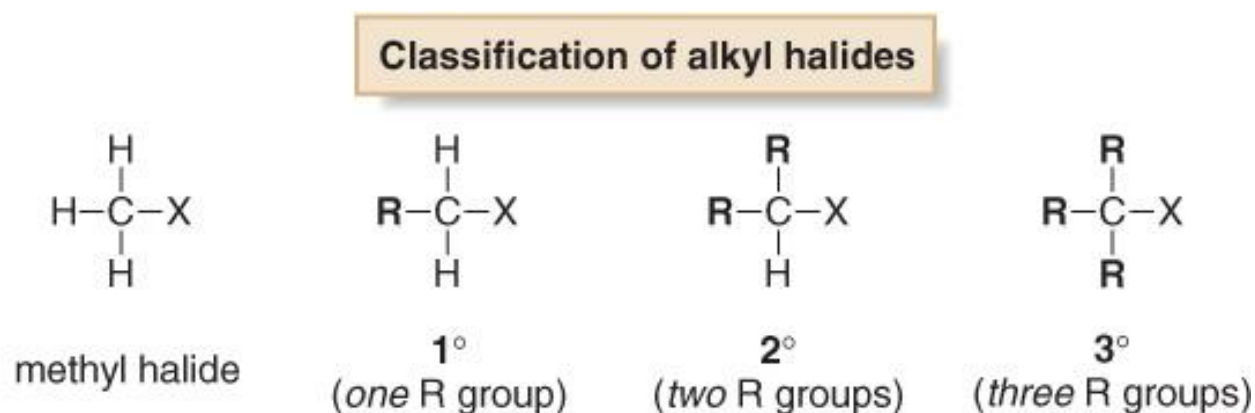
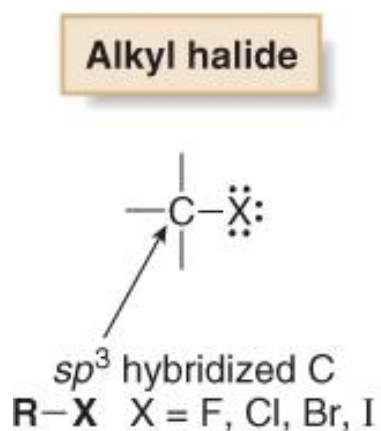


Alkyl Halides

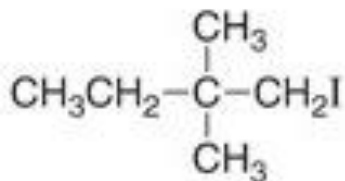
Chapter 10
Organic Chemistry, *8th Edition*
John McMurry

Introduction to Alkyl Halides

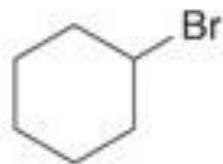
- **Alkyl halides** are organic molecules containing a halogen atom bonded to an sp^3 hybridized carbon atom.
- Alkyl halides are classified as **primary** (1°), **secondary** (2°), or **tertiary** (3°), depending on the number of carbons bonded to the carbon with the halogen atom.
- The halogen atom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



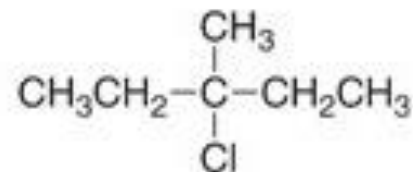
Introduction to Alkyl Halides



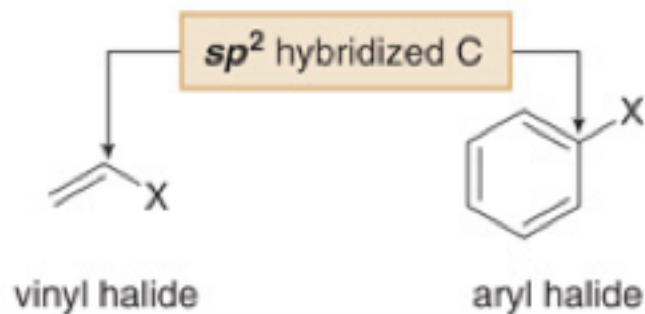
1° iodide



2° bromide



3° chloride



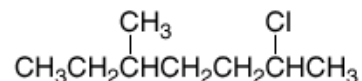
Different reactivity

Nomenclature

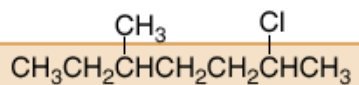
How To

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.



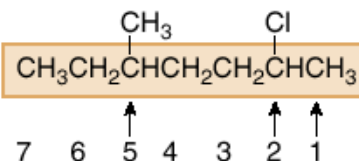
7 C's in the longest chain

7 C's ----> heptane

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

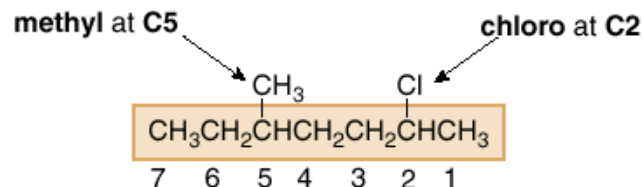
Step [2] Apply all other rules of nomenclature.

a. **Number** the chain.



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

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



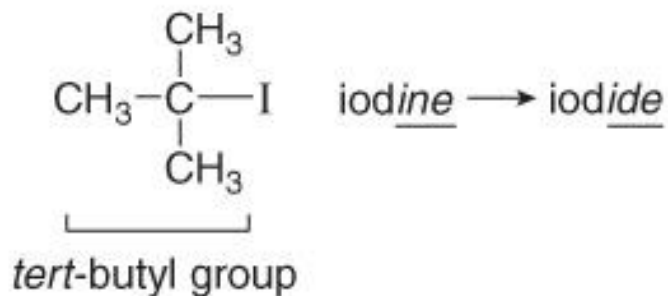
c. **Alphabetize**: c for chloro, then m for methyl.

ANSWER: 2-chloro-5-methylheptane

Nomenclature

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

Common names



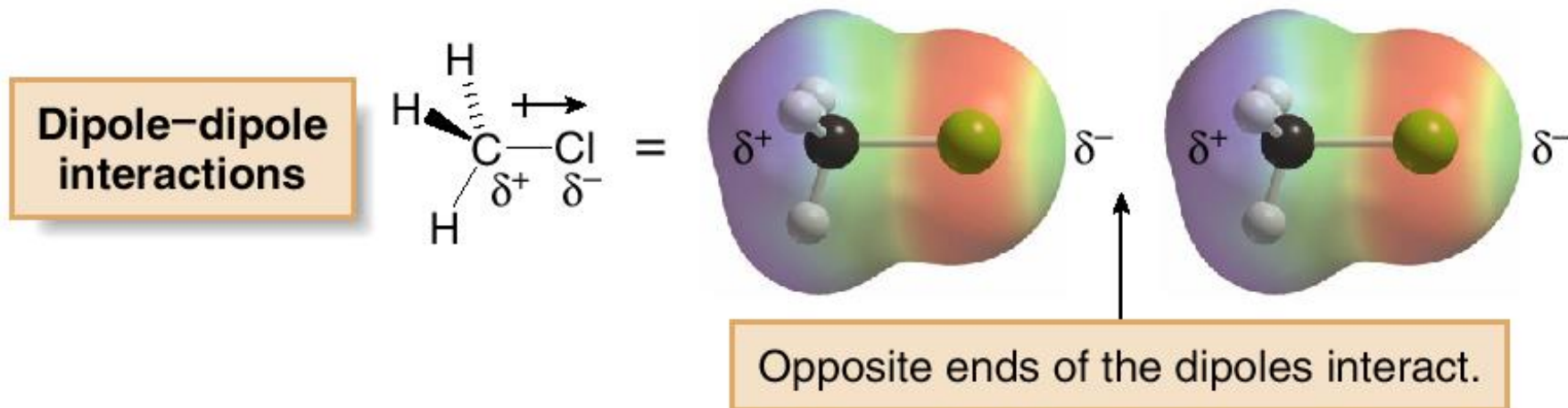
tert-butyl iodide



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.



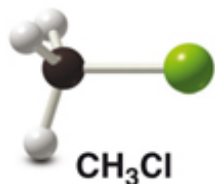
Physical Properties

Table 7.1

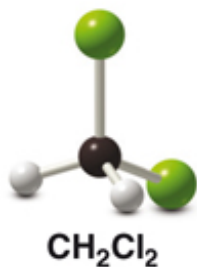
Physical Properties of Alkyl Halides

Property	Observation
Boiling point and melting point	<ul style="list-style-type: none"> Alkyl halides have higher bp's and mp's than alkanes having the same number of carbons. <div style="text-align: center; margin: 10px 0;"> CH_3CH_3 and $\text{CH}_3\text{CH}_2\text{Br}$ bp = -89°C bp = 39°C </div> Bp's and mp's increase as the size of R increases. <div style="text-align: center; margin: 10px 0;"> $\text{CH}_3\text{CH}_2\text{Cl}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ </div> <div style="display: flex; justify-content: space-around; align-items: center; margin: 5px 0;"> <div style="text-align: center;"> $\text{mp} = -136^\circ\text{C}$ $\text{bp} = 12^\circ\text{C}$ </div> <div style="text-align: center;"> $\text{mp} = -123^\circ\text{C}$ $\text{bp} = 47^\circ\text{C}$ </div> <div style="border: 1px solid black; padding: 5px; margin-left: 20px;"> larger surface area— higher mp and bp </div> </div> Bp's and mp's increase as the size of X increases. <div style="text-align: center; margin: 10px 0;"> $\text{CH}_3\text{CH}_2\text{Cl}$ and $\text{CH}_3\text{CH}_2\text{Br}$ </div> <div style="display: flex; justify-content: space-around; align-items: center; margin: 5px 0;"> <div style="text-align: center;"> $\text{mp} = -136^\circ\text{C}$ $\text{bp} = 12^\circ\text{C}$ </div> <div style="text-align: center;"> $\text{mp} = -119^\circ\text{C}$ $\text{bp} = 39^\circ\text{C}$ </div> <div style="border: 1px solid black; padding: 5px; margin-left: 20px;"> more polarizable halogen— higher mp and bp </div> </div>
Solubility	<ul style="list-style-type: none"> RX is soluble in organic solvents. RX is insoluble in water.

Interesting Alkyl Halides



- **Chloromethane (CH₃Cl)** is produced by giant kelp and algae and also found in emissions from volcanoes such as Hawaii's Kilauea. Almost all of the atmospheric chloromethane results from these natural sources.

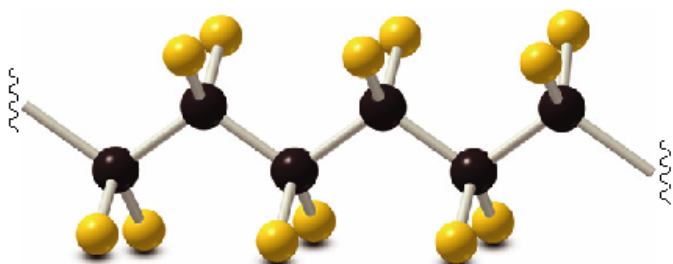
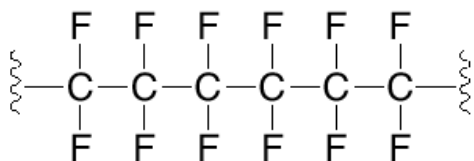


- **Dichloromethane (or methylene chloride, CH₂Cl₂)** is an important solvent, once used to decaffeinate coffee. Coffee is now decaffeinated by using supercritical CO₂ due to concerns over the possible ill effects of trace amounts of residual CH₂Cl₂ in the coffee. Subsequent studies on rats have shown, however, that no cancers occurred when animals ingested the equivalent of over 100,000 cups of decaffeinated coffee per day.

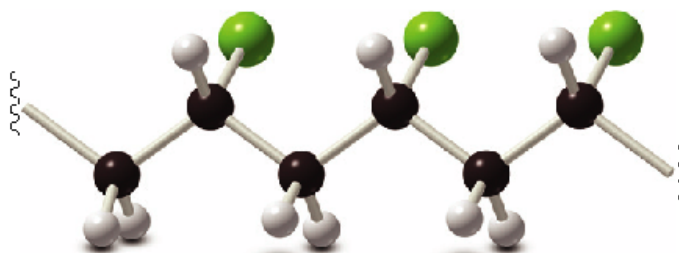
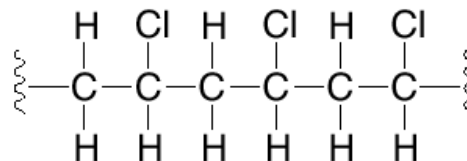


- **Halothane (CF₃CHClBr)** is a safe general anesthetic that has now replaced other organic anesthetics such as CHCl₃, which causes liver and kidney damage, and CH₃CH₂OCH₂CH₃ (diethyl ether), which is very flammable.

Interesting Alkyl Halides



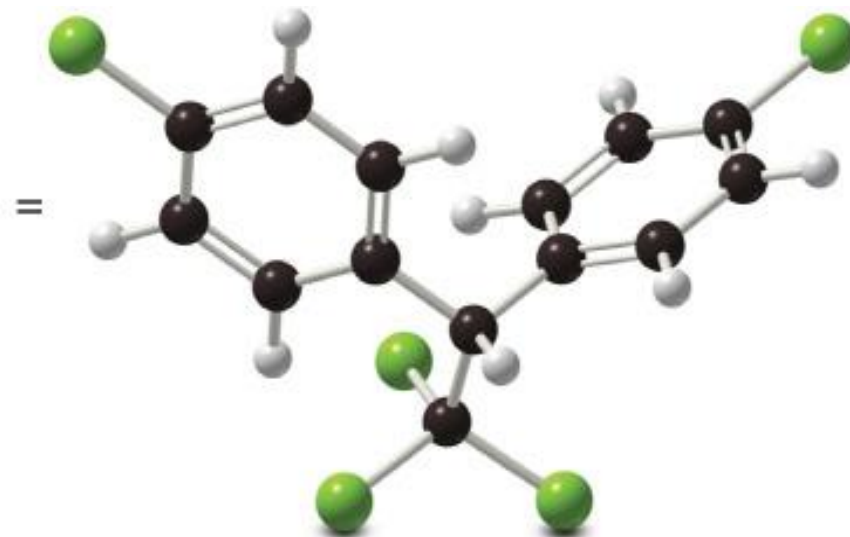
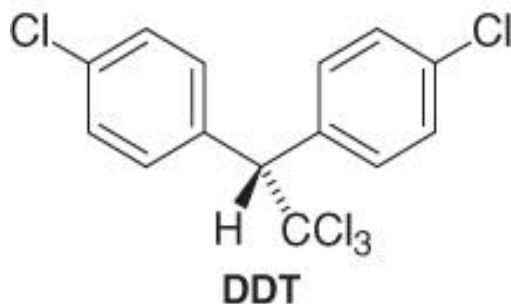
Teflon
(nonstick coating)



