

# Highlights of Elimination Reaction

- Elimination Reactions.
- E1 & E2 Reactions & Mechanisms.
- Energy Diagrams of E1 & E2.
- Transition States of E1 & E2.
- Characteristics of E1 & E2.
- The Saytzeff Rule (Z-rule).
- Elimination with Bulky Leaving Groups and Bulky Bases -- Hofmann Rule -- E2

# Elimination Reactions

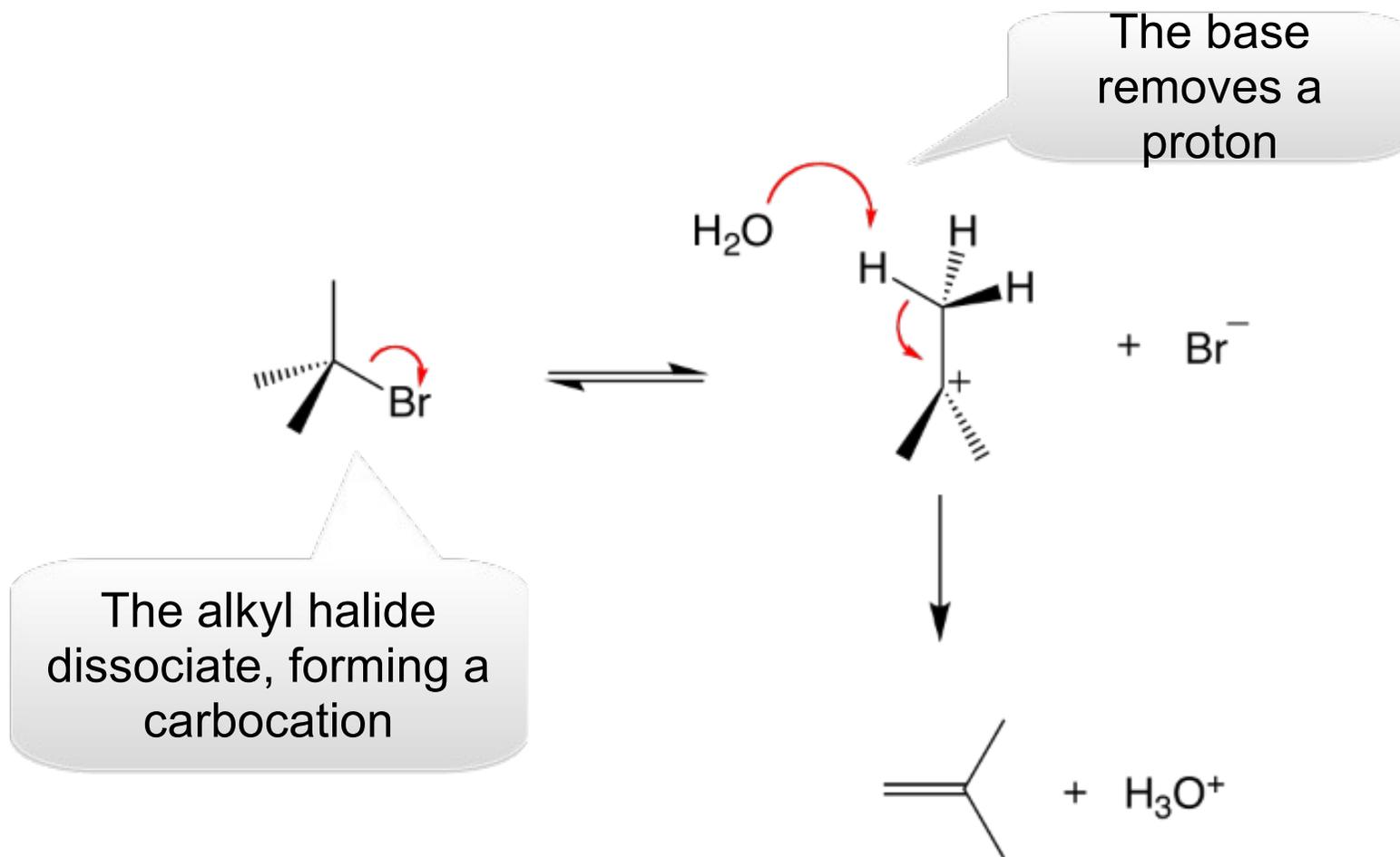
- An **elimination reaction** is a type of [organic reaction](#) in which two [substituents](#) are removed from a molecule in either a one or two-step mechanism.
- Either the [unsaturation](#) of the molecule increases (as in most organic elimination reactions) or the valence of an atom in the molecule decreases by two, a process known as [reductive elimination](#).
- An important class of elimination reactions are those involving [alkyl halides](#), or alkanes in general, with good [leaving groups](#), reacting with a [Lewis base](#) to form an [alkene](#) in the reverse of an [addition reaction](#). When the substrate is asymmetric, [regioselectivity](#) is determined by [Saytzeff rule](#).

The one and two-step mechanisms are named and known as **E2 reaction** and **E1 reaction**, respectively.

# E1 Reactions

- These reactions proceed under neutral conditions where a ***polar*** solvent helps to stabilize the carbocation intermediate.
- This solvent also acts as a weak base and removes a proton in the fast step.
- These types of reactions are referred to as ***solvolysis*** reactions.

# The E1 Reaction



The mechanism shows that an E1 reaction is a two-step reaction

# Alkyl Halides and Elimination Reactions

## Mechanisms of Elimination—E1

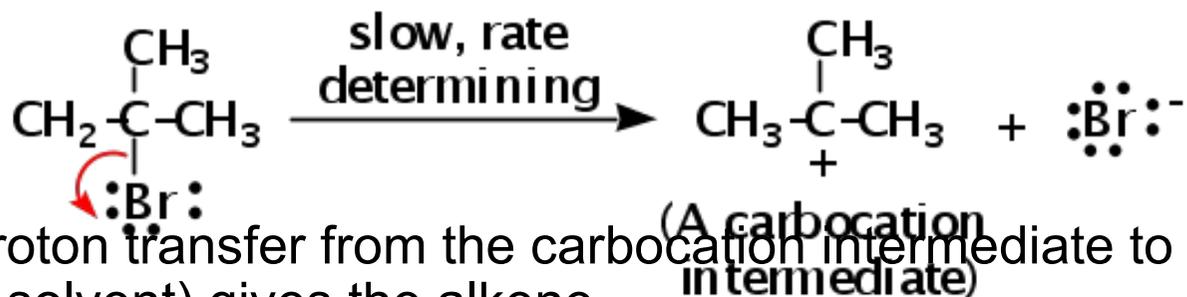
- An E1 reaction exhibits first-order kinetics:

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

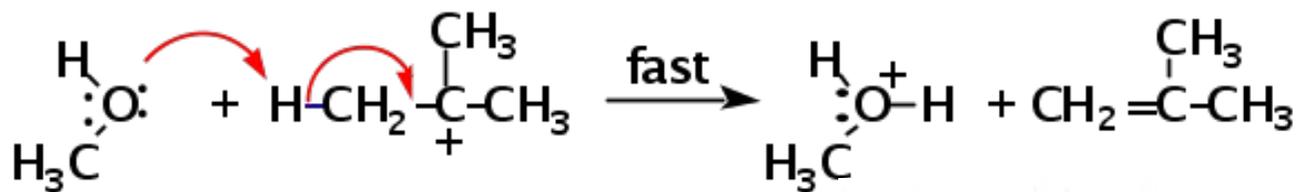
- The E1 reaction proceeds via a two-step mechanism: the bond to the leaving group breaks first before the  $\pi$  bond is formed. The slow step is unimolecular, involving only the alkyl halide.
- The E1 and E2 mechanisms both involve the same number of bonds broken and formed. The only difference is 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.

# E1 Mechanism

- Step 1: ionization of C-X gives a **carbocation intermediate**

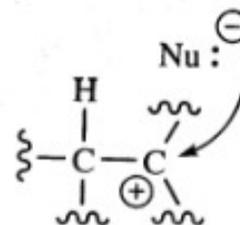


- Step 2: proton transfer from the carbocation intermediate to a base (in this case, the solvent) gives the alkene



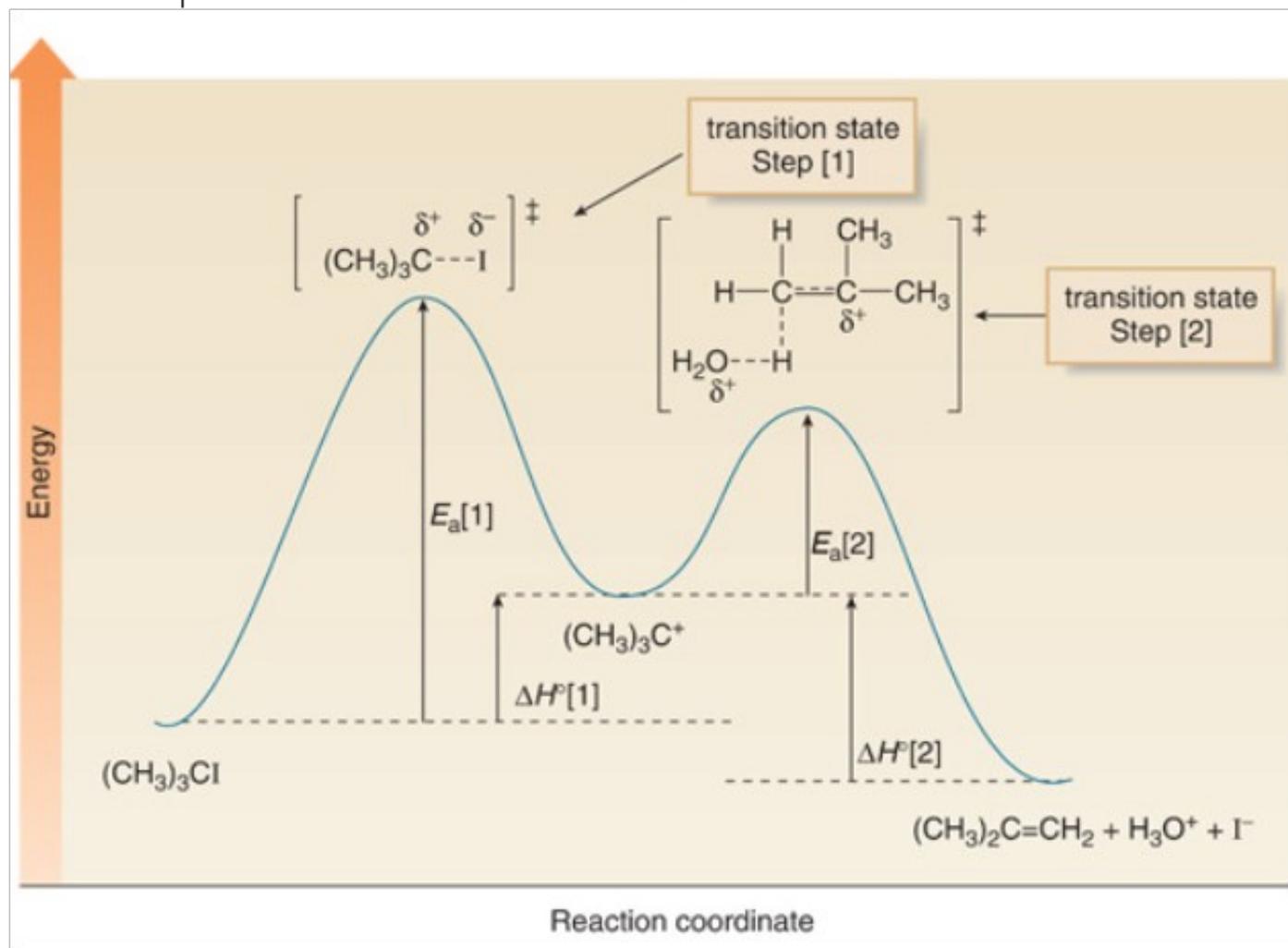
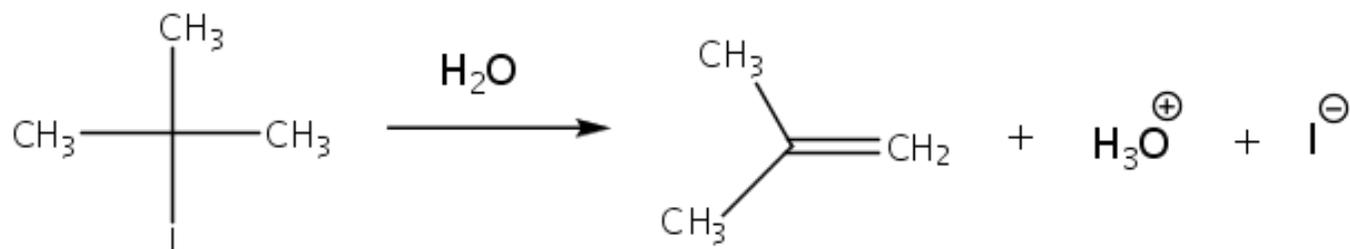
Nucleophile  
-> acting as a  
strong base

