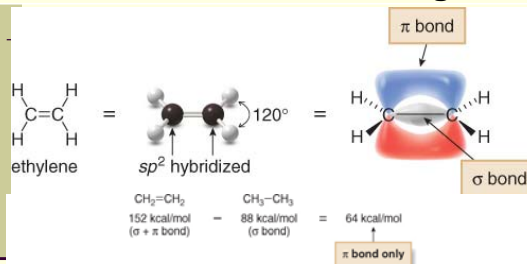


### Bonding in Ethylene

- Because of the  $\pi$ -bond, *free rotation is not possible* around carbon-carbon double bonds.



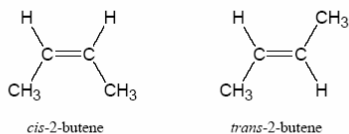
### Structure and Bonding



- The  $\pi$  bond is much weaker than the  $\sigma$  bond of a C-C double bond, making it much more easily broken. As a result, alkenes undergo many reactions that alkanes do not.

### Geometric Isomers in Alkenes

- Because free rotation is not possible around double bonds, there are two different forms of 2-butene, which are **geometric isomers** of each other:

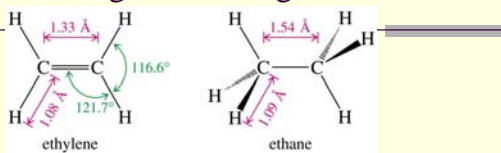


- The prefix *cis*- is used when the two arms of the longest chain are on the **same side** of the double bond; the prefix *trans*- is used when they are on **opposite sides** of the double bond.
- Geometric isomers can have drastically different chemical and physical properties.

### Orbital Description

- Sigma bonds around C are  $sp^2$  hybridized.
- Angles are approximately 120 degrees.
- No nonbonding electrons.
- Molecule is planar around the double bond.
- Pi bond is formed by the sideways overlap of parallel  $p$  orbitals perpendicular to the plane of the molecule.

## Bond Lengths and Angles

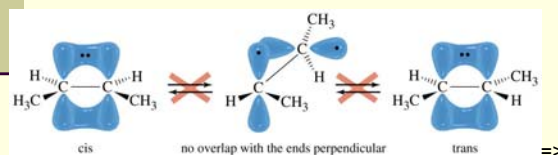


- Hybrid orbitals have more s character.
- Pi overlap brings carbon atoms closer.
- Bond angle with pi orbitals increases.
  - Angle C=C-H is 121.7°
  - Angle H-C-H is 116.6°

=>

## Pi Bond

- Sideways overlap of parallel  $p$  orbitals.
- No rotation is possible without breaking the pi bond (63 kcal/mole).
- Cis isomer cannot become trans without a chemical reaction occurring.



=>

## IUPAC Nomenclature

- Parent is longest chain containing the double bond.
- -ane changes to -ene. (or -diene, -triene)
- Number the chain so that the double bond has the lowest possible number.
- In a ring, the double bond is assumed to be between carbon 1 and carbon 2.

=>

## Naming Alkenes & Alkynes

Using the IUPAC alkane names:

Alkene names change the end to -ene.

Alkyne names change the end to -yne

### Comparison of Names for Alkanes, Alkenes, and Alkynes

Alkane	Alkene	Alkyne
H <sub>3</sub> C-CH <sub>3</sub>	H <sub>2</sub> C=CH <sub>2</sub>	HC≡CH
Ethane	Ethene (ethylene)	Ethyne (acetylene)
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>	CH <sub>3</sub> -CH=CH <sub>2</sub>	CH <sub>3</sub> -C≡CH
Propane	Propene (propylene)	Propyne

### Guide to Naming Alkenes and Alkynes

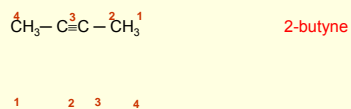
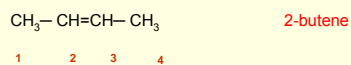
**STEP 1**  
Name of the longest carbon chain with a double or triple bond.