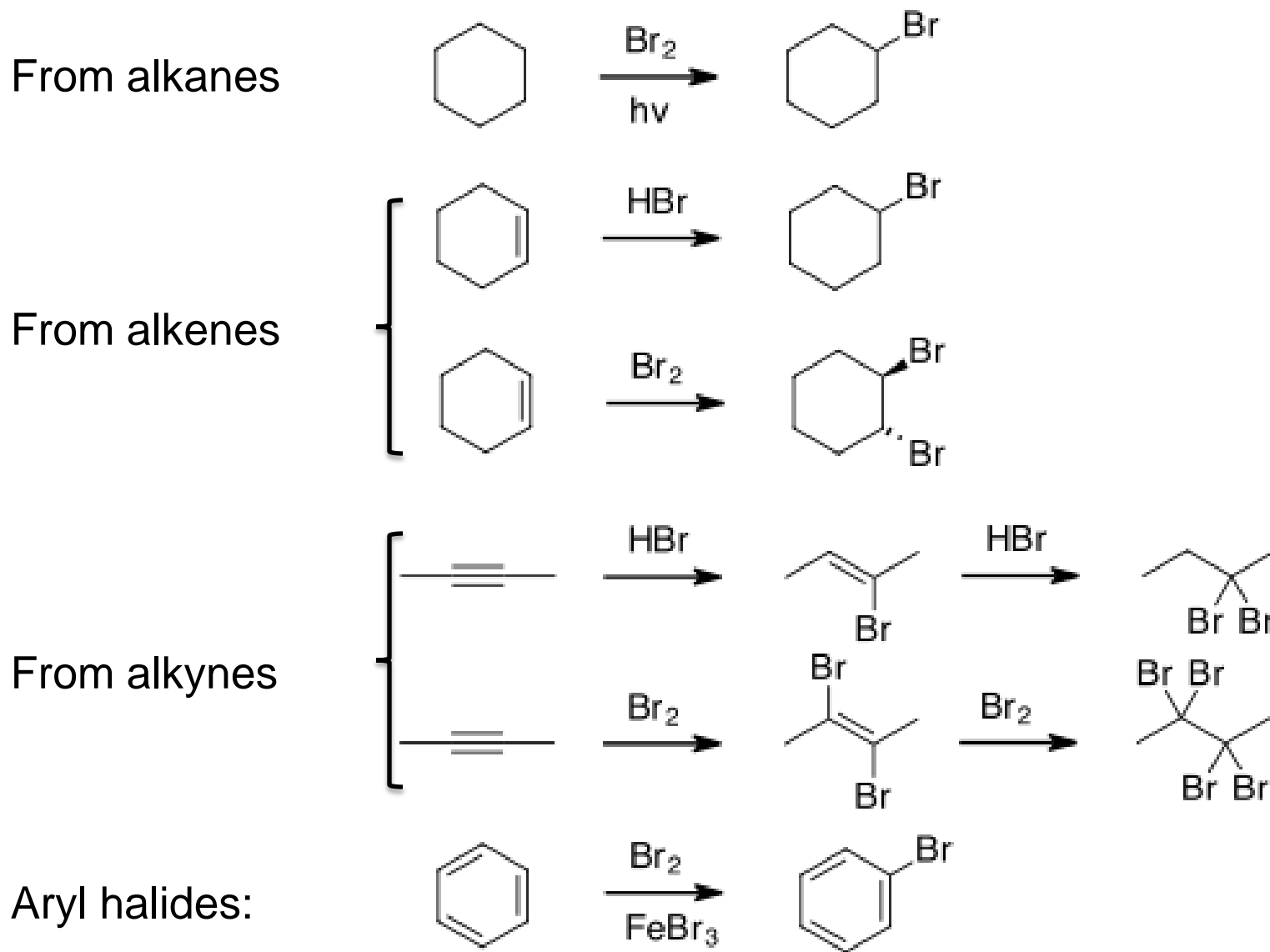
poly(vinyl chloride) (PVC)
(plastic used in films, pipes, and insulation)



CFCl₃
CFC 11
Freon 11

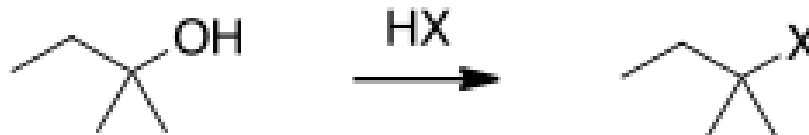


Preparation

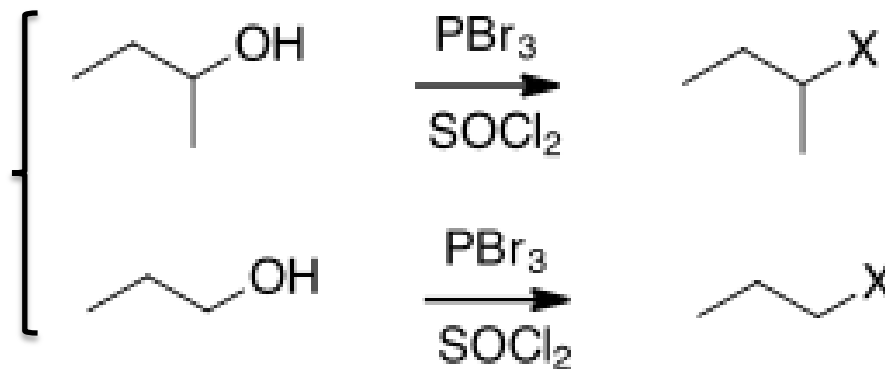


Preparation from alcohols

tertiary

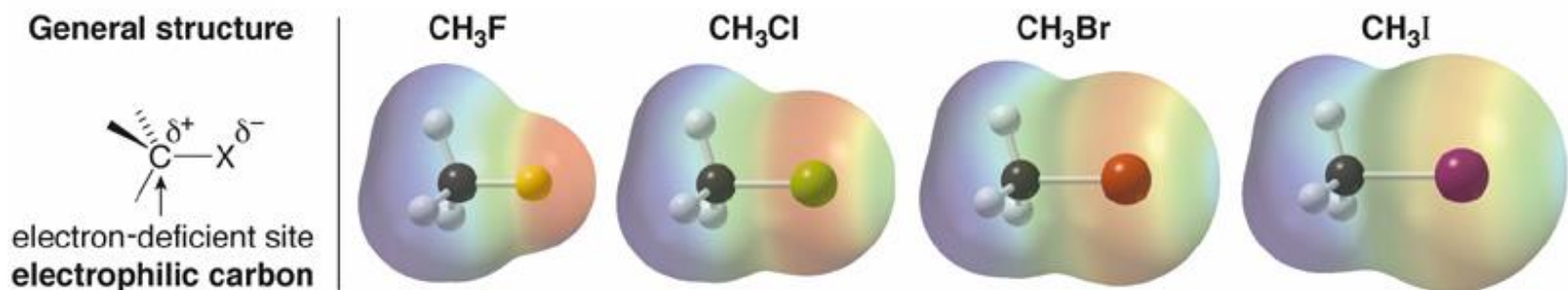


primary
and
secondary



The Polar Carbon-Halogen Bond

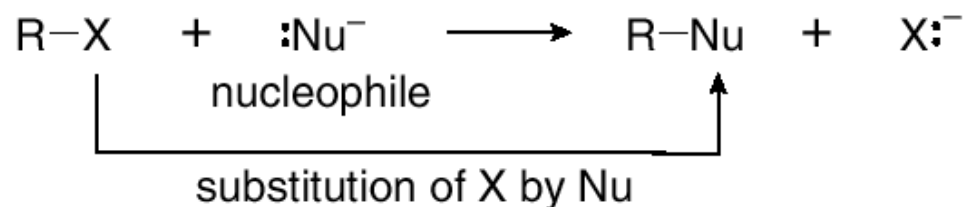
- The electronegative halogen atom in alkyl halides creates a polar C—X bond, making the carbon atom electron deficient. Electrostatic potential maps of four simple alkyl halides illustrate this point.



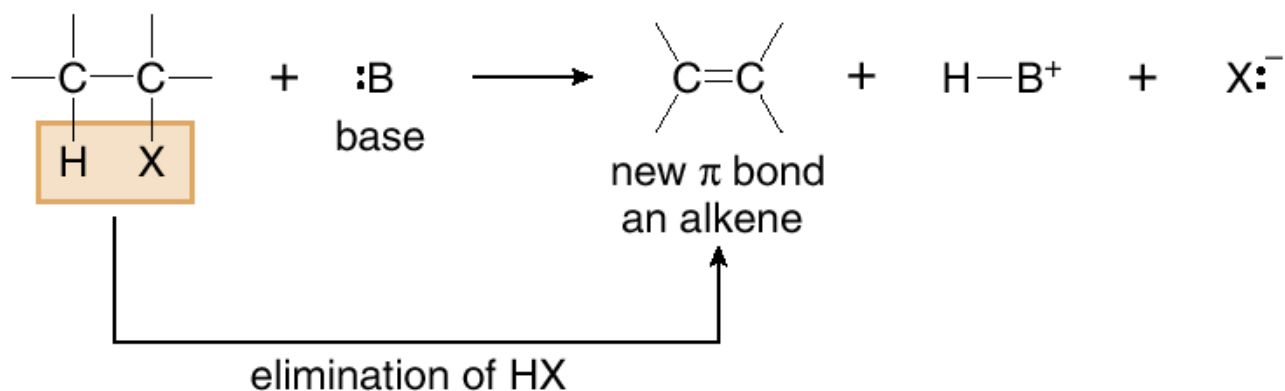
- The polar C—X bond makes the carbon atom *electron deficient* in each CH₃X molecule.

The Polar Carbon-Halogen Bond

- Alkyl halides undergo substitution reactions with nucleophiles.



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



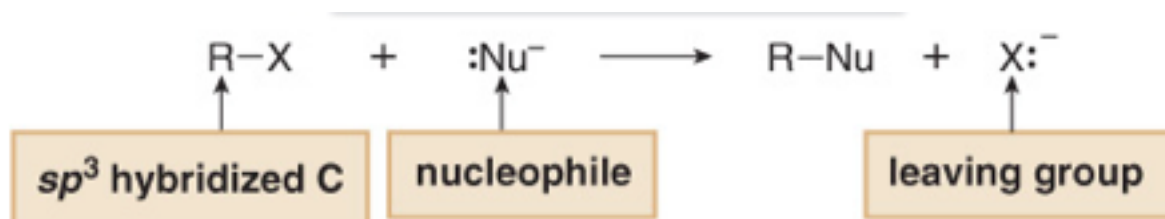
Nucleophilic Substitution

Chapter 11

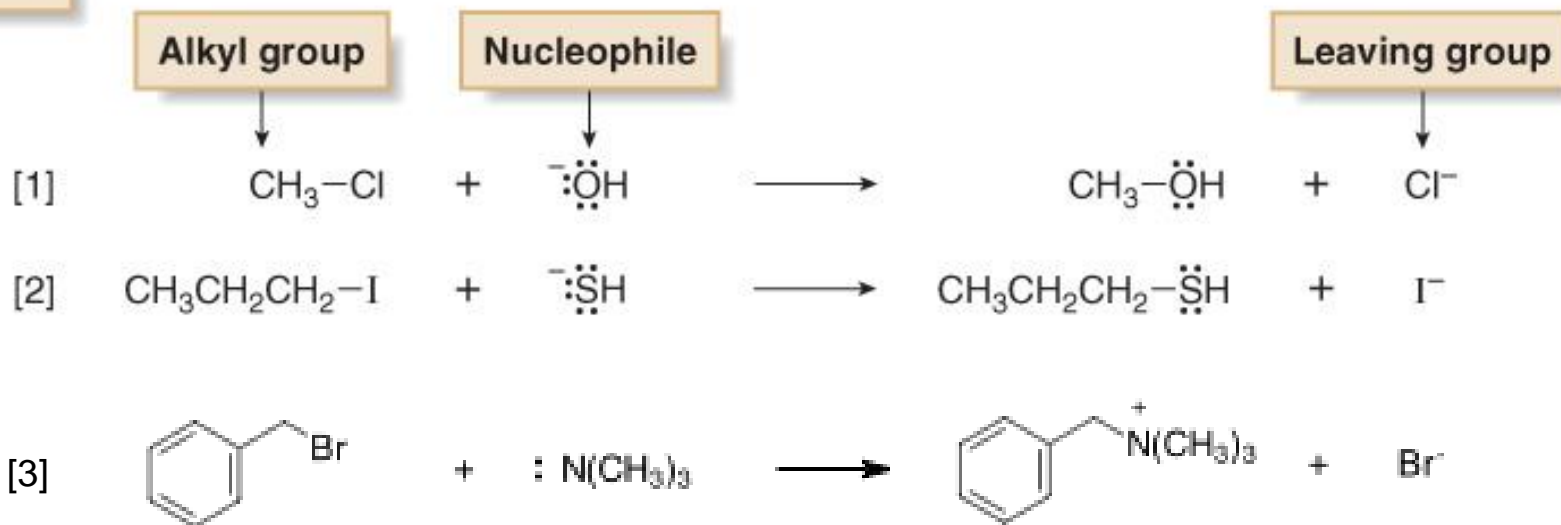
Organic Chemistry, *8th Edition*

John McMurry

General Features of Nucleophilic Substitution



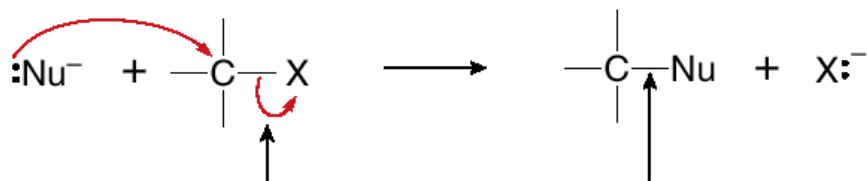
Examples



Mechanism

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

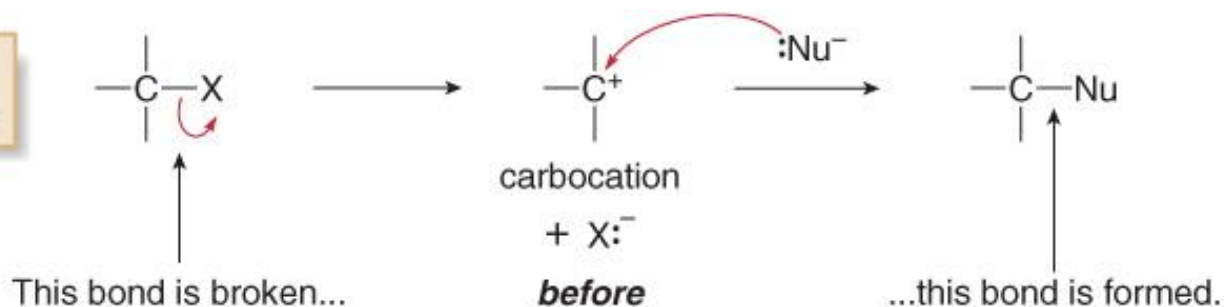
One-step
mechanism



This bond is broken... **as** ...this bond is formed.

Bond breaking occurs before bond making. **S_N1**

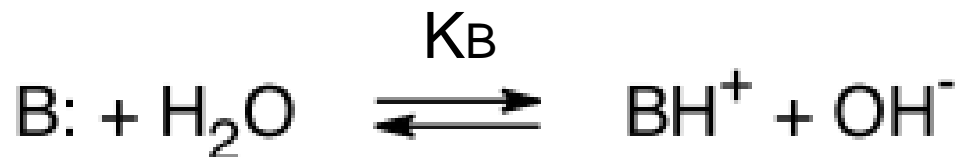
Two-step
mechanism



The Nucleophile

- 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.

HO^- is a stronger base and stronger nucleophile than CH_3COO^- .
($\text{p}K_a$: $\text{H}_2\text{O} = 15.7$, $\text{CH}_3\text{COOH} = 4.8$).

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

HO^- is a stronger base and stronger nucleophile than H_2O .

- Going down along a group nucleophilicity increases as polarizability increases:

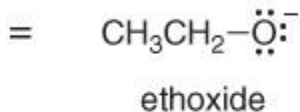
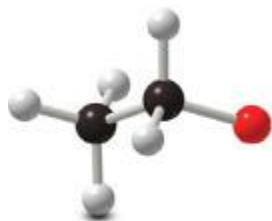
H_2S is a weaker base but a stronger nucleophile than H_2O . Nucleophilicity increases following the order $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$ while basicity follow the opposite order

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

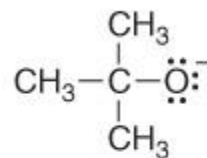
NH_3 is a stronger base and stronger nucleophile than H_2O .

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**.

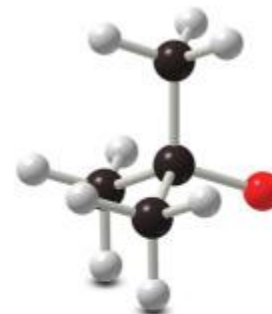


stronger nucleophile



tert-butoxide

stronger base



Three CH_3 groups sterically hinder the O atom, making it a **weaker nucleophile**.