compare an  $S_N1$   
mechanism



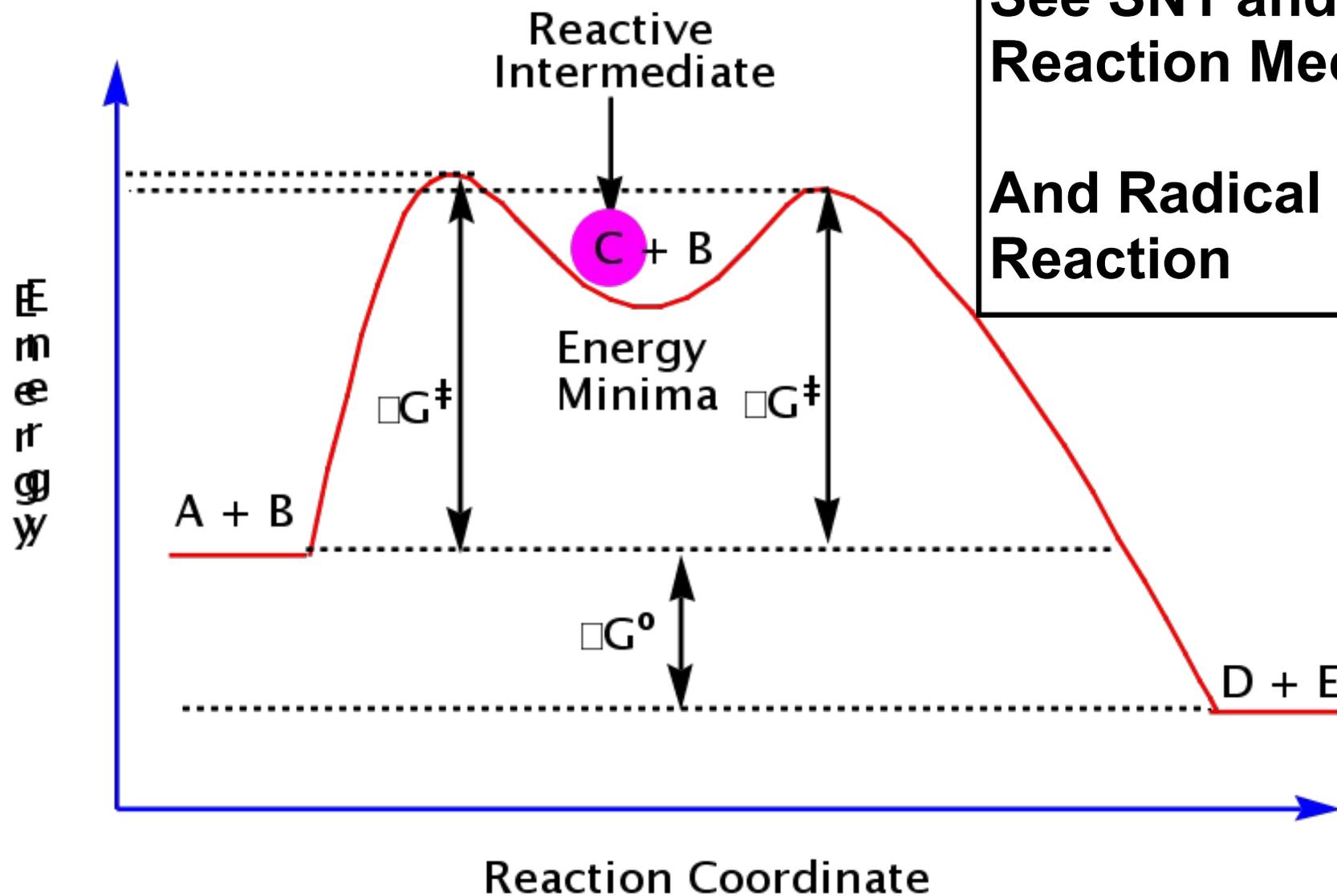
nucleophile  
(acting as  
a nucleophile)

# Energy Diagram for E1



# Transition States

$$\text{Rate} = k[A]$$



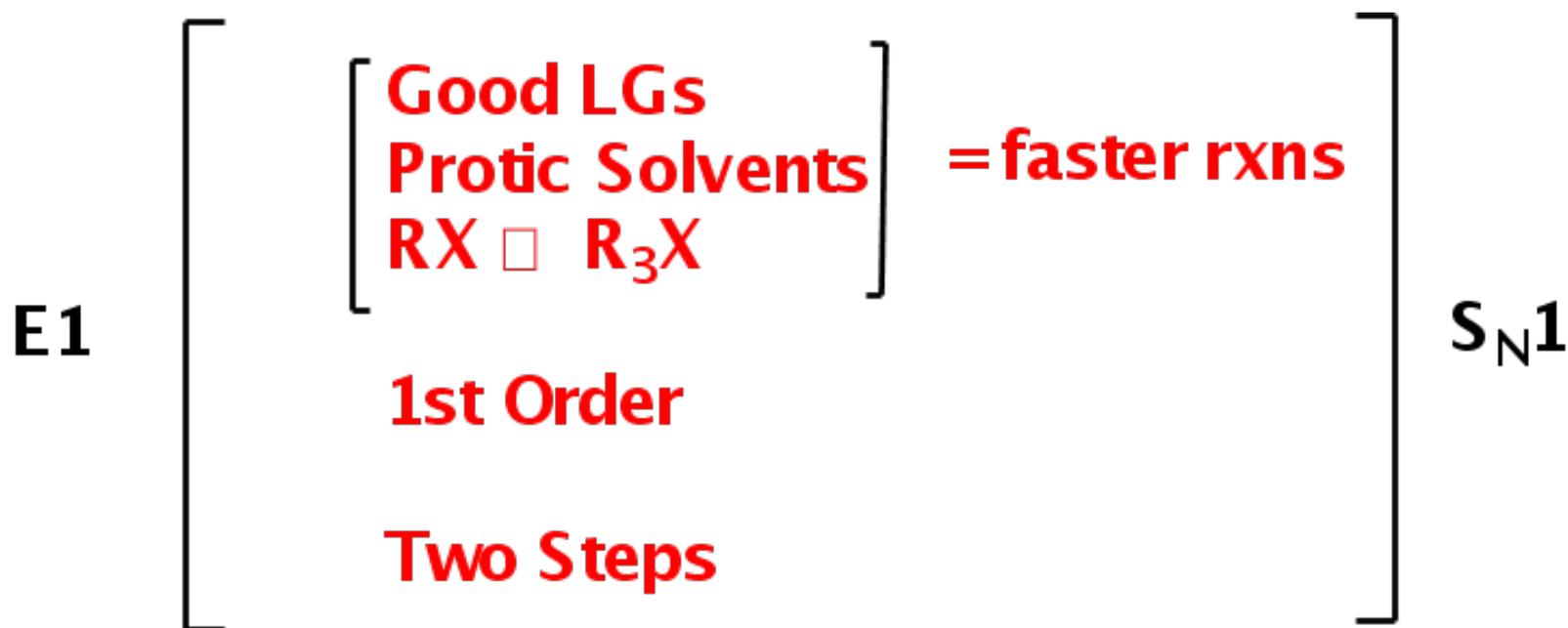
See SN1 and E1  
Reaction Mechanisms

And Radical Chain  
Reaction

**TABLE 8.3** Characteristics of the E1 Mechanism

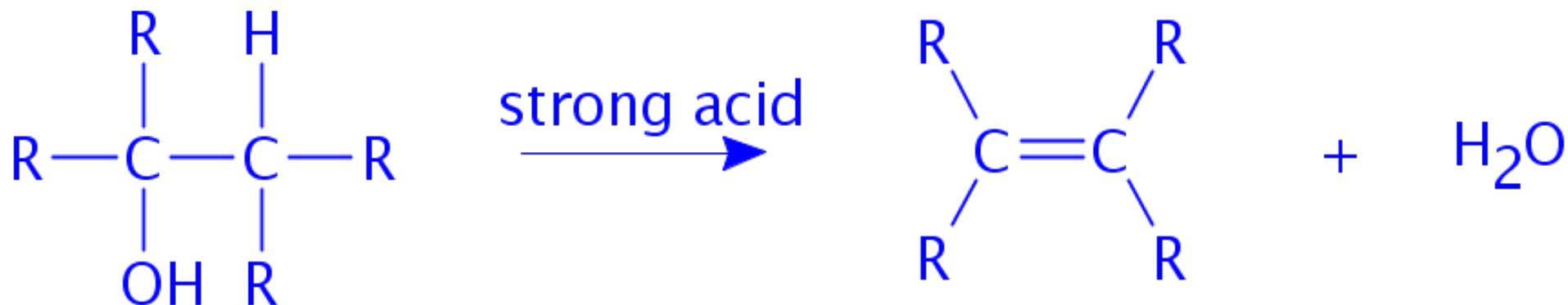
<b>Characteristic</b>	<b>Result</b>
Kinetics	<ul style="list-style-type: none"><li>• First order</li></ul>
Mechanism	<ul style="list-style-type: none"><li>• Two steps</li></ul>
Identity of R	<ul style="list-style-type: none"><li>• More substituted halides react fastest</li><li>• Rate: <math>R_3CX &gt; R_2CHX &gt; RCH_2X</math></li></ul>
Base	<ul style="list-style-type: none"><li>• Favored by weaker bases such as <math>H_2O</math> and <math>ROH</math></li></ul>
Leaving group	<ul style="list-style-type: none"><li>• A better leaving group makes the reaction faster because the bond to the leaving group is partially broken in the rate-determining step.</li></ul>
Solvent	<ul style="list-style-type: none"><li>• Polar protic solvents that solvate the ionic intermediates are needed.</li></ul>

