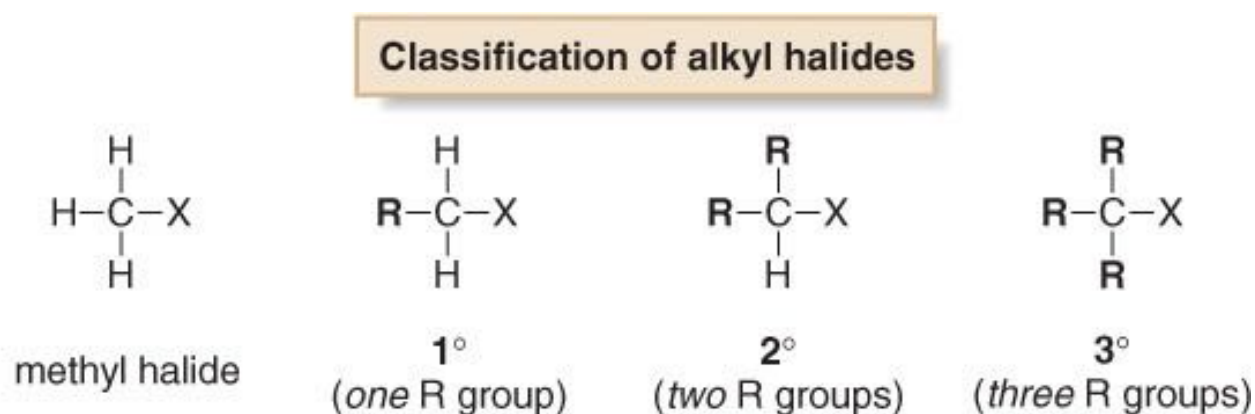
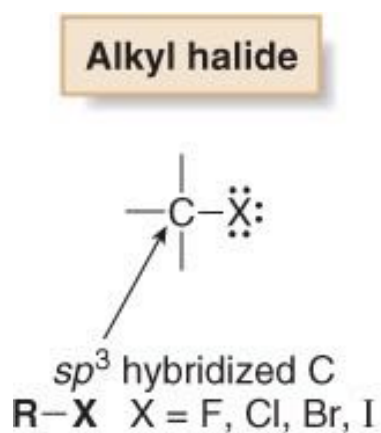


# Alkyl Halides

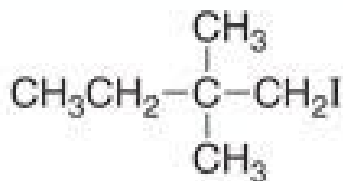
Chapter 10  
Organic Chemistry, *8th Edition*  
John McMurry

# Introduction to Alkyl Halides

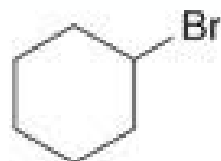
- **Alkyl halides** are organic molecules containing a halogen atom bonded to an  $sp^3$  hybridized carbon atom.
- Alkyl halides are classified as **primary** ( $1^\circ$ ), **secondary** ( $2^\circ$ ), or **tertiary** ( $3^\circ$ ), depending on the number of carbons bonded to the carbon with the halogen atom.
- The halogen atom in halides is often denoted by the symbol “X”.



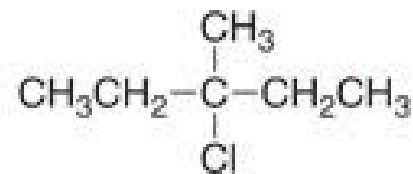
# Introduction to Alkyl Halides



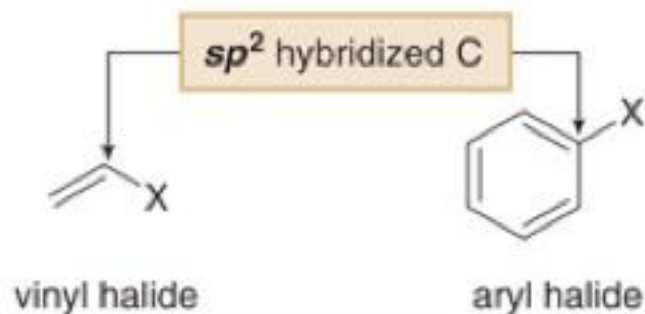
1° iodide



2° bromide



3° chloride



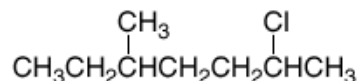
Different reactivity

# Nomenclature

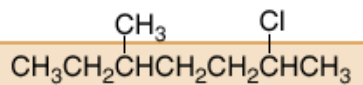
## How To

## Name an Alkyl Halide Using the IUPAC System

**Example** Give the IUPAC name of the following alkyl halide:



**Step [1]** Find the parent carbon chain containing the halogen.



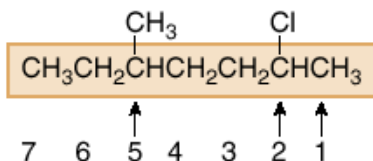
7 C's in the longest chain

7 C's ----> heptane

- Name the parent chain as an **alkane**, with the halogen as a substituent bonded to the longest chain.

**Step [2]** Apply all other rules of nomenclature.

a. **Number** the chain.

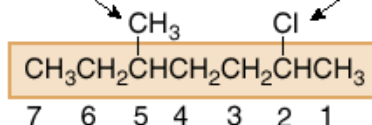


- Begin at the end nearest the first substituent, either alkyl or halogen.

b. **Name and number** the substituents.

methyl at C5

chloro at C2



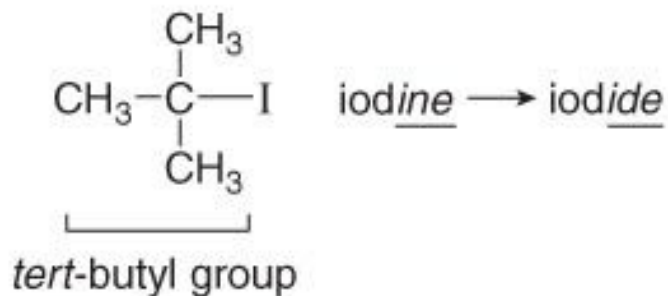
c. **Alphabetize**: c for chloro, then m for methyl.

**ANSWER: 2-chloro-5-methylheptane**

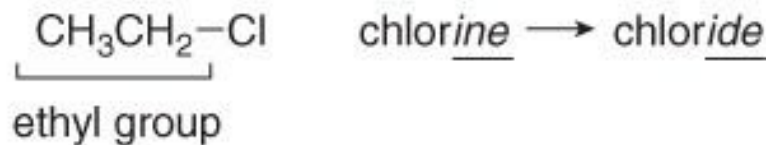
# Nomenclature

Common names are often used for simple alkyl halides. To assign a common name:

**Common  
names**



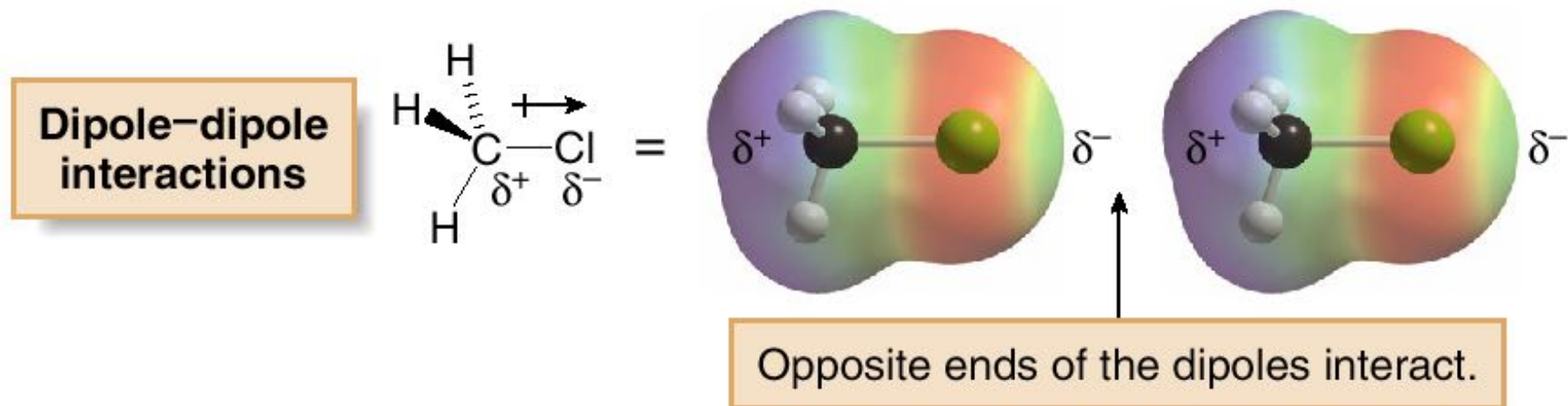
***tert*-butyl iodide**



**ethyl chloride**

# Physical Properties

Alkyl halides are weak polar molecules. They exhibit dipole-dipole interactions because of their polar C—X bond, but because the rest of the molecule contains only C—C and C—H bonds, they are incapable of intermolecular hydrogen bonding.



# Physical Properties

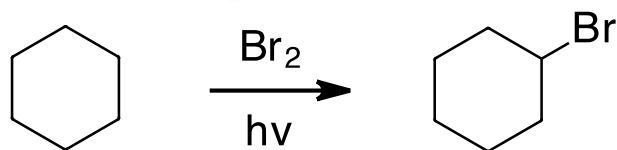
**Table 7.1**

**Physical Properties of Alkyl Halides**

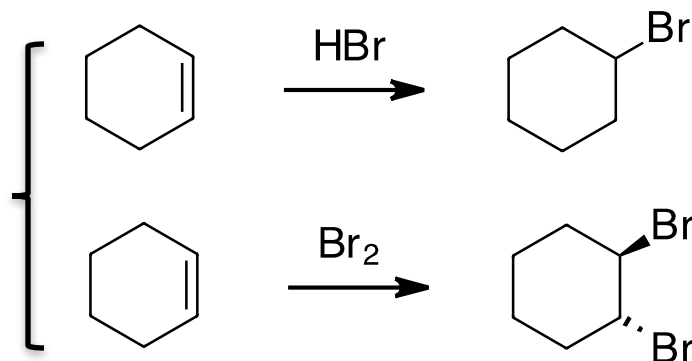
Property	Observation
Boiling point and melting point	<ul style="list-style-type: none"> <li>Alkyl halides have higher bp's and mp's than alkanes having the same number of carbons.                             <div style="display: flex; justify-content: space-around; align-items: center; margin-top: 10px;"> <div style="text-align: center;"> <math>\text{CH}_3\text{CH}_3</math> bp = <math>-89^\circ\text{C}</math> </div> <div>and</div> <div style="text-align: center;"> <math>\text{CH}_3\text{CH}_2\text{Br}</math> bp = <math>39^\circ\text{C}</math> </div> </div> </li> <li>Bp's and mp's increase as the size of R increases.                             <div style="display: flex; justify-content: space-around; align-items: center; margin-top: 10px;"> <div style="text-align: center;"> <math>\text{CH}_3\text{CH}_2\text{Cl}</math> mp = <math>-136^\circ\text{C}</math> bp = <math>12^\circ\text{C}</math> </div> <div>and</div> <div style="text-align: center;"> <math>\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}</math> mp = <math>-123^\circ\text{C}</math> bp = <math>47^\circ\text{C}</math> </div> <div style="margin-left: 20px;"> <div style="border: 1px solid black; padding: 5px; background-color: #fff9c4;">larger surface area— higher mp and bp</div> <div style="font-size: 2em;">←</div> </div> </div> </li> <li>Bp's and mp's increase as the size of X increases.                             <div style="display: flex; justify-content: space-around; align-items: center; margin-top: 10px;"> <div style="text-align: center;"> <math>\text{CH}_3\text{CH}_2\text{Cl}</math> mp = <math>-136^\circ\text{C}</math> bp = <math>12^\circ\text{C}</math> </div> <div>and</div> <div style="text-align: center;"> <math>\text{CH}_3\text{CH}_2\text{Br}</math> mp = <math>-119^\circ\text{C}</math> bp = <math>39^\circ\text{C}</math> </div> <div style="margin-left: 20px;"> <div style="border: 1px solid black; padding: 5px; background-color: #fff9c4;">more polarizable halogen— higher mp and bp</div> <div style="font-size: 2em;">←</div> </div> </div> </li> </ul>
Solubility	<ul style="list-style-type: none"> <li>RX is soluble in organic solvents.</li> <li>RX is insoluble in water.</li> </ul>

# Preparation

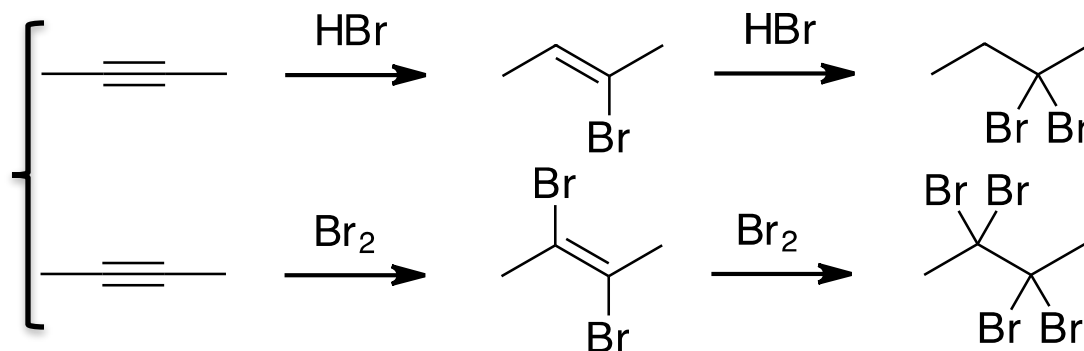
From alkanes



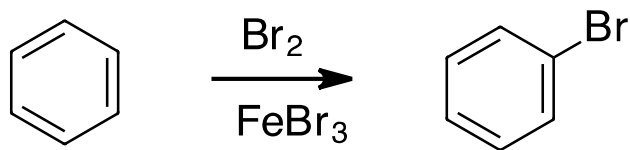
From alkenes



From alkynes

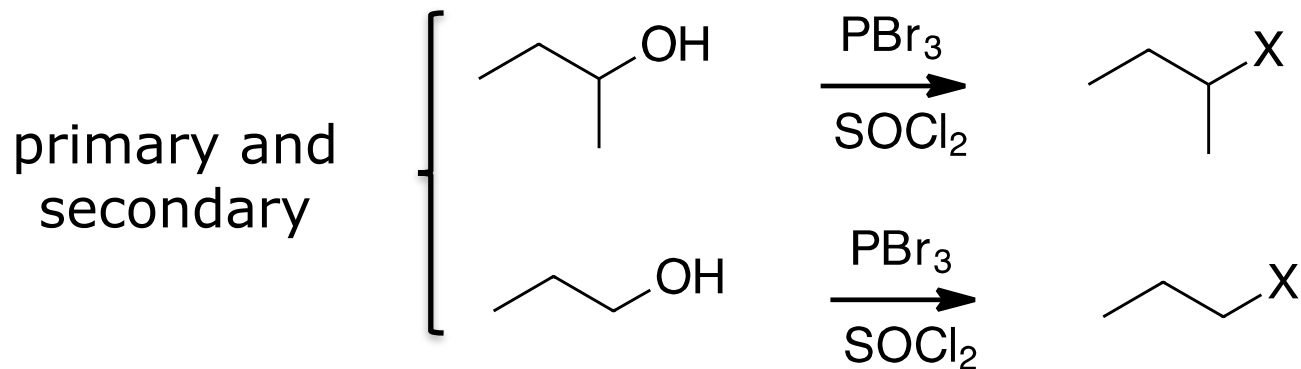
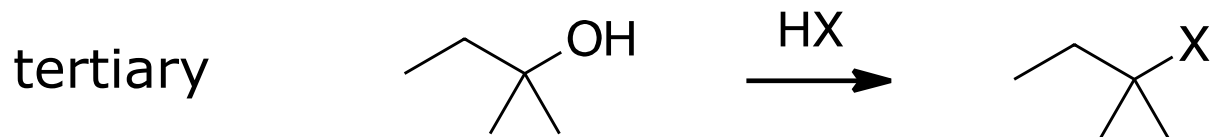