The Nucleophile

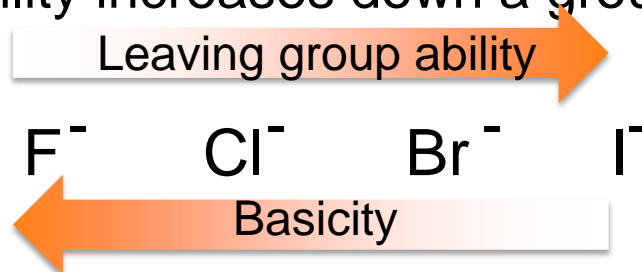
Some Common Nucleophiles

	Negatively charged nucleophiles			Neutral nucleophiles	
Oxygen	OH^-	OR^-	CH_3COO^-	H_2O	ROH
Nitrogen	N_3^-			NH_3	RNH_2
Carbon	CN^-	$\text{HC}\equiv\text{C}^-$			
Halogen	Cl^-	Br^-	I^-		
Sulfur	HS^-	RS^-		H_2S	RSH

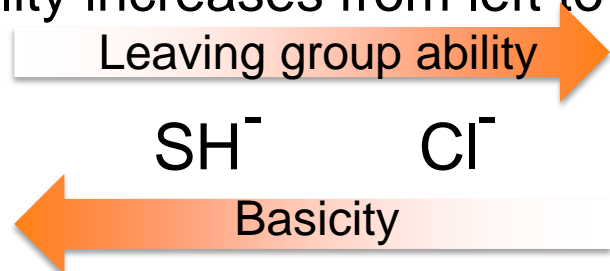
The Leaving Group

Stable (weak bases) species are good leaving groups.

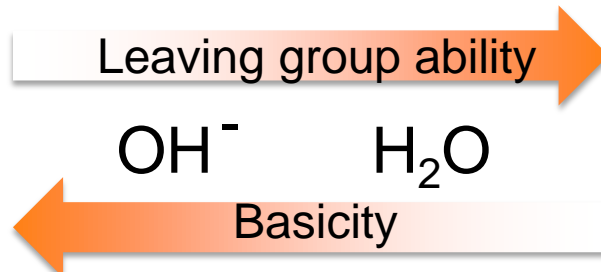
- Leaving group ability increases down a group:



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



- Neutral leaving groups are better than charged ones



The Leaving Group

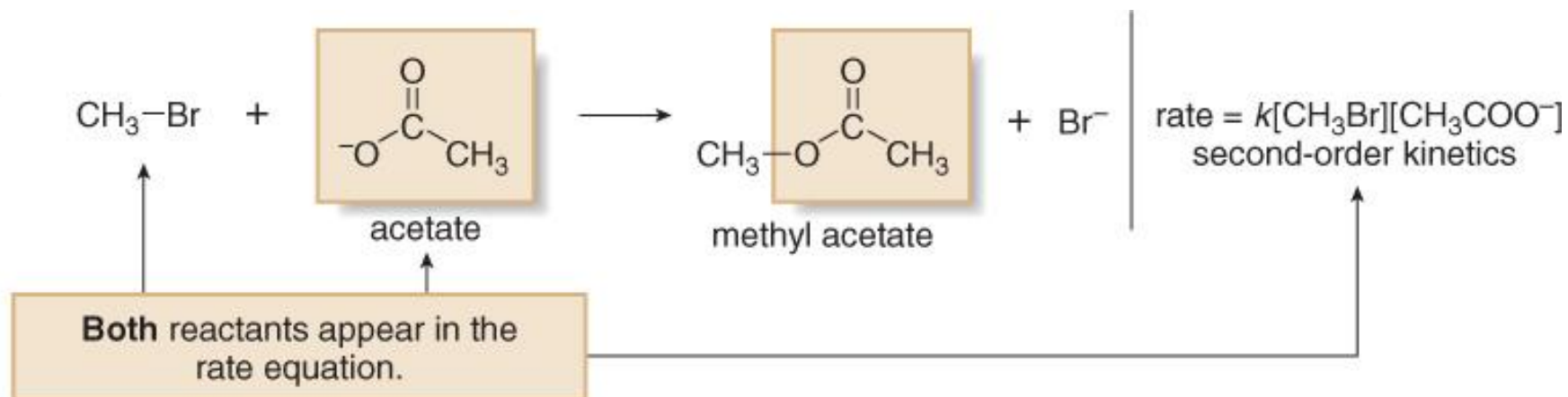
These molecules undergo nucleophilic substitution

Starting material	Leaving group	Conjugate acid	pK _a
R-Cl	Cl ⁻	HCl	-7
R-Br	Br ⁻	HBr	-9
R-I	I ⁻	HI	-10
R-OH ₂ ⁺	H ₂ O	H ₃ O ⁺	-1.7

These molecules do not undergo nucleophilic substitution

Starting material	Leaving group	Conjugate acid	pK _a
R-F	F ⁻	HF	3.2
R-OH	⁻ OH	H ₂ O	15.7
R-NH ₂	⁻ NH ₂	NH ₃	38
R-H	H ⁻	H ₂	35
R-R	R ⁻	RH	50

S_N2 Mechanism: Kinetics

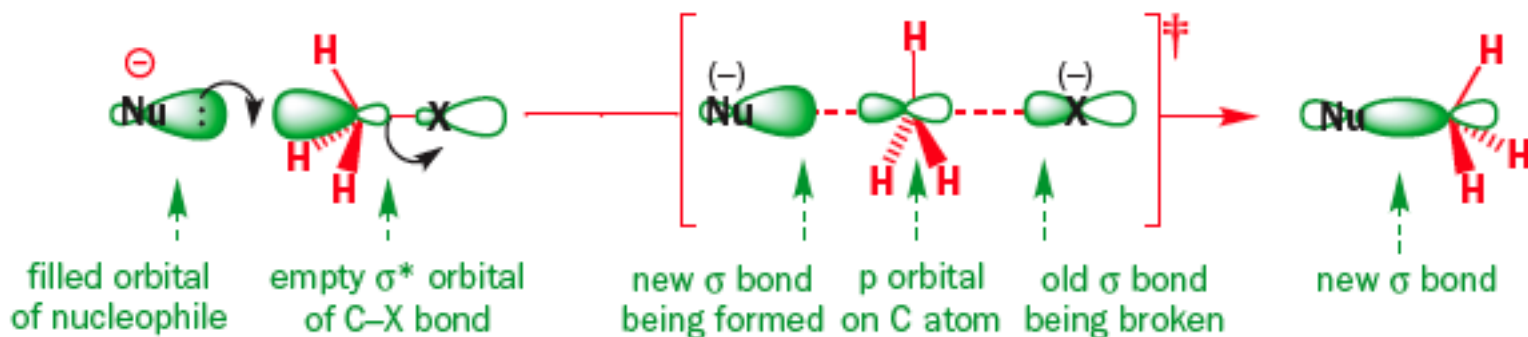


S_N2 Mechanism: Stereochemistry

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

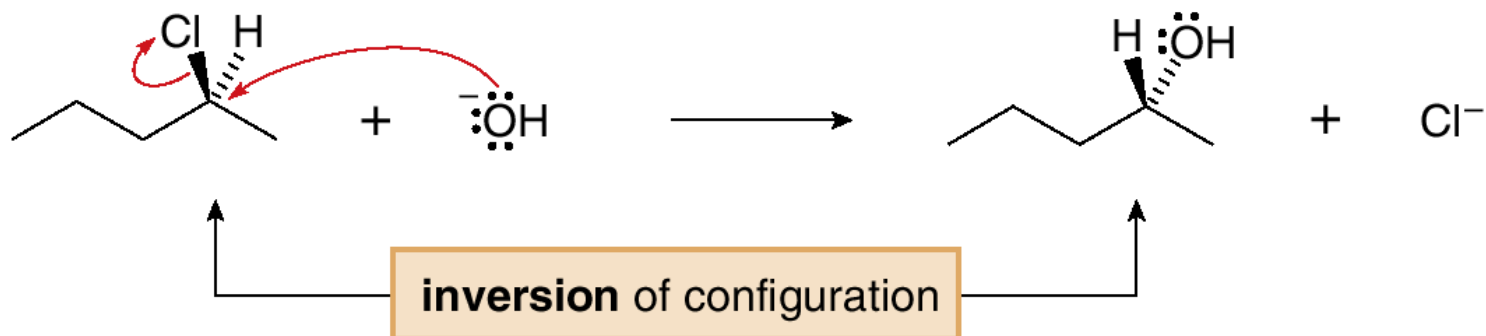
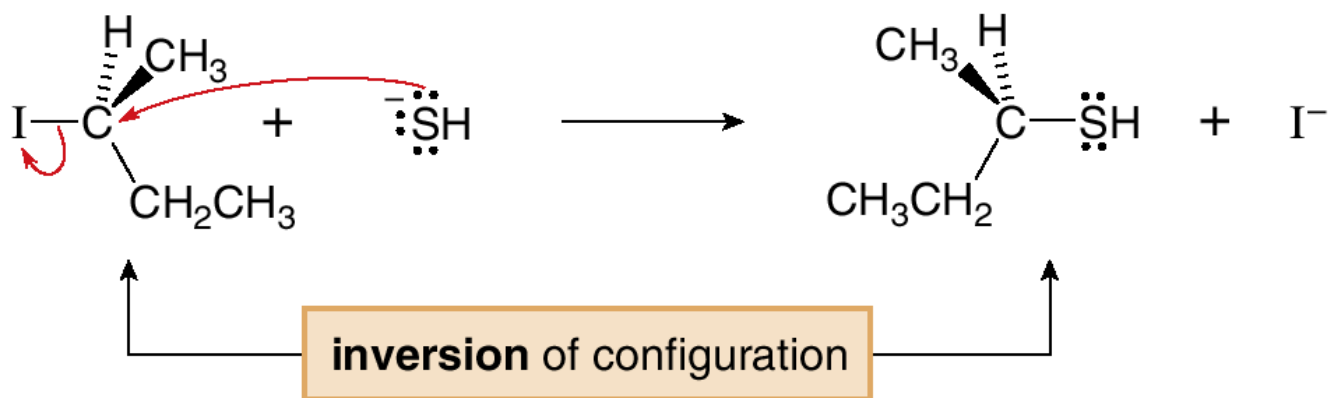


:Nu[⊖] and X[⊖] are 180° away from each other, on either side of a plane containing C, H, H, H



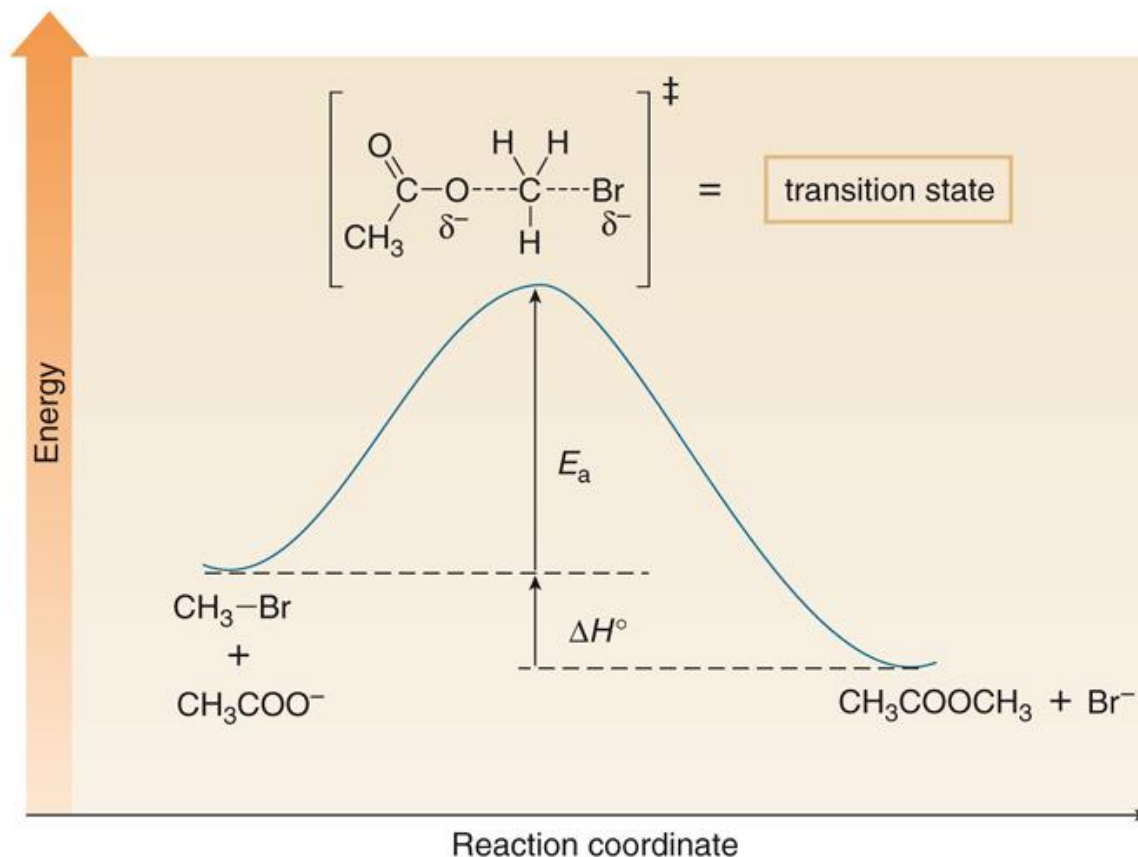
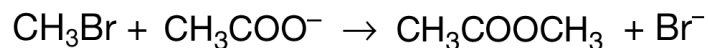
S_N2 Mechanism: Stereochemistry

- 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 Mechanism: Energy Profile

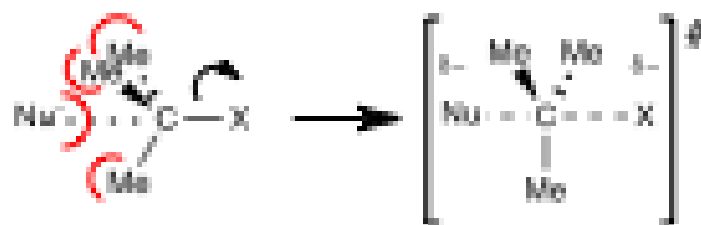
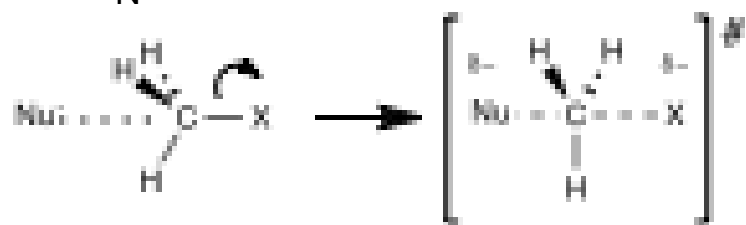
Energy profile for the reaction:



- 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.

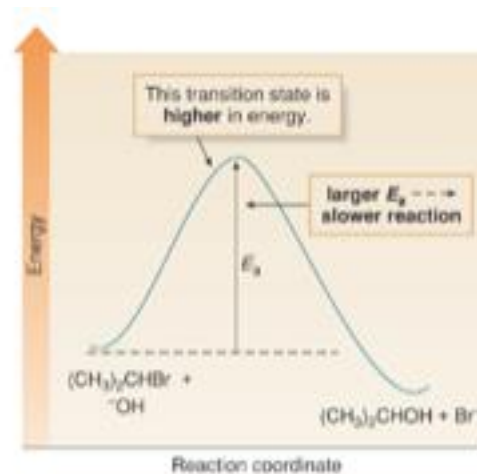
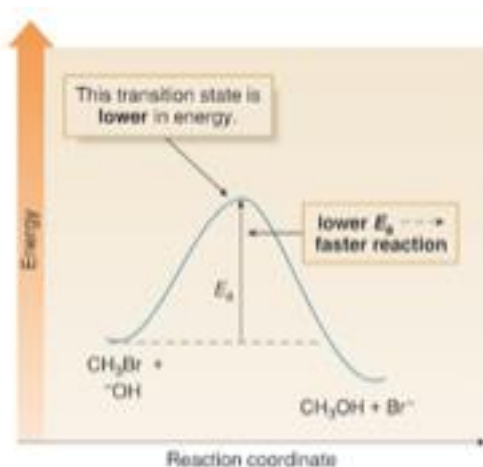
S_N2 Reaction: The Alkyl Substrate

- 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.



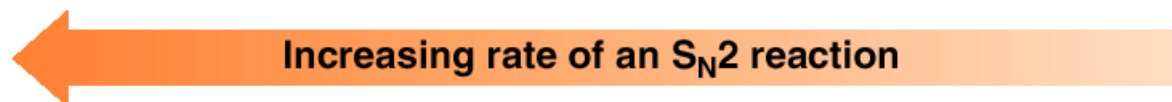
hindered
approach

crowded
transition state



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*.