Here are four characteristics that the **E1 / SN1** mechanisms have in common.



# Dehydration of Alcohols

Acid assisted reactions are always E1

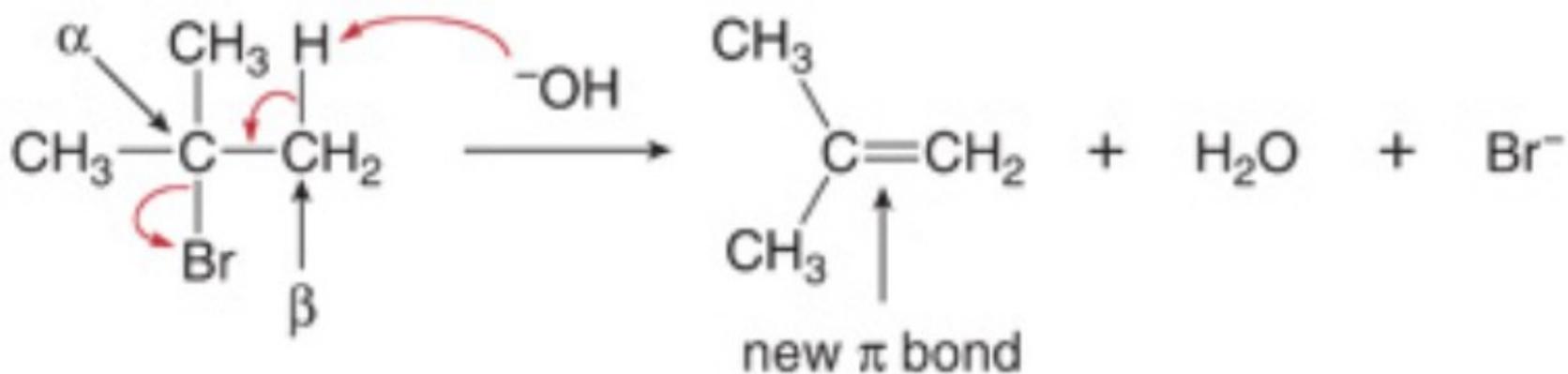


# The E2 Mechanism

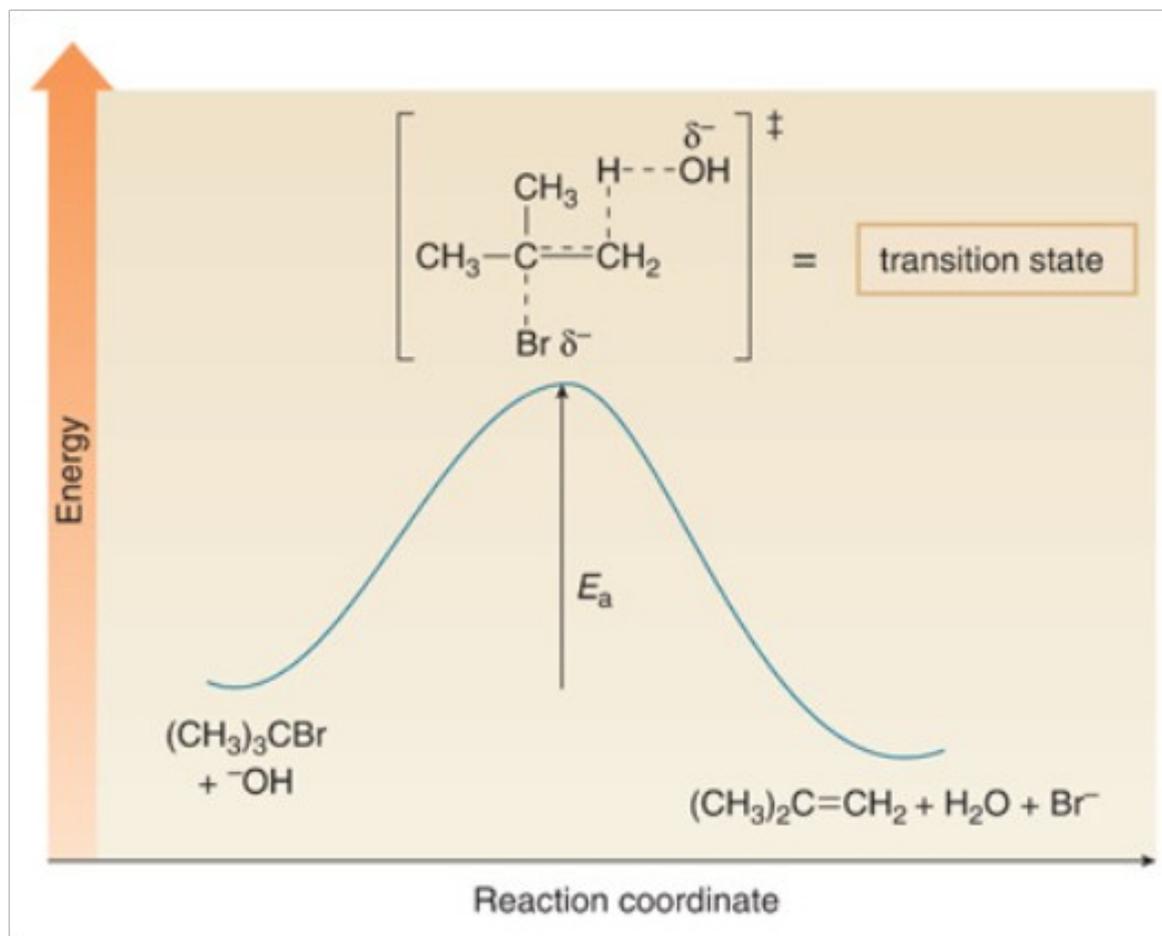


## MECHANISM 8.1

### The E2 Mechanism



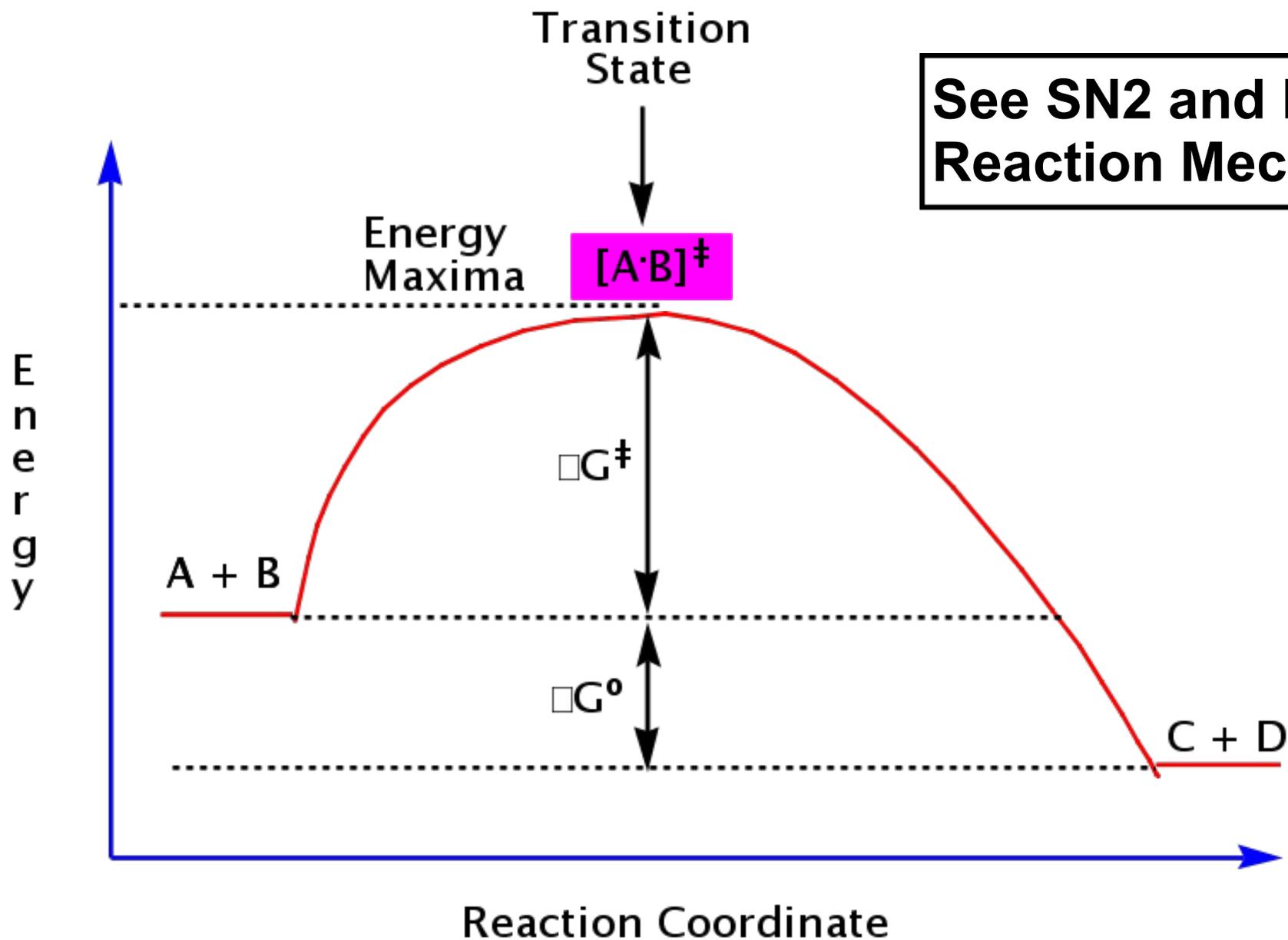
# Energy Diagram for the E2 Mechanism



# Transition States

$$\text{Rate} = k[A][B]$$

See SN2 and E2  
Reaction Mechanisms



**TABLE 8.2 Characteristics of the E2 Mechanism**

<b>Characteristic</b>	<b>Result</b>
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>

# Alkyl Halides and Elimination Reactions

## Mechanisms of Elimination—E2

- The most common mechanism for dehydrohalogenation is the E2 mechanism.
- It exhibits second-order kinetics, and both the alkyl halide and the base appear in the rate equation i.e.

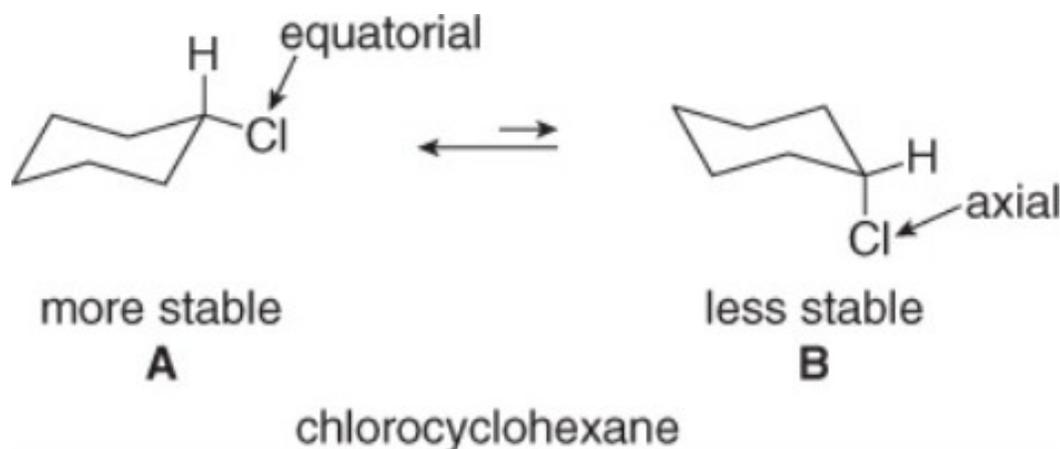


- The reaction is **concerted**—all bonds are broken and formed in a single step.

# Alkyl Halides and Elimination Reactions

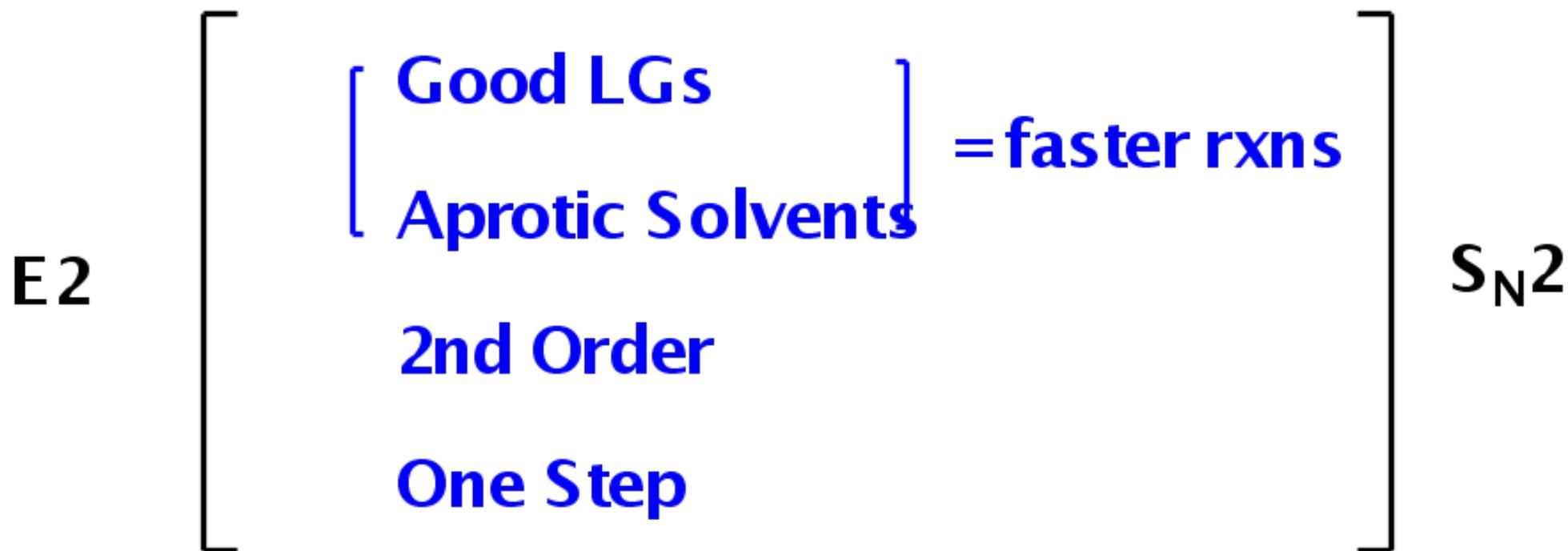
## Stereochemistry of the E2 Reaction:

- The stereochemical requirement of an anti periplanar geometry in an E2 reaction has important consequences for compounds containing six-membered rings.
- Consider chlorocyclohexane which exists as two chair conformations. Conformation A is preferred since the bulkier Cl group is in the equatorial position.

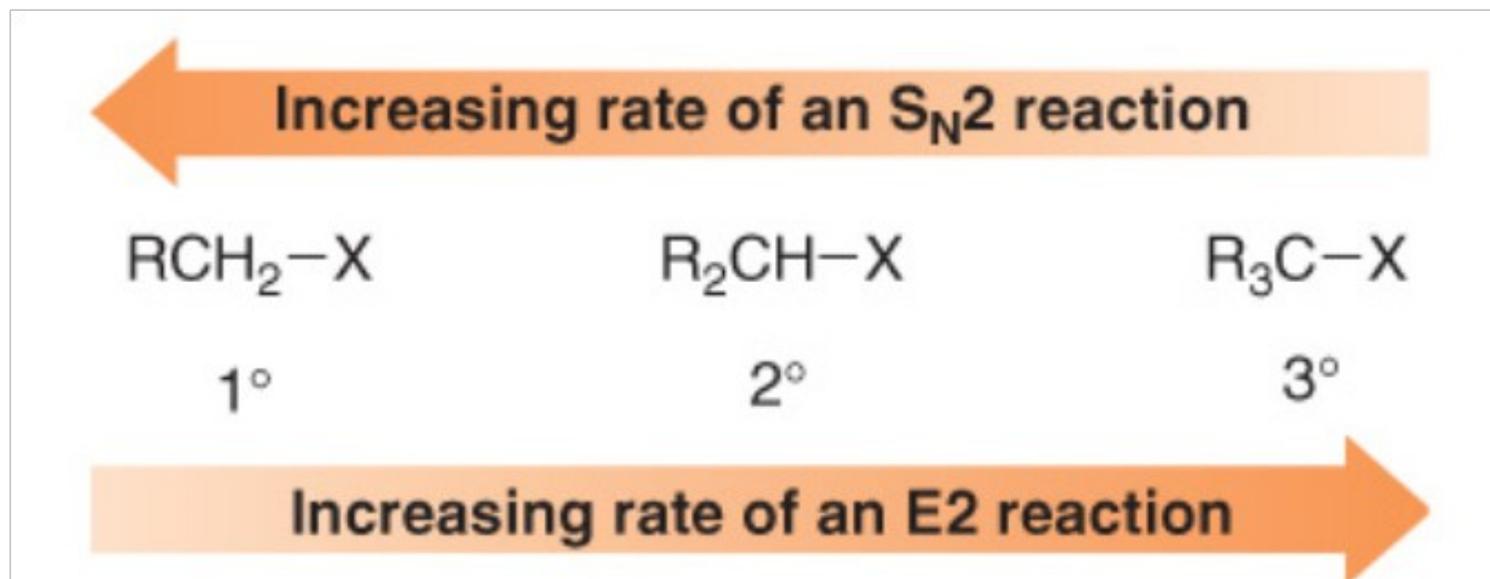


- For E2 elimination, the C-Cl bond must be anti periplanar to the C—H bond on a  Cl atoms are both in the axial position. The requirement for *trans* diaxial geometry means that elimination must occur from the less stable conformer, B.

Here are four characteristics that the **E2 / SN2** mechanisms have in common.

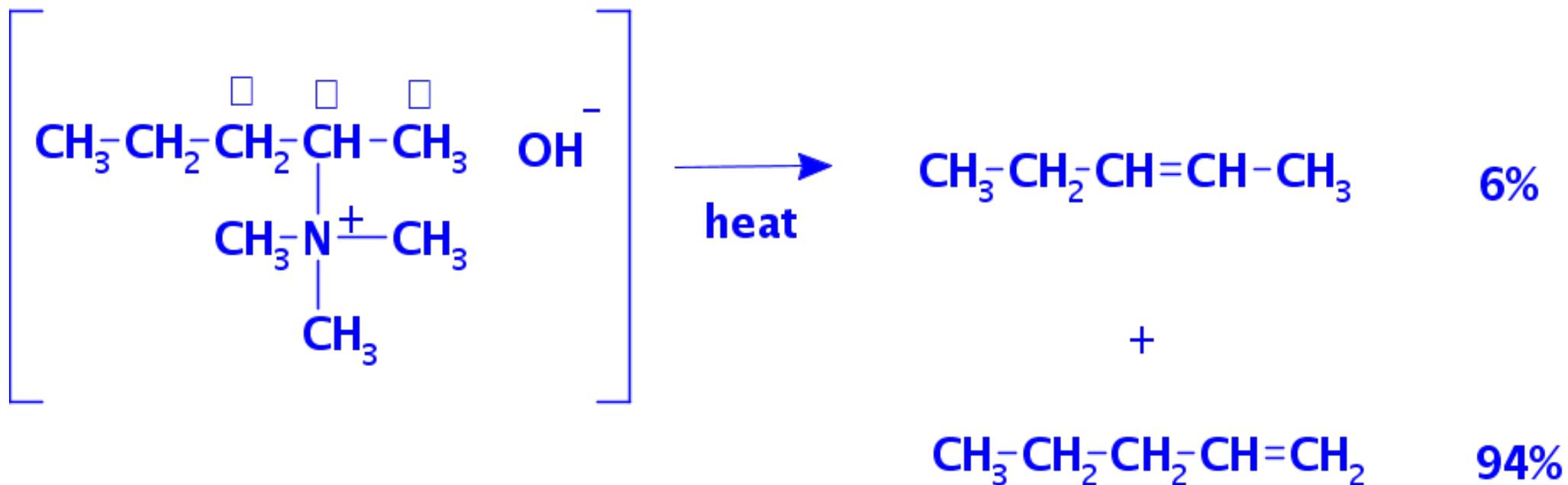


# Effect of the Substrate on E2 Reactivity



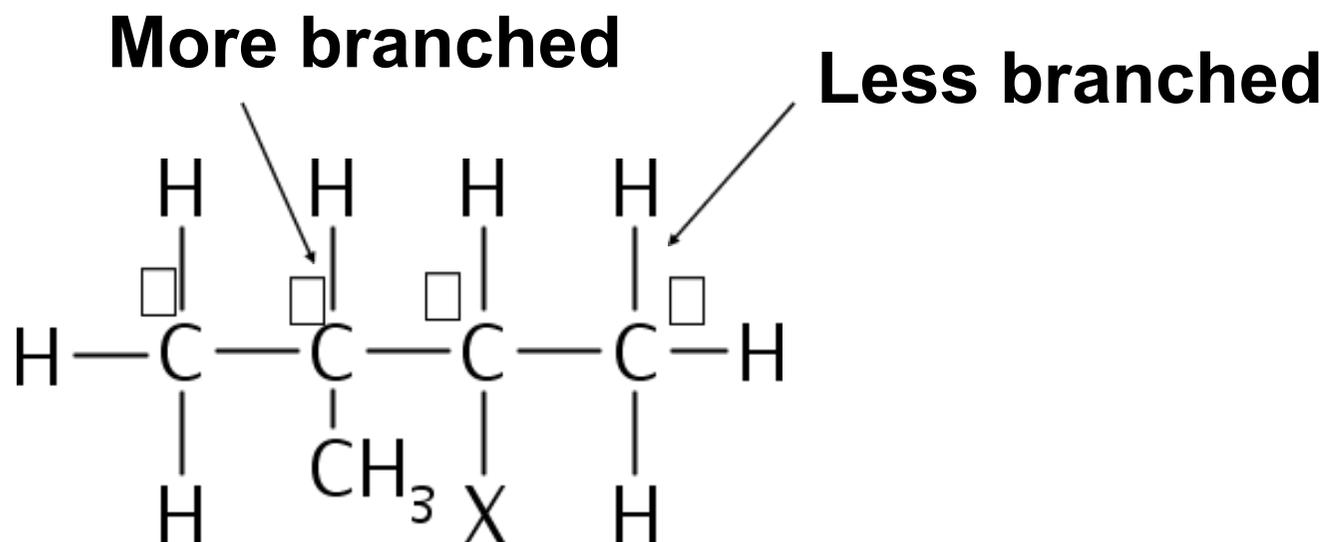
# Bulky leaving groups: Hofmann Elimination

This give the *anti-Saytzeff* product (least substituted product is formed)!



# Orientation of elimination: regiochemistry/ Hofmann's Rule

- In bimolecular elimination reactions in the presence of either a bulky leaving group or a bulky base, the *hydrogen* that is lost will come from the **LEAST** highly-branched *i*-carbon.

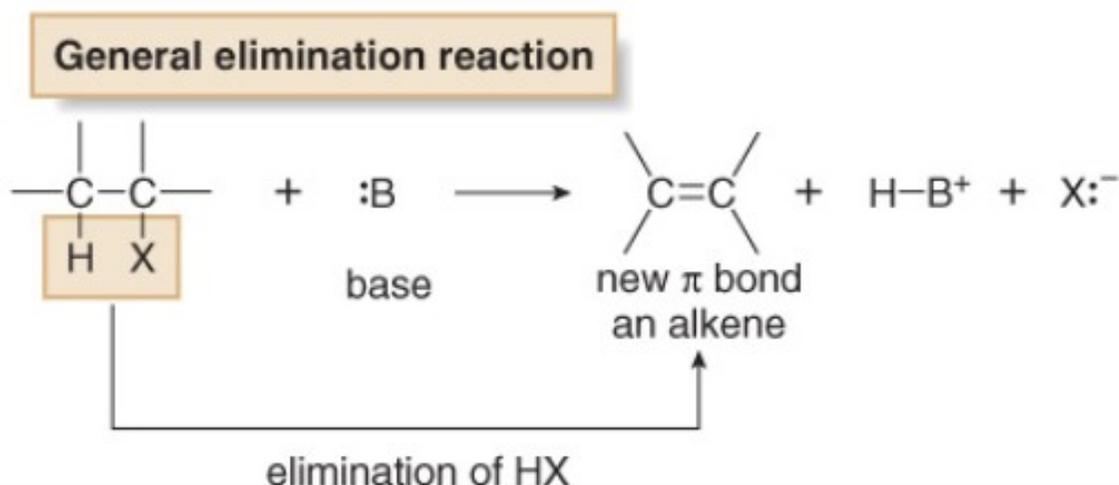


# Alkyl Halides and Elimination Reactions

## General Features of Elimination

- Elimination reactions involve the loss of elements from the starting material to form a new product.

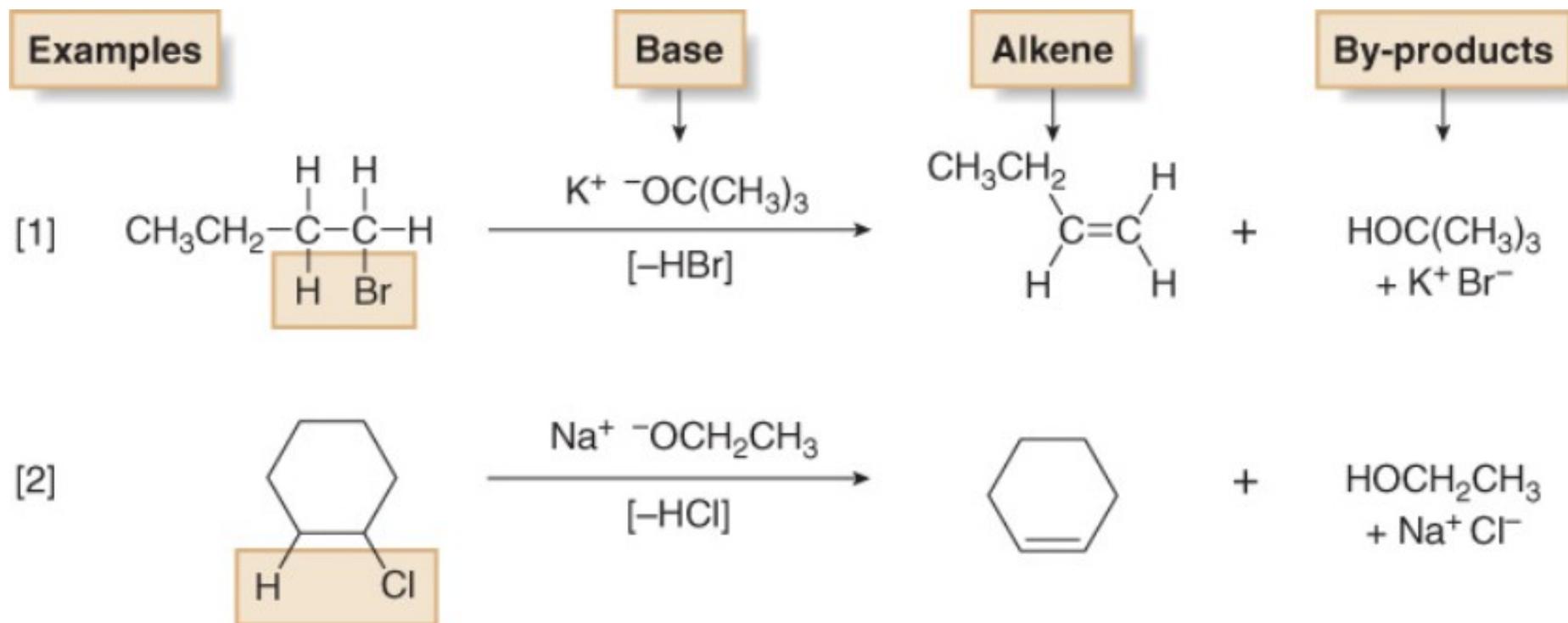
◆ Alkyl halides undergo elimination reactions with Brønsted–Lowry bases. The elements of HX are lost and an alkene is formed.



# Alkyl Halides and Elimination Reactions

## General Features of Elimination

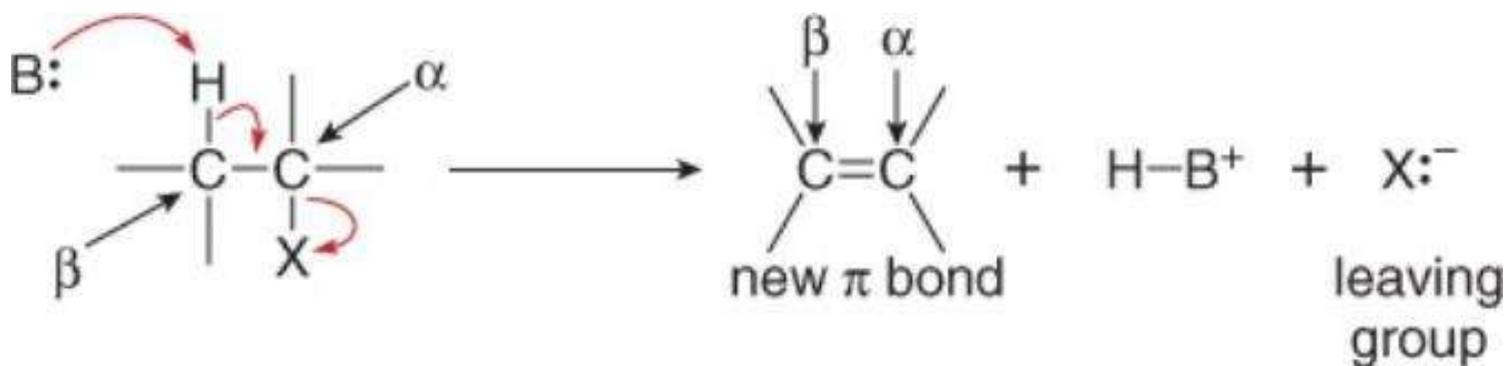
- Equations [1] and [2] illustrate examples of elimination reactions. In both reactions a base removes the elements of an acid, HX, from the organic starting material.



# Alkyl Halides and Elimination Reactions

## General Features of Elimination

- Removal of the elements HX is called dehydrohalogenation.
- Dehydrohalogenation is an example of  $n$  elimination.
- The curved arrow formalism shown below illustrates how four bonds are broken or formed in the process.



# Alkyl Halides and Elimination Reactions

## General Features of Elimination

- The most common bases used in elimination reactions are negatively charged oxygen compounds, such as  $\text{HO}^-$  and its alkyl derivatives,  $\text{RO}^-$ , called alkoxides.

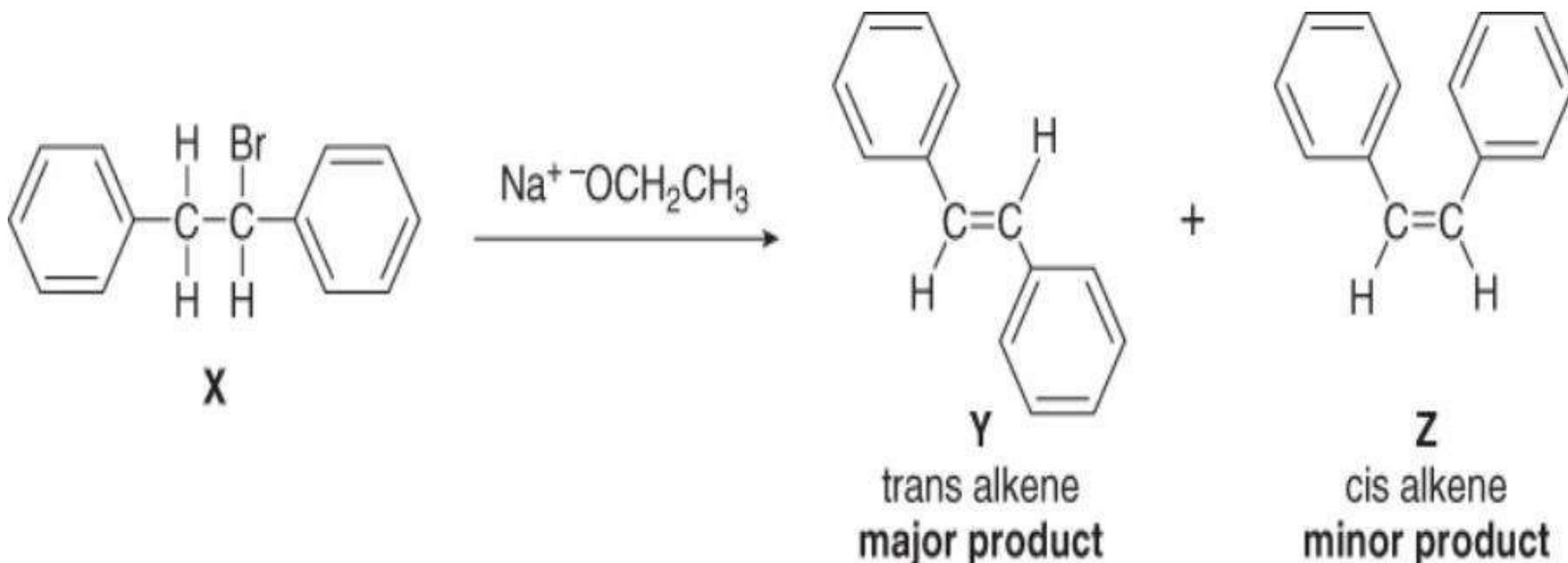
**TABLE 8.1 Common Bases Used in Dehydrohalogenation**

$\text{Na}^+ \text{}^- \text{OH}$	sodium hydroxide
$\text{K}^+ \text{}^- \text{OH}$	potassium hydroxide
$\text{Na}^+ \text{}^- \text{OCH}_3$	sodium methoxide
$\text{Na}^+ \text{}^- \text{OCH}_2\text{CH}_3$	sodium ethoxide
$\text{K}^+ \text{}^- \text{OC}(\text{CH}_3)_3$	potassium <i>tert</i> -butoxide

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# The Saytzeff) Rule (Z-rule)

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



# Summary

- Alkyl halides undergo two kinds of nucleophilic substitutions: **SN1** and **SN2**, and two kinds of elimination: **E1** and **E2**.
- SN2 and E2 are bimolecular one-step reactions
- SN1 and E1 are unimolecular two step reactions
- SN1 lead to a mixture of stereoisomers
- The major product of a elimination is the most stable alkene
- SN2 and E2 are favoured by strong nucleophile/strong base
- SN2 reactions are favoured by primary alkyl halides
- E2 reactions are favoured by tertiary alkyl halides

# Reference

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