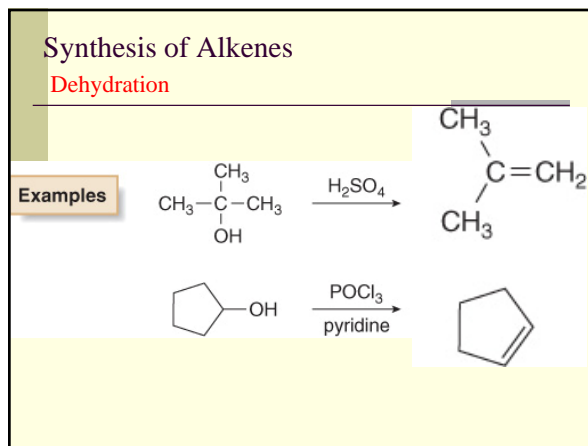
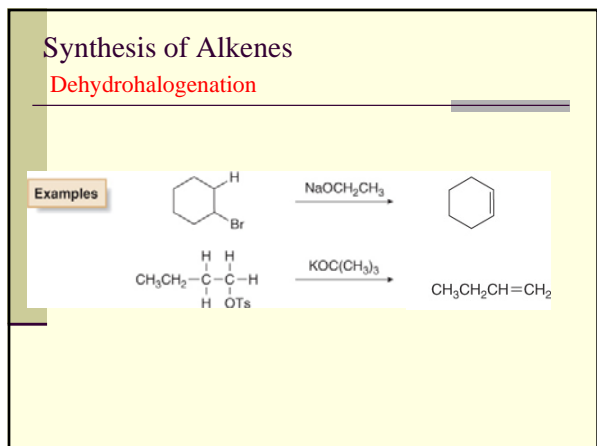
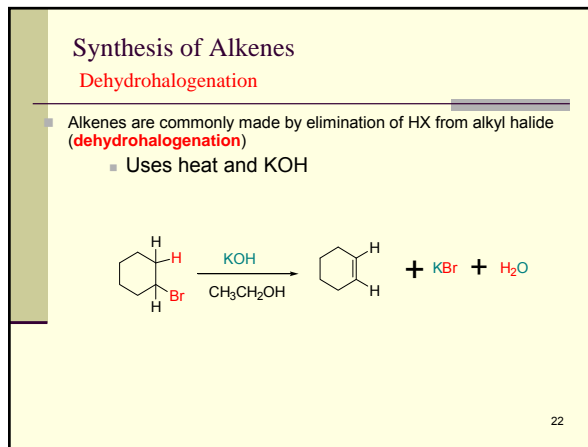
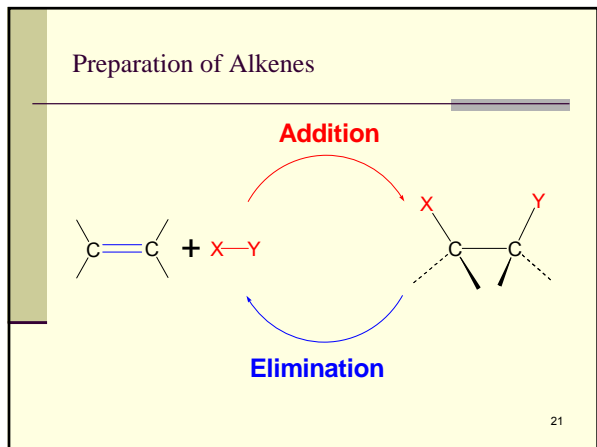
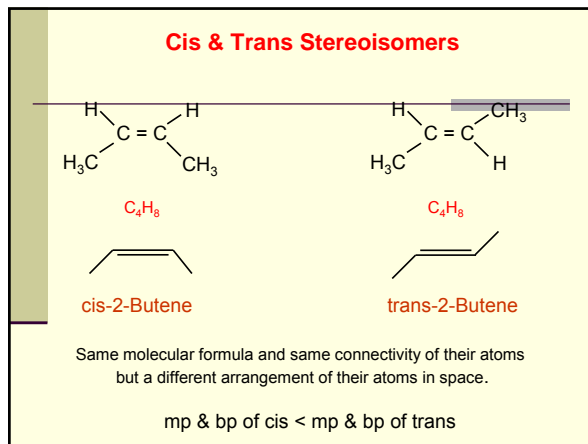
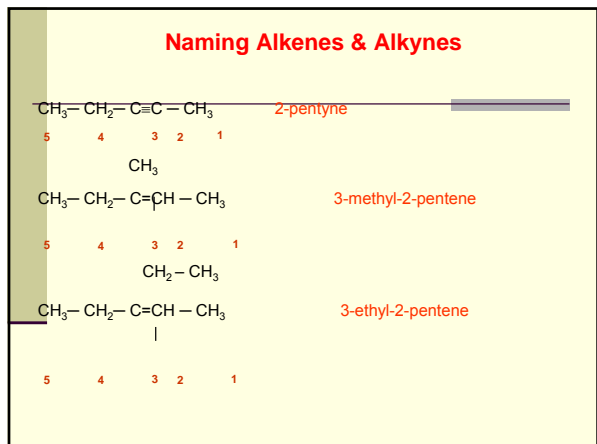
**STEP 2**  
Number the carbon chain starting from the end nearest a double or triple bond.

Give the location for double and triple bond.

**STEP 3**  
Give the location and name of each substituent (alphabetical order) as a prefix to the name.

## Naming Alkenes & Alkynes

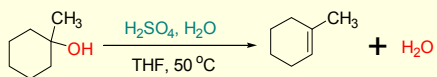




## Synthesis of Alkenes

### Dehydration

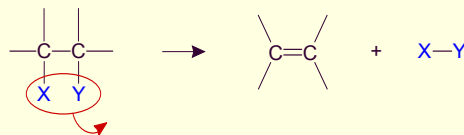
- elimination of H-OH from an alcohol (**dehydration**)
  - require strong acids (sulfuric acid, 50 °C)



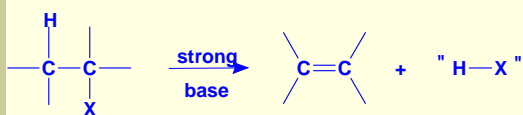
25

## Elimination Reactions

Dehydrohalogenation (-HX) and Dehydration (-H<sub>2</sub>O) are the main types of elimination reactions.



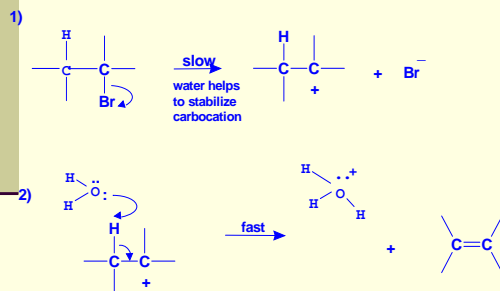
## Dehydrohalogenation (-HX)



X = Cl, Br, I

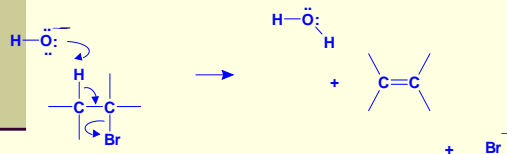
## E1 mechanism

This reaction is done in strong base at low concentration, such as 0.01 M NaOH in water)



## E2 mechanism

This reaction is done in strong base at high concentration, such as 1 M NaOH in water.



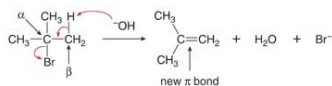
concerted mechanism

## The E2 Mechanism

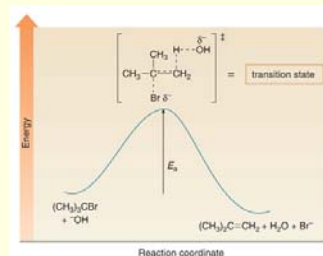


### MECHANISM 8.1

#### The E2 Mechanism



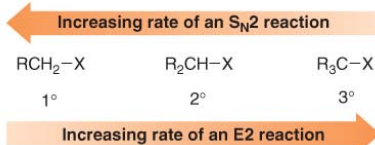
## Energy Diagram for the E2 Mechanism



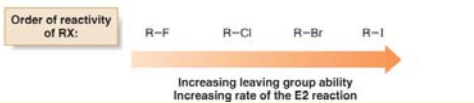
**TABLE 8.2** Characteristics of the E2 Mechanism

Characteristic	Result
Kinetics	• Second order
Mechanism	• One step
Identity of R	• More substituted halides react fastest • Rate: $R_3CX > R_2CHX > RCH_2X$
Base	• Favored by strong bases
Leaving group	• Better leaving group $\rightarrow$ faster reaction
Solvent	• Favored by polar aprotic solvents

## Effect of the Substrate on E2 Reactivity



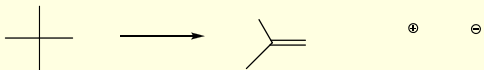
## Effect of the LG on E2 Reactivity



- ♦ Polar aprotic solvents increase the rate of E2 reactions.