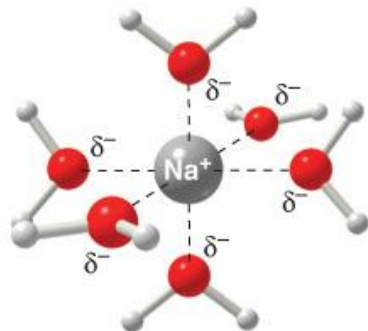
This order of reactivity can be explained by steric effects.

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

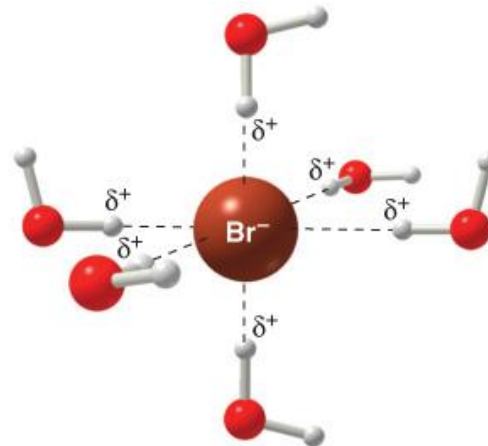
S_N2 Mechanism

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

The Solvent

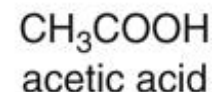
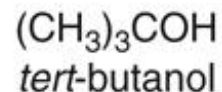
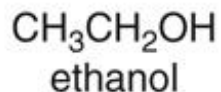


Na⁺ is solvated by ion-dipole interactions with H₂O.

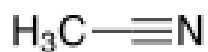


Br⁻ is solvated by hydrogen bonding with H₂O.

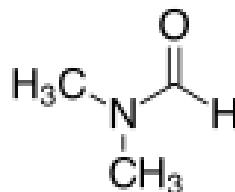
- Protic solvents slow down S_N2 reactions



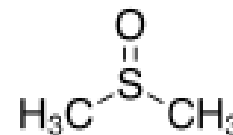
- S_N2 reactions are best carried out in **polar aprotic solvents**



acetonitrile



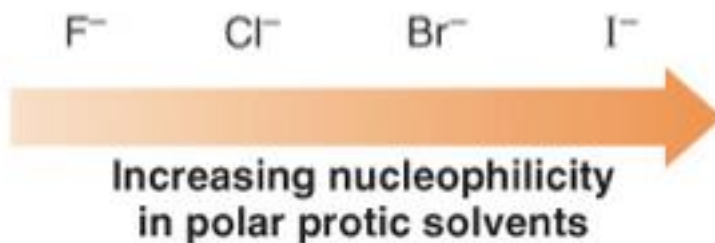
N,N-dimethylformamide
DMF



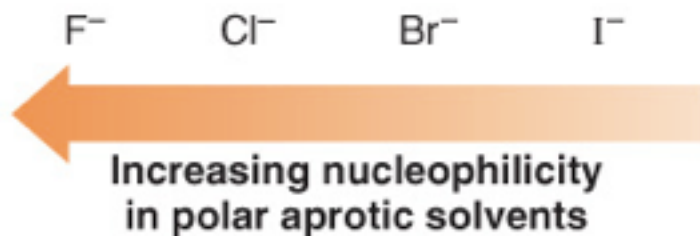
dimethylsulfoxide
DMSO

Solvent Effects on Nucleophilicity

- Hydrogen bonds are stronger with small anions
In **polar protic solvents**:



- In **polar aprotic solvents**, nucleophilicity parallels basicity.



S_N1 Mechanism

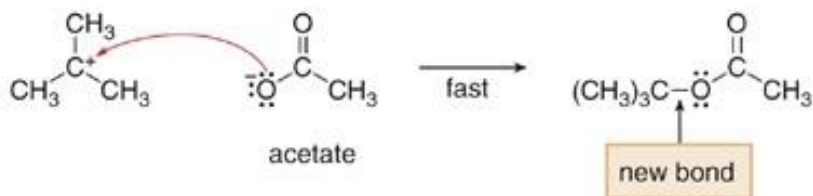
The S_N1 mechanism has two steps, and carbocations are formed as reactive intermediates.

Step [1] The C–Br bond is broken.



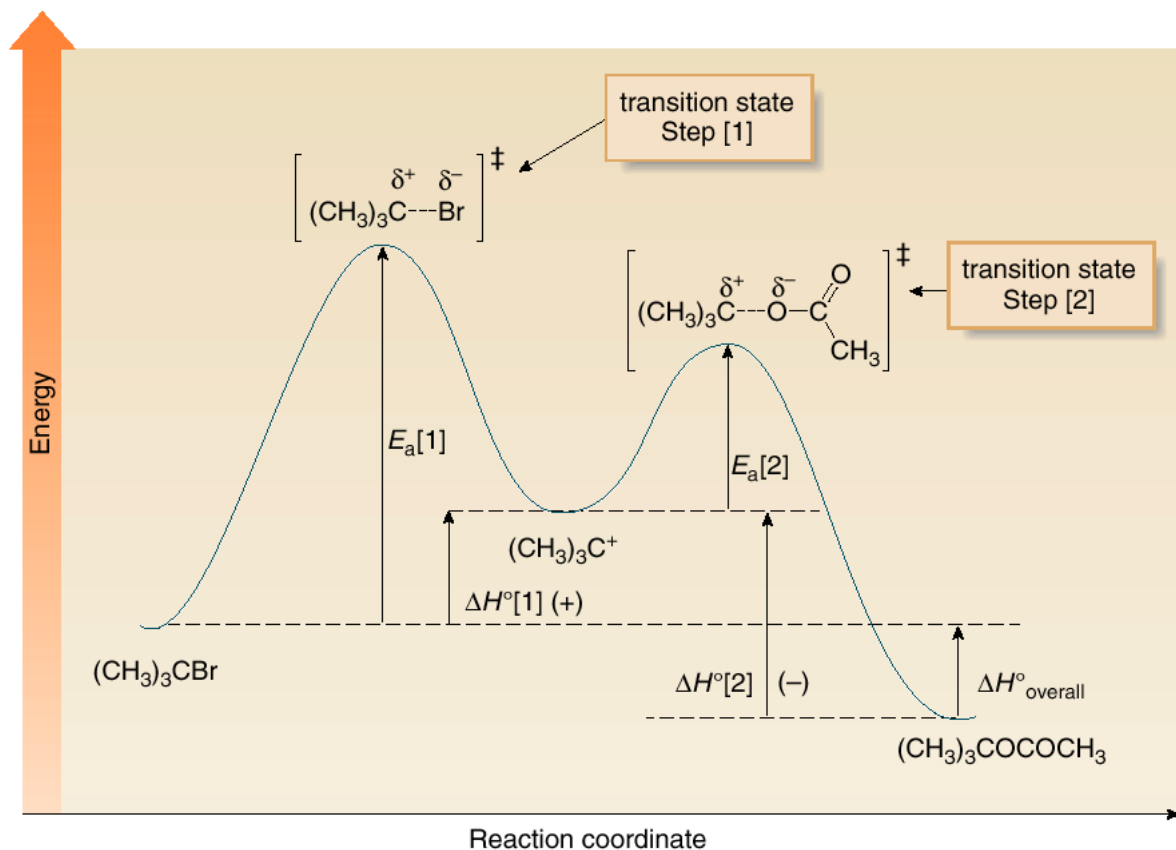
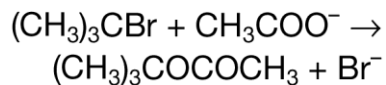
- **Heterolysis of the C–Br bond** forms an intermediate **carbocation**. This step is rate-determining because it involves only bond cleavage.

Step [2] The C–O bond is formed.



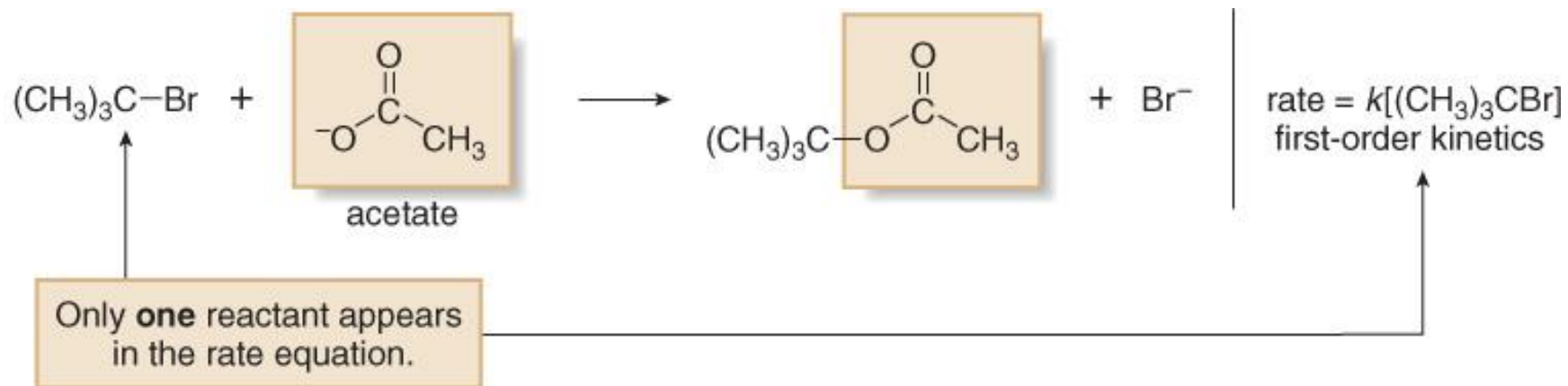
- **Nucleophilic attack of acetate** on the carbocation forms the new C–O bond in the product. This is a **Lewis acid–base reaction**; the nucleophile is the Lewis base and the carbocation is the Lewis acid. Step [2] is *faster* than Step [1] because no bonds are broken and one bond is formed.

S_N1 Mechanism: Energetics



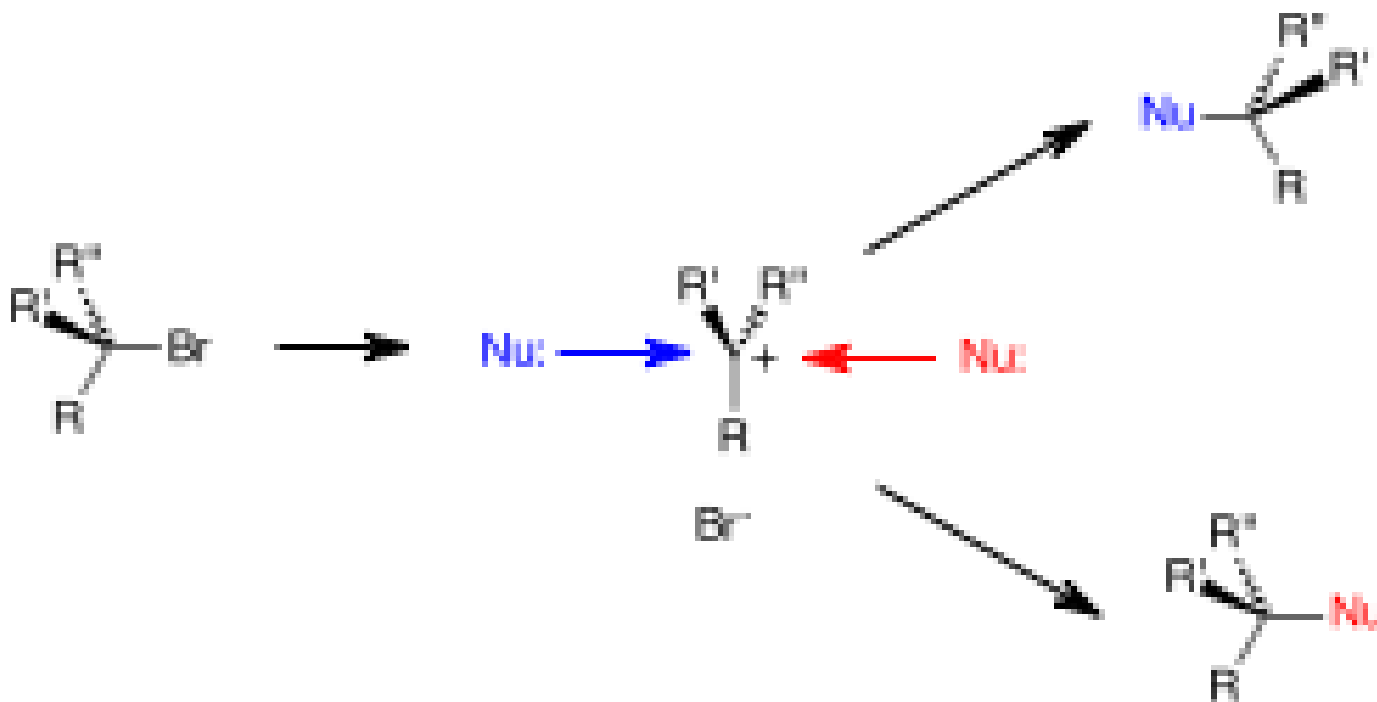
- Since the S_N1 mechanism has two steps, there are two energy barriers.
- E_a[1] > E_a[2] since Step [1] involves bond breaking and Step [2] involves bond formation.
- In each step only one bond is broken or formed, so the transition state for each step has one partial bond.
- The reaction is drawn with ΔH°_{overall} as a negative value, since the products are lower in energy than the starting materials.

S_N1 Mechanism: Kinetics

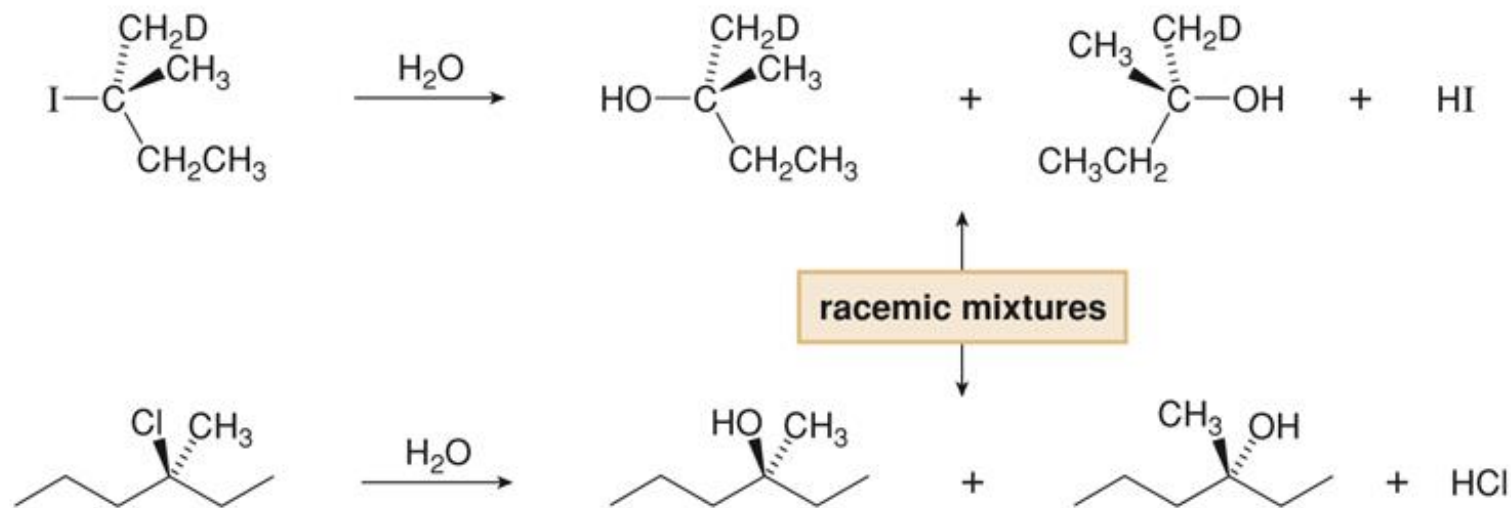


S_N1 Mechanism. Stereochemistry

- 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

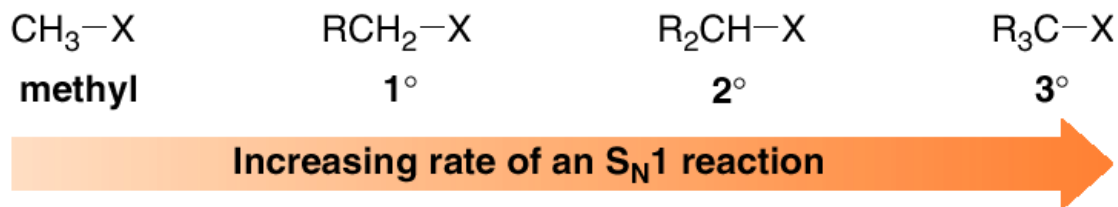


- Nucleophilic substitution of each starting material by an S_N1 mechanism forms a **racemic mixture** of two products.
- With H_2O , a neutral nucleophile, the initial product of nucleophilic substitution (ROH_2^+) loses a proton to form the final neutral product, ROH (Section 7.6).