Aryl halides:



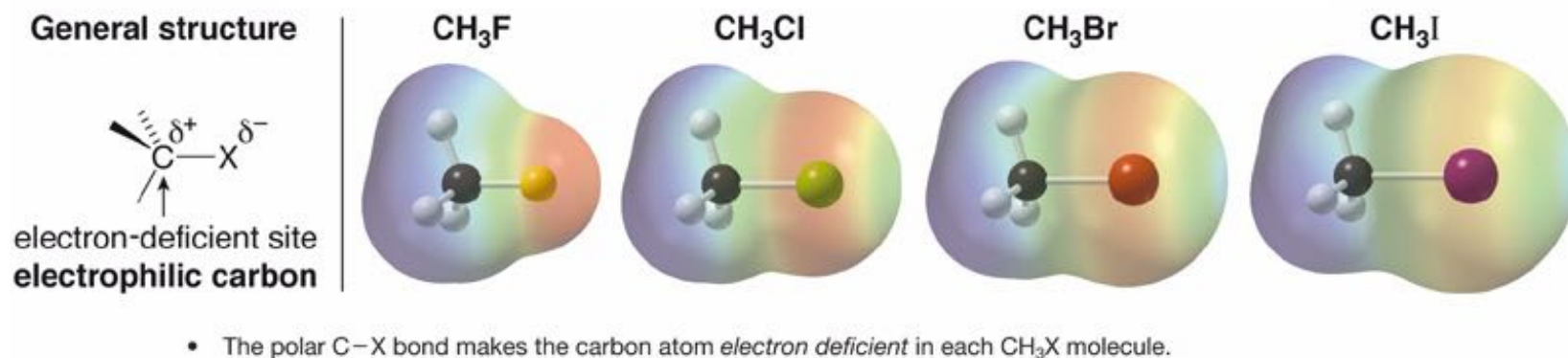


# Preparation from alcohols



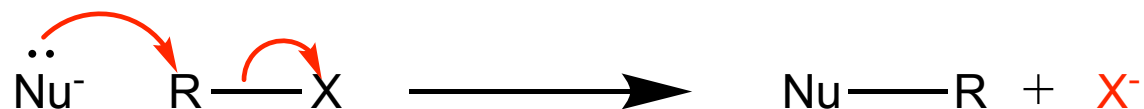
# The Polar Carbon-Halogen Bond

The electronegative halogen atom in alkyl halides creates a polar C—X bond, making the carbon atom electron deficient. Electrostatic potential maps of four simple alkyl halides illustrate this point.

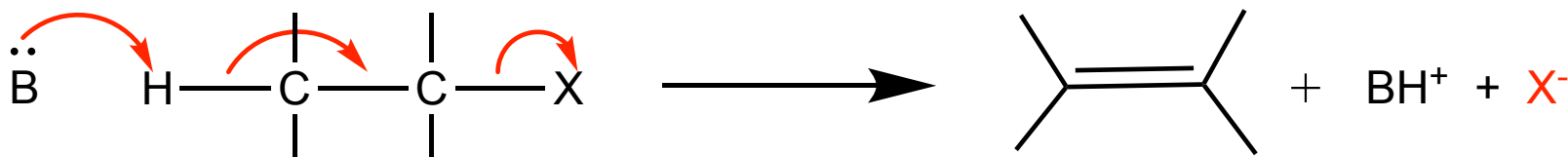


# The Polar Carbon-Halogen Bond

- Alkyl halides undergo substitution reactions with nucleophiles.



- Alkyl halides undergo elimination reactions with Brønsted-Lowry bases.



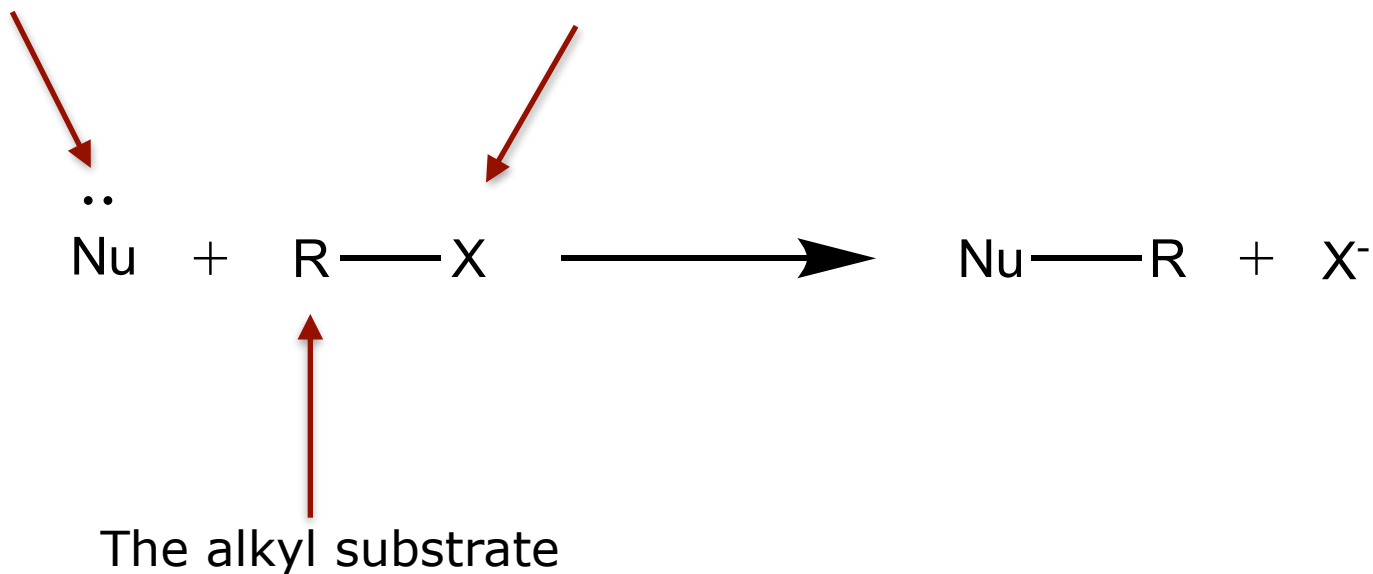
# Nucleophilic Substitution

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Organic Chemistry, *8th Edition*  
John McMurry

# Nucleophilic Substitutions

The nucleophile

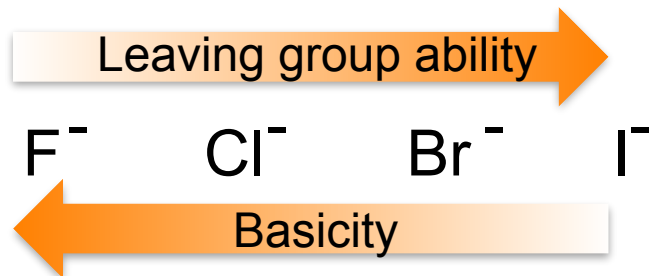
The leaving group



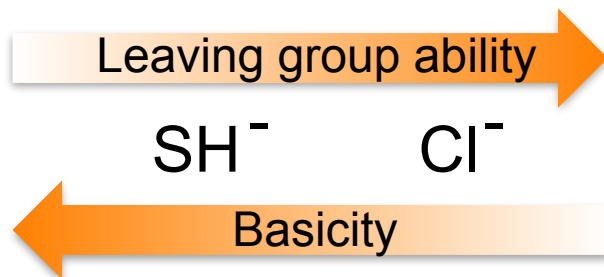
# The Leaving Group

Stable species are good leaving groups.

- Leaving group ability increases down a period:



- Leaving group ability increases from left to right across a group:



# The Leaving Group

These molecules undergo nucleophilic substitution

Starting material	Leaving group	Conjugate acid	pK <sub>a</sub>
R-Cl	Cl <sup>-</sup>	HCl	-7
R-Br	Br <sup>-</sup>	HBr	-9
R-I	I <sup>-</sup>	HI	-10
R-OH <sub>2</sub> <sup>+</sup>	H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>	-1.7

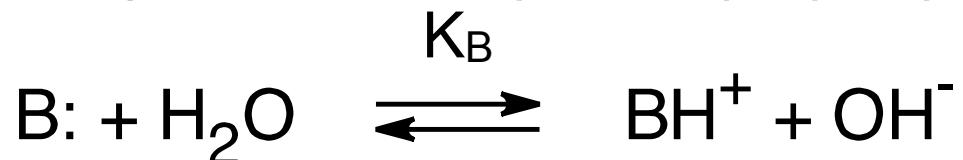
These molecules do not undergo nucleophilic substitution

Starting material	Leaving group	Conjugate acid	pK <sub>a</sub>
R-F	F <sup>-</sup>	HF	3.2
R-OH	<sup>-</sup> OH	H <sub>2</sub> O	15.7
R-NH <sub>2</sub>	<sup>-</sup> NH <sub>2</sub>	NH <sub>3</sub>	38
R-H	H <sup>-</sup>	H <sub>2</sub>	35
R-R	R <sup>-</sup>	RH	50

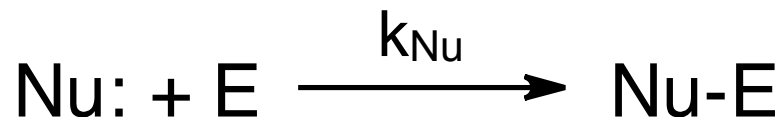
# The Nucleophile

- Nucleophilicity is correlated to basicity.
- Although nucleophilicity and basicity are interrelated, they are fundamentally different.

➡ Basicity is a **thermodynamic property**.



➡ Nucleophilicity is a **kinetic property**.





# The Nucleophile

- For two nucleophiles with the same nucleophilic atom, the stronger base is the stronger nucleophile.

$\text{HO}^-$  is a stronger nucleophile than  $\text{CH}_3\text{COO}^-$ .  
( $\text{p}K_{\text{a}}$ :  $\text{H}_2\text{O} = 15.7$ ,  $\text{CH}_3\text{COOH} = 4.8$ ).

- A negatively charged nucleophile is always a stronger nucleophile than its conjugate acid.

$\text{HO}^-$  is a stronger base and stronger nucleophile than  $\text{H}_2\text{O}$ .

- Right-to-left across a row of the periodic table, nucleophilicity increases as basicity increases:

$\text{NH}_3$  is a stronger base and stronger nucleophile than  $\text{H}_2\text{O}$ .

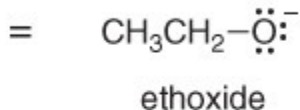
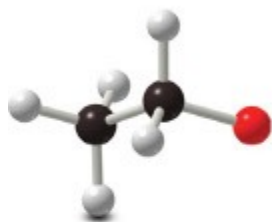
# The Nucleophile

**Tabella 11.1** Alcune reazioni  $S_N2$  con il bromometano

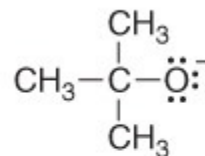
$\text{Nu:}^- + \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{Nu} + \text{Br}^-$				
Nucleofilo		Prodotto		Velocità relativa di reazione
Formula	Nome	Formula	Nome	
$\text{H}_2\text{O}$	Acqua	$\text{CH}_3\text{OH}_2^+$	Ione metilidronio	1
$\text{CH}_3\text{CO}_2^-$	Acetato	$\text{CH}_3\text{CO}_2\text{CH}_3$	Metil acetato	500
$\text{NH}_3$	Ammoniac	$\text{CH}_3\text{NH}_3^+$	Ione metilammonio	700
$\text{Cl}^-$	Cloruro	$\text{CH}_3\text{Cl}$	Clorometano	1000
$\text{HO}^-$	Idrossido	$\text{CH}_3\text{OH}$	Metanolo	10000
$\text{CH}_3\text{O}^-$	Metossido	$\text{CH}_3\text{OCH}_3$	Dimetil etere	25000
$\text{I}^-$	Ioduro	$\text{CH}_3\text{I}$	Iodometano	100000
$^- \text{CN}$	Cianuro	$\text{CH}_3\text{CN}$	Acetonitrile	125000
$\text{HS}^-$	Idrogenosolfuro	$\text{CH}_3\text{SH}$	Metantliolo	125000

# The Nucleophile

- Nucleophilicity does not parallel basicity when **steric hindrance** becomes important.
- **Steric hindrance** results from the presence of bulky groups at the site of a reaction.
- **Steric hindrance** decreases nucleophilicity but not basicity.
- Sterically hindered bases that are poor nucleophiles are called **non-nucleophilic bases**.



**stronger nucleophile**



*tert*-butoxide

**stronger base**



Three  $\text{CH}_3$  groups sterically hinder the O atom, making it a **weaker nucleophile**.

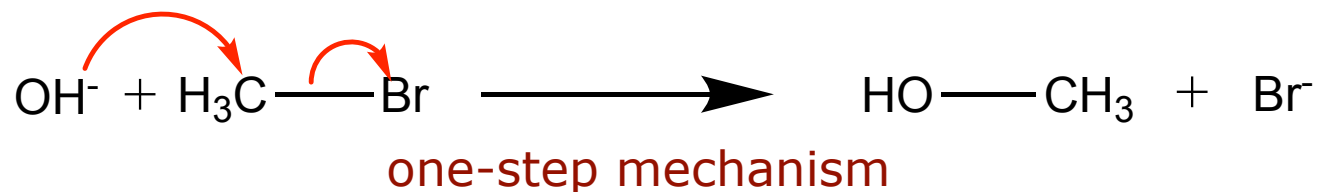
# The Nucleophile

## Some Common Nucleophiles

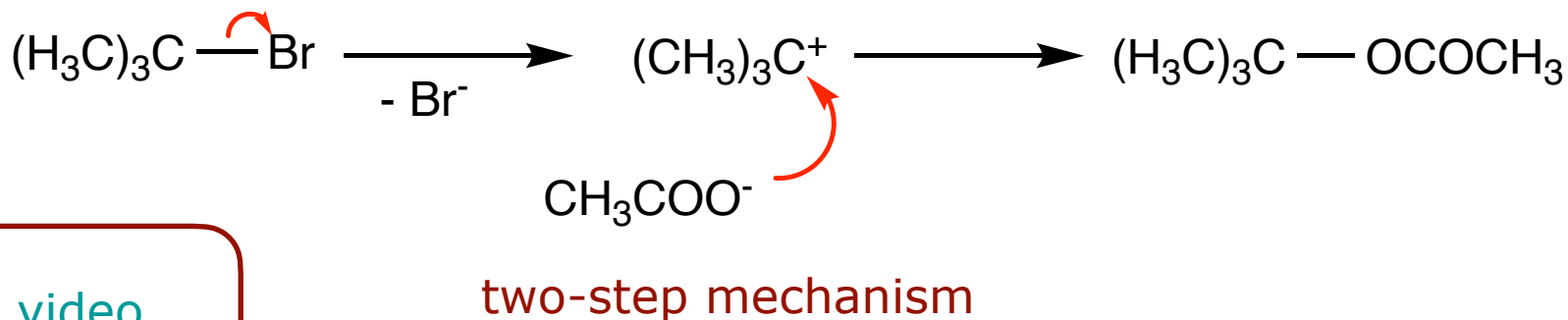
	Negatively charged nucleophiles			Neutral nucleophiles	
Oxygen	$\text{OH}^-$	$\text{OR}^-$	$\text{CH}_3\text{COO}^-$	$\text{H}_2\text{O}$	$\text{ROH}$
Nitrogen	$\text{N}_3^-$			$\text{NH}_3$	$\text{RNH}_2$
Carbon	$\text{CN}^-$	$\text{HC}\equiv\text{C}^-$			
Halogen	$\text{Cl}^-$	$\text{Br}^-$	$\text{I}^-$		
Sulfur	$\text{HS}^-$	$\text{RS}^-$		$\text{H}_2\text{S}$	$\text{RSH}$

# Mechanisms

Bond making and bond breaking occur at the same time.  $S_N2$



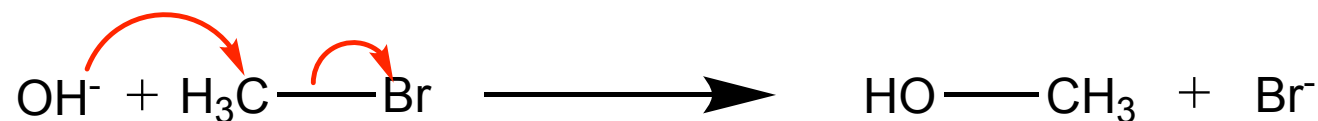
Bond breaking occurs before bond making.  $S_N1$



[video](#)

# $S_N2$ Mechanism: Kinetics

Bond making and bond breaking occur at the same time.