## The E1 Mechanism

Let's look at an E1 reaction mechanism using the rxn shown below.



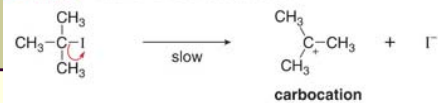
## The E1 Mechanism



### MECHANISM 8.2

#### The E1 Mechanism

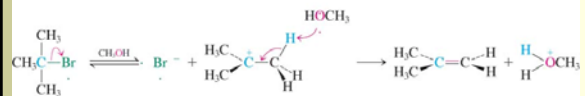
**Step [1]** The C-I bond is broken.



The **first step** of the E1 and S<sub>N</sub>1 mechanisms are identical.

First Step: Same as S<sub>N</sub>1

#### The E1 Reaction Mechanism

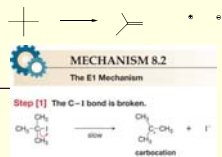


CH<sub>3</sub>

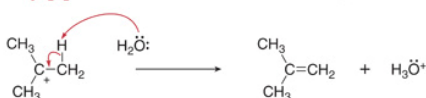
H<sub>2</sub>O

CH<sub>3</sub>

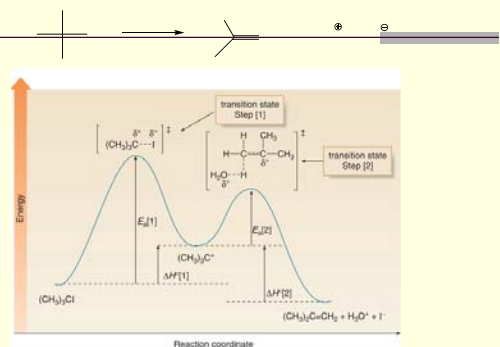
## The E1 Mechanism



**Step [2]** A C-H bond is cleaved and the π bond is formed

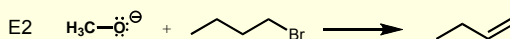
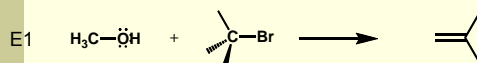
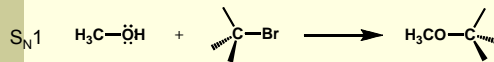
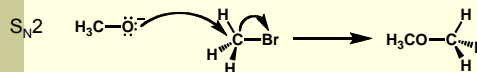


## Energy Diagram for E1



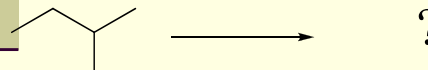
**TABLE 8.3 Characteristics of the E1 Mechanism**

Characteristic	Result
Kinetics	• First order
Mechanism	• Two steps
Identity of R	• More substituted halides react fastest • Rate: $R_2CX > R_2CHX > RCH_2X$
Base	• Favored by weaker bases such as $H_2O$ and $ROH$
Leaving group	• A better leaving group makes the reaction faster because the bond to the leaving group is partially broken in the rate-determining step.
Solvent	• Polar protic solvents that solvate the ionic intermediates are needed.

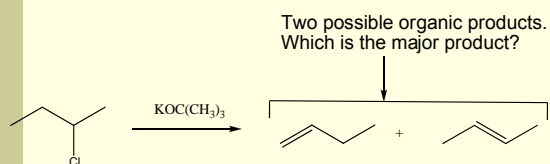


## The Zaitsev Rule

What about dehydrohalogenations involving  $RX$  with hydrogen atoms on different  $\beta$  carbon atoms



## The Zaitsev Rule- A Regioselective Rxn



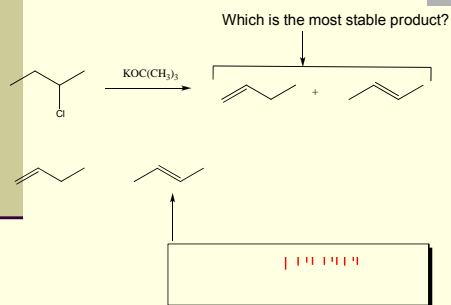
## The Zaitsev Rule (Z-rule)

According to the **Z-rule**, the major product in a dehydrohalogenation is the .....

**most stable product.**

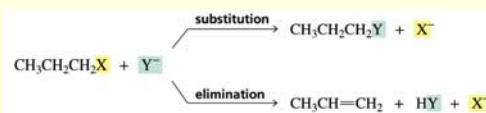


Let's ask a different question about the products.



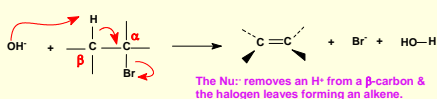
## Elimination Reactions

A compound with an electronegative atom bonded to an  $sp^3$  carbon, when approached by a nucleophile/base can undergo either a substitution reaction **OR** an elimination reaction



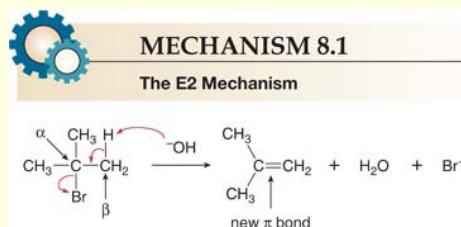
## Elimination Reactions

- There are 2 kinds of elimination reactions, E1 and E2.
- E2 = Elimination, Bimolecular (2nd order). Rate =  $k[\text{RX}][\text{Nu}:^-]$
- E2 reactions occur when a 2° or 3° alkyl halide is treated with a strong base such as  $\text{OH}^-$ ,  $\text{OR}^-$ ,  $\text{NH}_2^-$ ,  $\text{H}^-$ , etc.



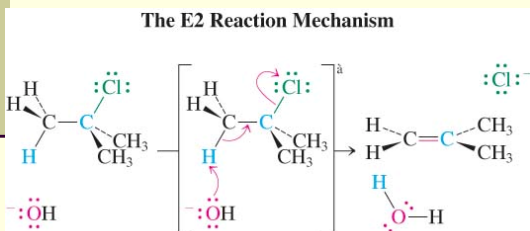
- All strong bases, like  $\text{OH}^-$ , are good nucleophiles. In 2° and 3° alkyl halides the α-carbon in the alkyl halide is hindered. In such cases, a strong base will 'abstract' (remove) a hydrogen ion ( $\text{H}^+$ ) from a β-carbon, before it hits the α-carbon. Thus strong bases cause elimination (E2) in 2° and 3° alkyl halides and cause substitution ( $\text{S}_{\text{N}}2$ ) in unhindered methyl° and 1° alkyl halides.

## The E2 Mechanism



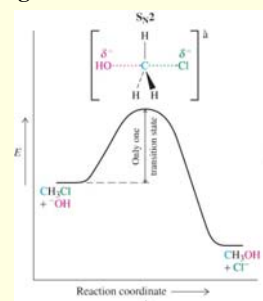
## The E2 Mechanism

E2: Deprotonation is First Step



## The E2 Mechanism

Energy Diagram



more stable  
has more

R groups attached at the  $sp^2$

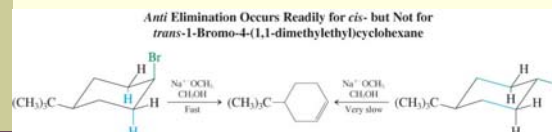
## The E2 Mechanism

**TABLE 8.2** Characteristics of the E2 Mechanism

Characteristic	Result
Kinetics	<ul style="list-style-type: none"> <li>• Second order</li> </ul>
Mechanism	<ul style="list-style-type: none"> <li>• One step</li> </ul>
Identity of R	<ul style="list-style-type: none"> <li>• More substituted halides react fastest</li> <li>• Rate: <math>R_3CX &gt; R_2CHX &gt; RCH_2X</math></li> </ul>
Base	<ul style="list-style-type: none"> <li>• Favored by strong bases</li> </ul>
Leaving group	<ul style="list-style-type: none"> <li>• Better leaving group <math>\rightarrow</math> faster reaction</li> </ul>
Solvent	<ul style="list-style-type: none"> <li>• Favored by polar aprotic solvents</li> </ul>

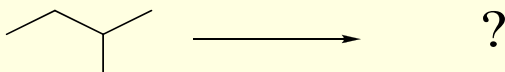
## The E2 Mechanism

Reaction proceeds by Anti Elimination



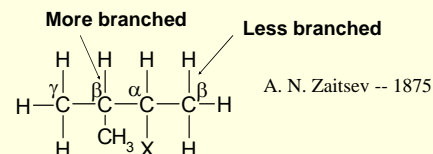
## The Zaitsev (Saytzeff) Rule Z Rule

What about dehydrohalogenations involving RX with hydrogen atoms on different  $\beta$  carbon atoms

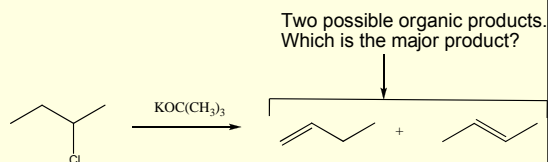


## The Zaitsev (Saytzeff) Rule Z Rule

- In reactions of removal of hydrogen halides from alkyl halides or the removal of water from alcohols, the *hydrogen* which is lost will come from the *more highly-branched*  $\beta$ -carbon.



## The Zaitsev (Saytzeff) Rule Z Rule



## The Zaitsev (Saytzeff) Rule Z Rule

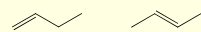
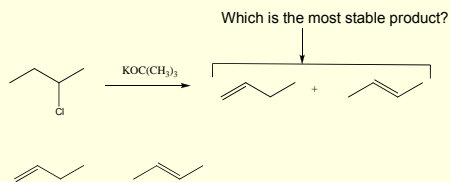
According to the **Z-rule**, the major product in a dehydrohalogenation is the

.....

**most stable product.**

## The Zaitsev (Saytzeff) Rule Z Rule

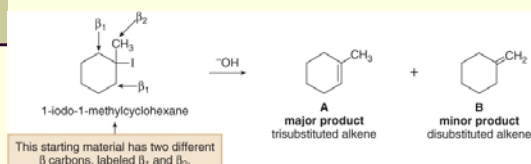
Let's ask a different question about the products.



1 1 1 1 1 1

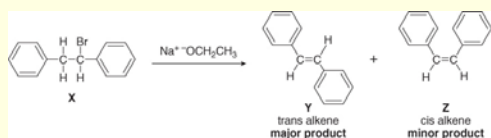
## The Zaitsev (Saytzeff) Rule Z Rule

- When alkyl halides have two or more different  $\beta$  carbons, more than one alkene product is formed.
- When this happens, one of the products usually predominates.
- The major product is the more stable product—the one with the more substituted double bond.
- This phenomenon is called the **Zaitsev rule**.



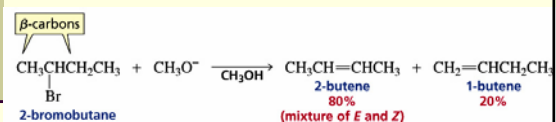
## The Zaitsev (Saytzeff) Rule Z Rule

- When a mixture of stereoisomers is possible from a dehydrohalogenation, the major product is the more stable stereoisomer.
- A reaction is **stereoselective** when it forms predominantly or exclusively one stereoisomer when two or more are possible.
- The E2 reaction is stereoselective because one stereoisomer is formed preferentially.



## The E2 Reaction: Regioselectivity

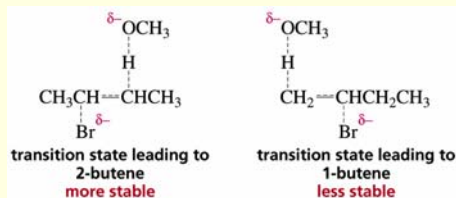
2-bromobutane has two structurally different  $\beta$ -carbons from which to abstract a hydrogen



E2 reactions give more stable alkene if possible

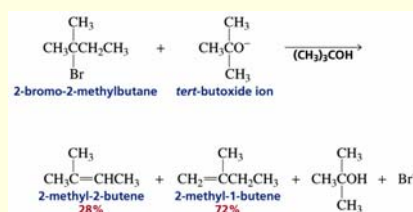
## The E2 Reaction: Regioselectivity

**Zaitsev's rule** (Saytzeff Rule): The more substituted alkene will be formed in elimination reactions



## The E2 Reaction: Regioselectivity

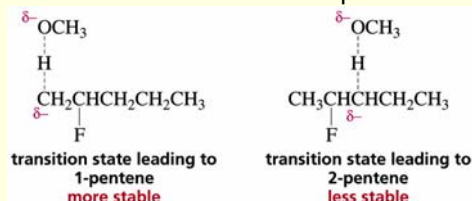
- Zaitsev's rule does not apply when the base is bulky
- E2 Rxn is kinetically-controlled



trans-2-Butene is **more**  
1-butene because it has  
**R groups** attached at t

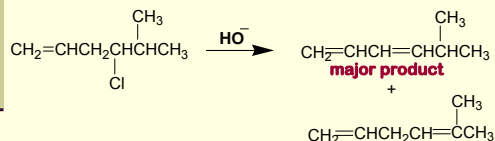
## The E2 Reaction: Regioselectivity

- Zaitsev's rule does not apply when the leaving group is poor
- E2-carbanion mechanism operative



## The E2 Reaction: Regioselectivity

Zaitsev's rule may not apply when conjugated dienes might be formed

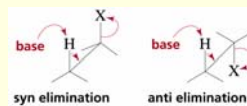


## The E2 Reaction: Regioselectivity

The major product of an E2 reaction is the more substituted alkene unless:

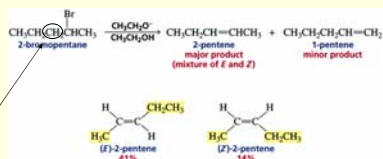
- the base is large (i.e. bulky)
- the leaving group is poor (i.e. F<sup>-</sup>)
- the less substituted β-carbon is allylic or benzylic (ie. more stable)

## The E2 Reaction: Stereochemistry



- If the elimination reaction removes two substituents from the same side of the molecule it is **syn elimination**
- If the elimination reaction removes two substituents from opposite sides of the molecule it is **anti elimination**

## The E2 Reaction: Stereochemistry



- The E2 Reaction is **stereoselective**, but **not stereospecific** if 2 β H's are available on carbon bearing eliminated H
- The H leading to more stable E isomer is selected to be extracted from β carbon regardless of stereochem at α carbon

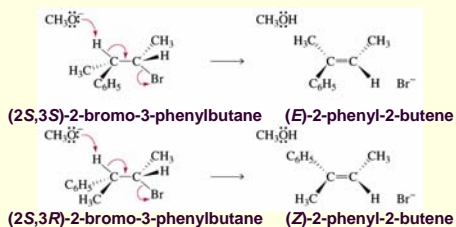
## The E2 Reaction: Stereochemistry

- In an E2 reaction, the bonds to the eliminated substituents must be in the same plane
- In this course E2 eliminations will all go via **anti-periplanar** conformation
- Product analysis possible by drawing Newman projections if only 1 β H is available

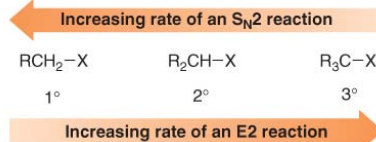


## The E2 Reaction: Stereochemistry

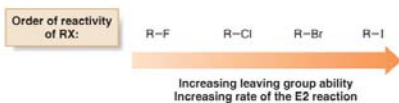
When only one hydrogen is on the  $\beta$  carbon predominantly anti elimination leads to high stereospecificity



## Effect of the Substrate on E2 Reactivity



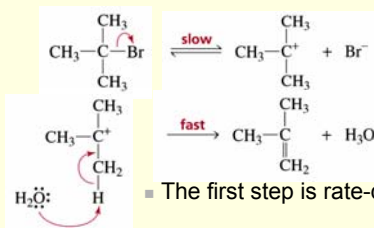
## Effect of the LG on E2 Reactivity



♦ Polar aprotic solvents increase the rate of E2 reactions.

