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# Organic Chemistry

# Alkyl Halides & Nucleophilic Substitution

## by
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*Communitising Technology*

# Expected Outcomes

In the end of this chapter, student will have the ability to:

- Classify alkyl halides
- Draw and name alkyl halides using IUPAC nomenclature
- Describe physical properties and example of alkyl halides
- Compare and write nucleophilic substitution ($S_N2$ and $S_N1$) and elimination (E1 and E2) of alkyl halides

# Contents

- Nomenclature
- Physical properties
- Nucleophilic substitution mechanism of alkyl halides
- Organic synthesis

# Alkyl Halides and Nucleophilic Substitution

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 (**R** groups) bonded to the carbon with the halogen atom (the *head* carbon).

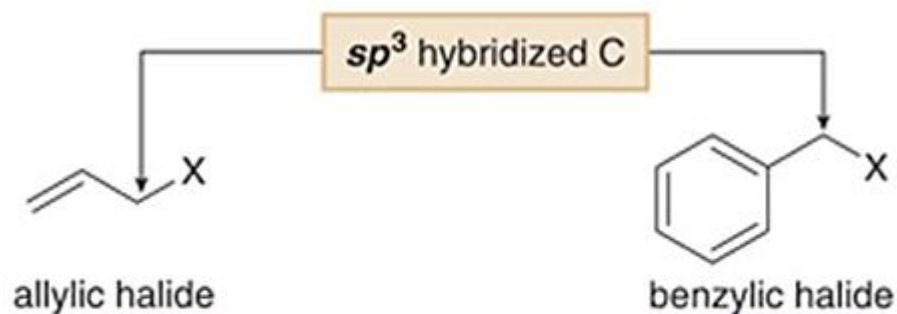- The halogen atom in halides is often denoted by the symbol "X".

| Alkyl halide | Classification of alkyl halides | | |
|---|---|---|---|
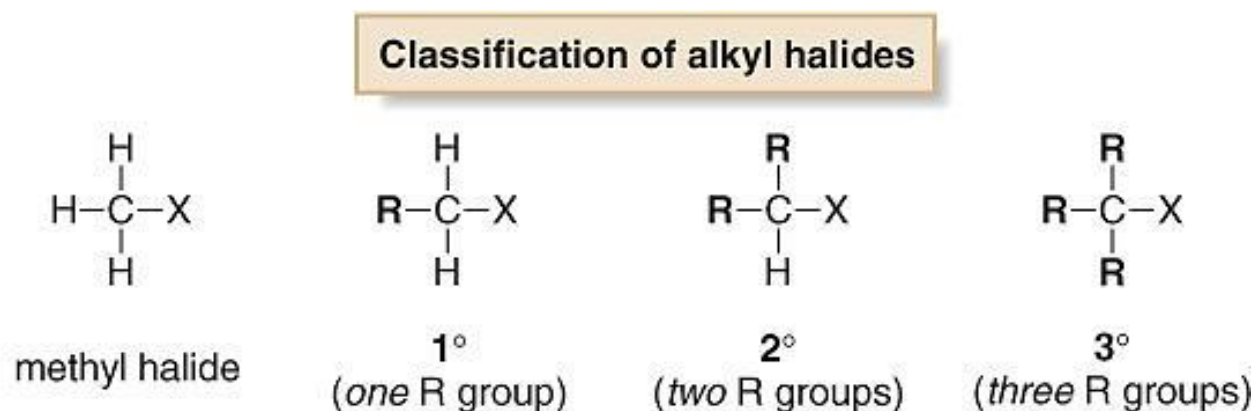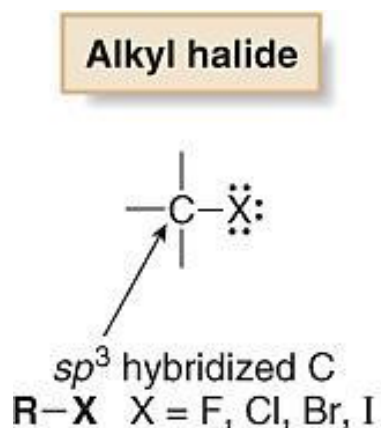
- There are other types of organic halides. These include vinyl halides, aryl halides, allylic halides and benzylic halides.

- **Vinyl halides** have a halogen atom (X) bonded to a carbon-carbon double bond.

- **Aryl halides** have a halogen atom bonded to a benzene ring.

- **Allylic halides** have X bonded to the carbon atom adjacent to a carbon-carbon double bond.

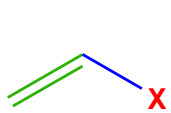- **Benzylic halides** have X bonded to the carbon atom adjacent to a benzene ring.