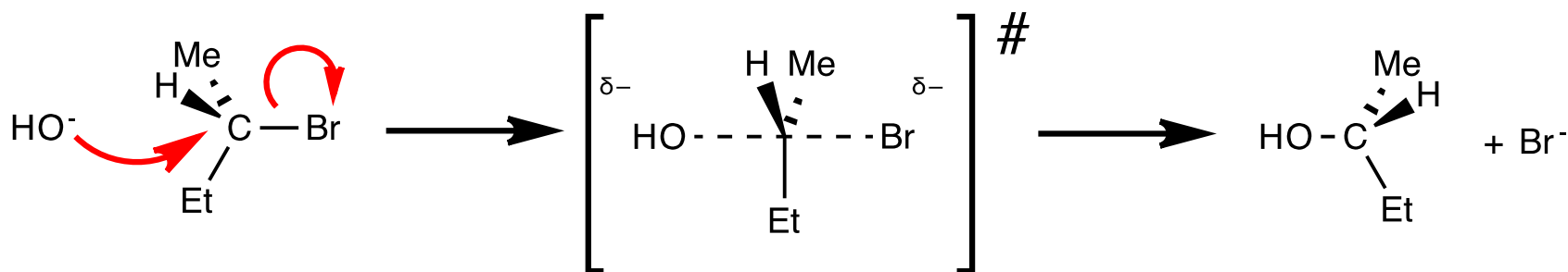
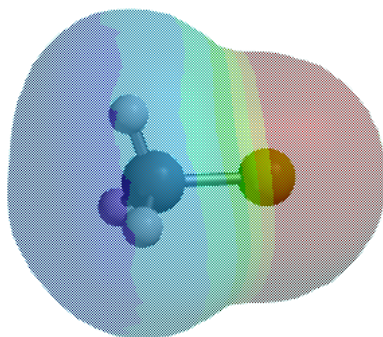


$$v = k[\text{OH}^-][\text{CH}_3\text{Br}]$$

2nd order rate equation; depends on both the nucleophile and the substrate

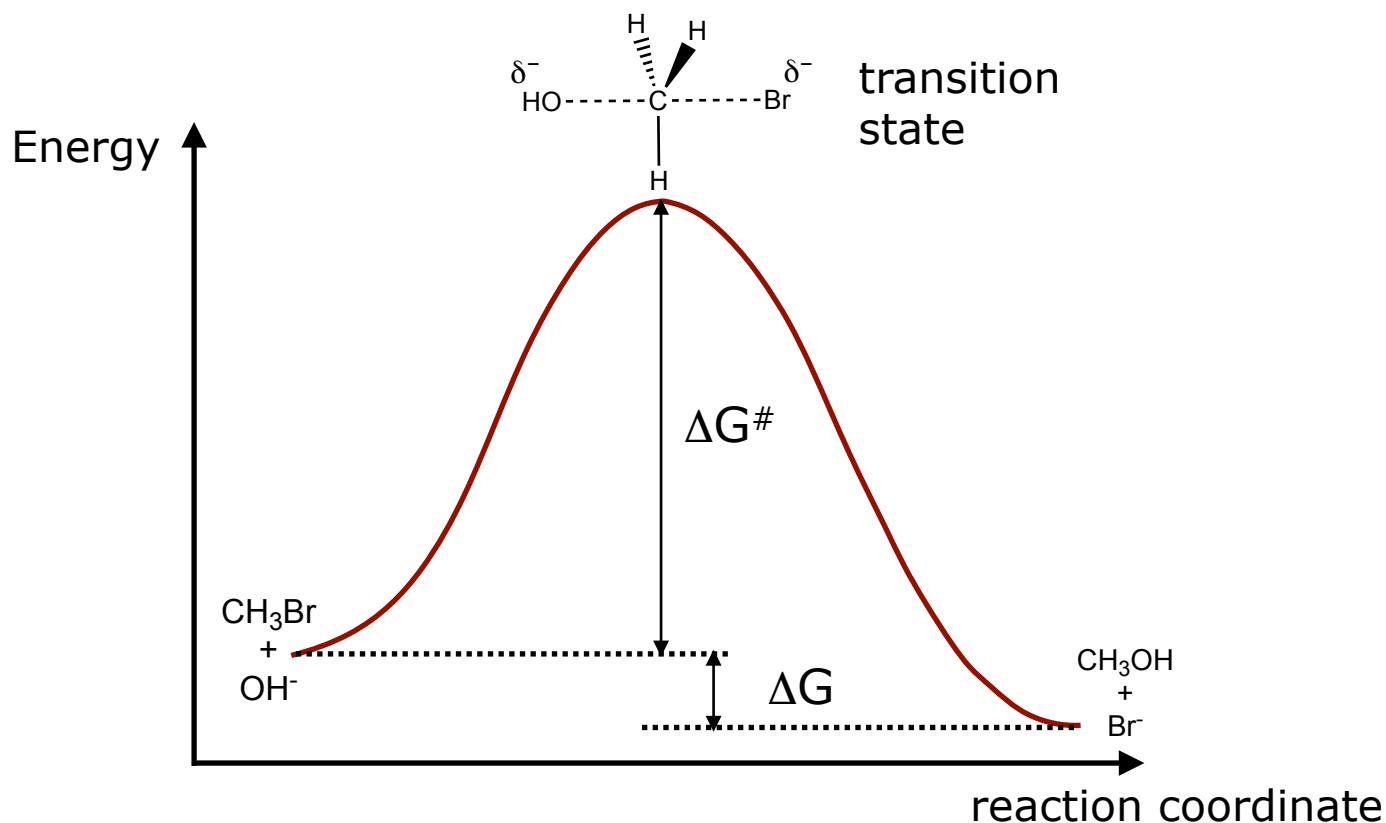
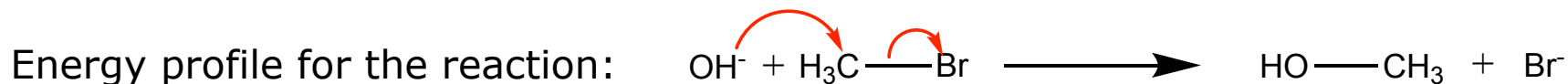
# $S_N2$ Mechanism: Stereochemistry

All  $S_N2$  reactions proceed with backside attack of the nucleophile, resulting in inversion of configuration at a stereogenic center.



:Nu<sup>-</sup> and Br<sup>-</sup> are 180° away from each other,  
on either side of a plane containing C, H, Me, Et

# $S_N2$ Mechanism: Energy Profile

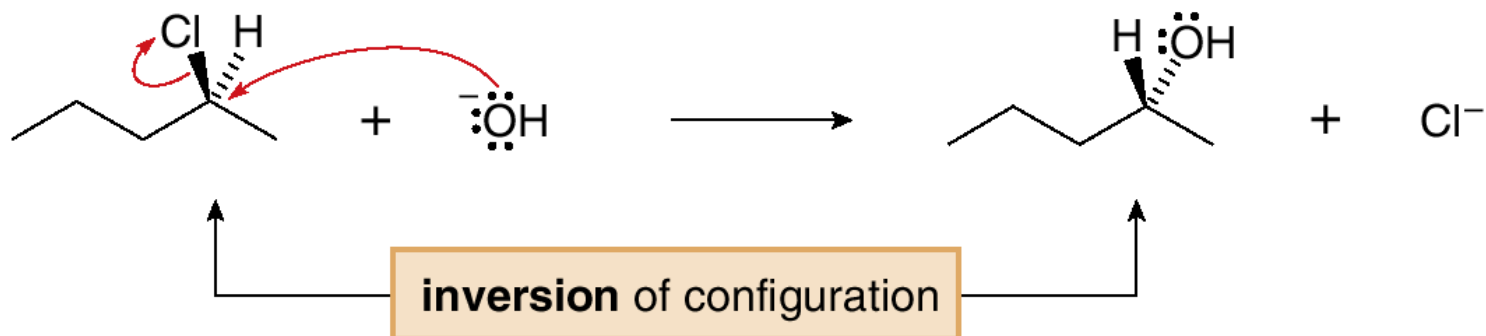
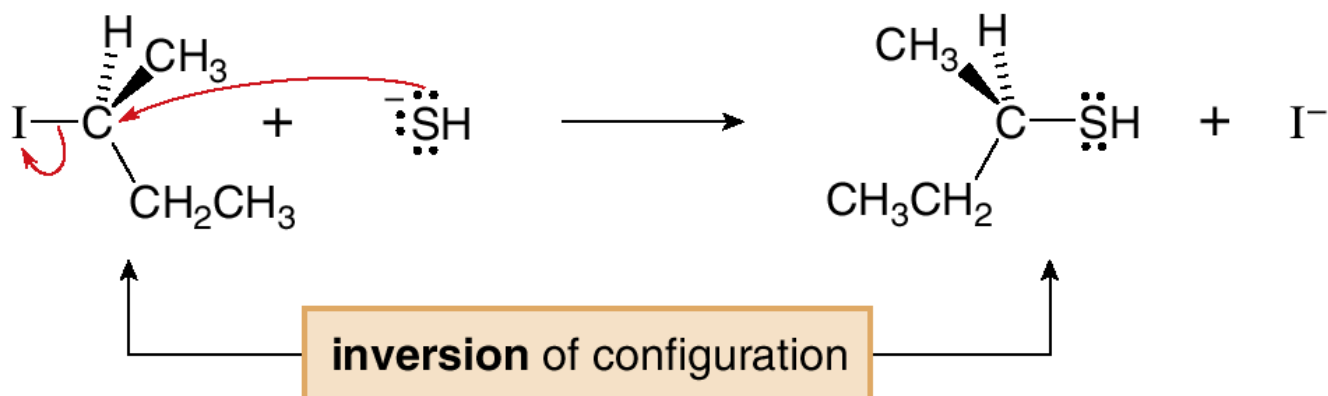


- In the transition state, the C–Br bond is partially broken, the C–O bond is partially formed, and both the attacking nucleophile and the departing leaving group bear a partial negative charge.



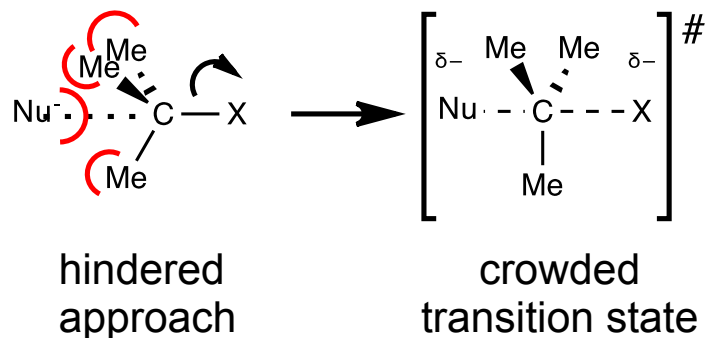
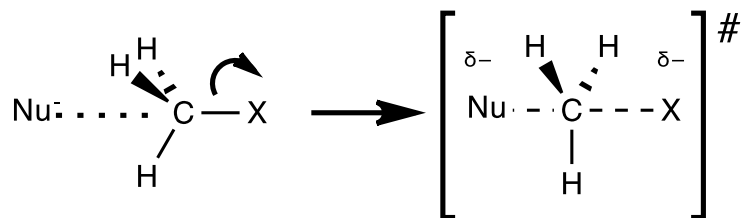
# S<sub>N</sub>2 Mechanism: Stereochemistry

- The bond to the nucleophile in the product is always on the **opposite side** relative to the bond to the leaving group in the starting material.



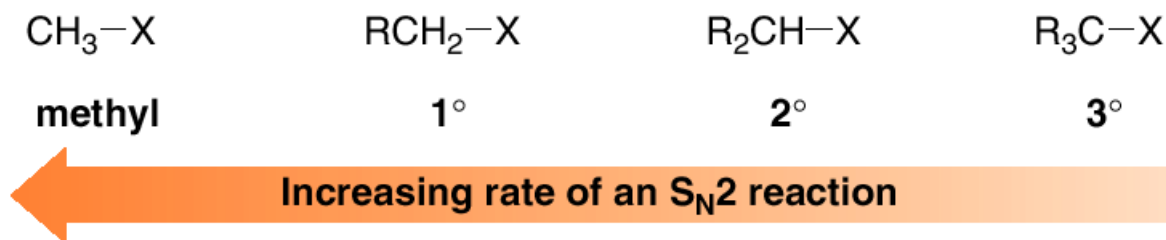
# $S_N2$ Reaction: The Alkyl Substrate

- Increasing the number of R groups on the carbon with the leaving group makes the approach of the nucleophile more difficult and increases crowding in the transition state.
- The  $S_N2$  reaction is fastest with unhindered halides.



# The Alkyl Substrate

- As the number of R groups on the carbon with the leaving group *increases*, the rate of an  $S_N2$  reaction *decreases*.



This order of reactivity can be explained by steric effects.

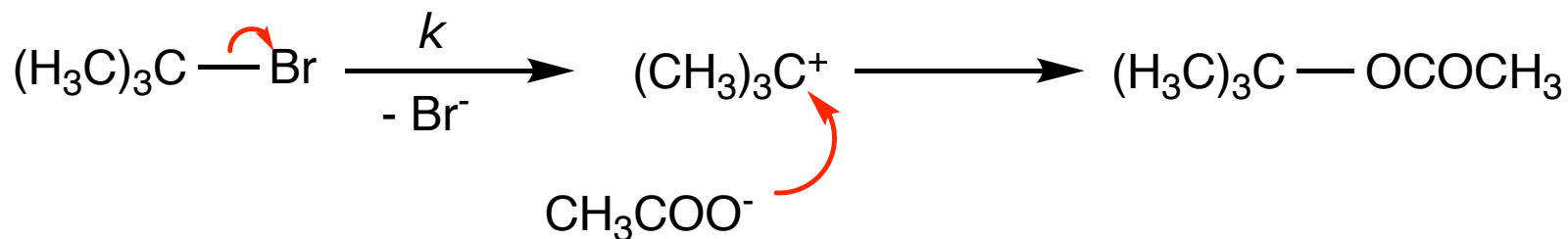
- Methyl and  $1^\circ$  alkyl halides undergo  $S_N2$  reactions with ease.
- $2^\circ$  Alkyl halides react more slowly.
- $3^\circ$  Alkyl halides do not undergo  $S_N2$  reactions.

# S<sub>N</sub>2 Mechanism

Characteristic	Result
Kinetics	<ul style="list-style-type: none"><li>• Second-order kinetics; rate = <math>k[\text{RX}][:\text{Nu}^-]</math></li></ul>
Mechanism	<ul style="list-style-type: none"><li>• One step</li></ul>
Stereochemistry	<ul style="list-style-type: none"><li>• Backside attack of the nucleophile</li><li>• Inversion of configuration at a stereogenic center</li></ul>
Identity of R	<ul style="list-style-type: none"><li>• Unhindered halides react fastest.</li><li>• Rate: <math>\text{CH}_3\text{X} &gt; \text{RCH}_2\text{X} &gt; \text{R}_2\text{CHX} &gt; \text{R}_3\text{CX}</math></li></ul>

# S<sub>N</sub>1 Mechanism: Kinetics

Bond breaking occurs before bond making.