The Alkyl Substrate

- The rate of an S_N1 reaction is affected by the type of alkyl halide involved.

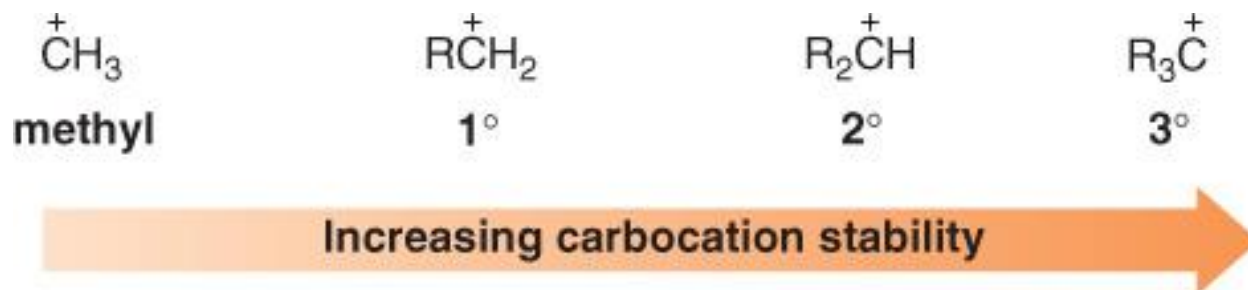
- As the number of R groups on the carbon with the leaving group *increases*, the rate of an S_N1 reaction *increases*.



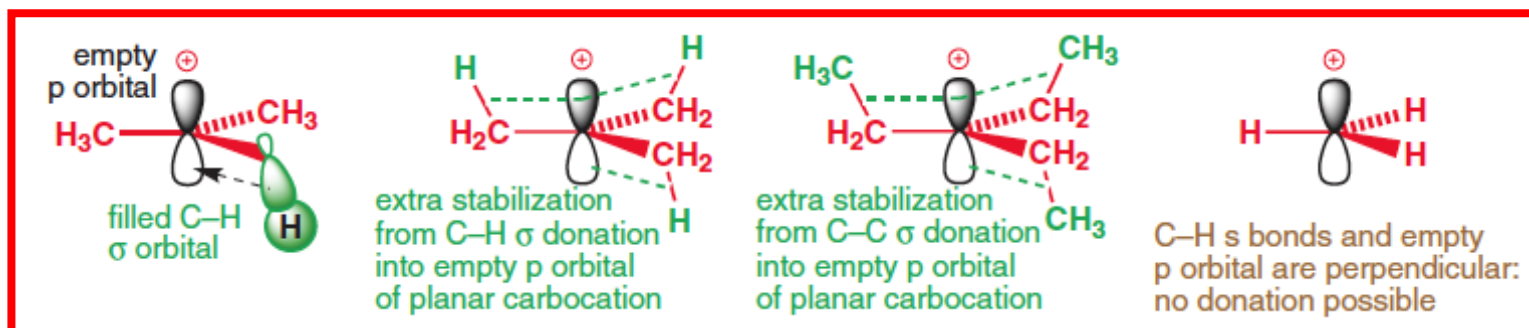
- 3° Alkyl halides undergo S_N1 reactions rapidly.
- 2° Alkyl halides react more slowly.
- Methyl and 1° alkyl halides do *not* undergo S_N1 reactions.

- This trend is exactly opposite to that observed in S_N2 reactions and reflects the **stability of the carbocation**.

Carbocation Stability

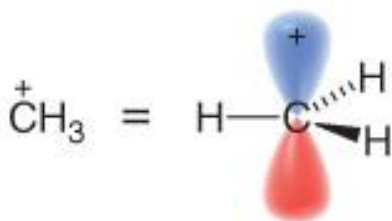


- Alkyl groups are **electron donating**. Since an alkyl group has several σ bonds, each containing electron density, it is more polarizable than a hydrogen atom, and better able to donate electron density.

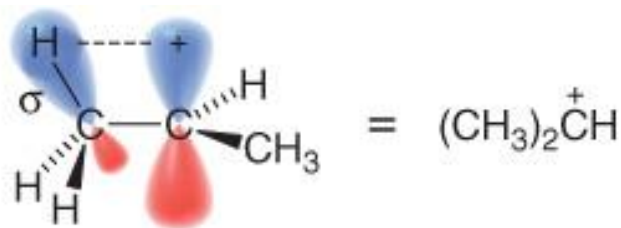


Carbocation Stability

- **Hyperconjugation** is the spreading out of charge by the overlap of an empty p orbital with an adjacent σ bond. This overlap (hyperconjugation) delocalizes the positive charge on the carbocation, spreading it over a larger volume, and this stabilizes the carbocation.
- Example: 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 C—H σ bond with the adjacent vacant p orbital stabilizes the carbocation.

S_N1 Mechanism

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

S_N1 Mechanism

- **Leaving group**: the same reactivity order as in S_N2 reactions.
- **Nucleophile**: has little effect in S_N1 reactions because it reacts after the slow step (must be nonbasic to prevent elimination) but good nucleophiles favour S_N2 reactions.
- **Solvent**: polar solvents favor the reaction by stabilizing the intermediate carbocation (Hammond postulate).

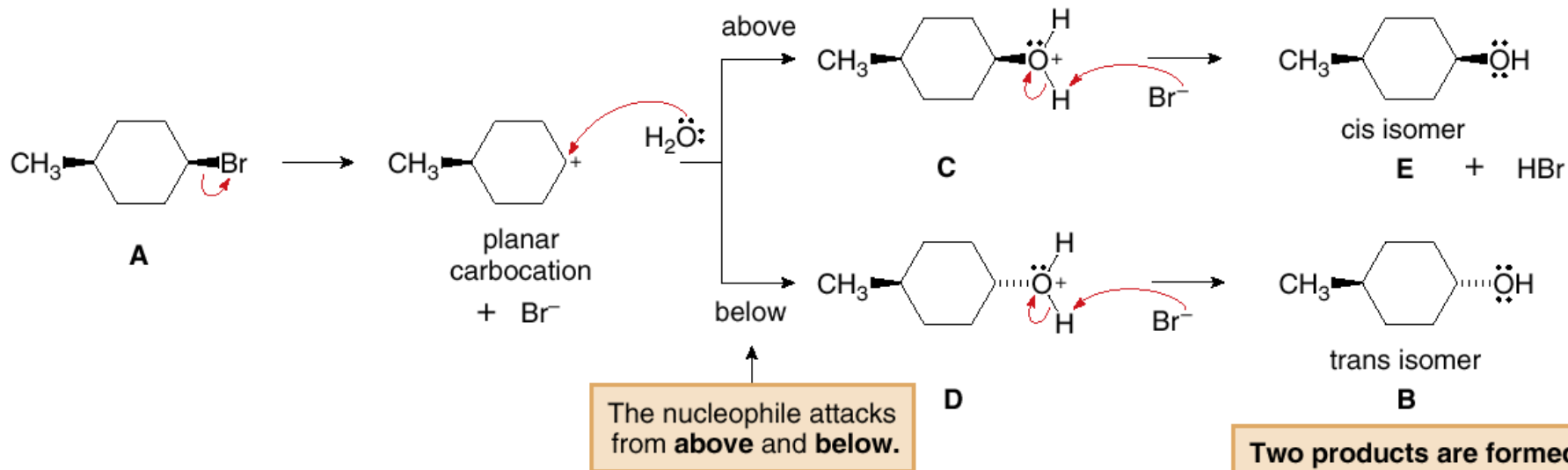
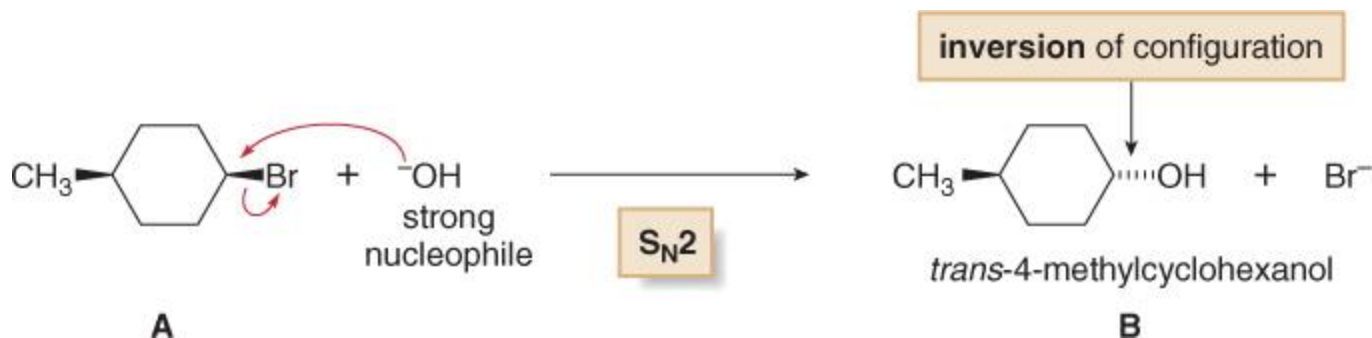


	ethanol	40% water/60% ethanol	80% water/20% ethanol	water
<i>Relative reactivity</i>	<i>1</i>	<i>100</i>	<i>14000</i>	<i>100000</i>

Predicting the Mechanism

Alkyl halide	Mechanism	Other factors
CH ₃ X RCH ₂ X (1°)	S _N 2	
R ₃ CX (3°)	S _N 1	
R ₂ CHX (2°)	S _N 1 or S _N 2	<p>The mechanism depends on the conditions.</p> <ul style="list-style-type: none">• Strong nucleophiles favor the S_N2 mechanism over the S_N1 mechanism. For example, RO⁻ is a stronger nucleophile than ROH, so RO⁻ favors the S_N2 reaction and ROH favors the S_N1 reaction.• Protic solvents favor the S_N1 mechanism and aprotic solvents favor the S_N2 mechanism. For example, H₂O and CH₃OH are polar protic solvents that favor the S_N1 mechanism, whereas acetone [(CH₃)₂C=O] and DMSO [(CH₃)₂S=O] are polar aprotic solvents that favor the S_N2 mechanism.

Predicting the Mechanism

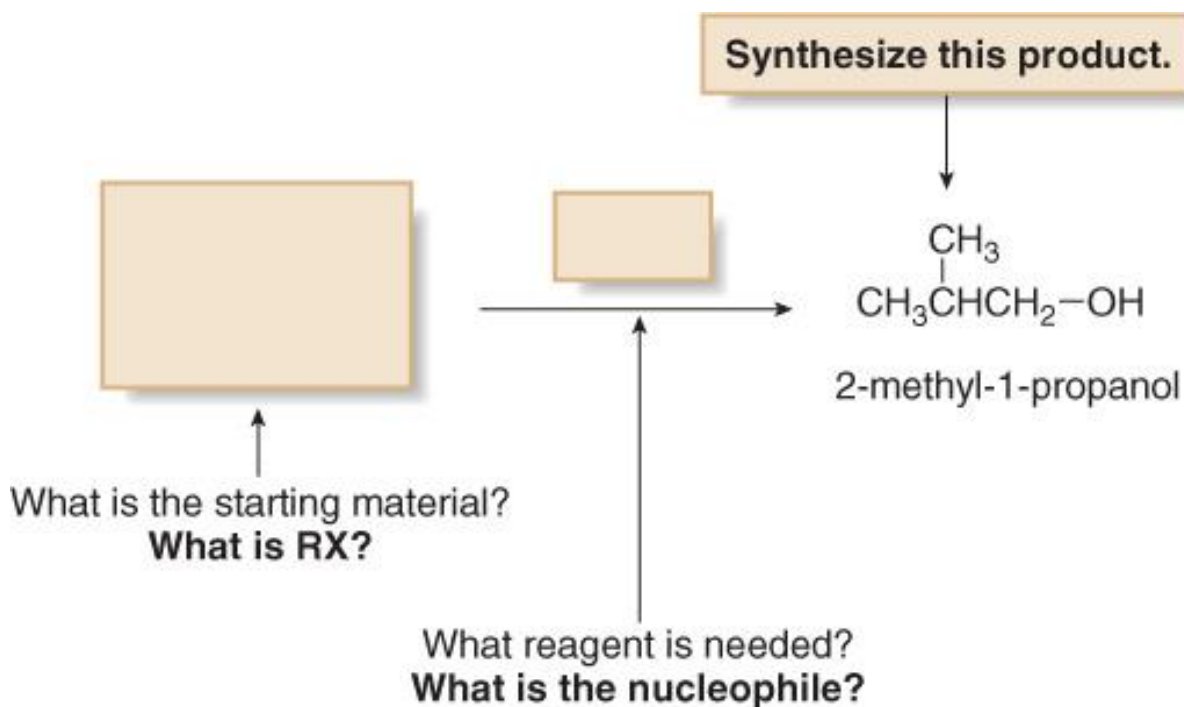


Organic Synthesis

	Nucleophile (:Nu ⁻)	Product	Name
Oxygen compounds	^-OH	R-OH	alcohol
	$^-OR'$	R-OR'	ether
	$\begin{array}{c} O \\ \\ ^-O-C-R' \end{array}$	$\begin{array}{c} O \\ \\ R-O-C-R' \end{array}$	ester
Carbon compounds	^-CN	R-CN	nitrile
	$^-C\equiv C-H$	R-C≡C-H	alkyne
Nitrogen compounds	N_3^-	R-N ₃	azide
	$:NH_3$	R-NH ₂	amine
Sulfur compounds	^-SH	R-SH	thiol
	$^-SR'$	R-SR'	sulfide
		↑	
		products of nucleophilic substitution	

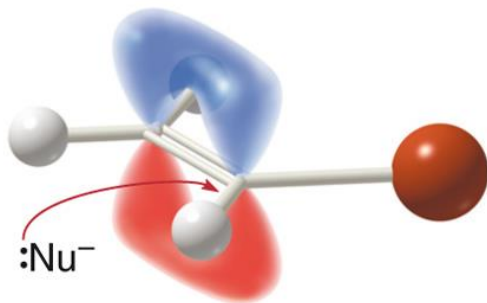
Organic Synthesis

- To carry out the synthesis of a particular compound, we must **think backwards**, and ask ourselves the question: What starting material and reagents are needed to make it?



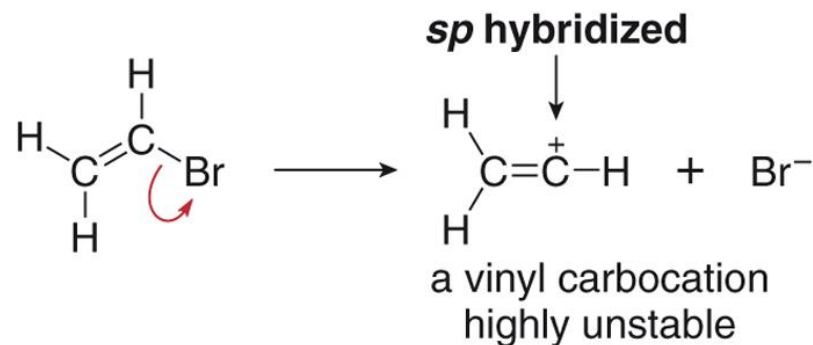
Vinyl Halides

- a. **Vinyl halides and the S_N2 mechanism:**
Backside attack of the nucleophile is not possible.



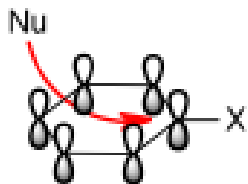
Backside attack would force the nucleophile to approach in the plane of the double bond.