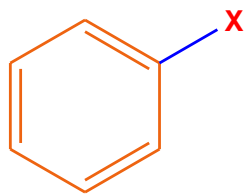**Four types of organic halides (RX) having X near a pi-bond**
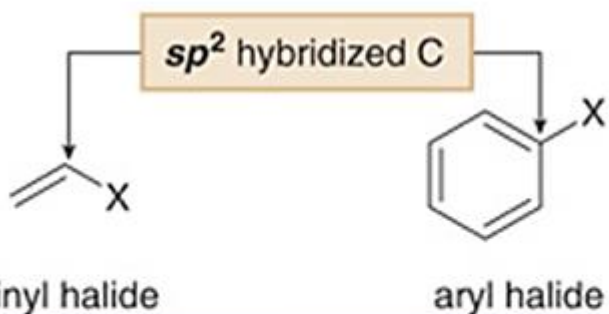


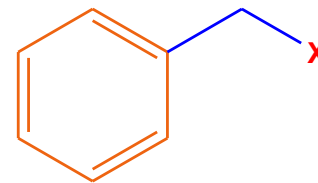| $sp^2$ hybridized C | $sp^3$ hybridized C |
|---|---|
| vinyl halide        aryl halide | allylic halide        benzylic halide |
| These organic halides are **unreactive** in the reactions | These organic halides do participate in the reactions |

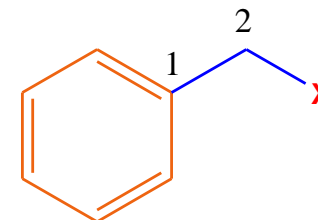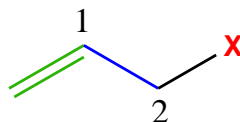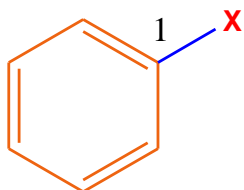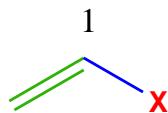**Vinyl halide**  **Aryl halide**  **Allylic halide**  **Benzylic halide**

**Examples of 1°, 2°, and 3° alkyl halides**
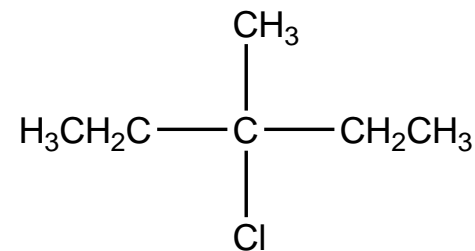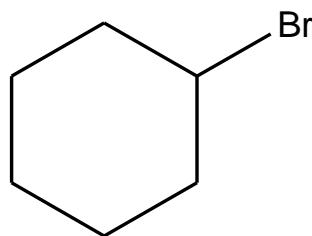
**Examples of 1°, 2°, and 3° alkyl halides**
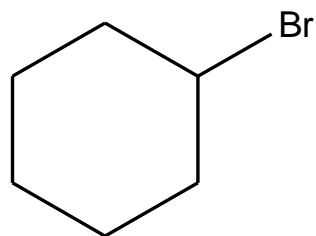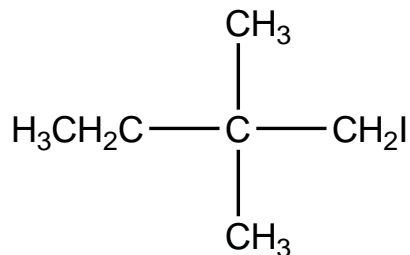
1°  2°  3°
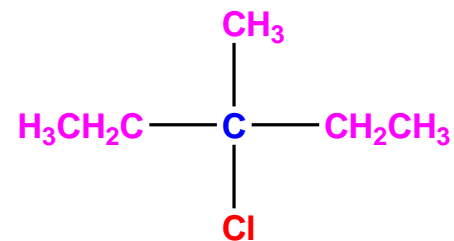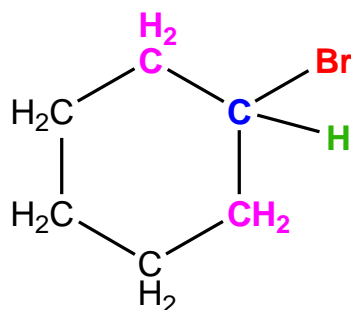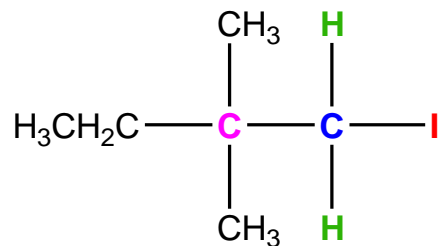
# Nomenclature

## How To    Name an Alkyl Halide Using the IUPAC System

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

$$CH_3CH_2CHCH_2CH_2CHCH_3$$

with $CH_3$ and $Cl$ substituents

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

$$CH_3CH_2CHCH_2CH_2CHCH_3$$
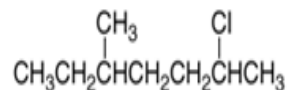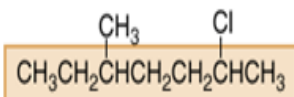
C's in the longest chain

• Name the parent chain as an **alkane,** with the halogen as a substituent bonded to the longest chain.
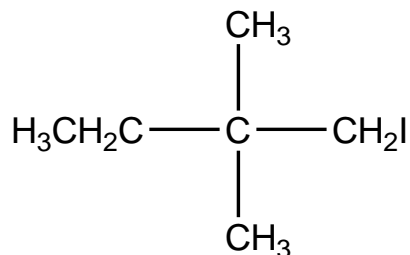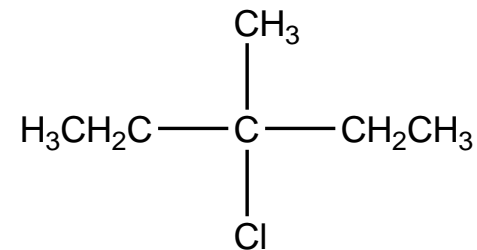
**Step [2]**   Apply all other rules of nomenclature.