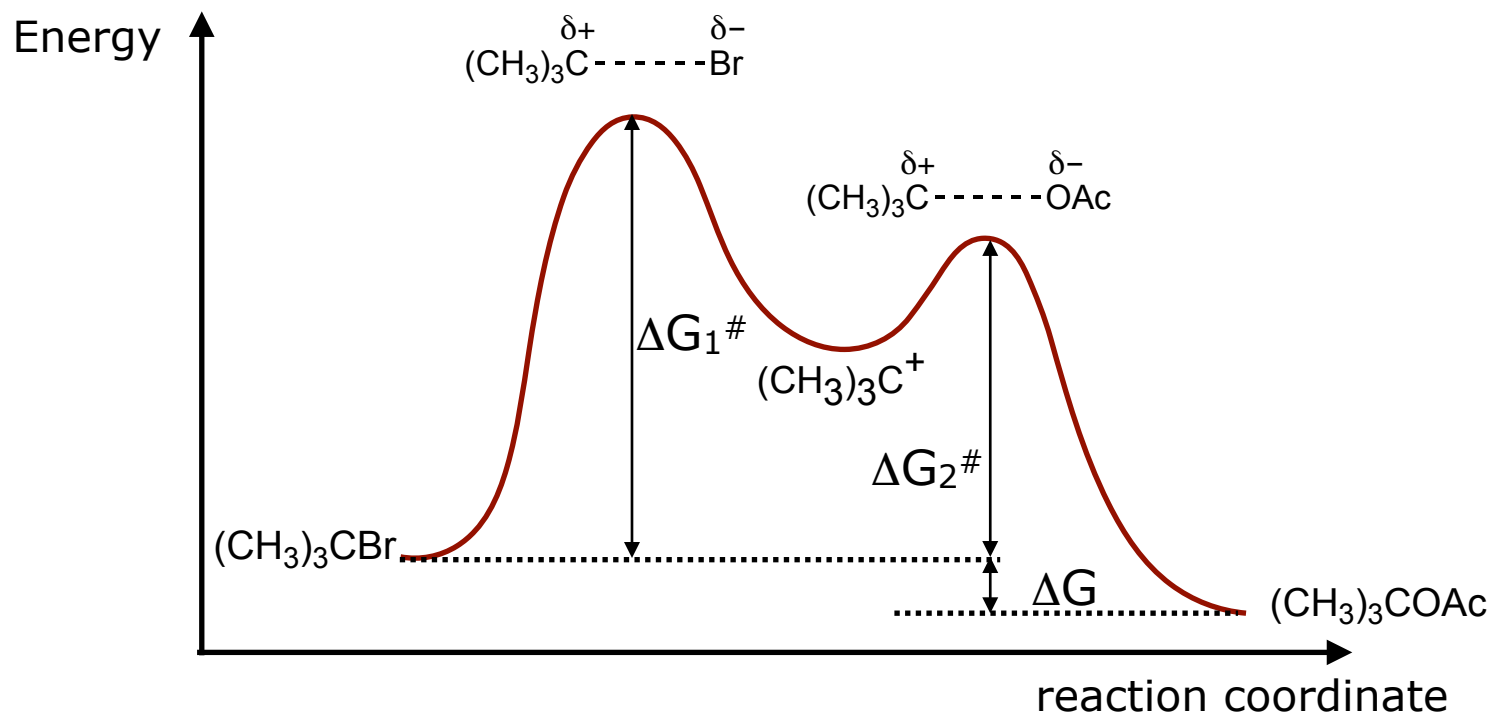
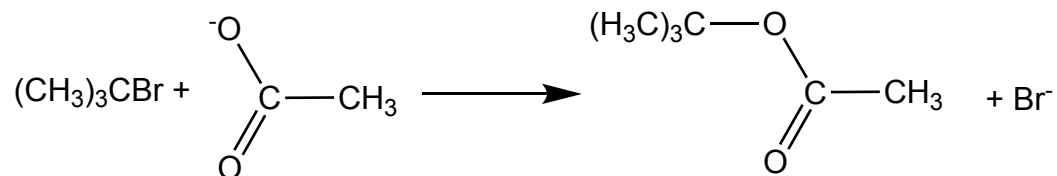


- In the S<sub>N</sub>1 mechanism carbocations are formed as reactive intermediates.
- The first step (bond breaking) is slow; the second step (bond making) is fast.

$$v = k[(\text{CH}_3)_3\text{CBr}]$$

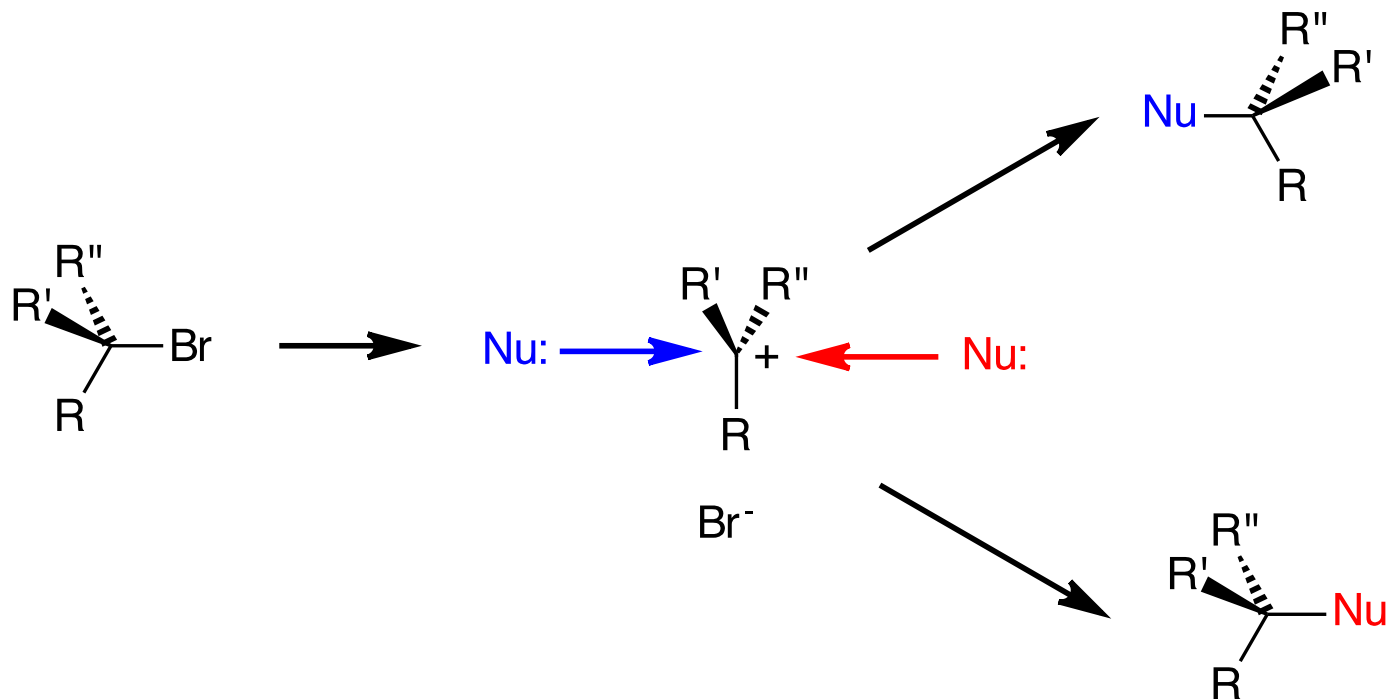
- 1st order rate equation; depends only on the substrate

# $S_N1$ Mechanism: Energetics

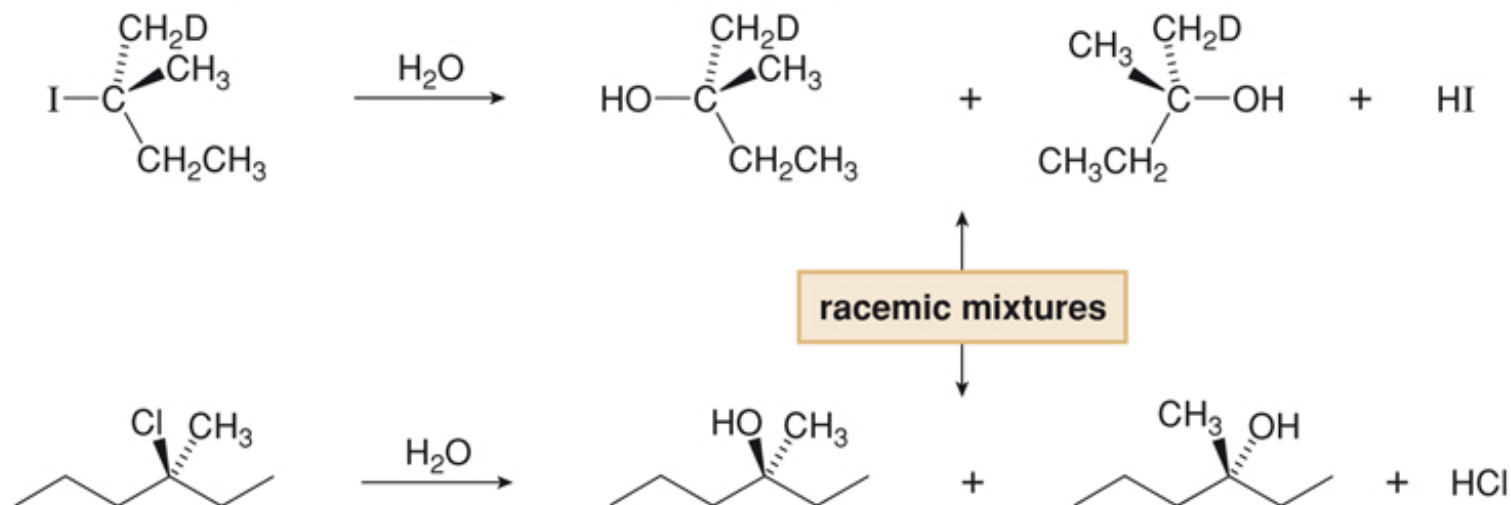


# $S_N1$ Mechanism. Stereochemistry

- Loss of the leaving group in Step [1] generates a planar carbocation that is achiral.
- In Step [2], attack of the nucleophile can occur on either side to afford two products which are a pair of enantiomers.  
**Racemization** has occurred.



# $S_N1$ Mechanism: Stereochemistry

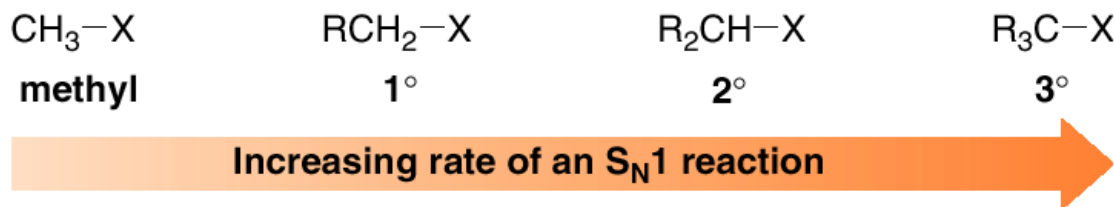


- Nucleophilic substitution of each starting material by an  $S_N1$  mechanism forms a **racemic mixture** of two products.
- With  $H_2O$ , a neutral nucleophile, the initial product of nucleophilic substitution ( $ROH_2^+$ ) loses a proton to form the final neutral product,  $ROH$  (Section 7.6).



# The Alkyl Substrate

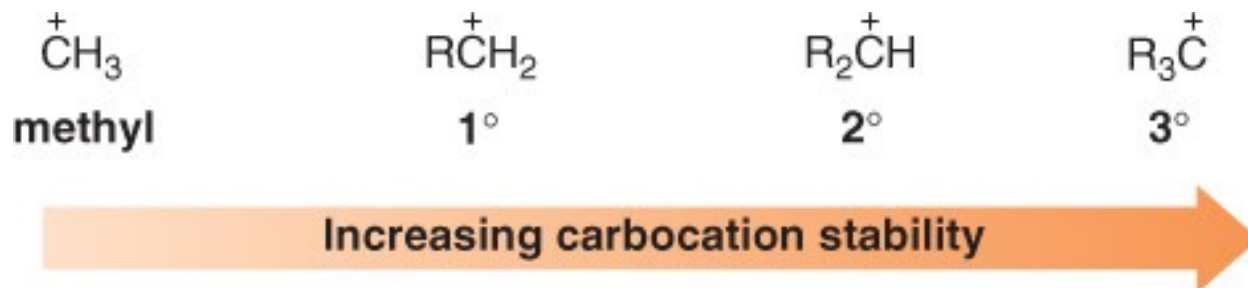
- As the number of R groups on the carbon with the leaving group *increases*, the rate of an S<sub>N</sub>1 reaction *increases*.



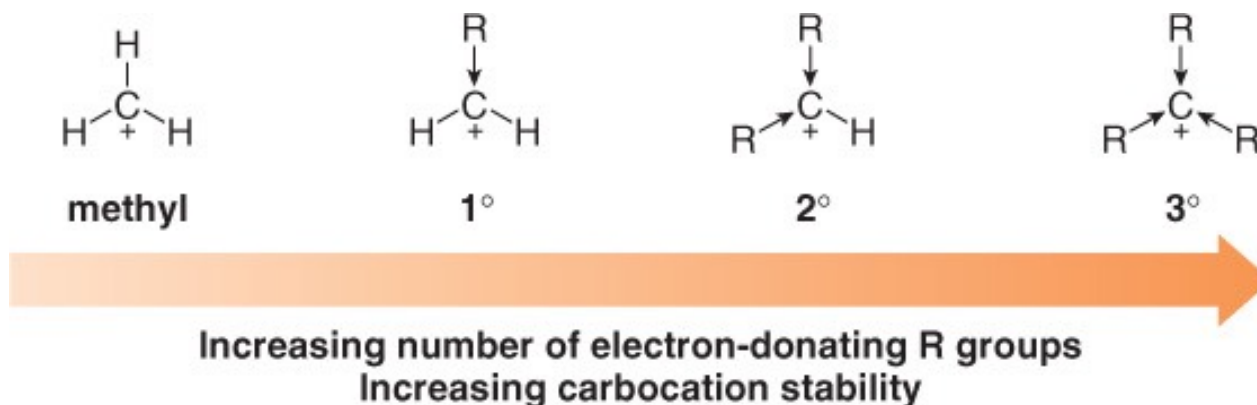
- 3° Alkyl halides undergo S<sub>N</sub>1 reactions rapidly.
- 2° Alkyl halides react more slowly.
- Methyl and 1° alkyl halides do *not* undergo S<sub>N</sub>1 reactions.

This trend is exactly opposite to that observed in S<sub>N</sub>2 reactions and reflects the **stability of the carbocation**.

# Carbocation Stability

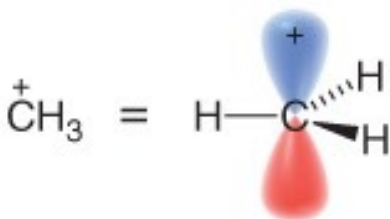


Alkyl groups are **electron donating**. Since an alkyl group has several  $\sigma$  bonds, each containing electron density, it is more polarizable than a hydrogen atom, and better able to donate electron density.

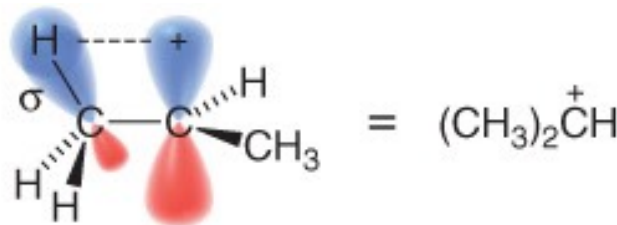


# Carbocation Stability

- **Hyperconjugation** is the spreading out of charge by the overlap of an empty  $p$  orbital with an adjacent  $\sigma$  bond. This overlap (hyperconjugation) delocalizes the positive charge on the carbocation, spreading it over a larger volume, and this stabilizes the carbocation.
- Example:  $\text{CH}_3^+$  cannot be stabilized by hyperconjugation, but  $(\text{CH}_3)_2\text{CH}^+$  can.



This carbocation has no opportunity for orbital overlap with the vacant  $p$  orbital.