- 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



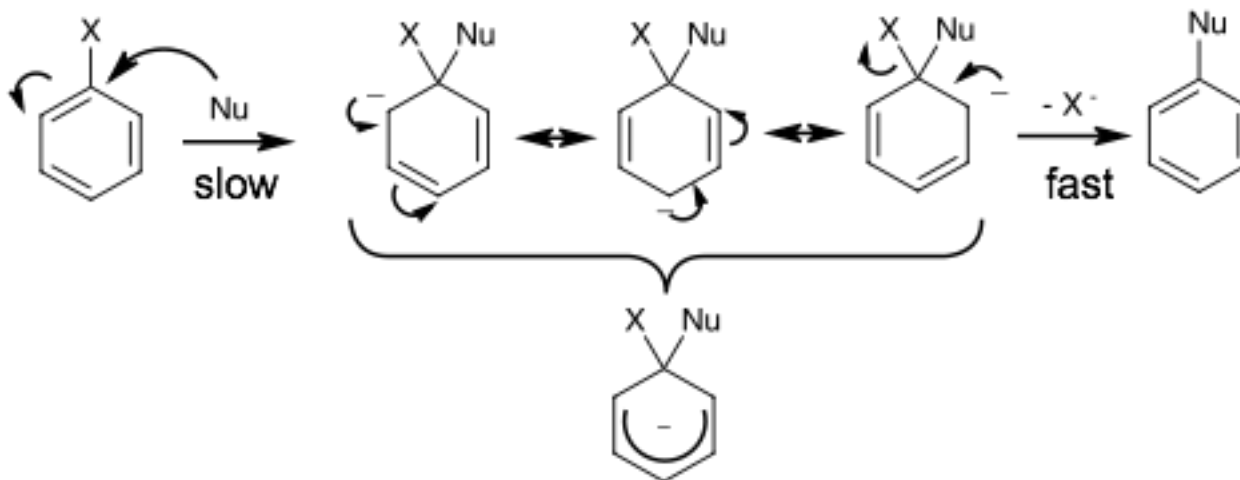
Backside attack
is impossible

S_N1



Very unstable
 sp^2 carbocation

S_NAr

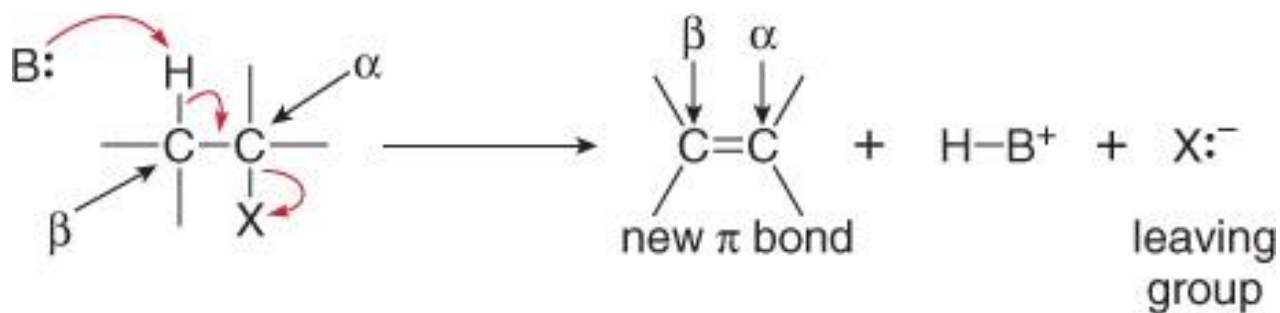


Eliminations

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

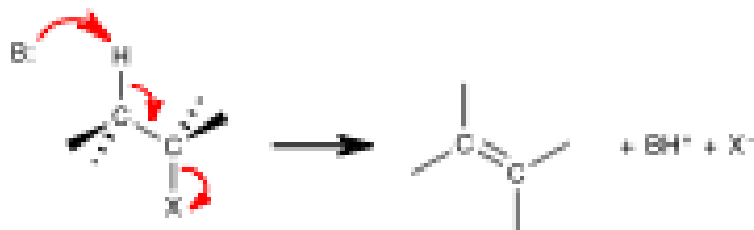
General Features of Elimination

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



Elimination Mechanisms

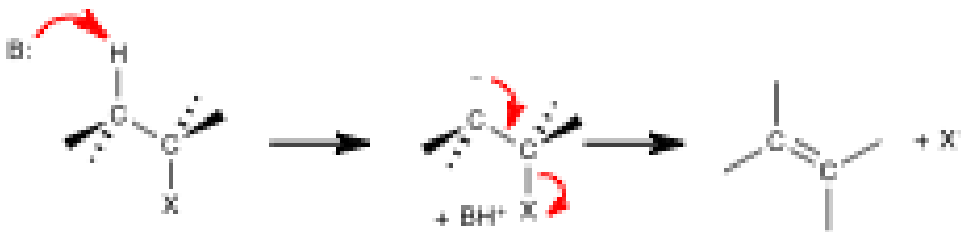
E2



E1

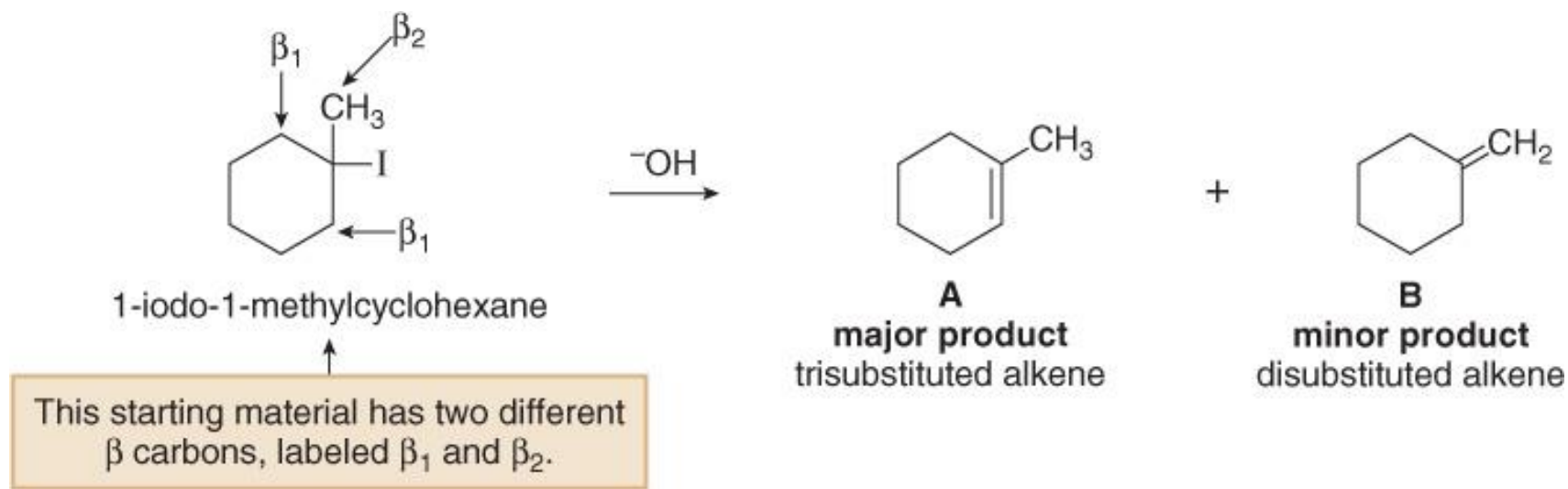


E1cb



The Zaitsev (Saytzeff) Rule

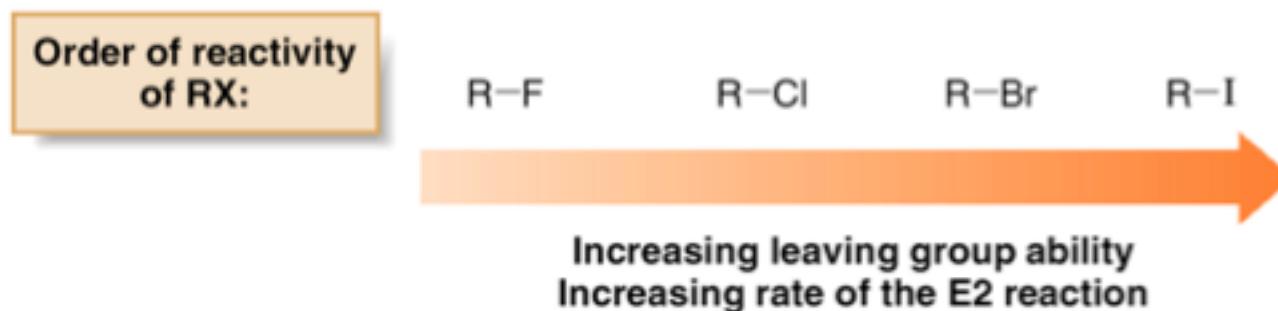
- The major product is the more stable product—the one with the more substituted double bond.



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

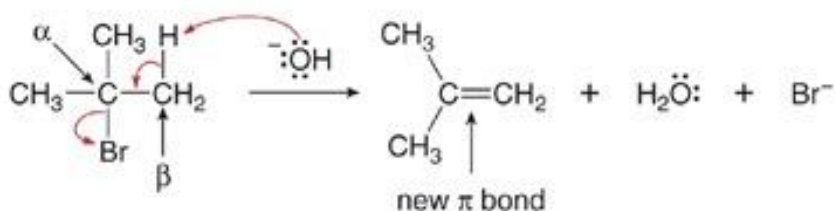
Leaving Groups in Elimination Reactions

Elimination reactions are faster with good leaving groups:



Mechanisms of Elimination—E2

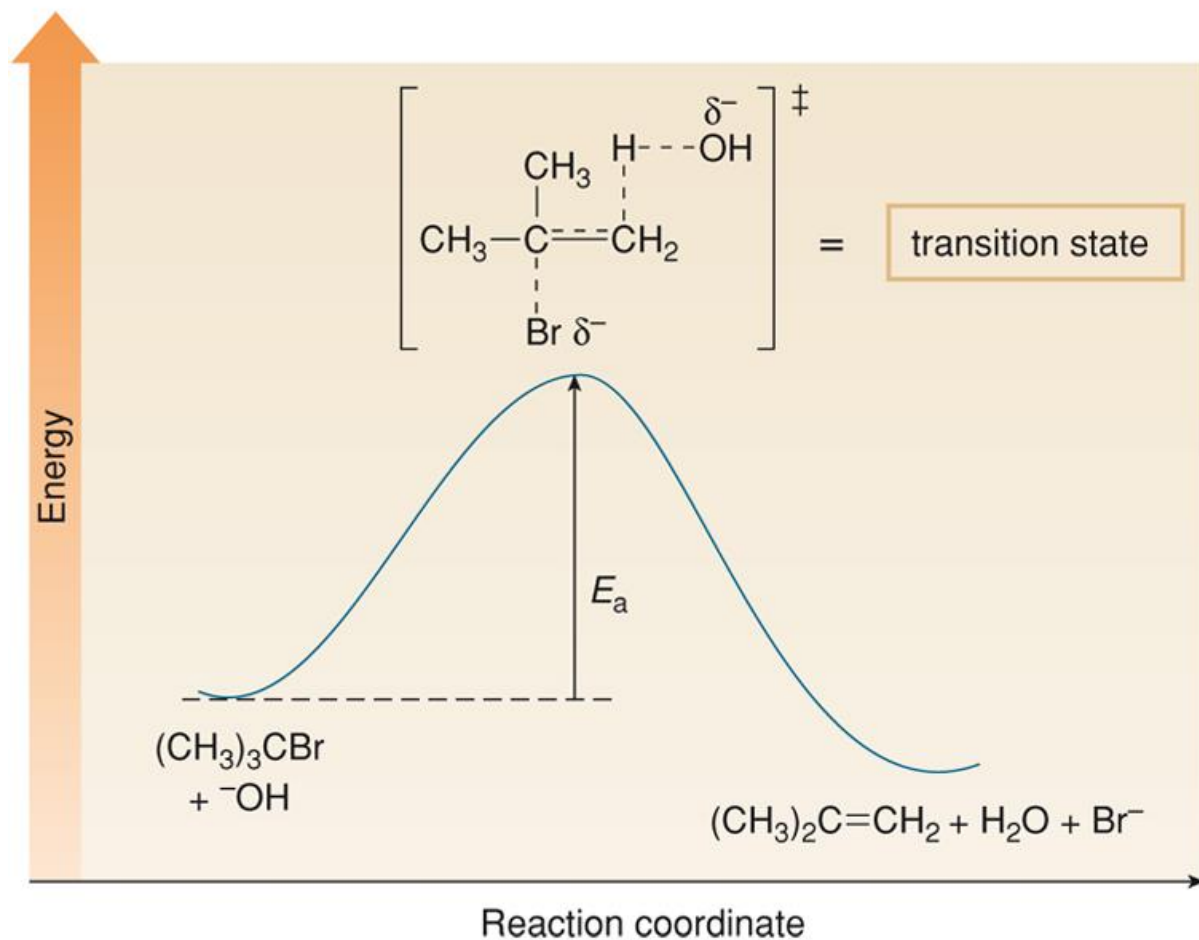
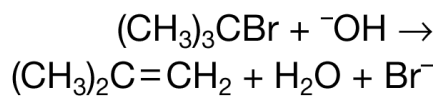
- The most common mechanism for dehydrohalogenation is the E2 mechanism.



- The base ^-OH removes a proton from the β carbon, forming H_2O (a by-product).
 - The electron pair in the β C-H bond forms the new π bond.
 - The leaving group Br^- comes off with the electron pair in the 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.,

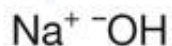
$$\text{rate} = k[(\text{CH}_3)_3\text{CBr}][^-\text{OH}]$$

Mechanisms of Elimination—E2

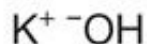


Mechanisms of Elimination—E2

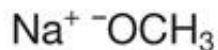
- E2 reactions are favoured by strong negatively charged bases, such as HO^- and its alkyl derivatives, RO^- , called alkoxides.
- Potassium t-butoxide is a strong, non-nucleophilic base.



sodium hydroxide



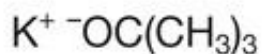
potassium hydroxide



sodium methoxide



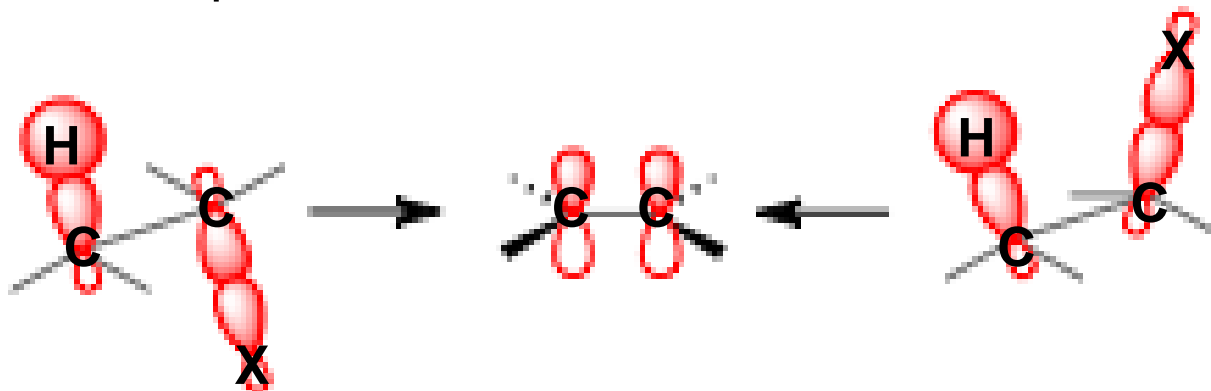
sodium ethoxide



potassium *tert*-butoxide

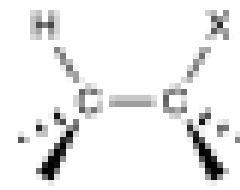
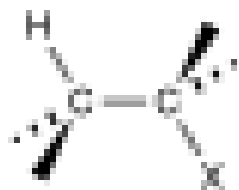
Stereochemistry of the E2 Reaction

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



anti periplanar

syn periplanar



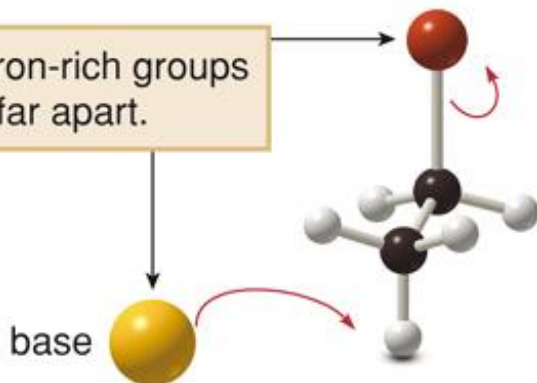
dihedral angle: 180°
staggered
favoured

dihedral angle: 0°
eclipsed
disfavoured

Stereochemistry of the E2 Reaction

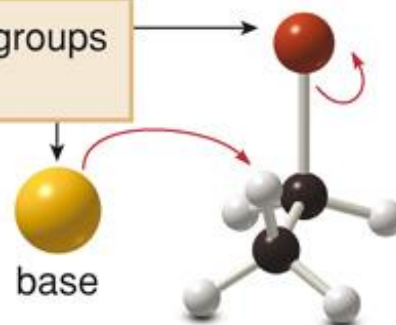
An **anti periplanar** arrangement has a **staggered** conformation.

Two electron-rich groups are far apart.



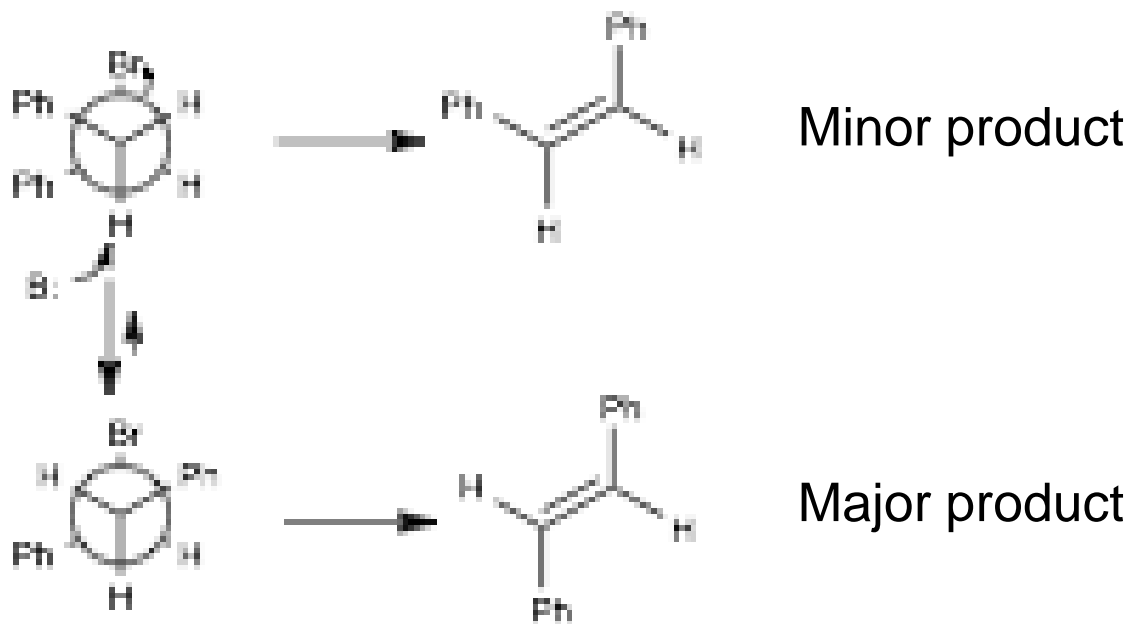
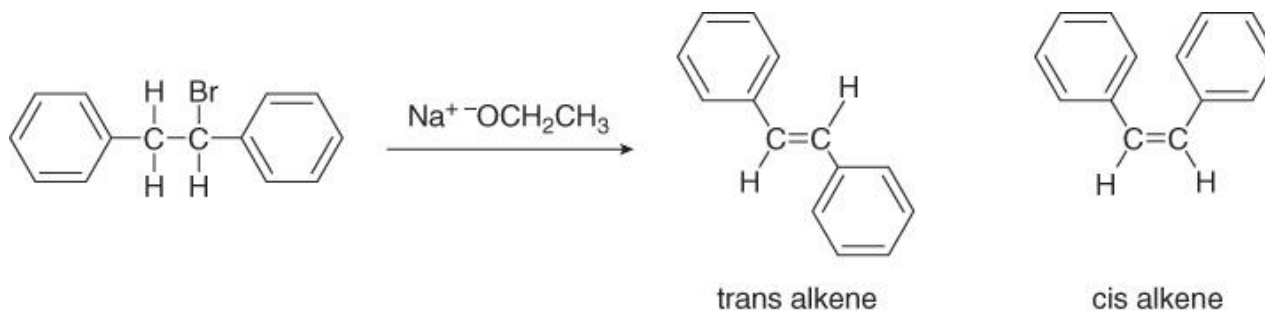
A **syn periplanar** arrangement has an **eclipsed** conformation.

Two electron-rich groups are close.



- E2 elimination occurs most often in the **anti periplanar geometry**.

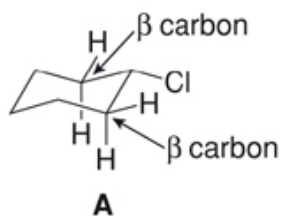
Stereochemistry of the E2 Reaction



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

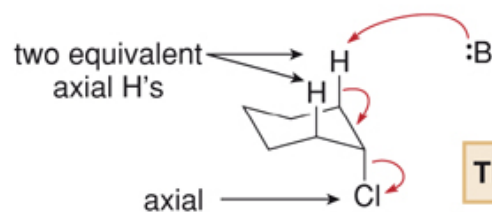
Stereochemistry of the E2 Reaction

Conformation A (equatorial Cl):

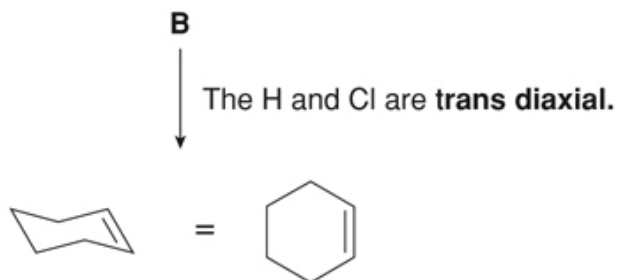


no reaction with this conformation

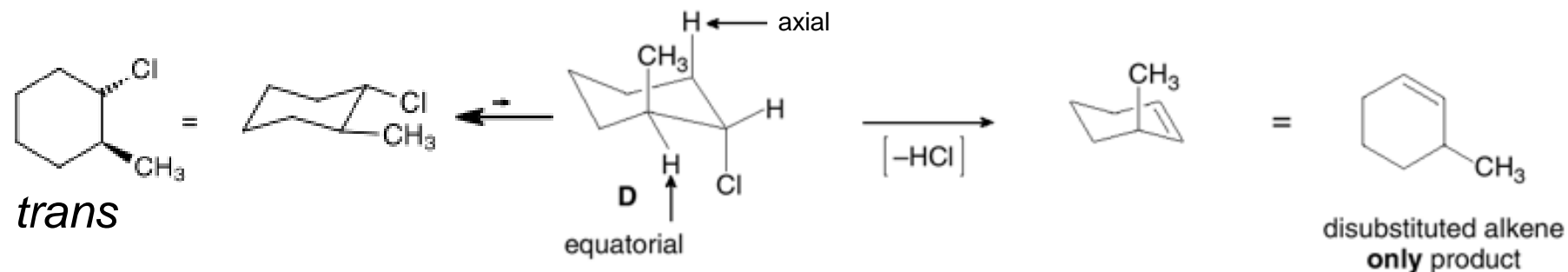
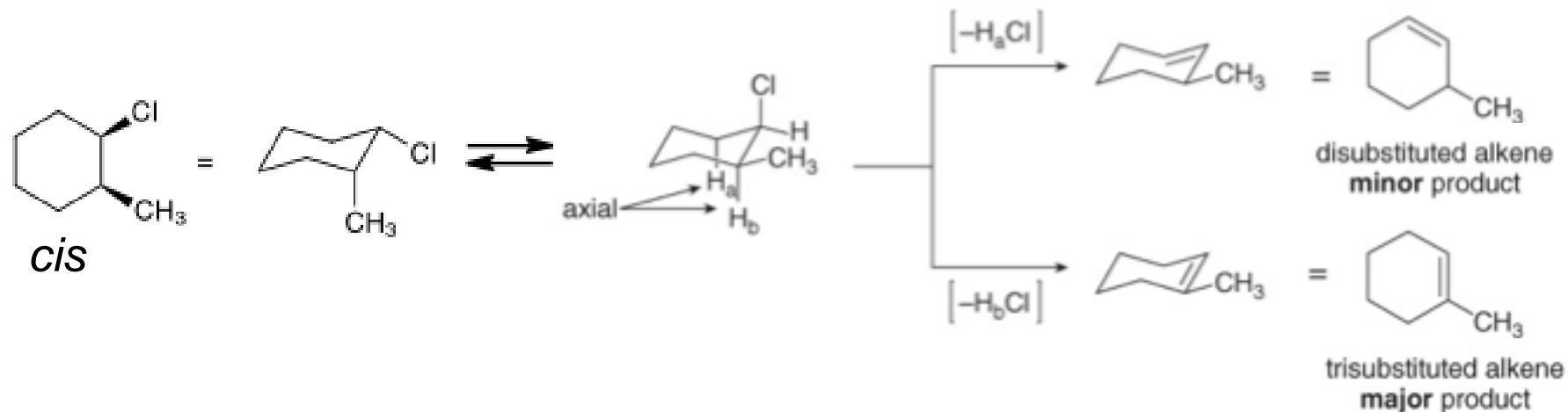
Conformation B (axial Cl):



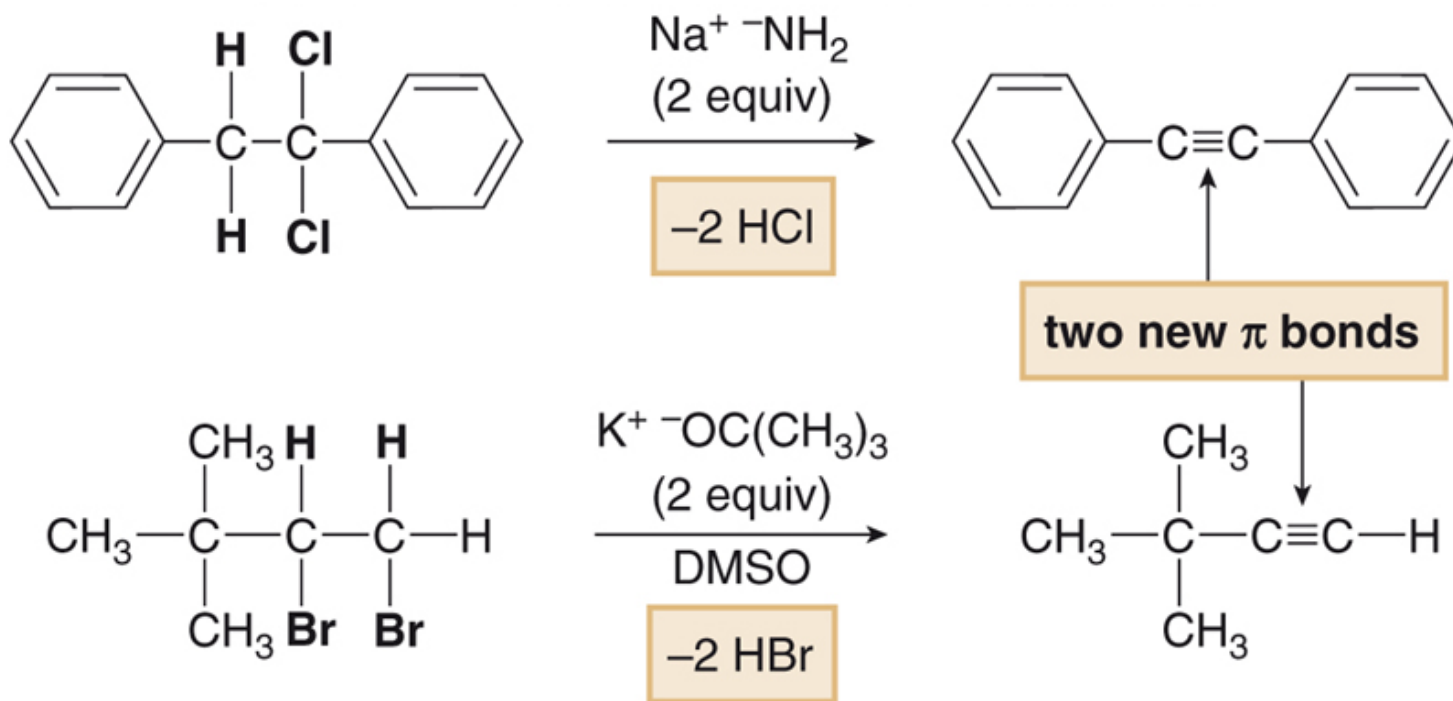
This conformation reacts.



Stereochemistry of the E2 Reaction

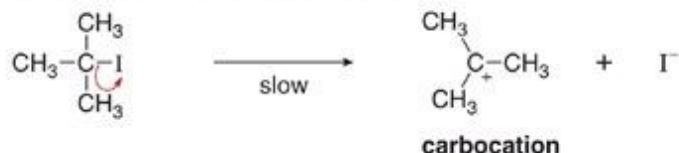


E2 Reactions and Alkyne Synthesis



Mechanisms of Elimination—E1

Step [1] The C–I bond is broken.



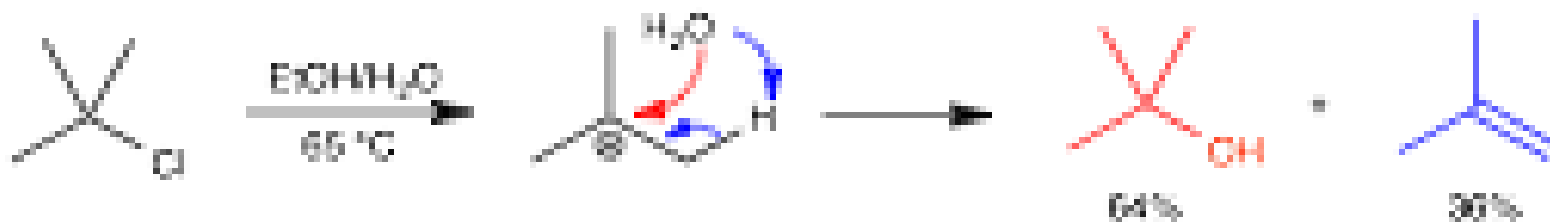
- **Heterolysis of the C–I bond** forms an intermediate **carbocation**. This is the same first step as the $\text{S}_{\text{N}}1$ mechanism. It is responsible for the first-order kinetics because it is rate-determining.

Step [2] A C–H bond is cleaved and the π bond is formed.