a. **Number** the chain.

$$CH_3CH_2CHCH_2CH_2CHCH_3$$

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

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

$$CH_3CH_2CHCH_2CH_2CHCH_3$$

c. **Alphabetize:**

ANSWER:

# Nomenclature

## *How To*  Name an Alkyl Halide Using the IUPAC System

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

$$CH_3CH_2CHCH_2CH_2CHCH_3$$

with $CH_3$ on one carbon and $Cl$ on another.

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

$CH_3CH_2CHCH_2CH_2CHCH_3$ (with $CH_3$ and $Cl$ substituents)
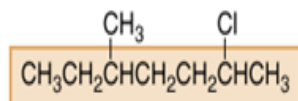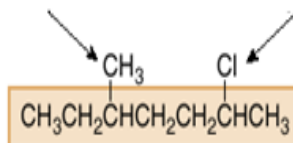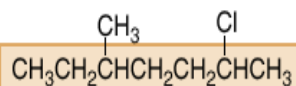
**7** C's in the longest chain

**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.

$CH_3CH_2CHCH_2CH_2CHCH_3$

7  6  5  4  3  2  1

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

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

**methyl** at **C5**          **chloro** at **C2**

$CH_3CH_2CHCH_2CH_2CHCH_3$

7  6  5  4  3  2  1
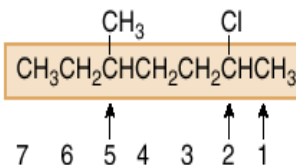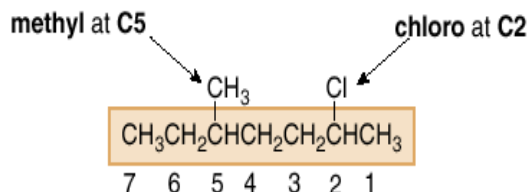
c. **Alphabetize: c** for **c**hloro, then **m** for **m**ethyl.

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

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

  - Name all the carbon atoms of the molecule as a single alkyl group.

  - Name the halogen bonded to the alkyl group.

  - Combine the names of the alkyl group and halide, separating the words with a space.
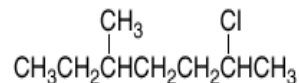
**Common names**

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-I$$

*tert*-butyl group

iod*ine* ⟶ iod*ide*

**tert-butyl iodide**

$CH_3CH_2-Cl$

ethyl group
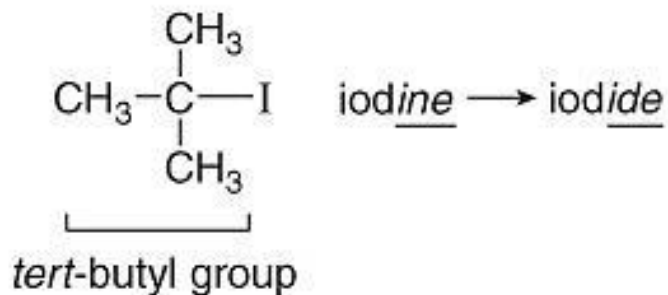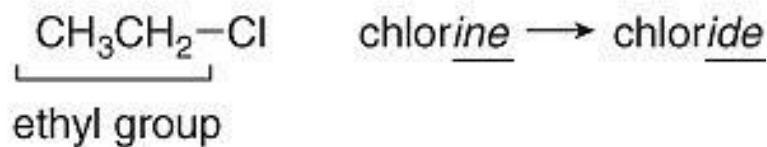
chlor*ine* ⟶ chlor*ide*