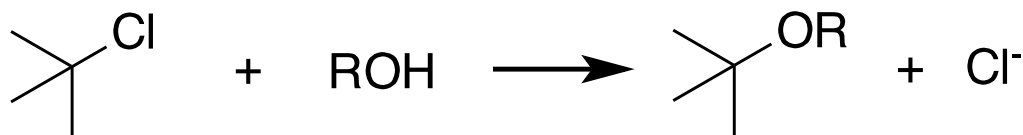
Overlap of the  $\text{C}-\text{H}$   $\sigma$  bond with the adjacent vacant  $p$  orbital stabilizes the carbocation.

# $S_N1$ Mechanism

Characteristic	Result
Kinetics	<ul style="list-style-type: none"><li>• First-order kinetics; rate = <math>k[\text{RX}]</math></li></ul>
Mechanism	<ul style="list-style-type: none"><li>• Two steps</li></ul>
Stereochemistry	<ul style="list-style-type: none"><li>• Trigonal planar carbocation intermediate</li><li>• Racemization at a single stereogenic center</li></ul>
Identity of R	<ul style="list-style-type: none"><li>• More substituted halides react fastest.</li><li>• Rate: <math>\text{R}_3\text{CX} &gt; \text{R}_2\text{CHX} &gt; \text{RCH}_2\text{X} &gt; \text{CH}_3\text{X}</math></li></ul>

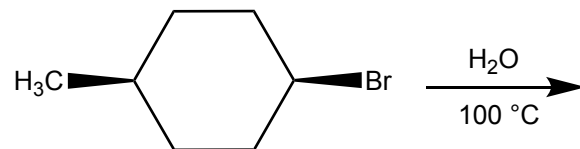
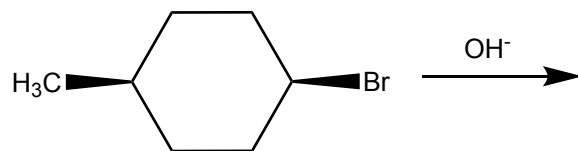
# $S_N1$ and $S_N2$ Mechanisms

- **Substrate:** 1<sup>ry</sup> -  $S_N2$ ; 2<sup>ry</sup> -  $S_N2$  or  $S_N1$ ; 3<sup>ry</sup> -  $S_N1$
- **Leaving group:** the same reactivity order in  $S_N1$  and  $S_N2$  reactions.
- **Nucleophile:** has little effect in  $S_N1$  reactions because it reacts after the slow step (must be nonbasic to prevent elimination). Good nucleophiles favour  $S_N2$  reactions.
- **Solvent:** polar solvents favor the  $S_N1$  reaction by stabilizing the intermediate carbocation.

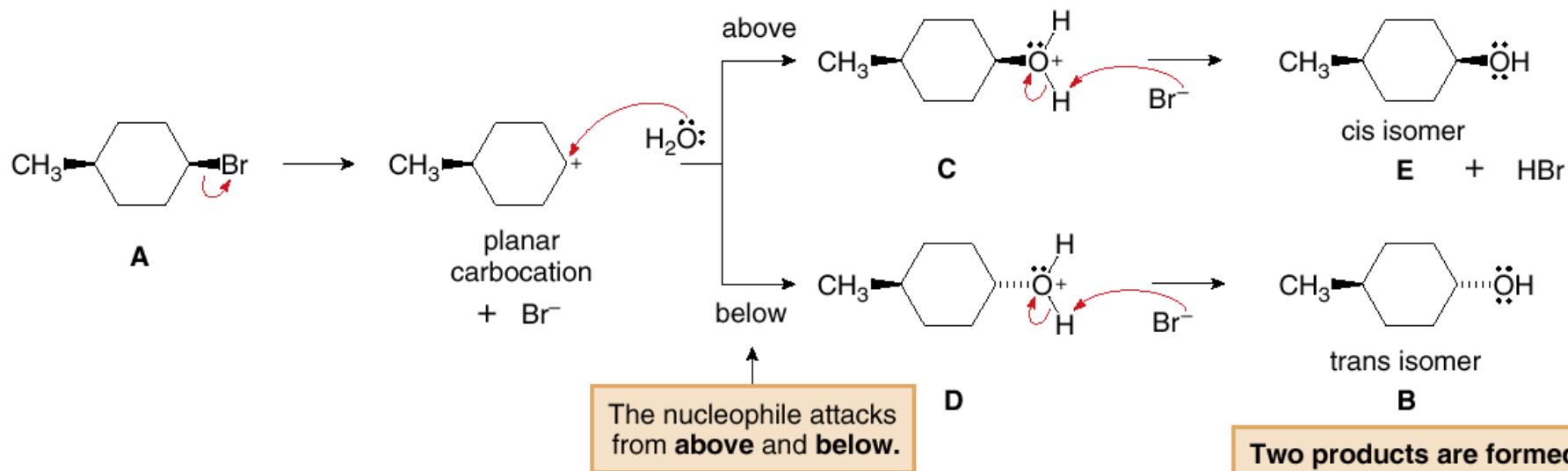
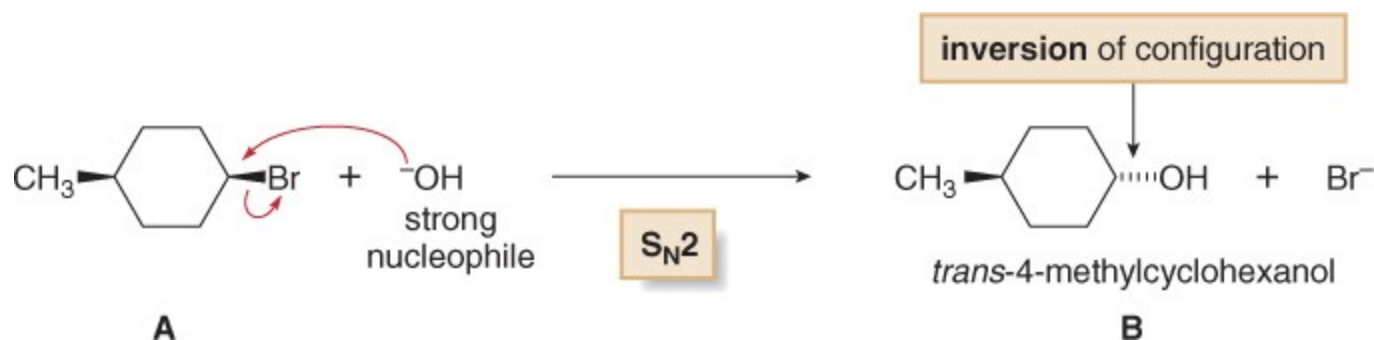


	ethanol	40% water/ 60% ethanol	80% water/20% ethanol	water
<b>Relative reactivity</b>	<b>1</b>	<b>100</b>	<b>14000</b>	<b>100000</b>

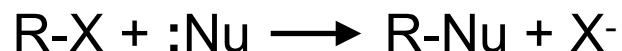
# Predicting the Mechanism




# Predicting the Mechanism



# Alkyl Halides in Organic Synthesis



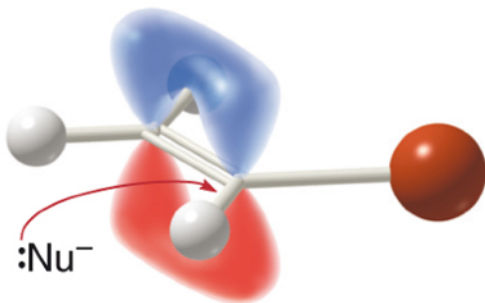
	Nucleophile (:Nu <sup>-</sup> )	Product	Name
Oxygen compounds	<sup>-</sup> OH	R-OH	alcohol
	<sup>-</sup> OR'	R-OR'	ether
	$\begin{array}{c} \text{O} \\ \parallel \\ \text{^-O}-\text{C}-\text{R}' \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{O}-\text{C}-\text{R}' \end{array}$	ester
Carbon compounds	<sup>-</sup> CN	R-CN	nitrile
	<sup>-</sup> :C≡C-H	R-C≡C-H	alkyne
Nitrogen compounds	N <sub>3</sub> <sup>-</sup>	R-N <sub>3</sub>	azide
	:NH <sub>3</sub>	R-NH <sub>2</sub>	amine
Sulfur compounds	<sup>-</sup> SH	R-SH	thiol
	<sup>-</sup> SR'	R-SR'	sulfide
<div style="text-align: center;">    <b>products of nucleophilic substitution</b> </div>			



# Vinyl Halides

## a. Vinyl halides and the $S_N2$ mechanism:

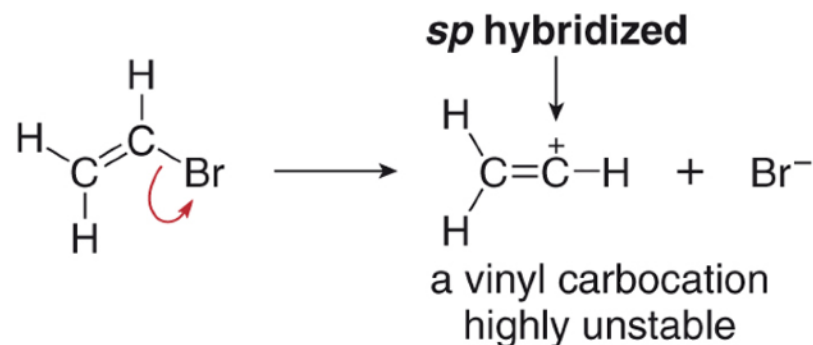
Backside attack of the nucleophile is not possible.



Backside attack would force the nucleophile to approach in the plane of the double bond.

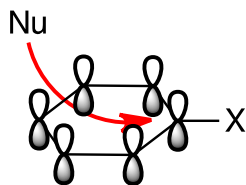
## b. Vinyl halides and the $S_N1$ mechanism:

Heterolysis of the C–X bond forms a very unstable carbocation, making the rate-determining step very slow.



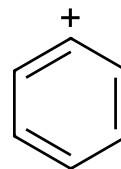
# Aryl Halides

$S_N2$



Backside  
attack is  
impossible

$S_N1$



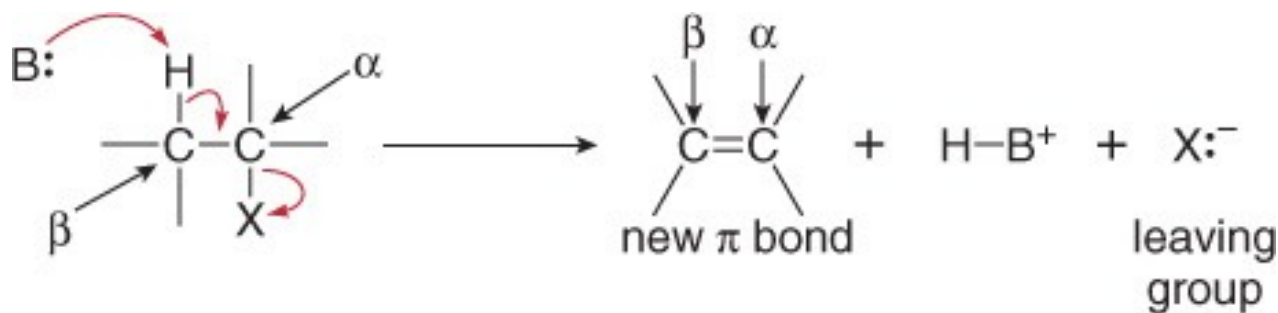
Unstable  $sp^2$   
carbocation

# Eliminations

Chapter 11  
Organic Chemistry, *8th Edition*  
John McMurry

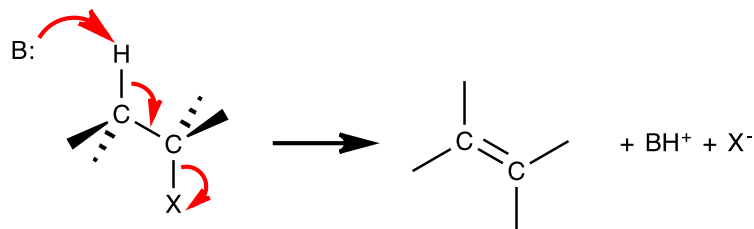
# General Features of Elimination

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

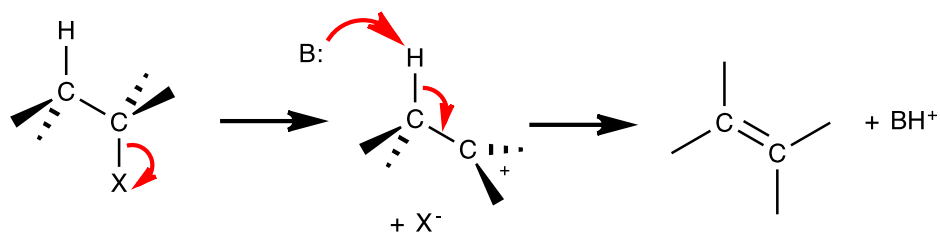


# Elimination Mechanisms

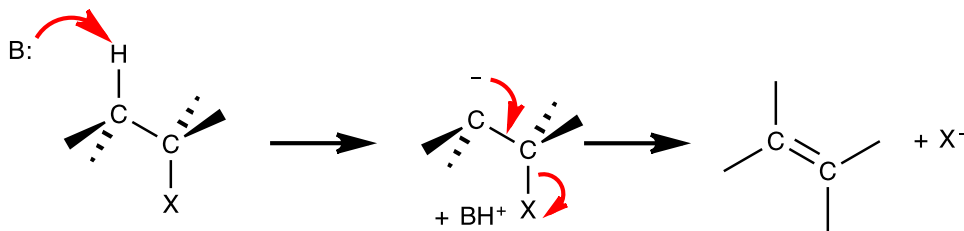
E2



E1



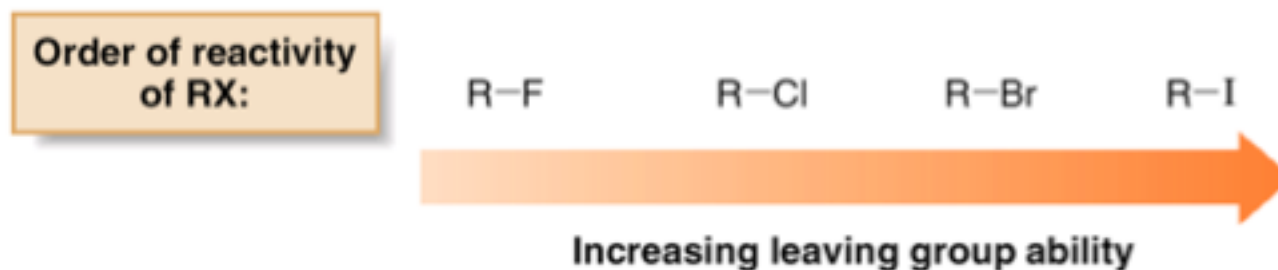
E1cb



[video](#)

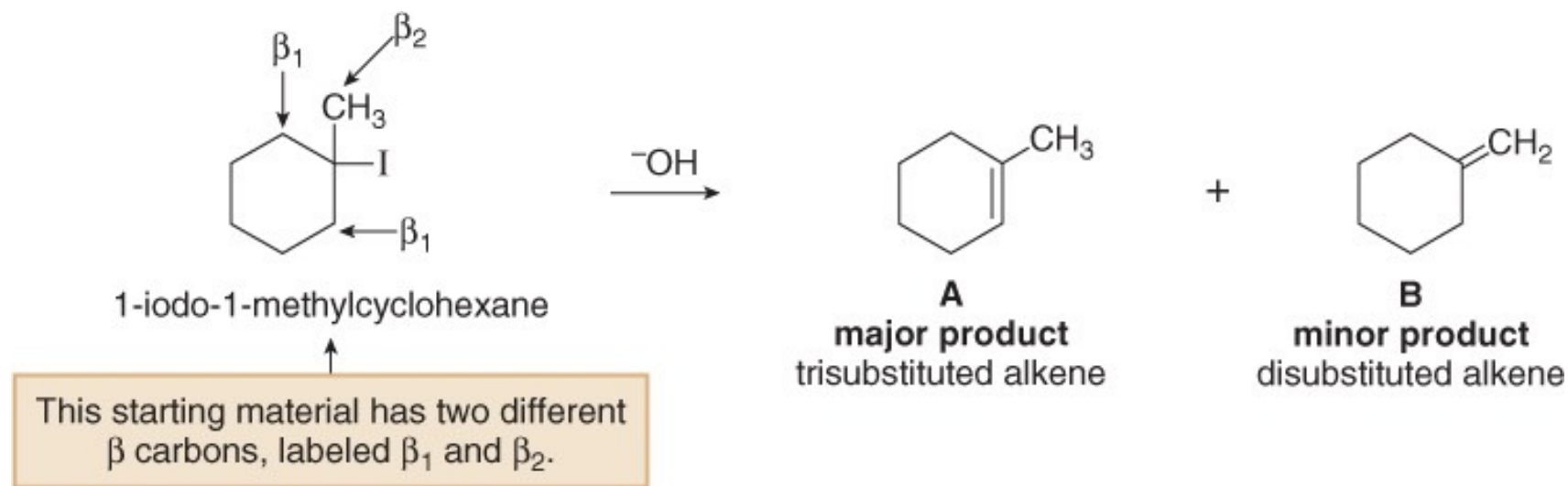
# Leaving Groups in Elimination Reactions

Elimination reactions are faster with good leaving groups:



# The Zaitsev (Saytzeff) Rule

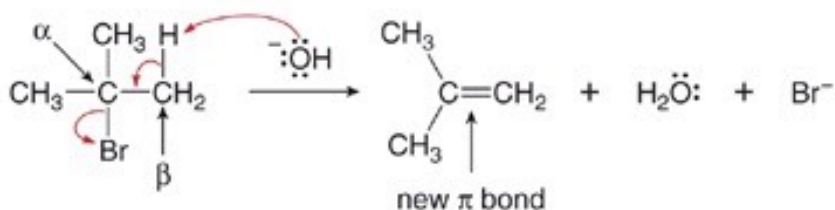
- The major product is the more stable product—the one with the more substituted double bond.



- A reaction is **regioselective** when it yields predominantly or exclusively one constitutional isomer when more than one is possible. Thus, elimination reactions are regioselective.

# Mechanisms of Elimination: E2

- The most common mechanism for dehydrohalogenation is the E2 mechanism.

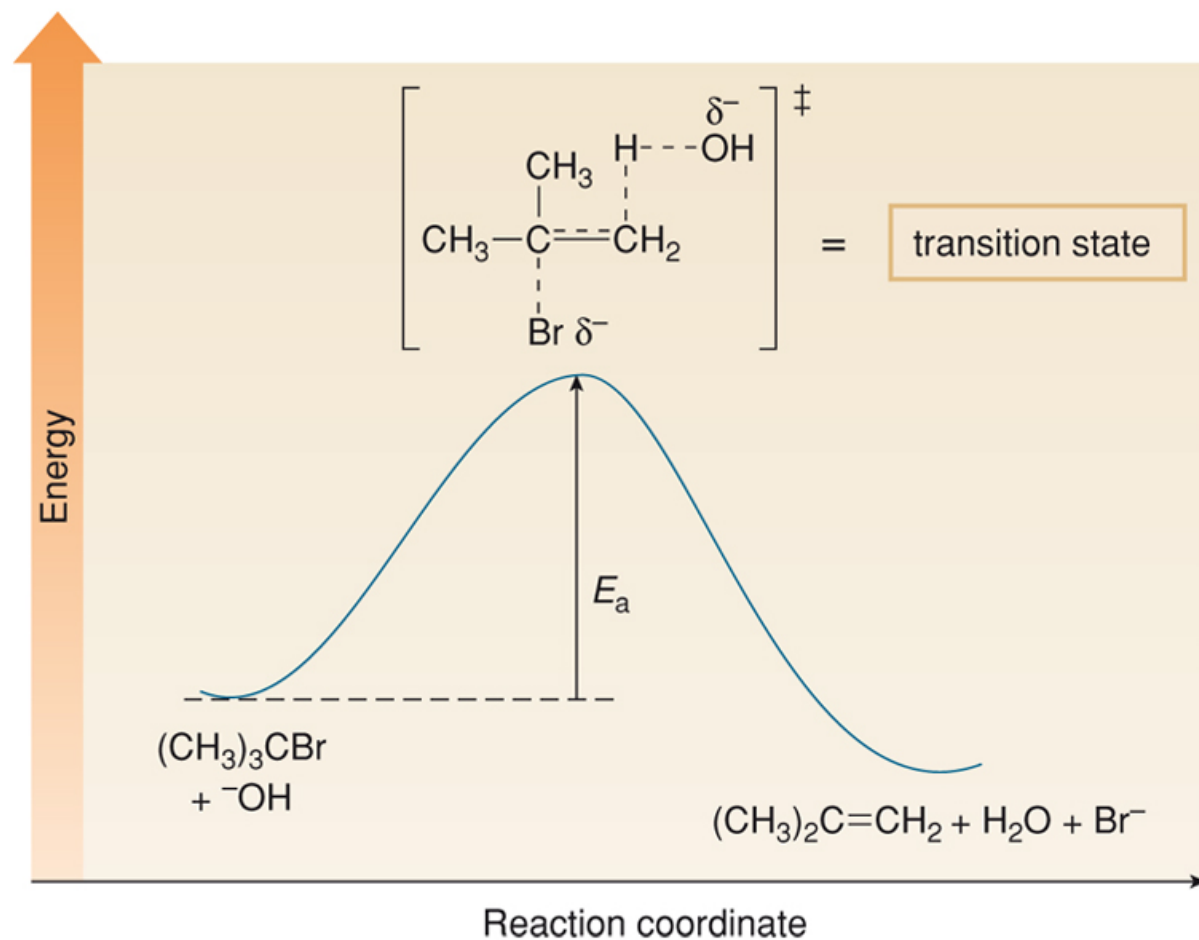
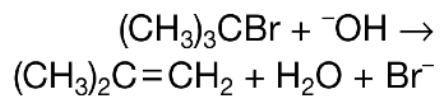


- The base  $\text{OH}^-$  removes a proton from the  $\beta$  carbon, forming  $\text{H}_2\text{O}$  (a by-product).
  - The electron pair in the  $\beta$   $\text{C-H}$  bond forms the new  $\pi$  bond.
  - The leaving group  $\text{Br}^-$  comes off with the electron pair in the  $\text{C-Br}$  bond.
- The reaction is **concerted**—all bonds are broken and formed in a single step.
  - It exhibits **second-order kinetics**, and both the alkyl halide and the base appear in the rate equation, i.e.,

$$v = k[(\text{CH}_3)_3\text{CBr}][\text{OH}^-]$$

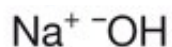


# Mechanisms of Elimination: E2

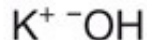


# Mechanisms of Elimination: E2

- E2 reactions are favoured by strong negatively charged bases, such as  $\text{HO}^-$  and its alkyl derivatives,  $\text{RO}^-$ , called alkoxides.



sodium hydroxide



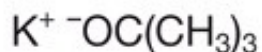
potassium hydroxide



sodium methoxide



sodium ethoxide

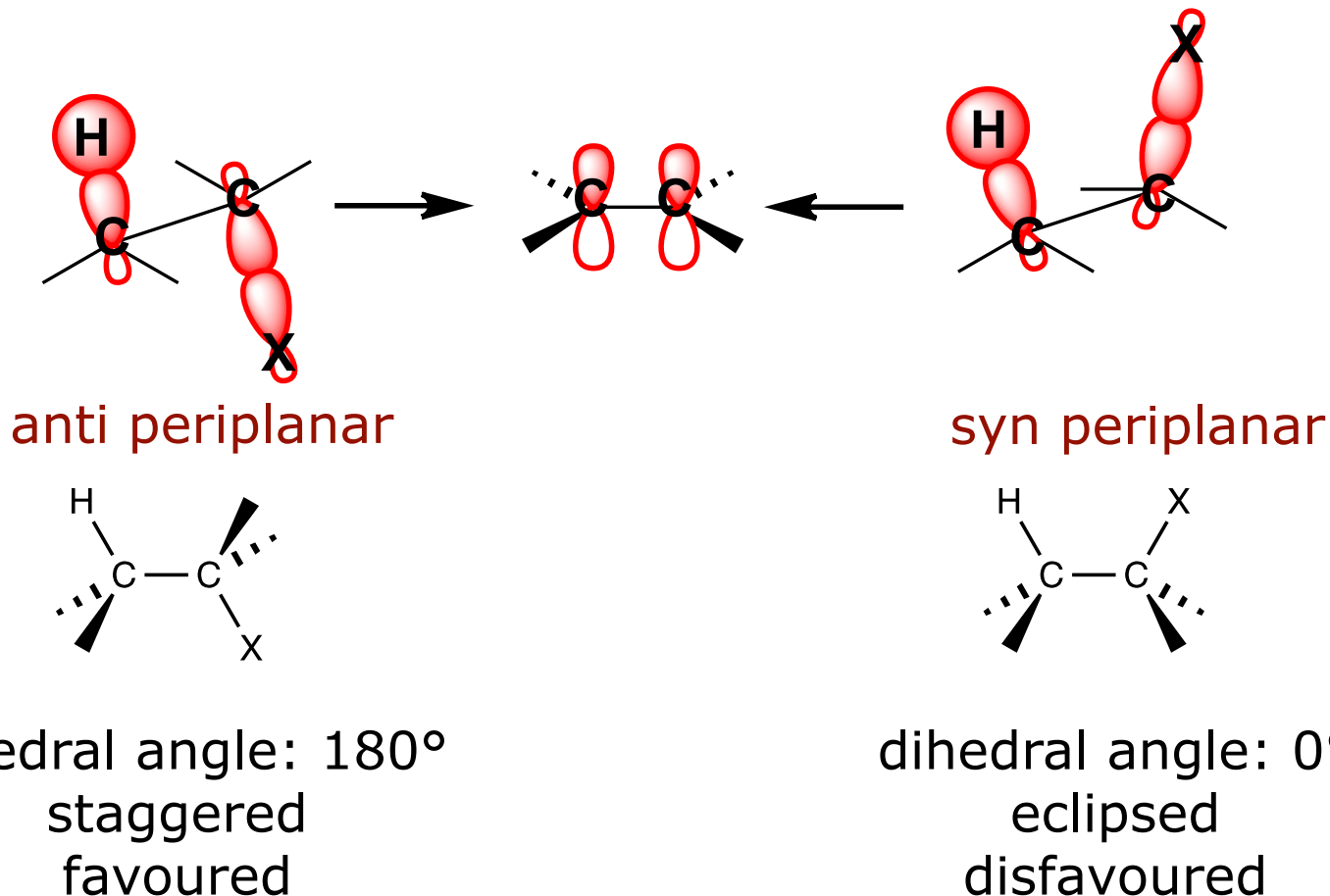


potassium *tert*-butoxide

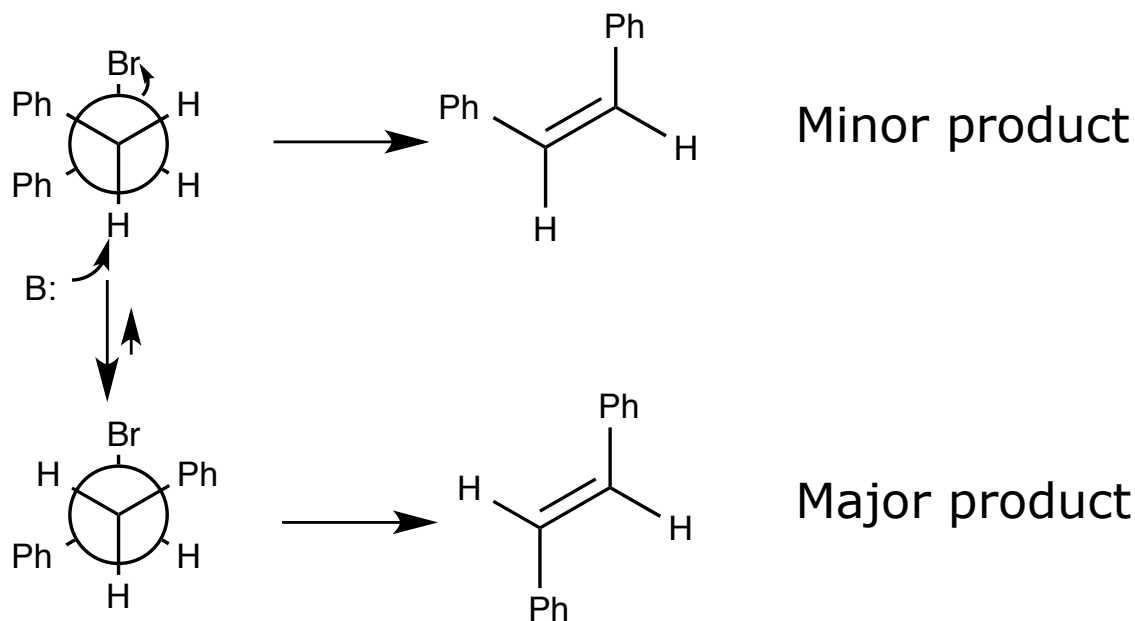
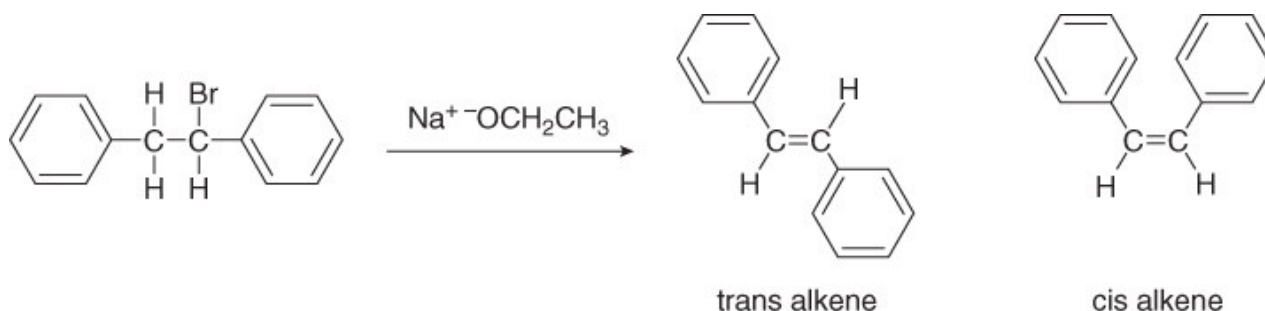
- 
- Potassium *t*-butoxide is a strong, non-nucleophilic base.

# Stereochemistry of the E2 Reaction

- For efficient overlap the C—H and C—X bonds must be **coplanar**.

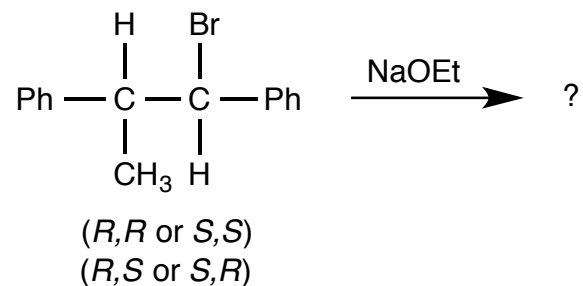


# Stereochemistry of the E2 Reaction



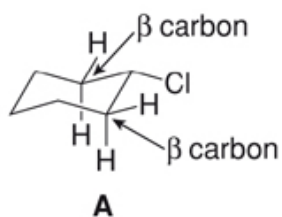
The E2 reaction is **stereoselective** because one stereoisomer is formed preferentially.

# Stereochemistry of the E2 Reaction



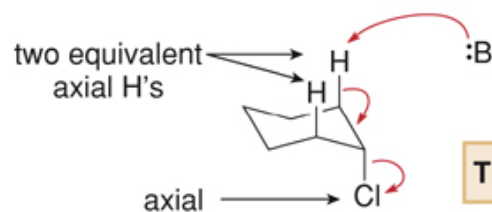
# E2 Reactions in Cyclohexanes

**Conformation A** (equatorial Cl):



no reaction with this conformation

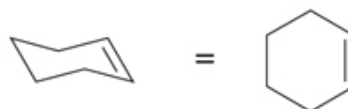
**Conformation B** (axial Cl):



**This conformation reacts.**

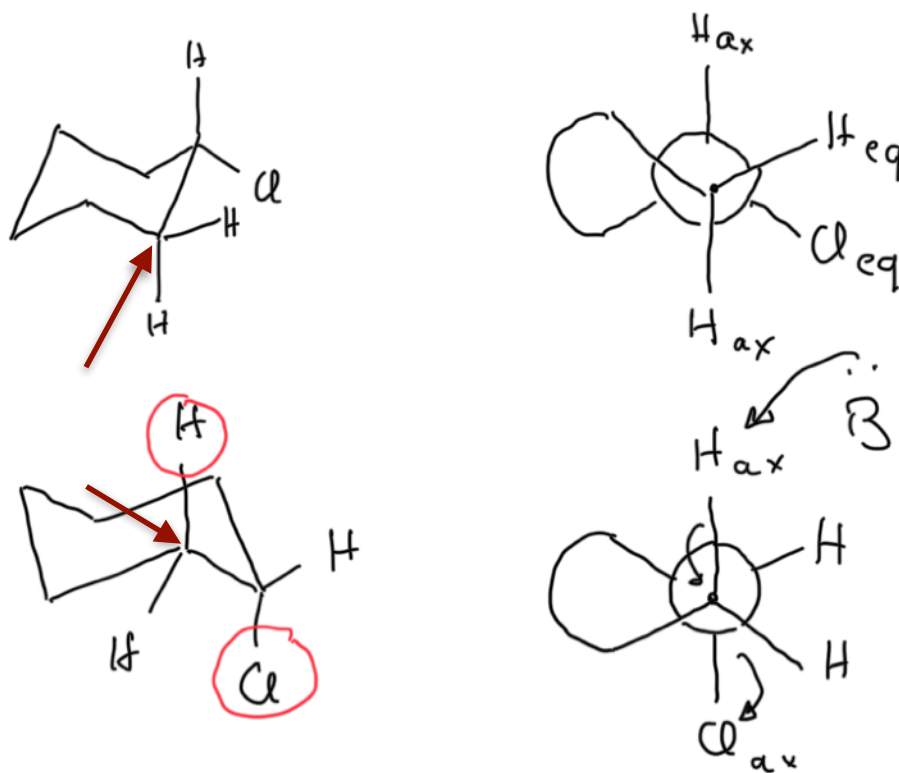
**B**

The H and Cl are **trans diaxial**.

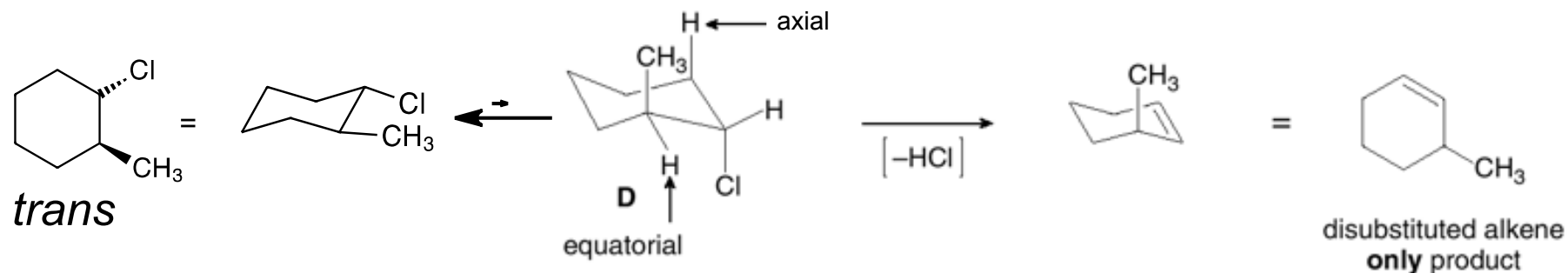
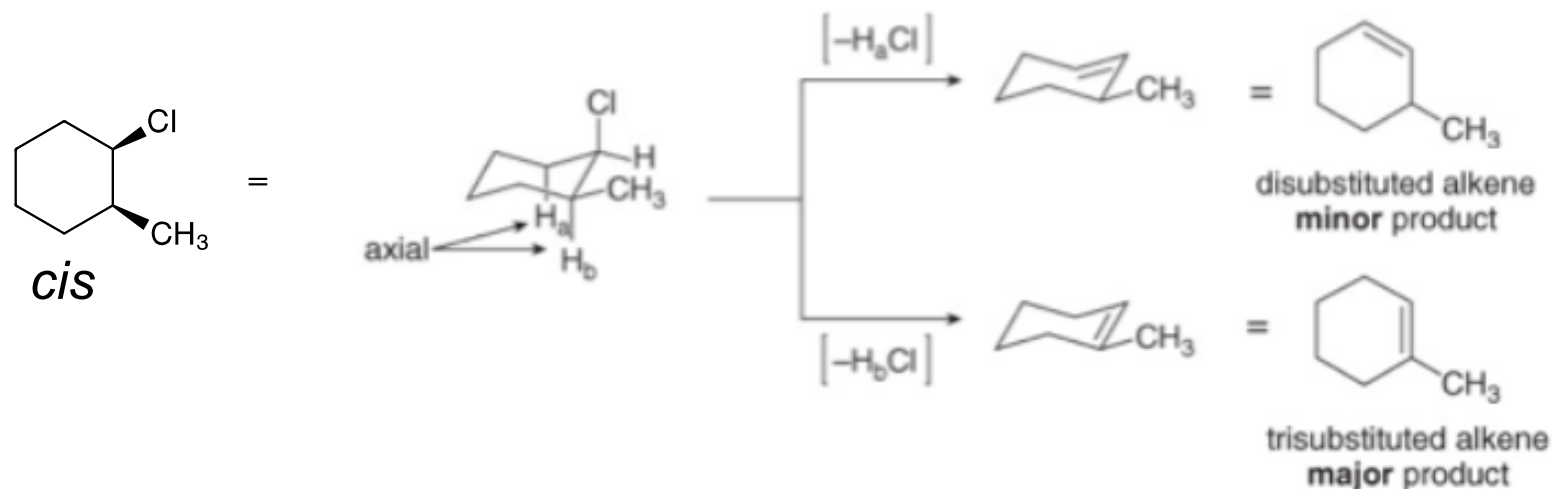


# E2 Reactions in Cyclohexanes

Proiezioni di Newman lungo i legami indicati dalla freccia



# E2 Reactions in Cyclohexanes





# Mechanisms of Elimination: E1

Step [1] The C–I bond is broken.



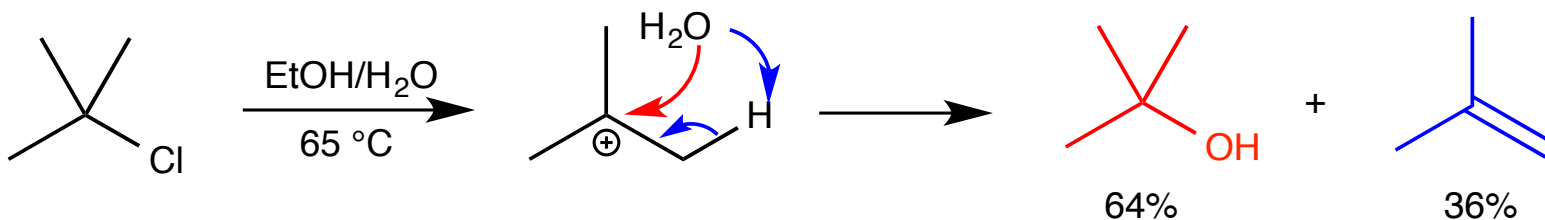
- **Heterolysis of the C–I bond** forms an intermediate **carbocation**. This is the same first step as the  $\text{S}_{\text{N}}1$  mechanism. It is responsible for the first-order kinetics because it is rate-determining.

Step [2] A C–H bond is cleaved and the  $\pi$  bond is formed.

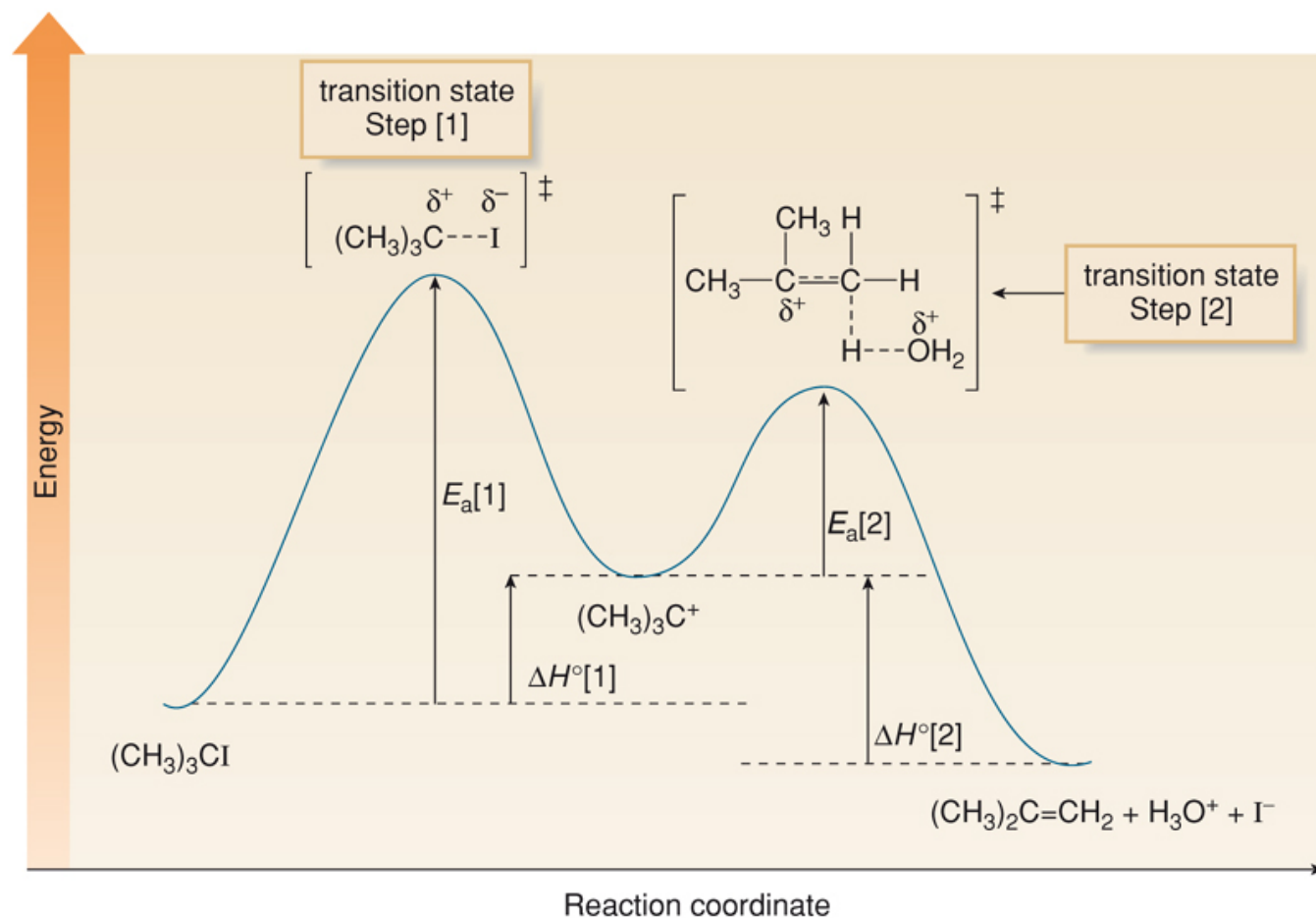
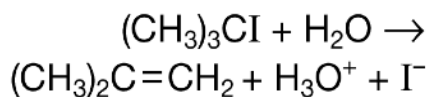


- A base (such as  $\text{H}_2\text{O}$  or  $\text{I}^-$ ) **removes a proton from a carbon adjacent to the carbocation** (a  $\beta$  carbon). The electron pair in the C–H bond is used to form the new  $\pi$  bond.

- E1 reactions exhibit first-order kinetics:  $v = k[(\text{CH}_3)_3\text{I}]$
- E1 reactions frequently accompany  $\text{S}_{\text{N}}1$  reactions

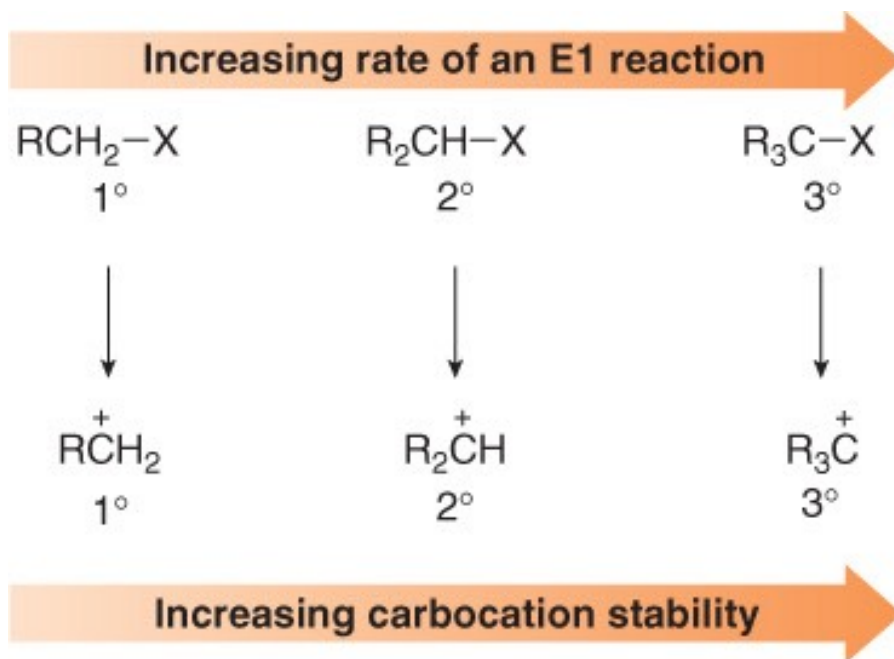


# Mechanisms of Elimination: E1



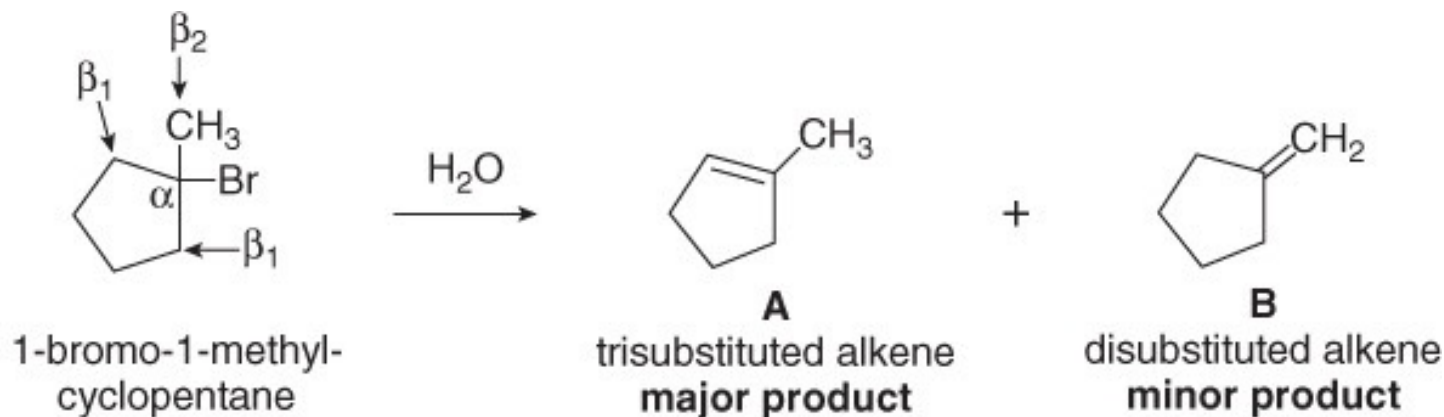
# Mechanisms of Elimination: E1

The rate of an E1 reaction increases as the number of R groups on the carbon with the leaving group increases.



# Mechanisms of Elimination: E1

E1 reactions are regioselective, favoring formation of the more substituted, more stable alkene (Zaitsev's rule)

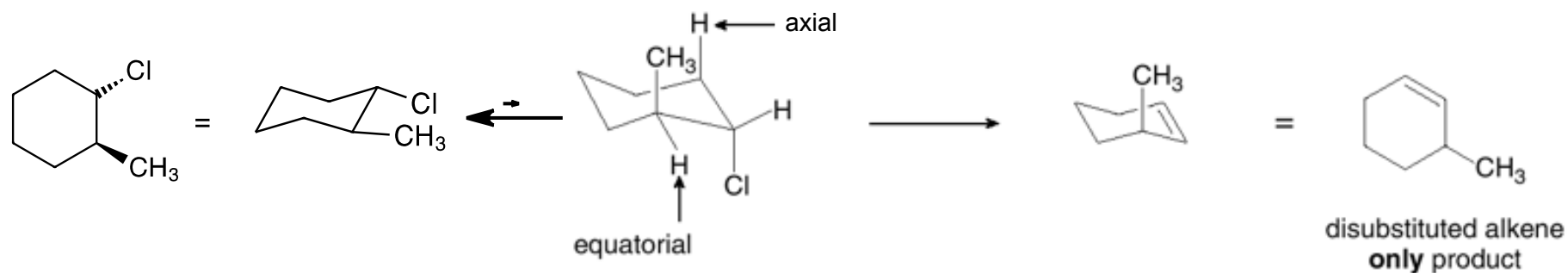


# Mechanisms of Elimination

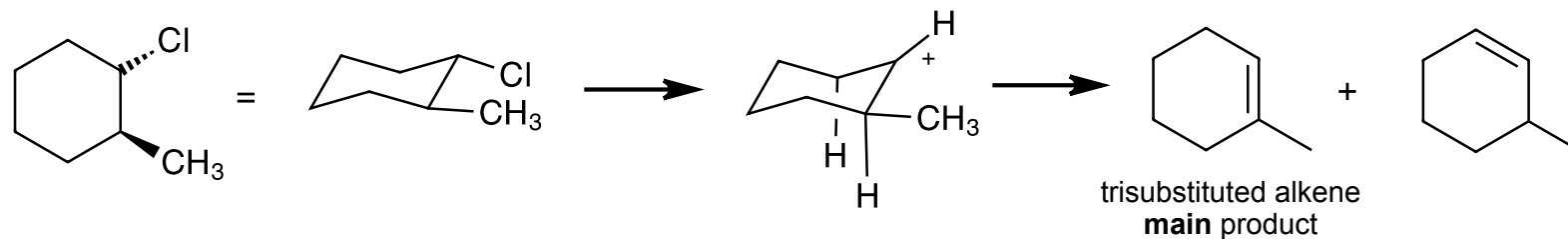
	E2	E1
Mechanism	One step	Two steps
Kinetics	Second order	First order
Substrate	1ry, 2ry and 3ry halides	3ry (and 2ry) halides
Leaving group	Favored by good leaving groups	Favored by good leaving groups
Base	Favored by strong bases	Favored by weak bases (H <sub>2</sub> O, ROH)
Stereochemistry	Antiperiplanar-stereoselective	Not stereoselective
Solvent	Favored by non polar solvents	Favored by polar protic solvents.

# When is the Mechanism E1 or E2?

E2 conditions: 1M NaOEt, EtOH, 100 °C

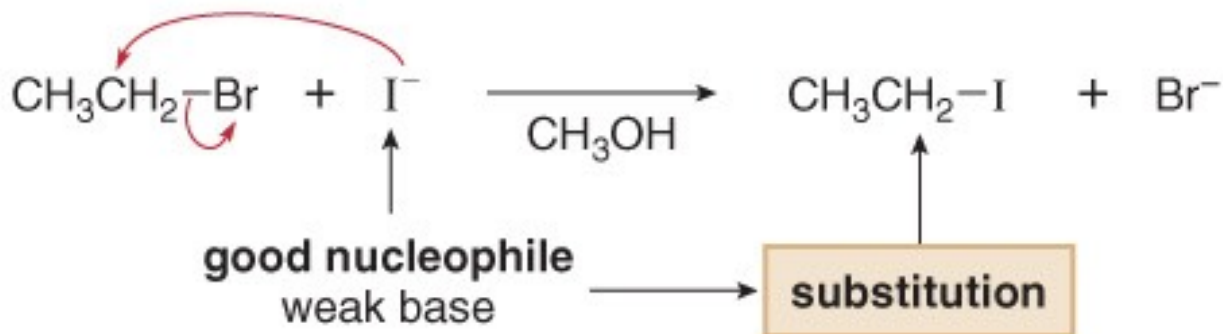


E1 conditions: 0.01M NaOEt, 80% EtOH, 160 °C

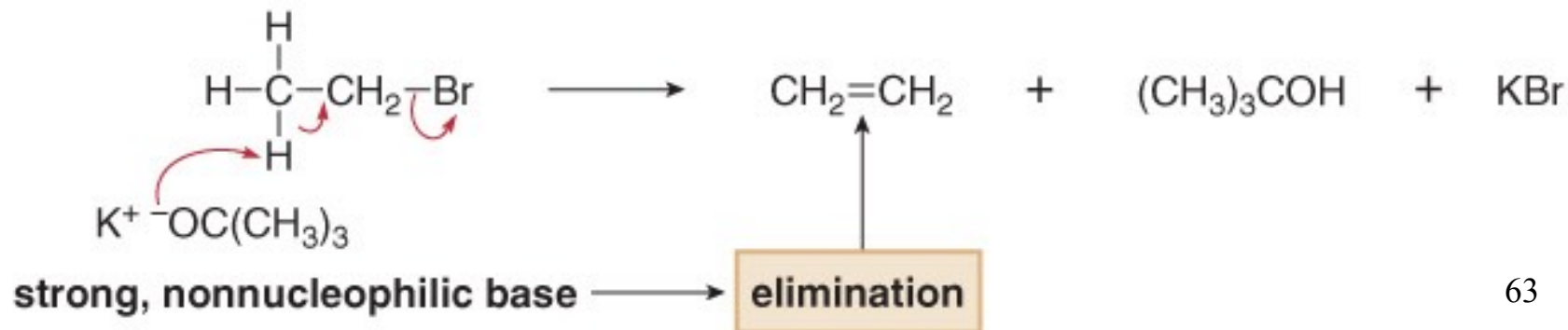


# Substitution vs Elimination

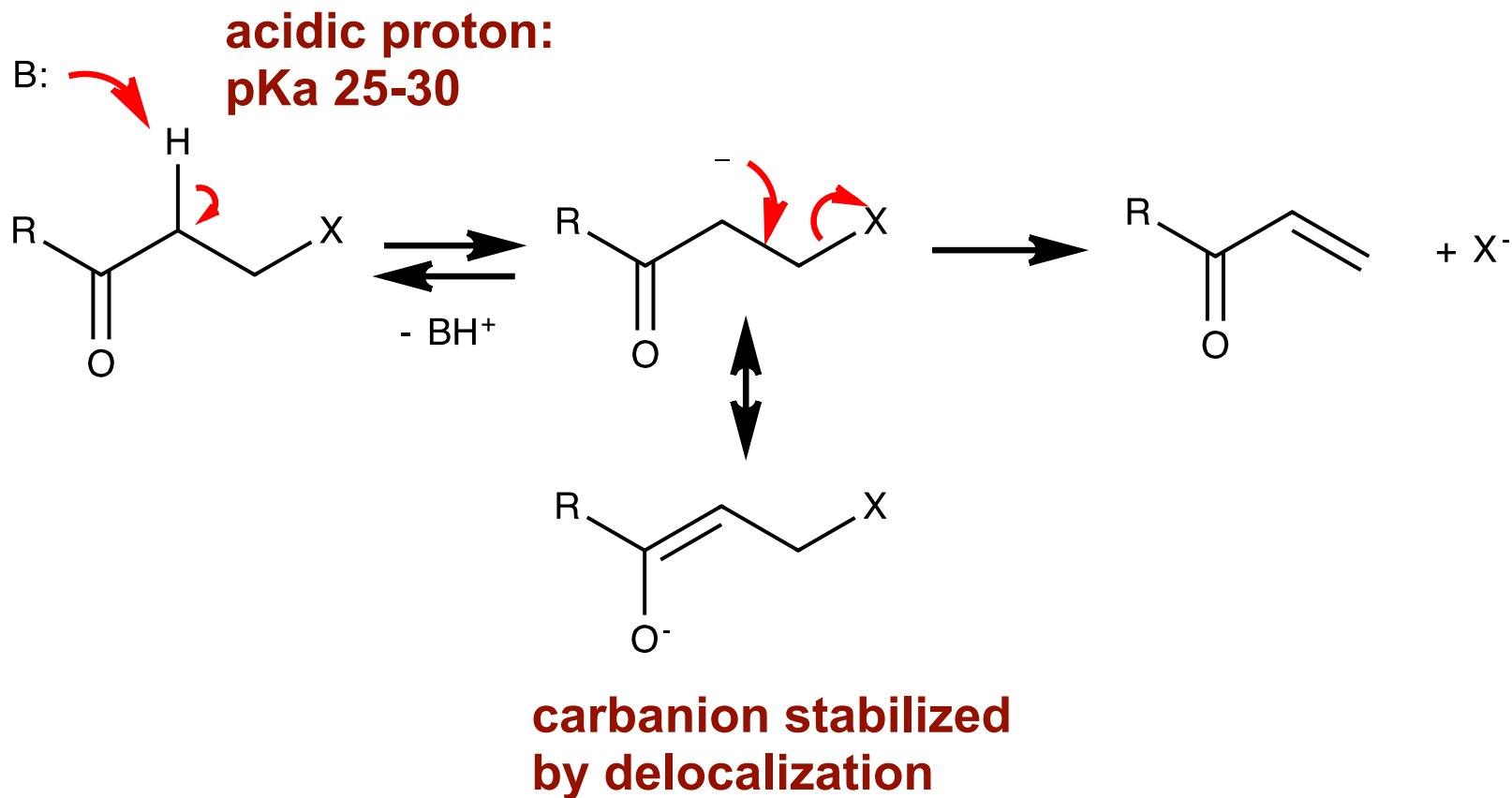
- Good nucleophiles that are weak bases favor substitution over elimination. These include  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{HS}^-$ ,  $\text{CN}^-$ , and  $\text{CH}_3\text{COO}^-$ .



- Bulky nonnucleophilic bases ( $\text{KOC}(\text{CH}_3)_3$ ) favor elimination over substitution.



# Mechanisms of Elimination—E1cb





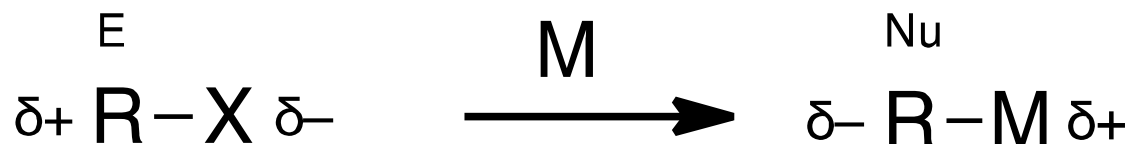
# Substitution and Elimination

<i>Alkyl halide</i>	SN2	SN1	E2	E1	E1cb
methyl	yes				
primary	<i>with good, weakly basic nucleophiles</i>		<i>with strong, non-nucleophilic bases</i>		<i>with activated substrates</i>
secondary allylic benzylic	<i>with good nucleophiles in aprotic solvents</i>	<i>with weak nucleophiles in protic solvents</i>	<i>with strong bases in aprotic solvents</i>	<i>with weak bases in protic solvents</i>	<i>with activated substrates</i>
tertiary		<i>with non basic nucleophiles</i>	<i>with strong bases</i>	<i>with weak bases</i>	<i>with activated substrates</i>

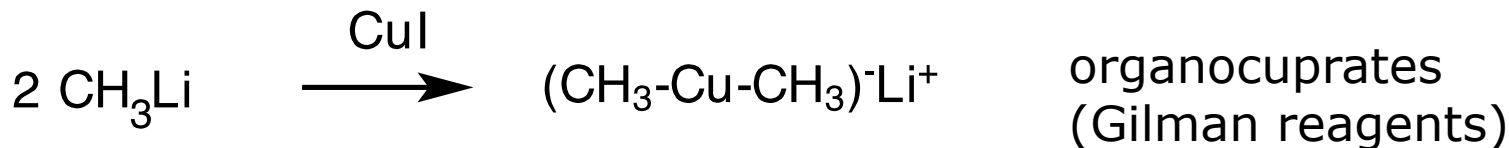
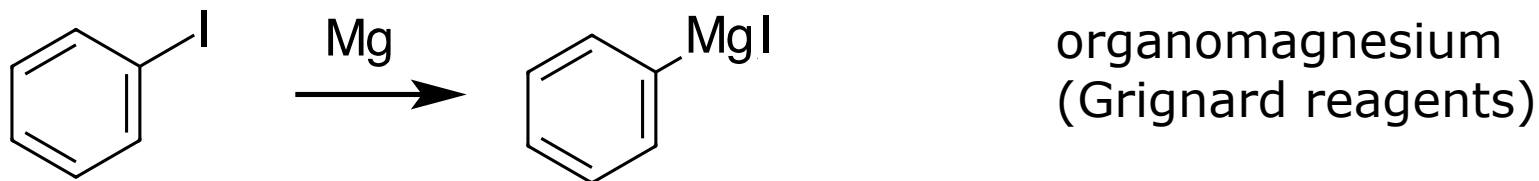
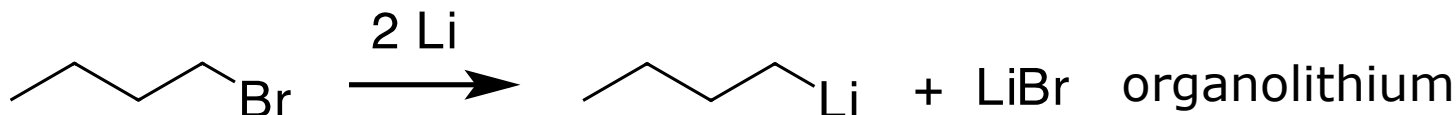
# Competition Between Substitution and Elimination

<i>Alkyl halide/ base-nucleophile</i>	strong bases strong nucleophiles (F <sup>-</sup> , Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup> , HO <sup>-</sup> , RO <sup>-</sup> , RS <sup>-</sup> , CN <sup>-</sup> , acetylides, R-M, NH <sub>3</sub> , amines)	strong bases non nucleophilic (tBuO <sup>-</sup> )	weak bases weak nucleophiles (H <sub>2</sub> O, ROH, RCOOH)
methyl	<i>SN2</i>	-	-
primary	<i>SN2/E2</i>	<i>E2</i>	-
secondary allylic benzylic	<i>SN2/E2</i>	<i>E2</i>	<i>SN1/E1</i>
tertiary	<i>E2</i>	<i>E2</i>	<i>SN1/E1</i>

# Reverse of Polarity. Organometallic Compounds

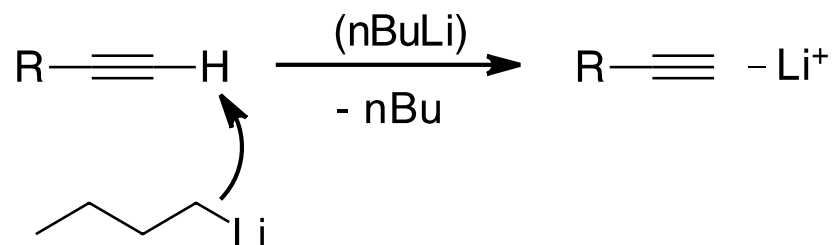


Examples:



# Reverse of Polarity. Organometallic Compounds

strong bases:



strong nucleophiles:

