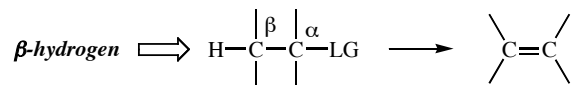




Elimination Reactions

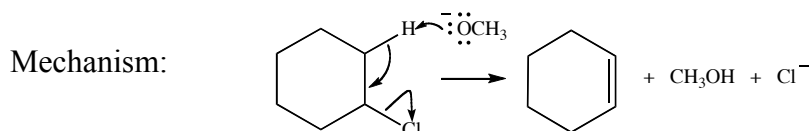
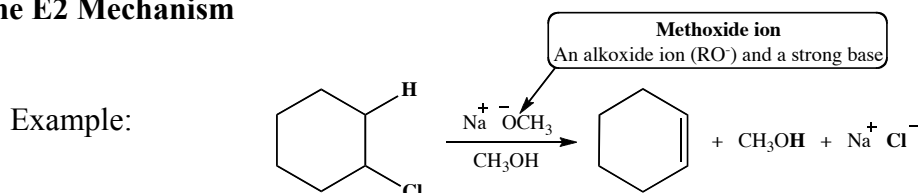
Elimination reaction: A reaction in which a molecule loses atoms or groups of atoms, usually from adjacent atoms, often resulting in a new pi bond.



- Called β -elimination (most common elimination reaction)
- Useful reaction to synthesize alkenes, alkynes, other pi bond functional groups

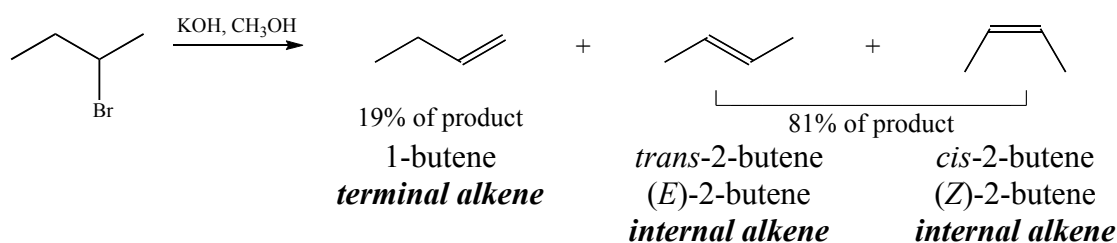
Alkene stereochemistry nomenclature	
<u>Cis and trans: carbon chain position</u>	<u>E and Z: Cahn-Ingold-Prelog priorities</u>
 <p>cis trans</p>	 <p>Z E</p> <p>(zusammen = together) (entgegen = against)</p>
<i>May be ambiguous</i>	<i>Never ambiguous</i>

The E2 Mechanism



Kinetics: rate = k [R-Cl] [CH₃O⁻] Elimination Bimolecular → **E2**

What if more than one alkene product is possible?



Zaitsev's Rule: Major product of E2 reaction is more substituted alkene.

How can we rationalize the major product?

Two explanations to explore....

- When reactions compete, fastest reaction gives major product (kinetic control)
- More stable product is major (thermodynamic control)

Explanation #1: Fastest reaction gives major product

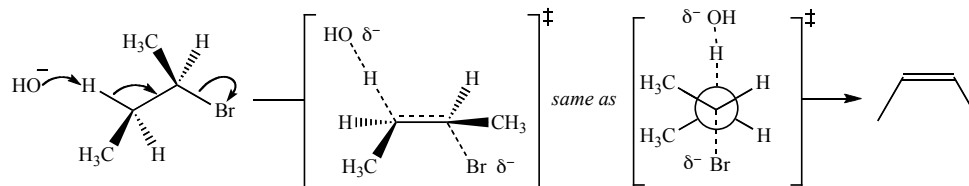
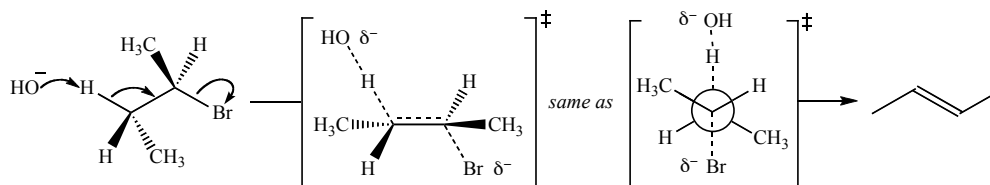
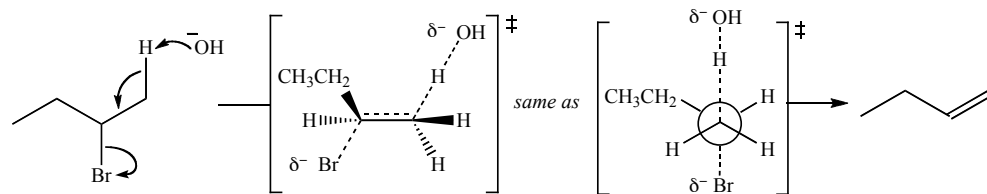
Example: Reactants \rightarrow A + B

When $E_{\text{act}}(\text{A}) < E_{\text{act}}(\text{B}) \rightarrow \text{Rate A} > \text{rate B}$
 \rightarrow A is major product
 \rightarrow **Faster product is major**

Transition state energy: torsional strain considerations

Useful vocabulary:

- Dihedral angle: angle formed between two planes (three atoms define a plane)
- Periplanar = coplanar: lying in the same plane
- Anti-periplanar: dihedral angle is 180° Syn-periplanar: dihedral angle is 0°



- Anti-periplanar arrangement of H-C and C-Br bonds: When H-C and C-Br bonds cannot be periplanar E2 cannot occur via this conformation. *Syn-periplanar E2 possible, but rare.*
- Transition state stability: Torsional strain influences E_{act} .

Prediction based on transition state torsional strain:

1-butene (greatest amount formed) > (*E*)-2-butene > (*Z*)-2-butene (least amount)

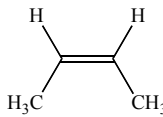
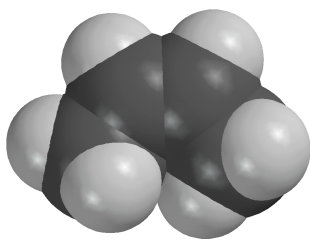
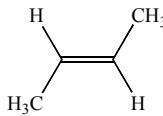
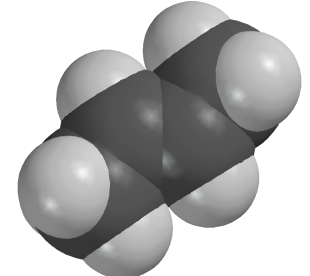
Transition state considerations alone are not sufficient to explain E2 major product.

Explanation #2: More stable product is major

- Transition state energy also influenced by product stability

Alkene stability: steric strain

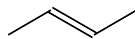
- Atoms/groups attached to alkene sp^2 carbons lie in same plane \rightarrow eclipsed!
- Prediction: Increasing steric strain decreases alkene stability

<u>Alkene</u>	<u>Structure</u>	<u>Space Filling Model</u>	<u>Strain</u>
<i>cis</i> -2-butene			More steric strain
<i>trans</i> -2-butene			Less steric strain

Conclusion: Trans alkene more stable than cis alkene

Warning!!! E not always more stable than Z

Alkene stability: internal versus terminal



An internal alkene



A terminal alkene

General rule: Internal alkene more stable than terminal alkene

Alkene stability: number of $C_{sp^2}-C_{sp^3}$ bonds

- Fact: Bonds to sp^2 carbon are stronger (i.e., more stable) than bonds to sp^3 carbon.

BDE = Bond dissociation energy. Higher BDE = stronger bond

Relevant BDE (kcal mol^{-1}):

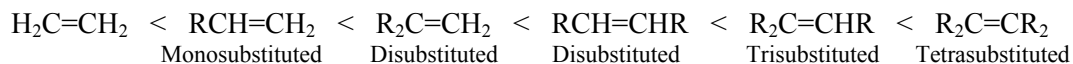
$C_{sp^3}-C_{sp^3}$	89	$C_{sp^2}-C_{sp^3}$	102
$C_{sp^3}-H$	98	$C_{sp^2}-H$	109 ← sp^2 bonds stronger

- Conclusion: Alkene isomer with more bonds to $C=C$ is more stable.

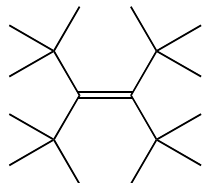
Example: 1-butene versus *E*-2-butene

$C_{sp^2}-C_{sp^3}$	2 x 102 = 204	1 x 102 = 102
$C_{sp^3}-C_{sp^3}$	0 x 89 = 0	1 x 89 = 89
$C_{sp^2}-H$	2 x 109 = 218	3 x 109 = 327
$C_{sp^3}-H$	6 x 98 = 588	5 x 98 = 490
Total (kcal mol^{-1})	= 1010 <i>more stable</i>	= 1008 <i>less stable</i>

General alkene stability trend



Caveat: Steric strain can become quite severe!

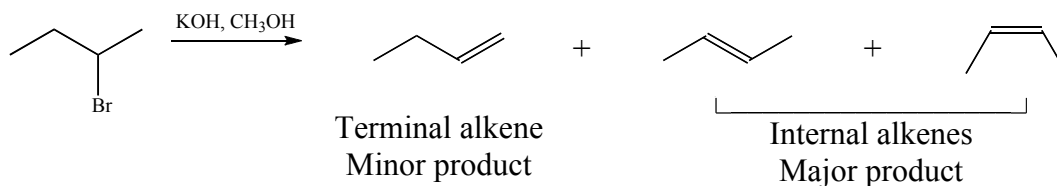


Tetra-*tert*-butylethylene

- Tetrasubstituted alkene
- Severe steric strain
- Has never been synthesized

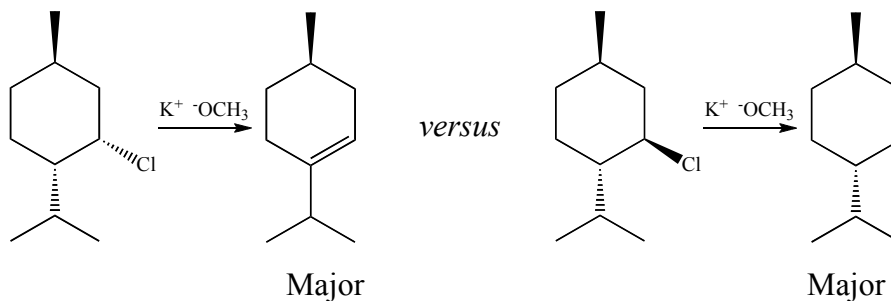
General rule: For alkene stability, number of alkyl groups outweighs steric strain unless steric strain is severe.

E2 major product prediction based on alkene stability:



This is consistent with empirical data and Zaitsev's Rule.

Caution: Periplanarity requirement can override alkene stability...



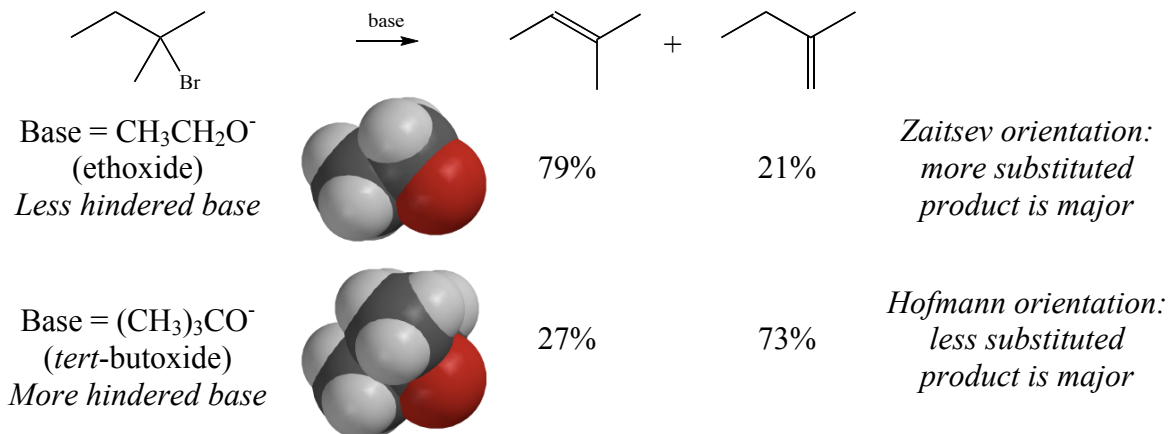
Explore this example in more depth in Thinkbook practice problems.

General rule: Reaction major product = most stable product, unless other factors override.

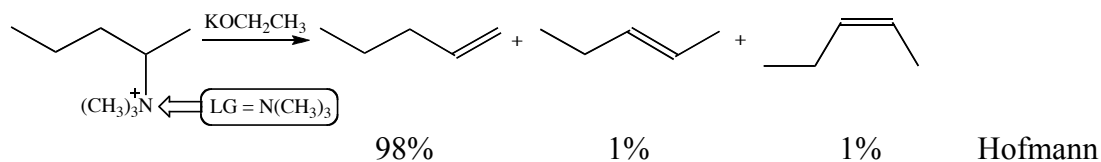
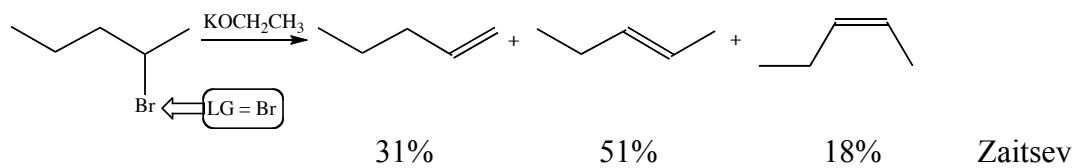
Exceptions to Zaitsev's Rule

Hofmann's Rule: Less substituted alkene is major.

(a) Less substituted alkene is major when base is sterically hindered.

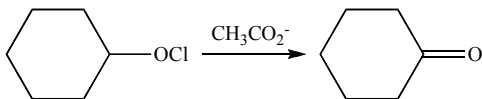
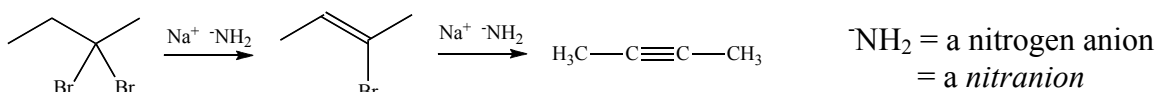


(b) Less substituted alkene is major when leaving group is NR_3 , SR_2 , or F^- .



E2 reactions of alkyl fluorides require harsh conditions, and are thus not very practical.

Other E2 Examples

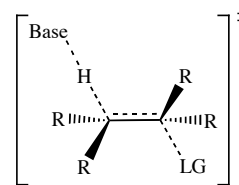


Work out the mechanisms!

E2 Reaction Requirements

Does my E2 reaction occur at a useful rate?

How to make E_{act} low enough for reaction to proceed at a useful rate?

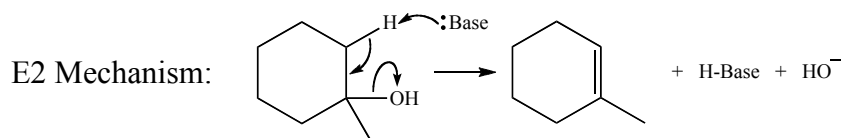
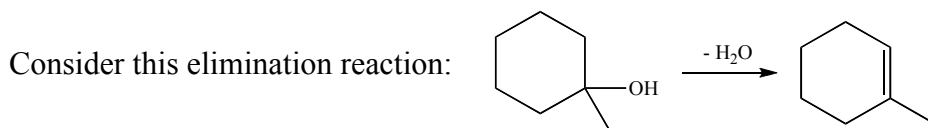


The E2 Reaction Checklist

- Strong base: usually HO^- or RO^- ; *not* ROH .
 - Leaving group: Must be moderate or better.
 - Molecular geometry: C-leaving group and β C-H bonds must be periplanar.
- } Interdependent

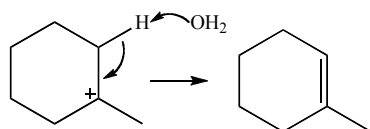
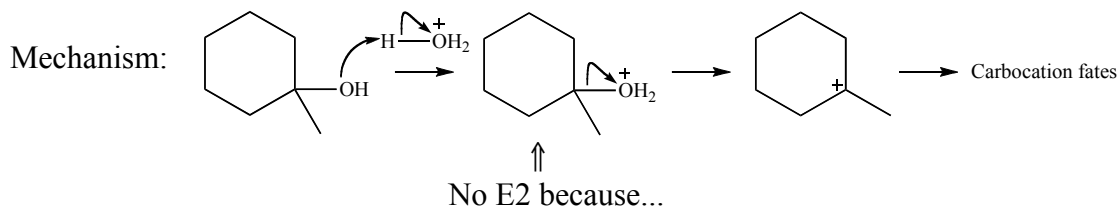
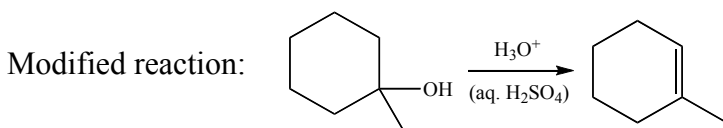
* *Despite reduction of basicity by H-bonding, HO^- and RO^- in ROH are still sufficiently basic for E2.*

The E1 Mechanism



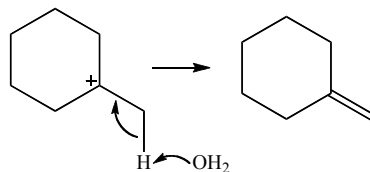
This E2 mechanism is unacceptable because...

Solution:



Trisubstituted, internal alkene

- More stable alkene
- *Major product*



Disubstituted, terminal alkene

- Less stable alkene
- *Minor product*

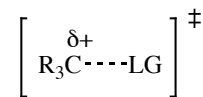
Kinetics: rds = ionization to form carbocation (similar to $\text{S}_{\text{N}}1$).

Rate = $k [\text{ROH}_2^+]$ Elimination Unimolecular \rightarrow **E1**

E1 Reaction Requirements

Does my E1 reaction occur at a useful rate?

How to make E_{act} low enough for reaction to proceed at a useful rate?



- Same rds as S_N1 → Same requirements as S_N1

The E1 Reaction Checklist

Leaving group: Must be moderate or better.

Carbocation: 2° or higher stability

Solvent: High polarity necessary; protic preferred

} Interdependent

Elimination vs. Substitution: Which Mechanism?

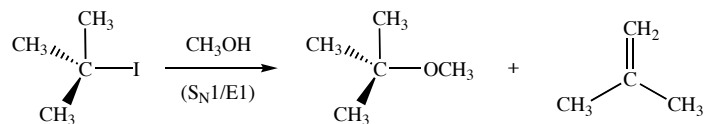
- *Carbocation formation is energetically expensive.* Consider E2 and S_N2 (mechanisms without carbocations) before E1 and S_N1 (mechanisms with carbocations).
- Consider E2 before S_N2 . **Exception:** 1° alkyl halides: consider S_N2 before E2.

Therefore the order of preference is:

E2 } S_N2 } E1/ S_N1	Except 1° alkyl halides where S_N2 is considered before E2.
--------------------------------	---

Borderline cases involve a hybrid or mixed mechanism.

A Final Thought Concerning S_N1 and E1 Reaction Rates



Rate data: $k_{\text{Artic}} \sim k_{\text{Antarctic}} \gg k_{\text{Equator}}$

Why these rates? Consider transition state of rate-determining step (ionization of carbon-iodine bond)...