**ethyl chloride**

# Examples of different type of alkyl halides
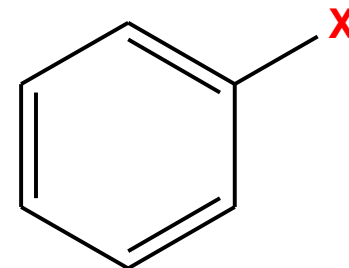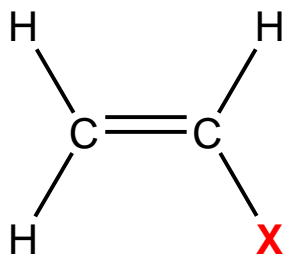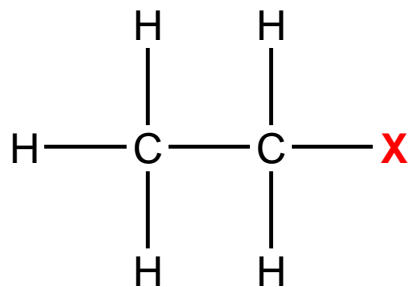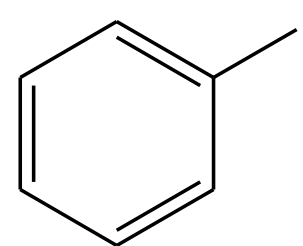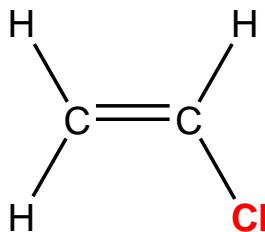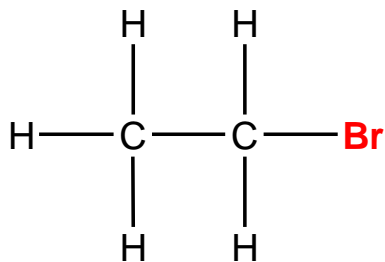
∴   X = F
        Cl
        Br
         I
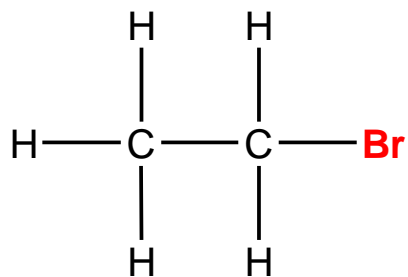
alkyl halide
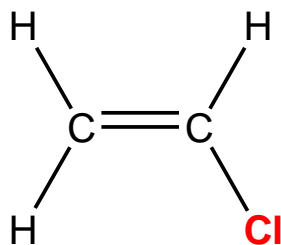
vinyl halide
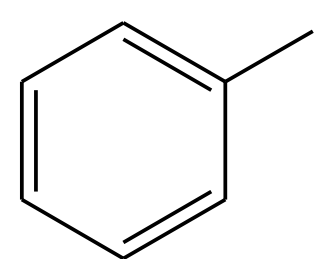
aryl halide

# 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.



Opposite ends of the dipoles interact.
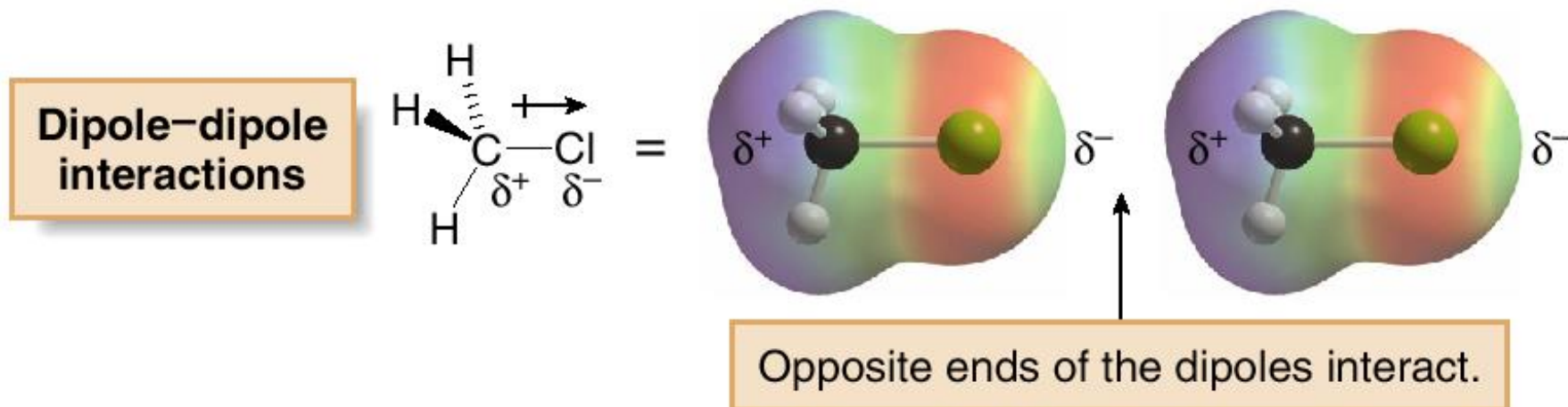
## Table 7.1   Physical Properties of Alkyl Halides

| Property | Observation |
|---|---|
| Boiling point and melting point | • Alkyl halides have higher bp's and mp's than alkanes having the same number of carbons.<br><br>$CH_3CH_3$    and    $CH_3CH_2Br$<br>bp = −89 °C      bp = 39 °C<br><br>• Bp's and mp's increase as the size of R increases.<br><br>$CH_3CH_2Cl$    and    $CH_3CH_2CH_2Cl$ ◄── larger surface area— higher mp and bp<br>mp = −136 °C      mp = −123 °C<br>bp = 12 °C      bp = 47 °C<br><br>• Bp's and mp's increase as the size of X increases.<br><br>$CH_3CH_2Cl$    and    $CH_3CH_2Br$ ◄── more polarizable halogen— higher mp and bp<br>mp = −136 °C      mp = −119 °C<br>bp = 12 °C      bp = 39 °C |
| Solubility | • RX is soluble in organic solvents.<br>• RX is insoluble in water. |

