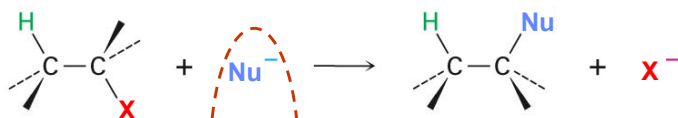
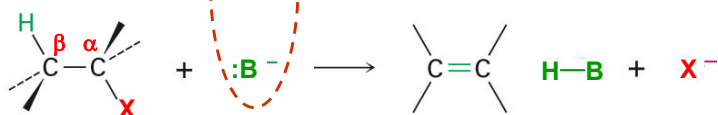


β-Elimination Reactions

Substitution



Elimination



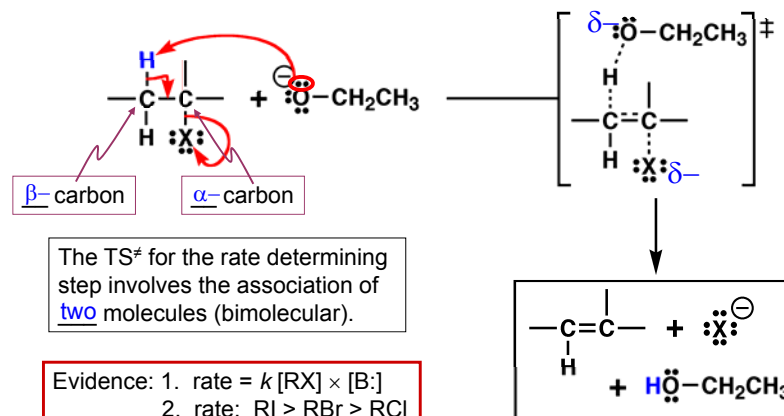
As **nucleophiles** more than often are **basic** reagents, in many cases substitution and elimination reactions simultaneously occur as competitive processes.

6-1

β-Elimination Mechanism I

There are two mechanisms by which β-elimination reactions take place

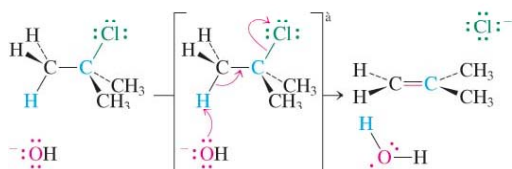
(1) All bond breaking happens simultaneously with pi-bond making. The __ pathway (**E**limination, **B**imolecular)



6-2

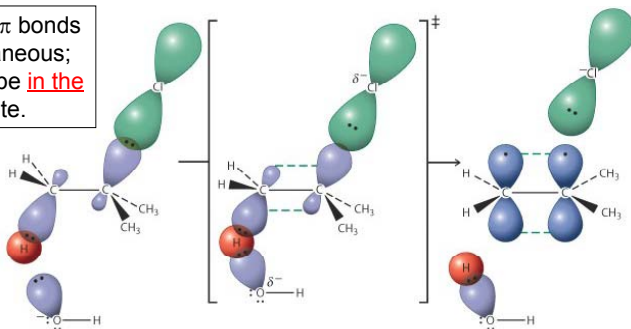
Stereochemistry of the E2 Mechanism

The E2 Reaction Mechanism



The E2 reaction pathway has very specific requirements: There must be **continuous overlap** among the orbitals in which σ bonds are broken and π bonds are made.

σ bonds dissociation and π bonds formation must be simultaneous; all orbitals involved must be **in the same plane** in the TS[‡] state.

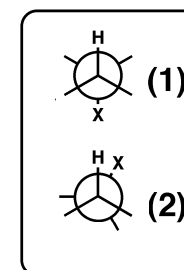


Conformational Requirements of the E2 Elimination

Two conformations satisfy the requirement:

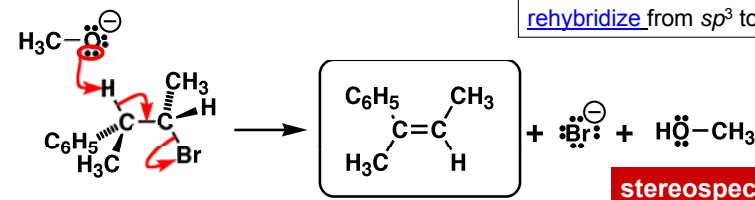
(1) -X and -H oriented **anti-periplanar**