## The E1 Reaction

- “E1” stands for “Elimination unimolecular”
- The E1 reaction is a two-step reaction

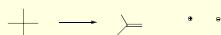
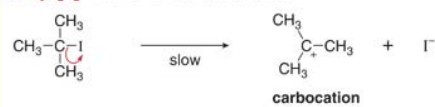


## The E1 Mechanism

### MECHANISM 8.2

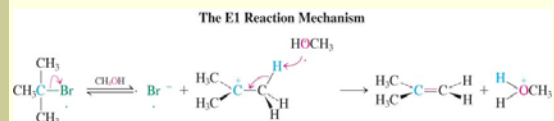
#### The E1 Mechanism

**Step [1]** The C–I bond is broken.



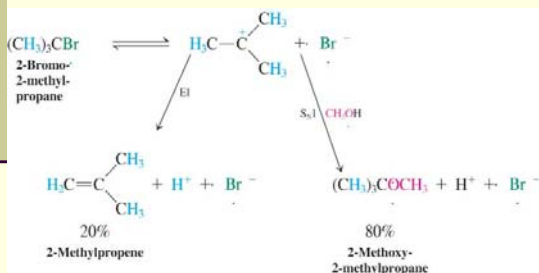
## The E1 Mechanism

First Step: Same as  $S_N1$



## The E1 Mechanism

The E1 Pathway Competes with S<sub>N</sub>1



## Mechanisms of Elimination—E1

- The dehydrohalogenation of  $(\text{CH}_3)_3\text{CI}$  with  $\text{H}_2\text{O}$  to form  $(\text{CH}_3)_2\text{C}=\text{CH}_2$  can be used to illustrate the second general mechanism of elimination, the E1 mechanism.
- An E1 reaction exhibits first-order kinetics:

$$\text{rate} = k[(\text{CH}_3)_3\text{CI}]$$

- The E1 reaction proceeds via a two-step mechanism: the bond to the leaving group breaks first before the  $\pi$  bond is formed. The slow step is unimolecular, involving only the alkyl halide.
- The E1 and E2 mechanisms both involve the same number of bonds broken and formed. The only difference is timing. In an E1, the leaving group comes off before the  $\beta$  proton is removed, and the reaction occurs in two steps. In an E2 reaction, the leaving group comes off as the  $\beta$  proton is removed, and the reaction occurs in one step.

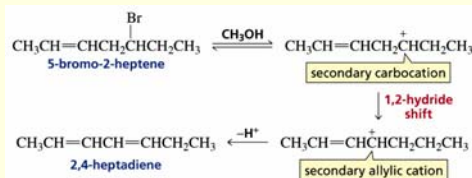
## Mechanisms of Elimination—E1

TABLE 8.3 Characteristics of the E1 Mechanism

Characteristic	Result
Kinetics	• First order
Mechanism	• Two steps
Identity of R	• More substituted halides react fastest • Rate: $\text{R}_2\text{CX} > \text{RCH}_2\text{X} > \text{RCH}_2\text{X}$
Base	• Favored by weaker bases such as $\text{H}_2\text{O}$ and $\text{ROH}$
Leaving group	• A better leaving group makes the reaction faster because the bond to the leaving group is partially broken in the rate-determining step.
Solvent	• Polar protic solvents that solvate the ionic intermediates are needed.

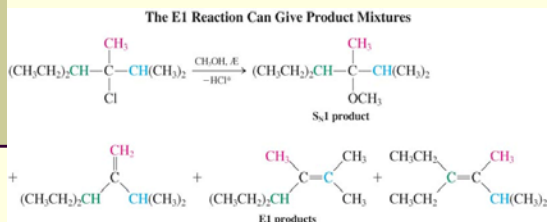
## The E1 Reaction

- E1 reaction involves a carbocation
- Therefore rearrangements must be considered



## The E1 Mechanism

Several Products are Possible



## The E1 Reaction: Stereochemistry

- With C<sup>+</sup> both syn and anti elimination can occur, so E1 reaction forms both E and Z products regardless of whether  $\beta$ -carbon is bonded to one or two H's
- Product stability leads to stereoselectivity but not stereospecificity