# 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.

**Electrostatic potential maps of four halomethanes ($CH_3X$)**



| General structure | $CH_3F$ | $CH_3Cl$ | $CH_3Br$ | $CH_3I$ |

electron-deficient site
electrophilic carbon
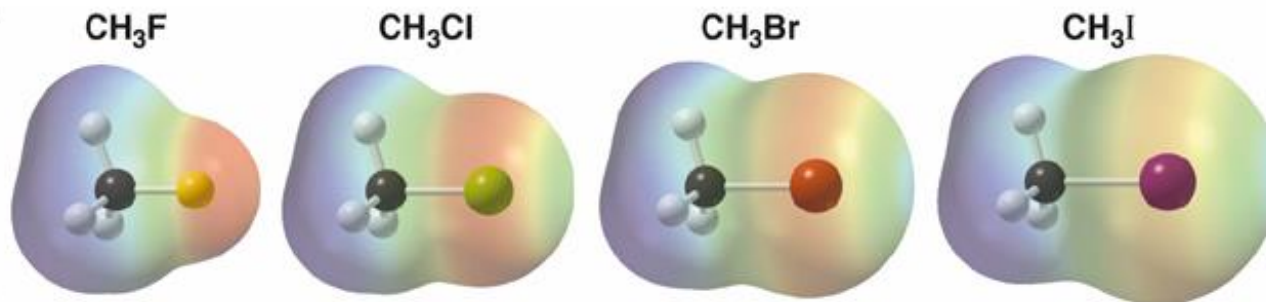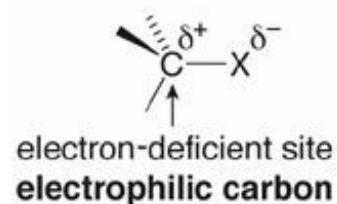
- The polar C−X bond makes the carbon atom *electron deficient* in each $CH_3X$ molecule.

- **Alkyl halides undergo substitution reactions with nucleophiles.**

$$R-X \quad + \quad :Nu^- \quad \longrightarrow \quad R-Nu \quad + \quad X:^-$$

nucleophile

substitution of X by Nu

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

$$\underset{\substack{\phantom{x}\\ H \quad X}}{-\overset{|}{C}-\overset{|}{C}-} \quad + \quad :B \quad \longrightarrow \quad C=C \quad + \quad H-B^+ \quad + \quad X:^-$$

base

new π bond
an alkene

elimination of HX

# Substitution Reaction

$$H-\overset{\ominus}{\underset{..}{\overset{..}{O}}}: \quad CH_3-\overset{..}{\underset{..}{Cl}}: \quad \rightleftharpoons \quad H-\overset{..}{\underset{..}{O}}-CH_3 \quad + \quad :\overset{..}{\underset{..}{Cl}}:^{\ominus}$$

nu:           $E^{\oplus}$           product          LG

## Nucleophile
- $e^-$ rich (lone pair or $\pi$ bond), can be $\ominus$ charge
- Seeks $e^-$ deficient species

## Electrophile
- $e^-$ poor
- seeks $e^-$ rich species

## Leaving Group (LG)
- group leaves and takes $2e^-$ with it
- stable groups (weak bases) make good LG

General reaction:

$$Nu:^{\ominus} + \quad R\text{-}LG \quad \longrightarrow \quad R\text{-}Nu \quad + \quad LG$$

• Three components are necessary in any substitution reaction.

**General substitution reaction**

$$R-X \quad + \quad :Nu^- \quad \longrightarrow \quad R-Nu \quad + \quad X:^-$$

$sp^3$ hybridized C     nucleophile     leaving group

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**Examples**

| | Alkyl group | | Nucleophile | | | | Leaving group |
|---|---|---|---|---|---|---|---|

[1]    $CH_3-Cl$   +   $^-:\ddot{O}H$       $\longrightarrow$       $CH_3-\ddot{O}H$   +   $Cl^-$

[2]    $CH_3CH_2CH_2-I$   +   $^-:\ddot{S}H$       $\longrightarrow$       $CH_3CH_2CH_2-\ddot{S}H$   +   $I^-$

[3]    $CH_3CH_2-Br$   +   $^-:\ddot{O}CH_3$       $\longrightarrow$       $CH_3CH_2-\ddot{O}CH_3$   +   $Br^-$

A new C–Nu bond forms.
The leaving group comes off.
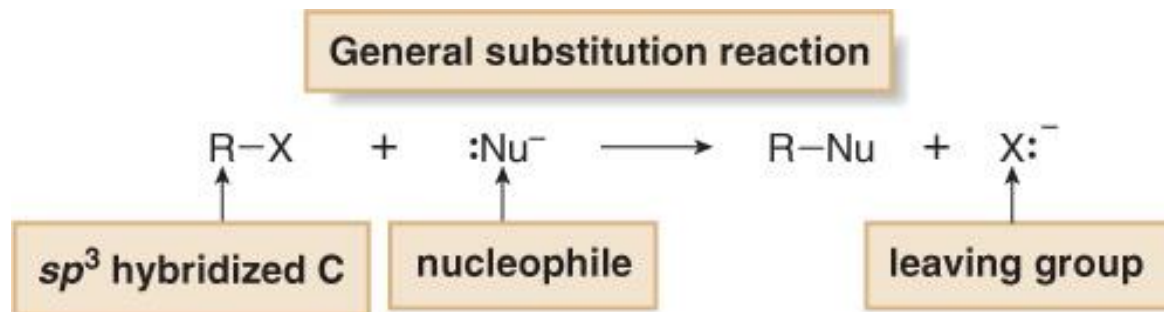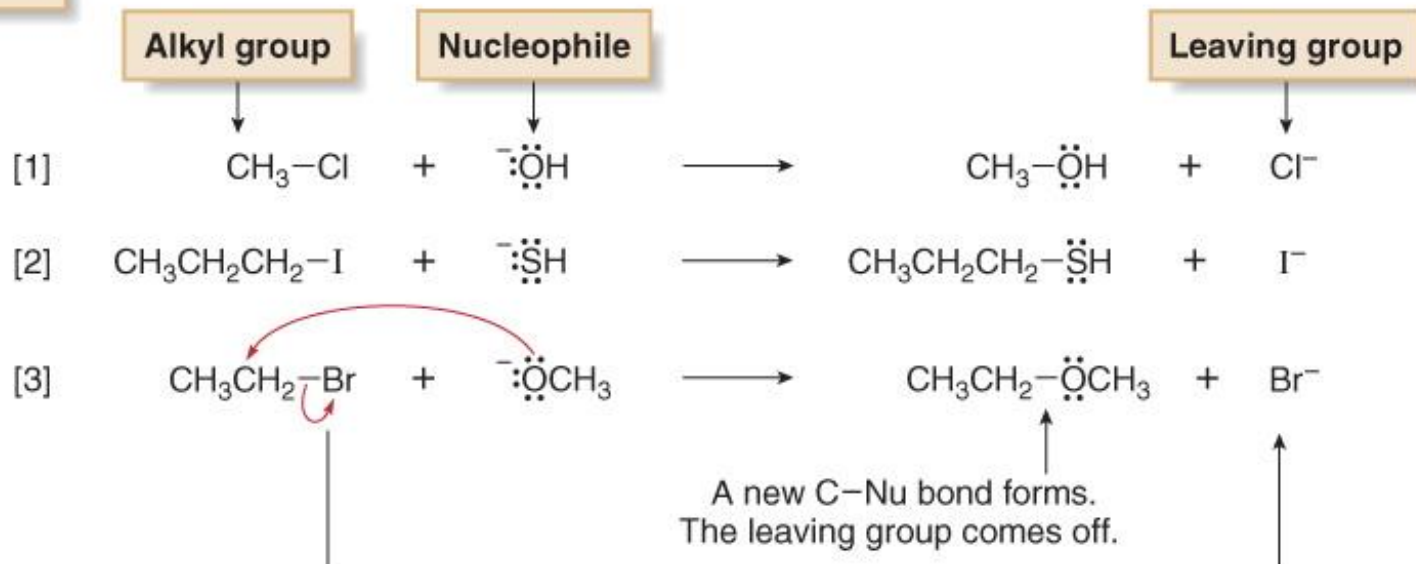
- Negatively charged nucleophiles like HO⁻ and HS⁻ are used as salts with Li⁺, Na⁺, or K⁺ counterions to balance the charge. Since the identity of the counterion is usually inconsequential, it is often omitted from the chemical equation.
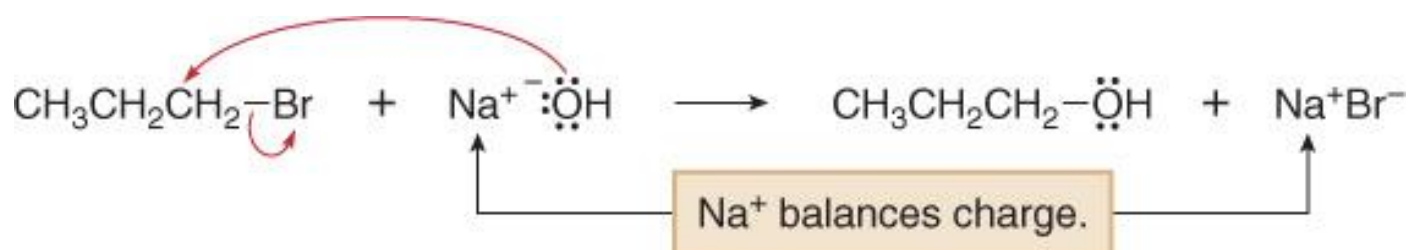


- When a neutral nucleophile is used, the substitution product bears a positive charge.
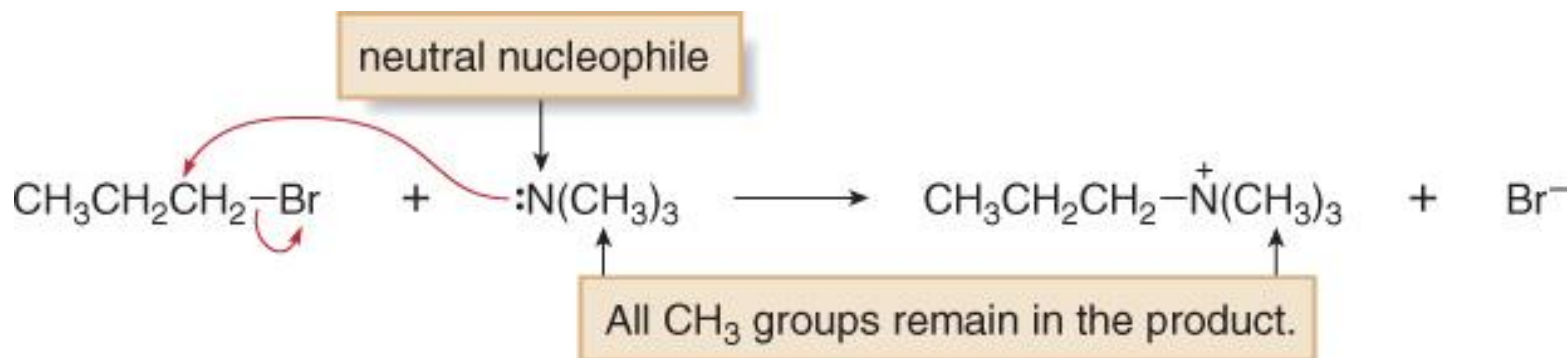
- Furthermore, when the substitution product bears a positive charge and also contains a proton bonded to O or N, the initially formed substitution product readily loses a proton in a BrØnsted-Lowry acid-base reaction, forming a neutral product.



**Step [1]:**
Nucleophilic substitution

**Step [2]:**
Proton transfer

The overall result:
**a neutral product**
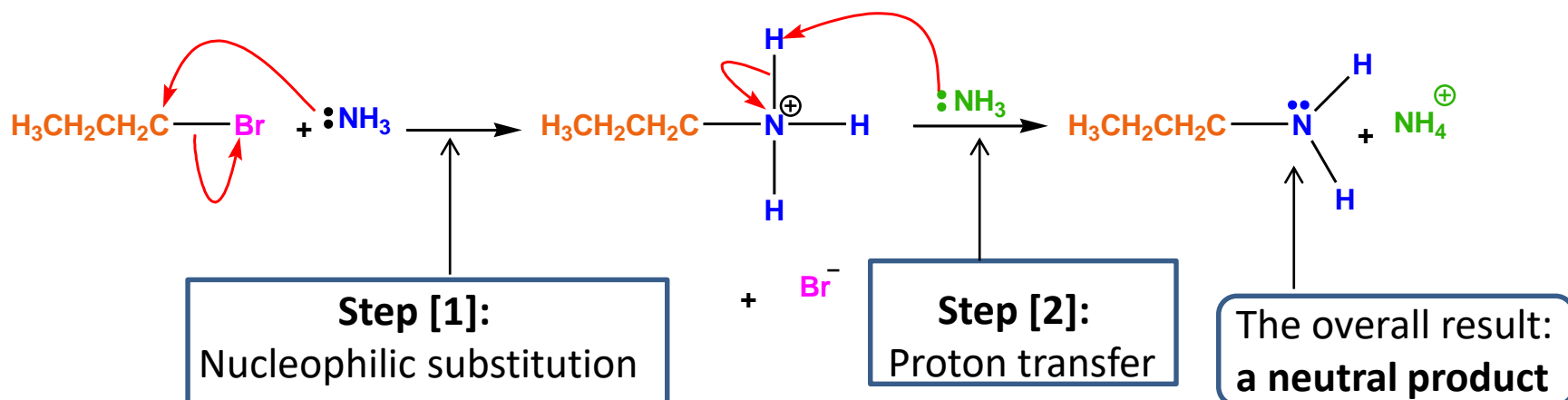
# The Leaving Group

- In a nucleophilic substitution reaction of R—X, the C—X bond is heterolytically cleaved, and the leaving group departs with the electron pair in that bond, forming X:⁻. The more stable the leaving group X:⁻, the better able it is to accept an electron pair.

- In comparing two leaving groups, the better leaving group is the weaker base.



Nucleophilic substitution occurs with **leaving groups that are weak bases.**
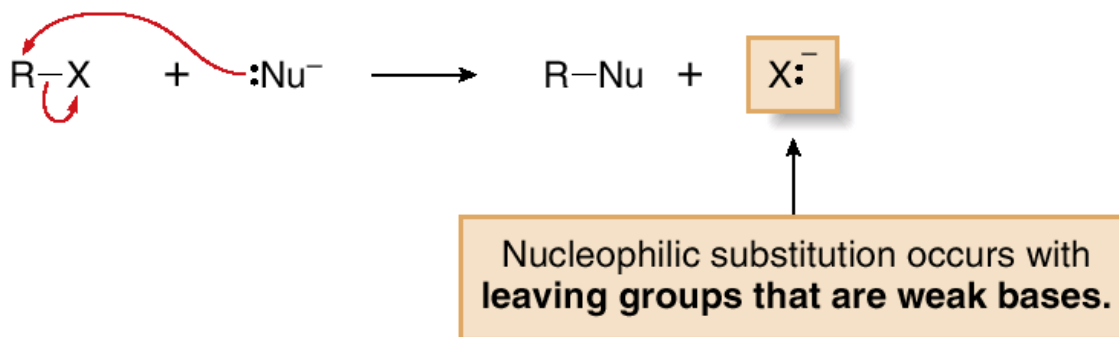
- For example, $H_2O$ is a better leaving group than $HO^-$ because $H_2O$ is a weaker base.