(2) -X and -H oriented **syn-periplanar**



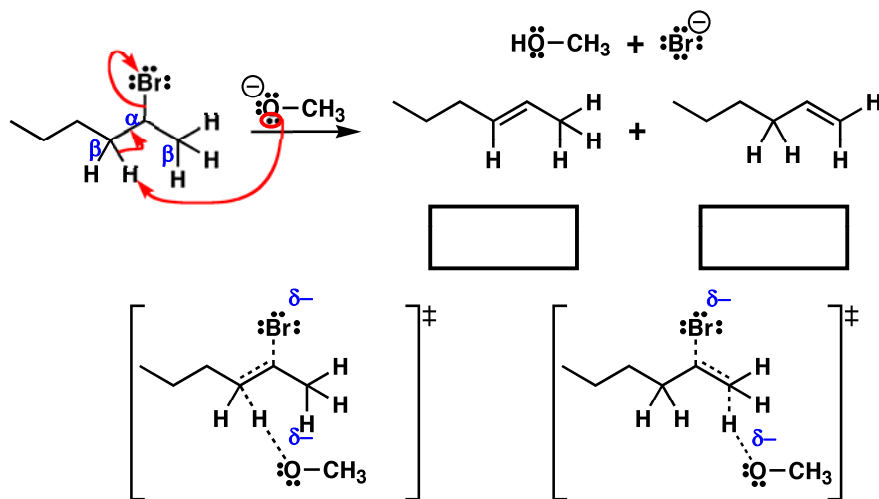
Most E2 reactions proceed through (1) leading to important stereochemical implications

The carbon atoms smoothly **rehybridize** from sp^3 to sp^2



6-4

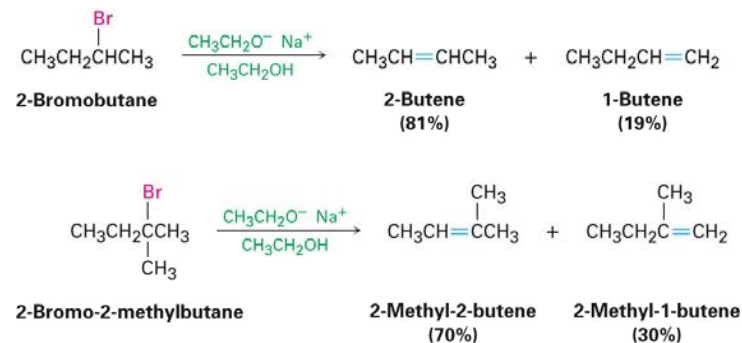
Regiochemistry of E2 Elimination Reactions



6-5

Regioselectivity of β -Elimination: Zaitsev's Rule

Zaitsev's rule: In the elimination of HX from an alkyl halide, the more highly substituted alkene product predominates.

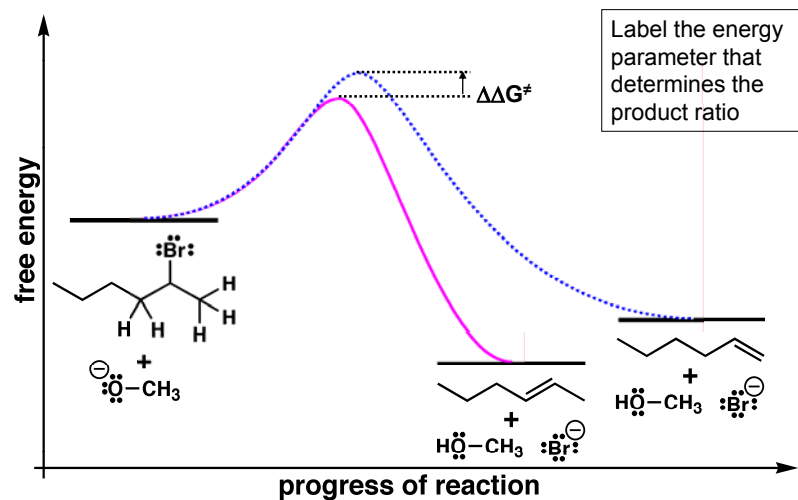


E2: Double bond character is highly developed in the TS[‡] so the relative stability of possible alkenes determines the major product.

The more stable the alkene product, the faster the reaction proceeds.

6-6

Product Ratio for E2 Elimination Reactions

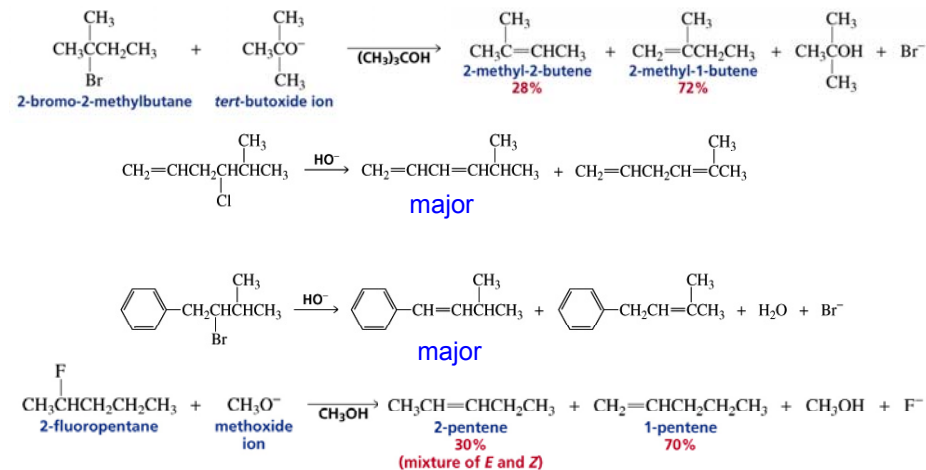


6-7

Exceptions to Zaitsev's Rule

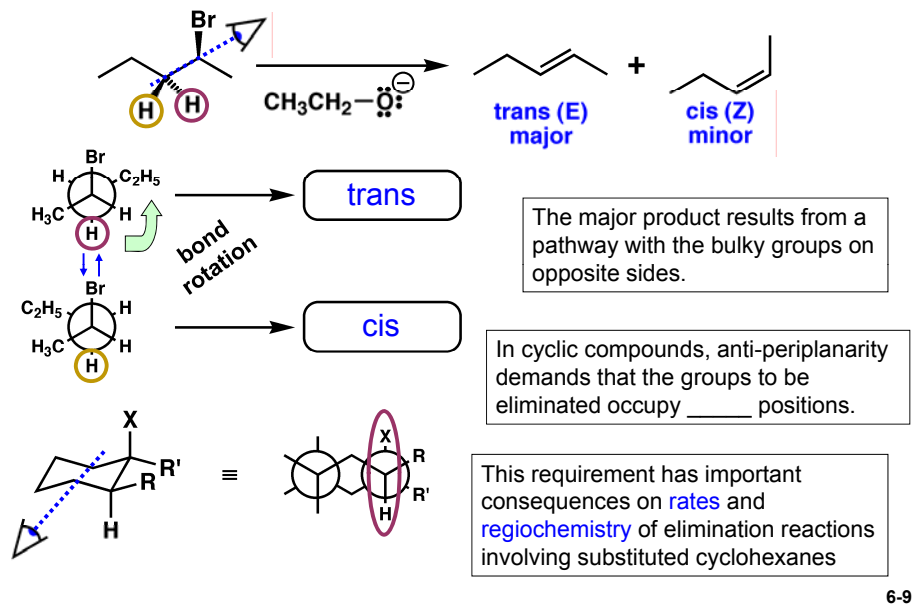
The less substituted product is major when

- A bulky base is used (a steric issue)
- A conjugated double bond can form
- The leaving group is -F



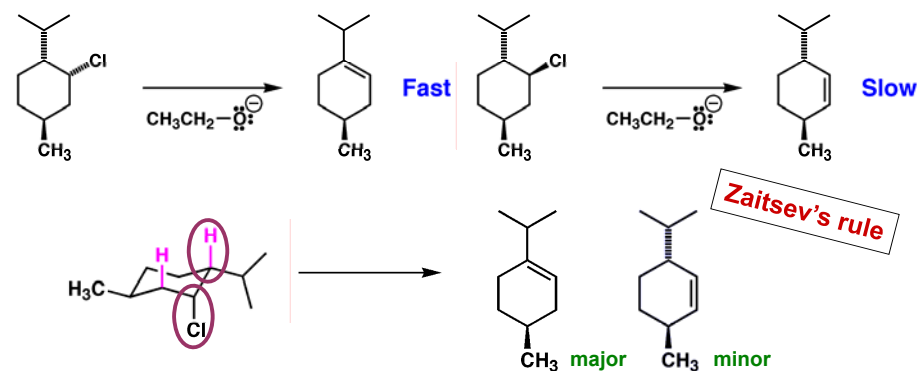
6-8

Stereochemistry in E2 Pathway



E2 Elimination Reactions in Substituted Cyclohexanes

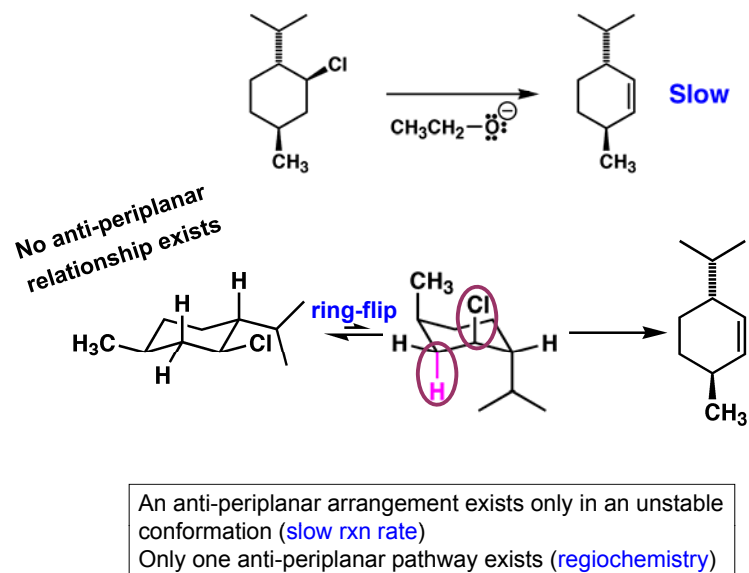
Explain the reason for the difference in relative **rates** and **regiochemistry** in the following examples:



Two anti-periplanar pathways are possible from the most stable chair conformation. The observed product follows the pathway leading to the more substituted alkene

6-10

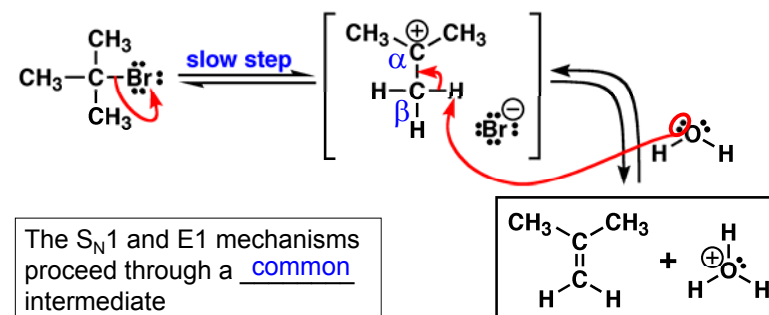
E2 Reactions in Substituted Cyclohexanes



6-11

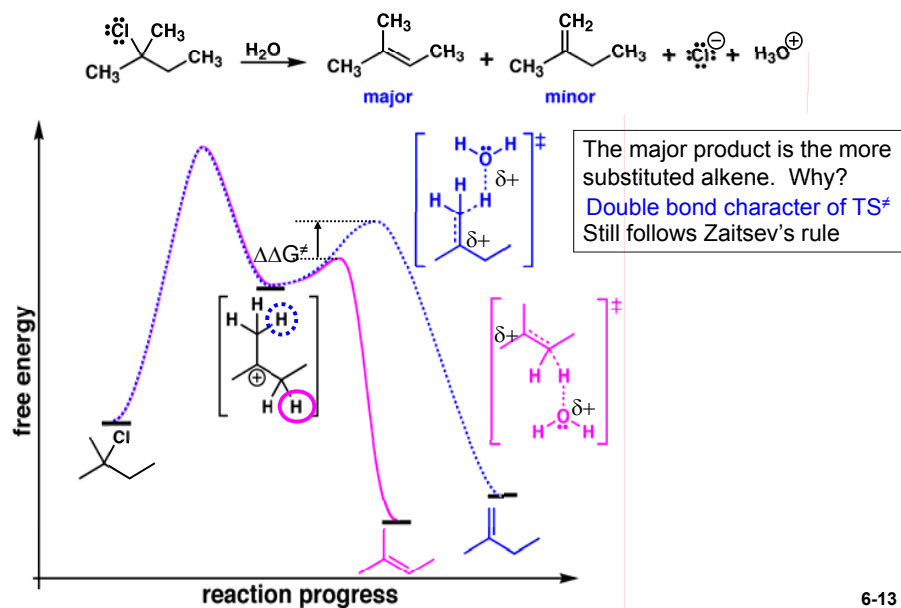
β -Elimination Mechanism II

(2) Bond breaking **precedes** bond making. The _____ pathway (**E**limination, **U**nimolecular)



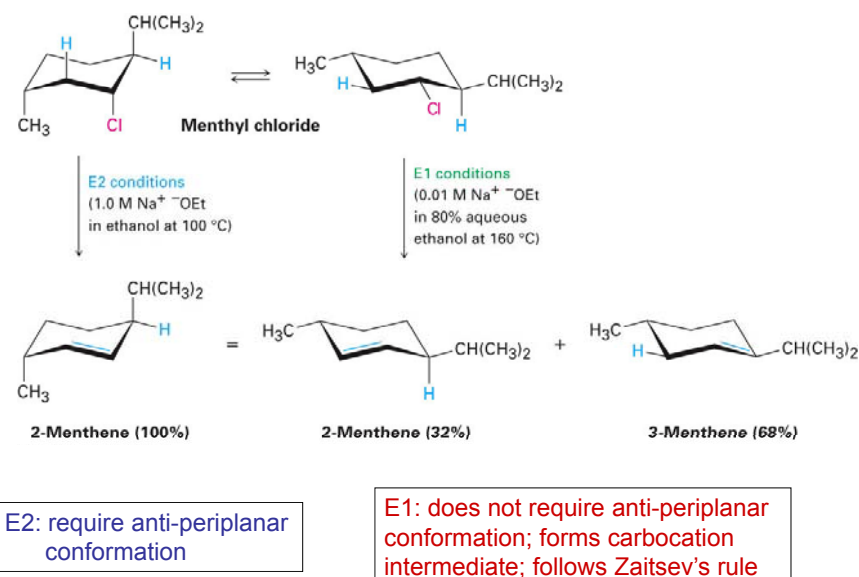
6-12

Regiochemistry of E1 Elimination Reactions



6-13

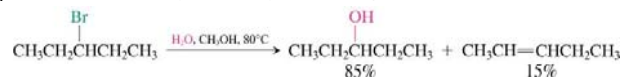
Stereochemistry of E1 Reaction



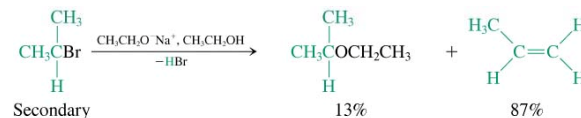
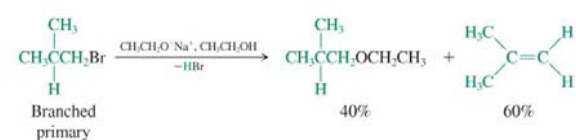
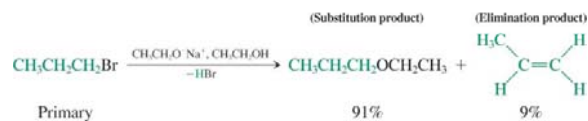
6-14

Competition between Substitution and Elimination

- S_N1 and E1 pathways usually occur together with weak nucleophiles

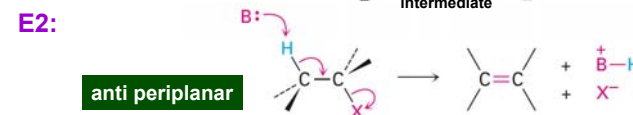
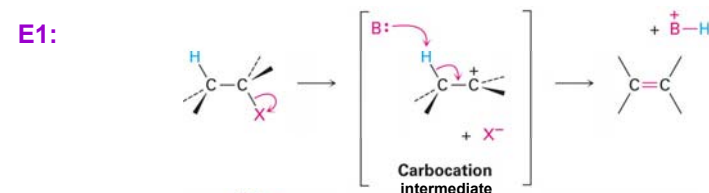


- More elimination than substitution occurs as steric bulk increases.

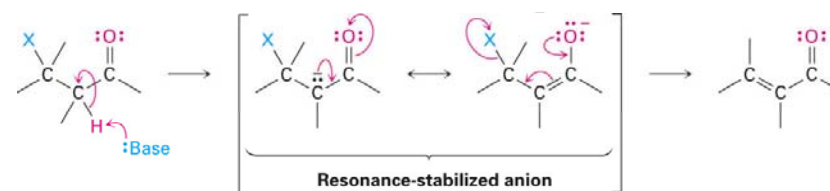


6-15

E1cb Reaction: a Third Mechanism of β-Elimination



E1cb: Elimination, Unimolecular, conjugate base intermediate



6-16