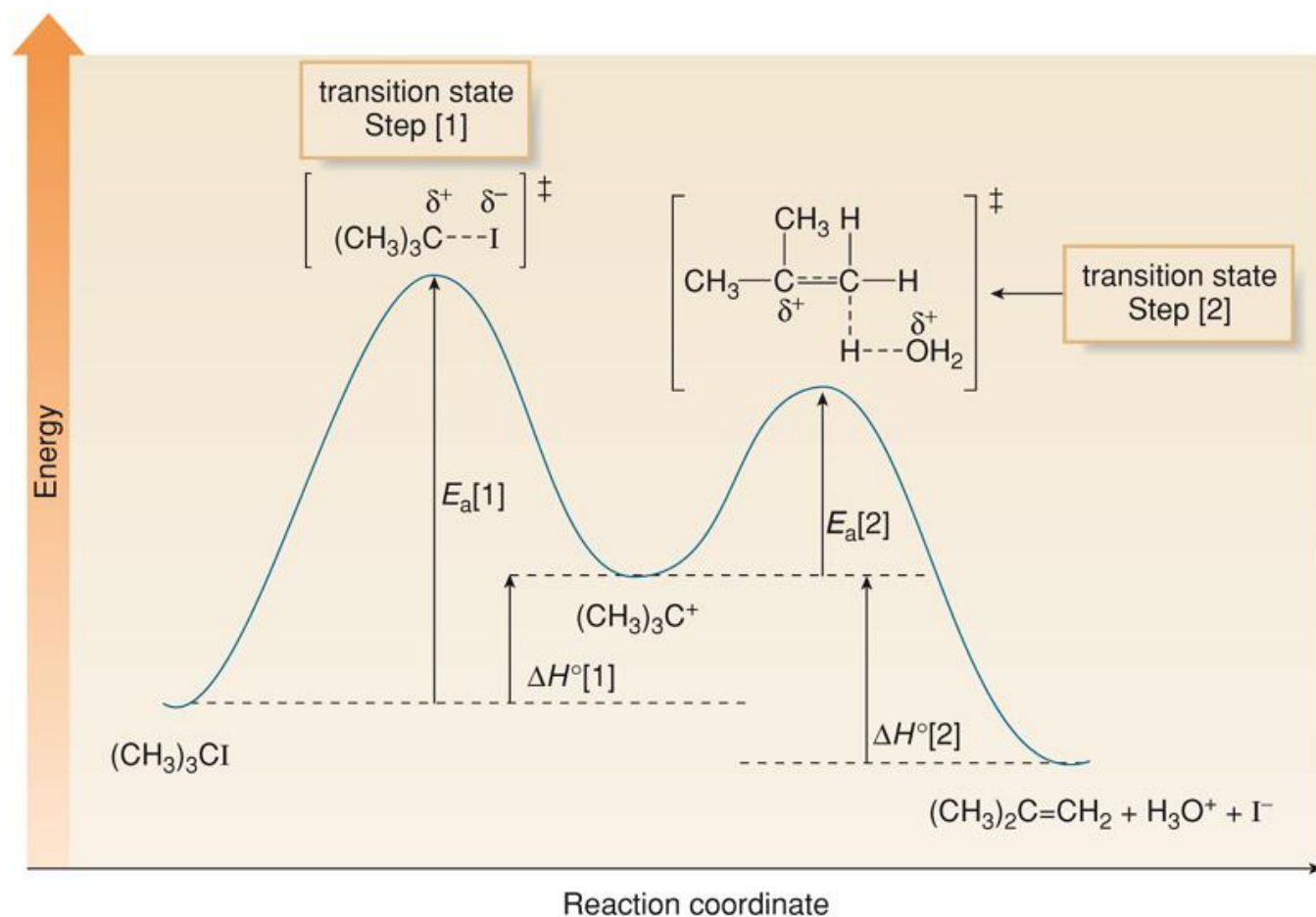
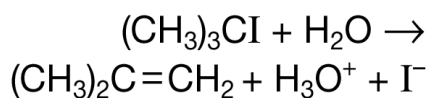


- **A base** (such as H_2O or I^-) **removes a proton from a carbon adjacent to the carbocation** (a β carbon). The electron pair in the C–H bond is used to form the new π bond.

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

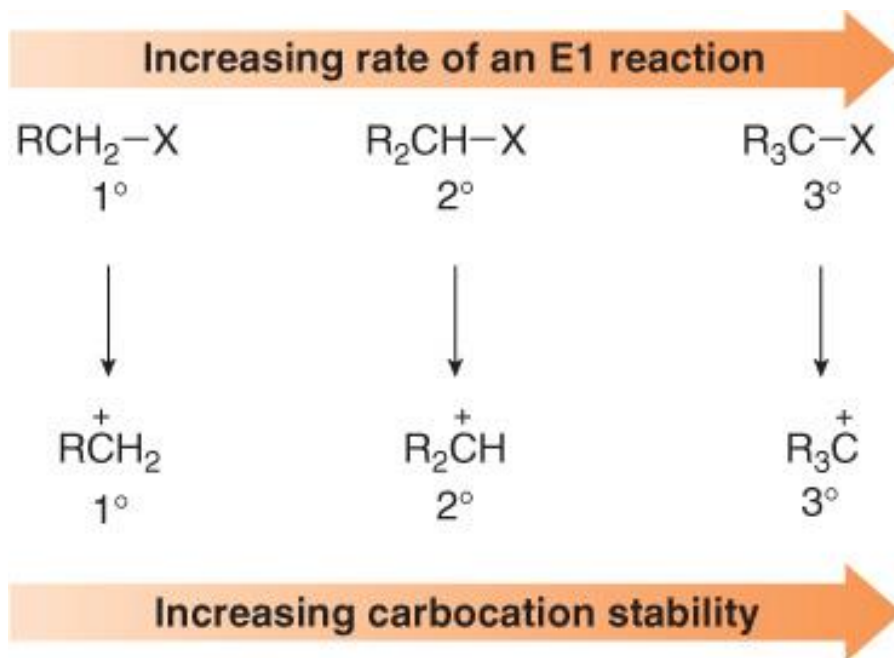


Mechanisms of Elimination—E1



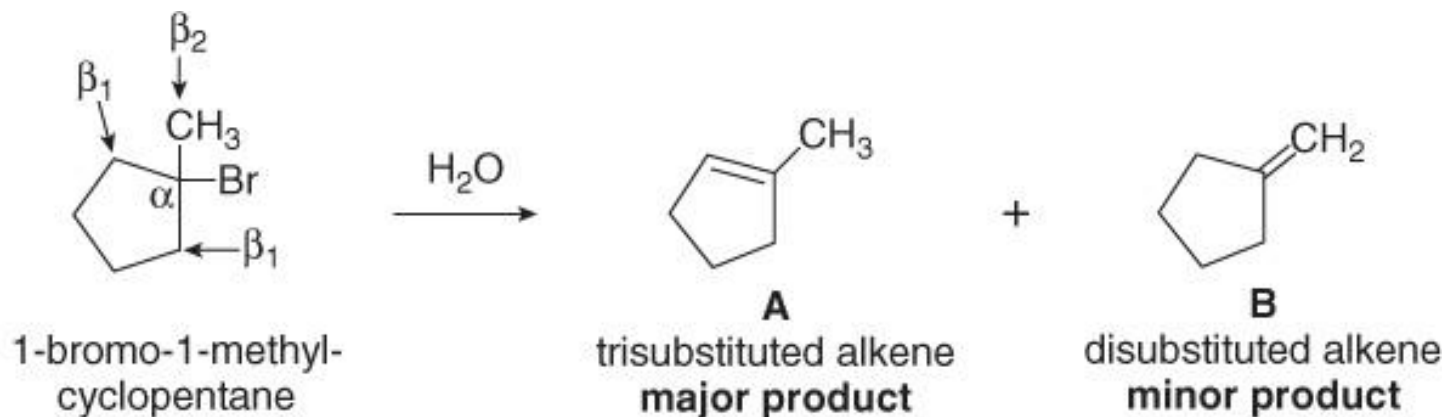
Mechanisms of Elimination—E1

- 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)

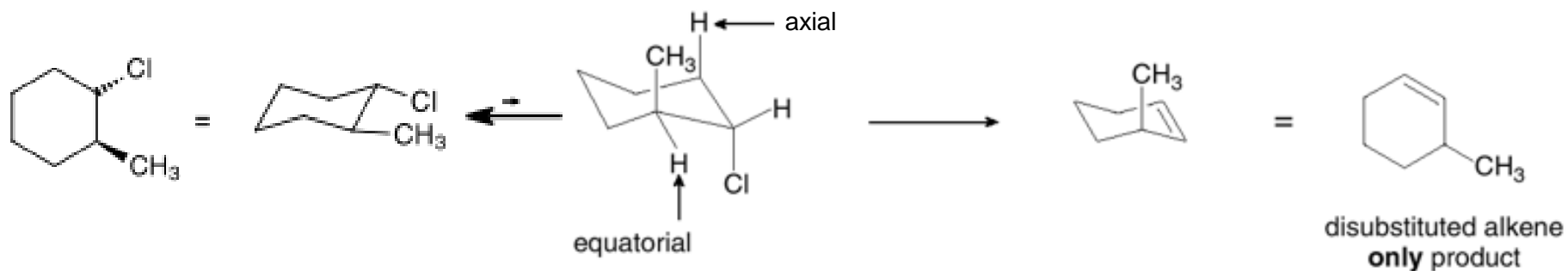


Mechanisms of Elimination

	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 ₂ O, ROH)
Stereochemistry	Antiperiplanar-stereoselective	Favors the most stable alkene
Solvent	Favored by dipolar aprotic solvents	Favored by polar protic solvents

When is the Mechanism E1 or E2?

E2 conditions: 1M NaOEt, EtOH, 100 °C

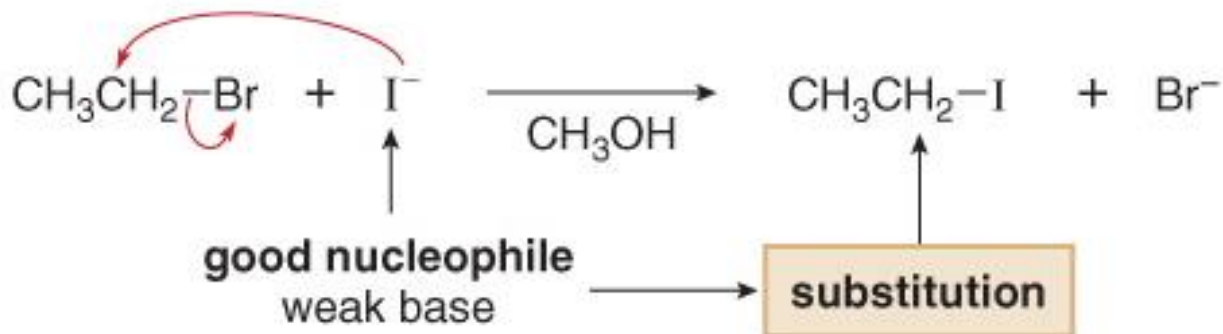


E1 conditions: 0.01M NaOEt, 80% EtOH, 160 °C

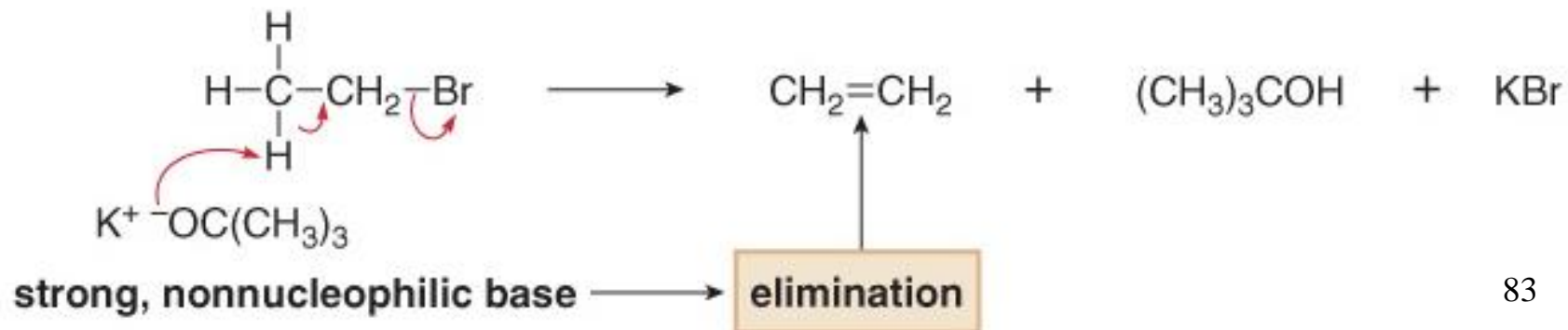


Substitution vs Elimination

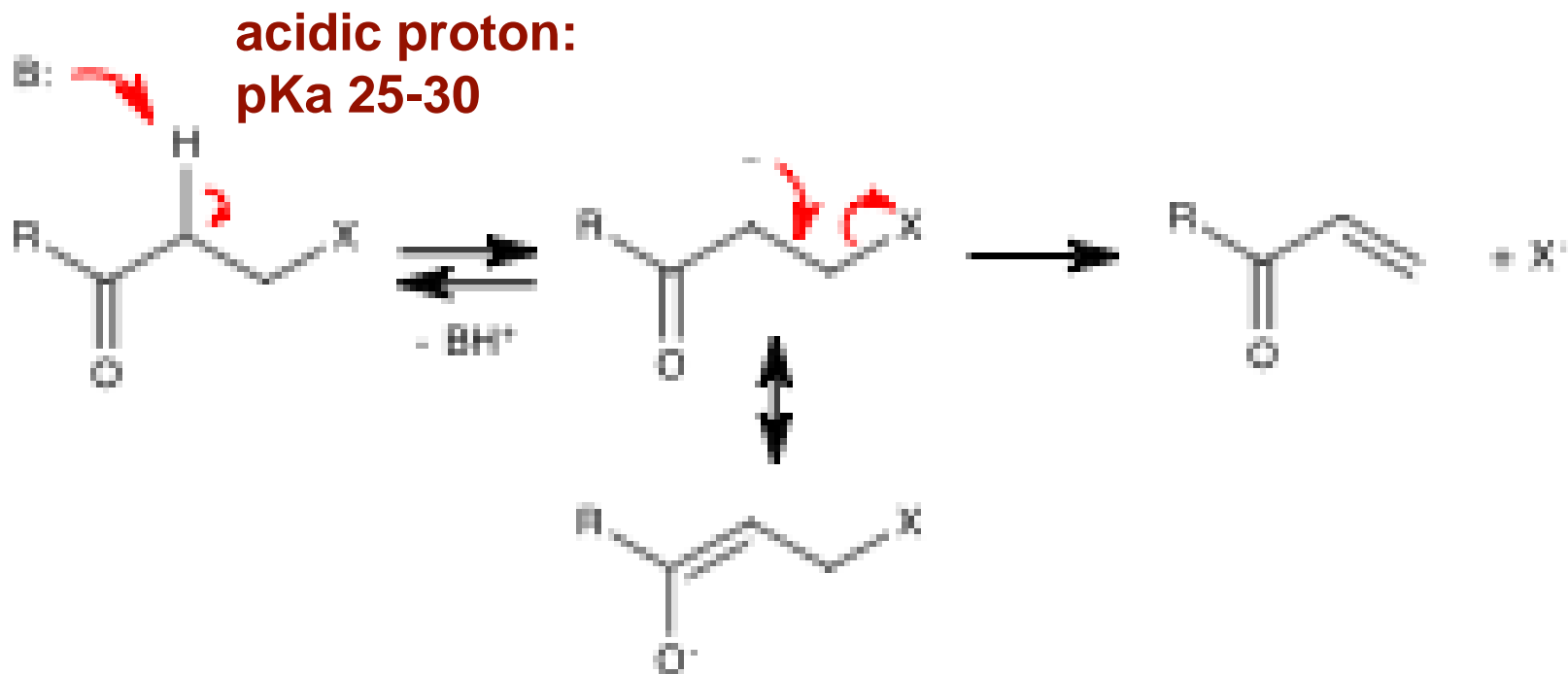
- Good nucleophiles that are weak bases favor substitution over elimination. These include I^- , Br^- , HS^- , CN^- , and CH_3COO^- .



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



Mechanisms of Elimination—E1cb



**carbanion stabilized
by delocalization**

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>		yes
secondary allylic benzylic	<i>with good nucleophiles in polar 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>	yes
tertiary		<i>with non basic nucleophiles</i>	<i>with strong bases</i>	<i>with weak bases</i>	yes

Reverse of Polarity. Organometallic Compounds

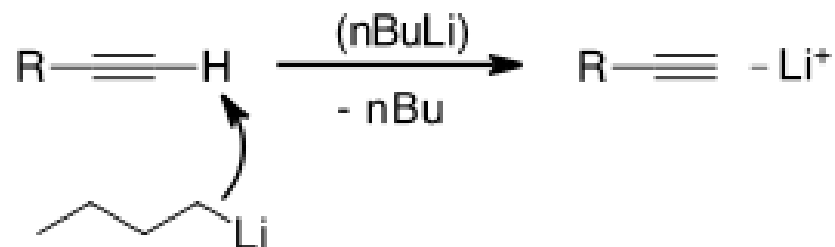


Examples:



Reverse of Polarity. Organometallic Compounds

strong bases:



strong nucleophiles:

