

# **Alkenes**

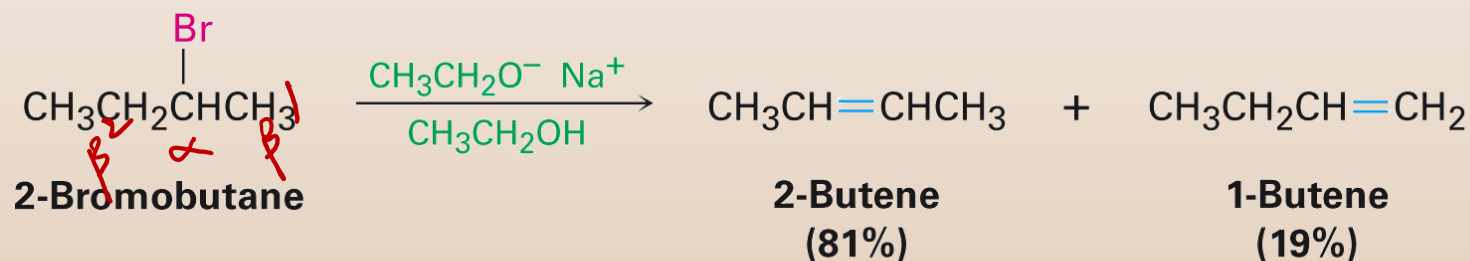
## **3- Elimination**

### **Other Considerations**

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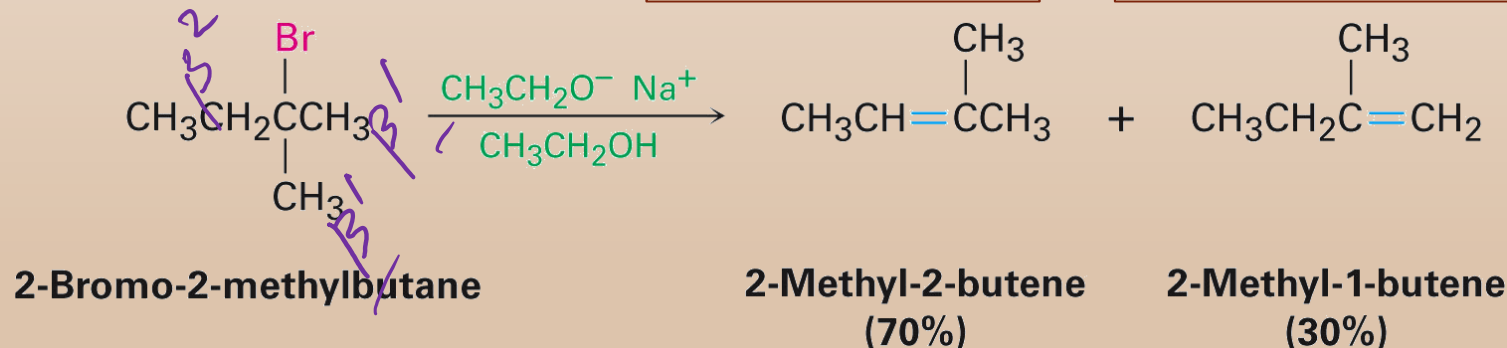
# Regioselectivity - Zaitsev's Rule

- In the elimination of HX from an alkyl halide, the more highly substituted alkene product predominates.
- Occurs in E1 and E2



Zaitsev's product

Hoffman's product

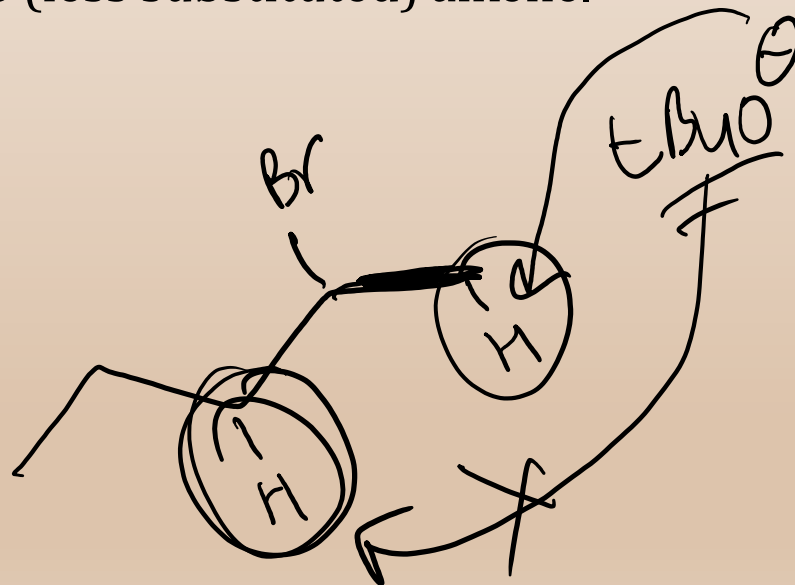


Zaitsev's product

Hoffman's product

# Regioselectivity - ...contd

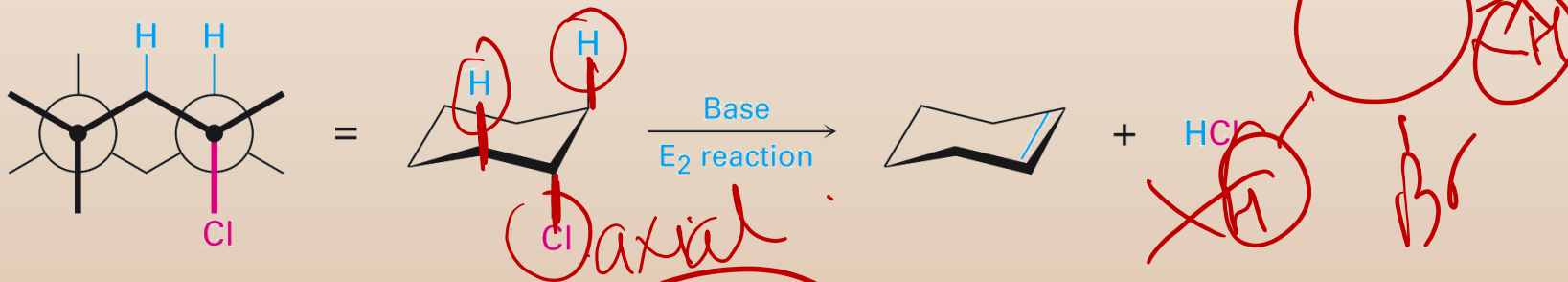
- E1: major product is ALWAYS the more stable alkene (Zaitsev's product)
- E2: with strong base, the major product is the more stable (more substituted) alkene (Zaitsev's product).
- E2: with a strong, sterically hindered base such as *tert*-butoxide, the major product is often the less stable (less substituted) alkene.



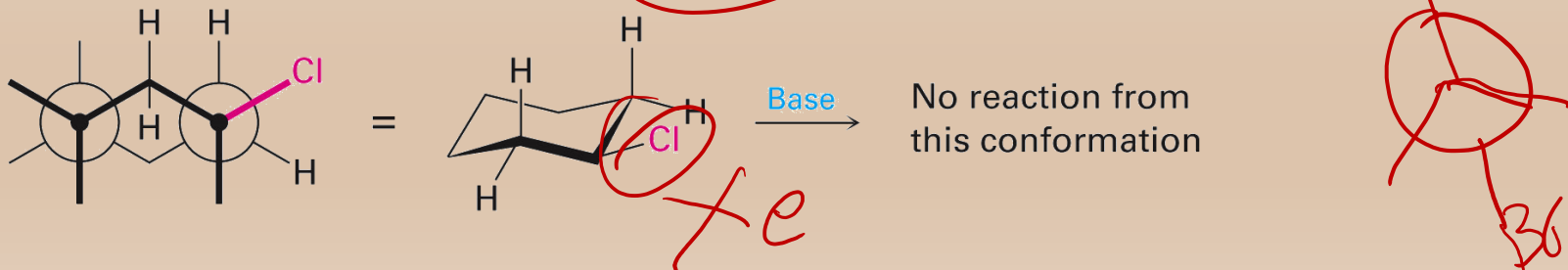
# Stereoselectivity –in E2 only

- E2 is most favorable (lowest activation energy) when H and LG are oriented anti and coplanar.
- In the examples below for anti periplanar elimination in cyclohexane, the equatorial groups are not in proper alignment for elimination.

**Axial chlorine: H and Cl are anti periplanar**

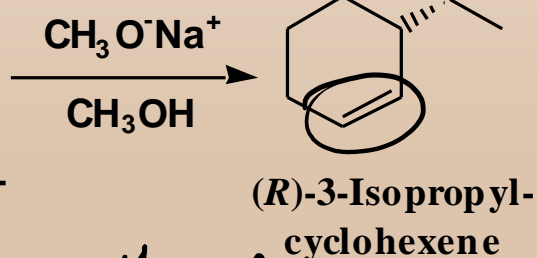
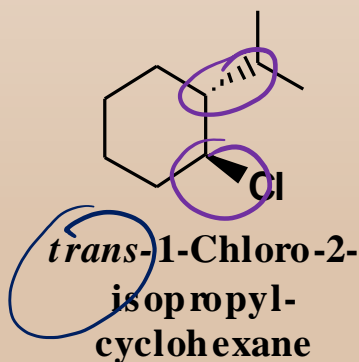
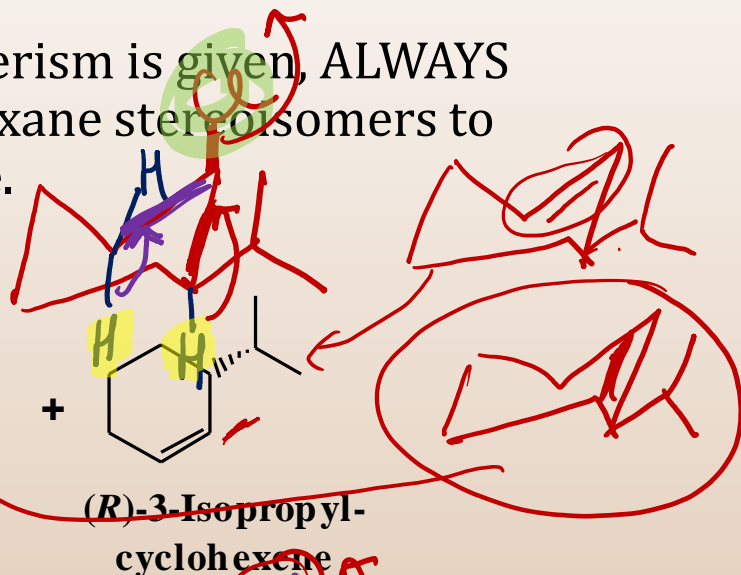
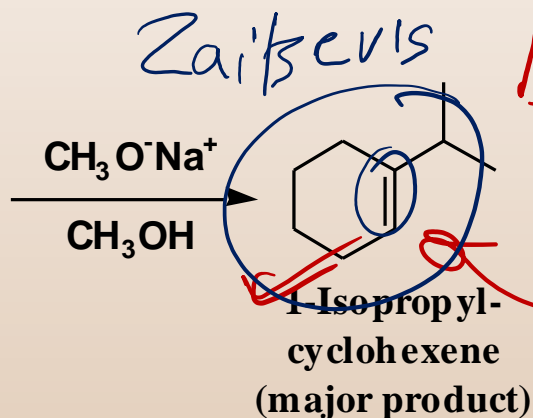
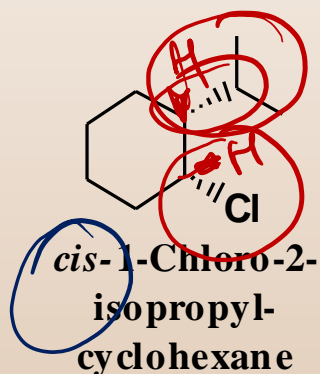


**Equatorial chlorine: H and Cl are not anti periplanar**

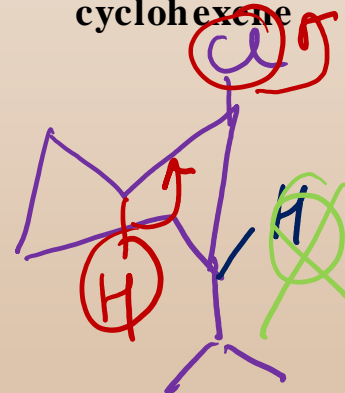


# Problem

In a problem like below, where cis/trans isomerism is given, ALWAYS draw the conformers for the following cyclohexane stereoisomers to identify the antiperiplanar groups to eliminate.



Hoffman



# Review – Synthesis of Alkenes

- Most synthesis of alkenes are elimination reactions.
  - Elimination – dehydrohalogenation
  - Elimination – dehydration
- Elimination gives two kinds of products
  - Zaitsev's product
  - Non-Zaitsev's product (Hoffman product)
- Anti periplanar elimination occurs in very specific conformations
- Rearrangements during carbocation transition state formation

# Conditions of Elimination

Condition	E1	E2
Mechanism	1 <sup>st</sup> order	2 <sup>nd</sup> order
Rate	Dependent on only one chemical – the substrate	dependent on two chemicals – the substrate and Nu <sup>-</sup>
Substrate	should form a stable carbocation, so 3 <sup>o</sup>	should be 1 <sup>o</sup> for better results
Bases	Does not need a strong base	Needs a strong base to cause elimination
Solvent	polar	Non polar
Competes	With S <sub>N</sub> <sup>1</sup>	With S <sub>N</sub> 2
Stereochemistry	Regiospecific (gives Zaitsev's product as major product)	Stereospecific (needs the H and leaving groups to be anti-periplanar)

# Substitution or Elimination?

	Substitution	Elimination
Nucleophile strength	Strong Nu but weak base – S <sub>N</sub> 2	Strong Nu – E2
Nucleophile size	Small	Bulky
Substrate	Primary – S <sub>N</sub> 2	Tertiary - S <sub>N</sub> 1, E1 or E2
Temperature		Higher temp - > more E

## E2 vs S<sub>N</sub>2

3° halide and bulky base promote E2

## E1 vs S<sub>N</sub>1

High heat promotes E1

## Types of Alkyl Halides

1° – will almost always give S<sub>N</sub>2

2° – primarily S<sub>N</sub>2 except when using a bulky base

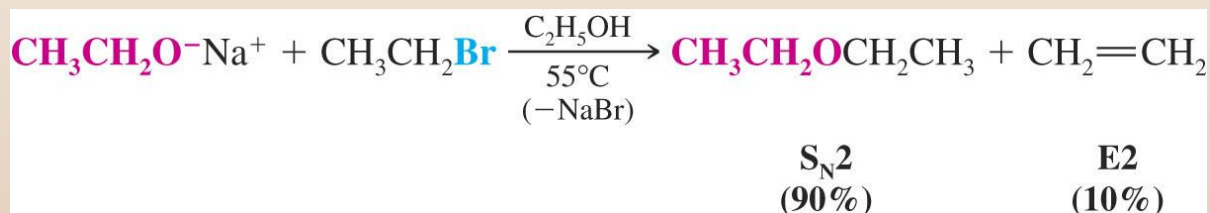
3° – S<sub>N</sub>1, E1 or E2. Strong base and high temperature promotes E



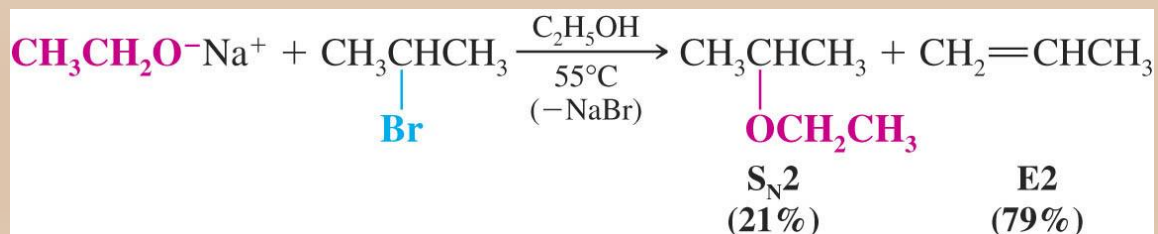
# Substitution or Elimination?

Look at the conditions and then decide.

- Primary substrate
  - If the base is small,  $S_N2$  competes strongly because approach at carbon is unhindered



- Secondary substrate
  - Approach to carbon is sterically hindered and E2 elimination is favored



# Key Words/Concepts

- Dehydrohalogenation
- Dehydration of alcohols
- Zaitsev's and Hoffman's product
- Anti coplanar elimination
- Stability of carbocation
- Rearrangement of carbocation intermediate
- Hydride, methyl and phenyl group shifts