- There are periodic trends in leaving group ability:

- Left-to-right across a row of the periodic table, basicity *decreases* so leaving group ability *increases*.

**Increasing basicity** →

With second-row elements:
$:NH_3$   $H_2\ddot{O}:$   ← better leaving group

**Increasing leaving group ability** →
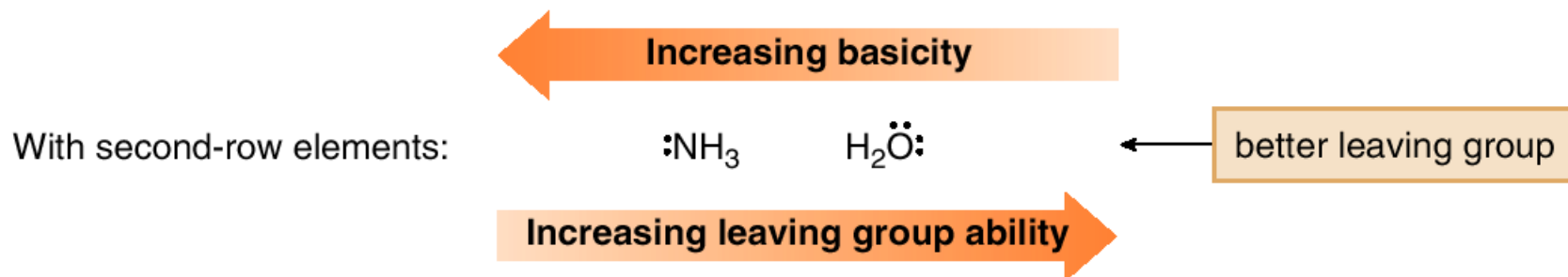
- Down a column of the periodic table, basicity *decreases* so leaving group ability *increases*.

**Increasing basicity** →

$F^-$   $Cl^-$   $Br^-$   $I^-$ ← weakest base best leaving group

**Increasing leaving group ability** →
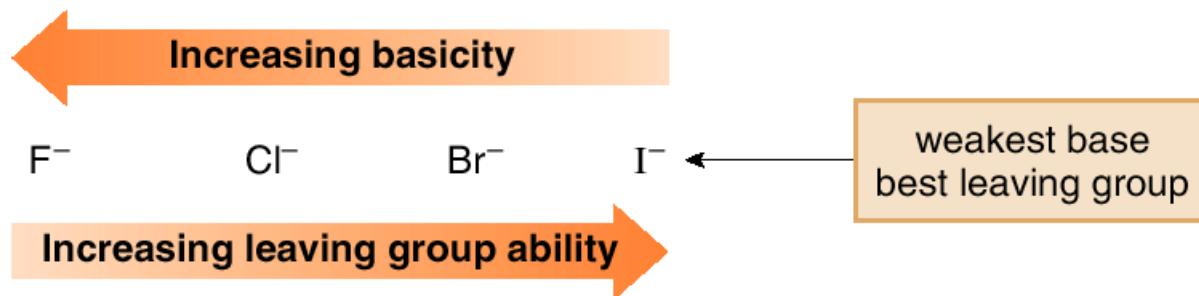
# The Nucleophile

- Nucleophiles and bases are structurally similar: both have a lone pair or a $\pi$ bond. They differ in what they attack.

- Bases attack protons. Nucleophiles attack other electron-deficient atoms (usually carbons).

Nucleophiles attack carbons.

Bases attack protons.
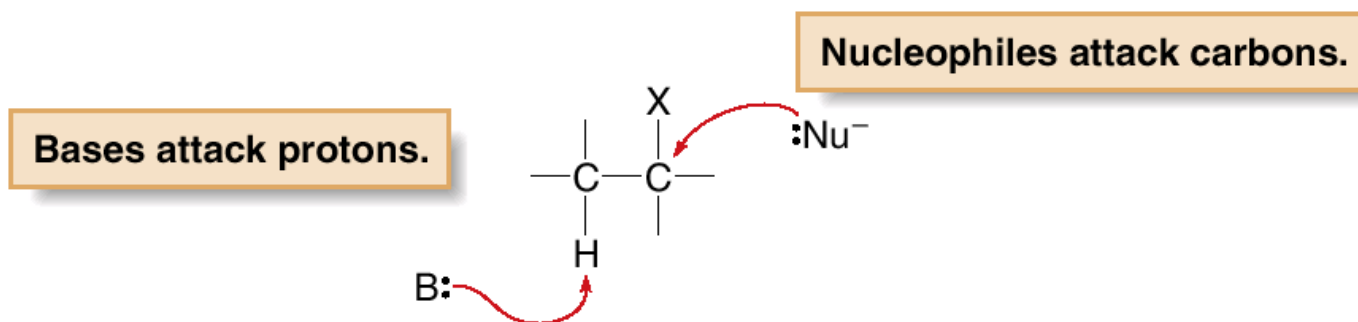
- Although Nucleophilicity and basicity are interrelated, they are fundamentally different.

  ➡ Basicity is a measure of how readily an atom donates its electron pair to a proton. It is characterized by an equilibrium constant, $K_a$ in an acid-base reaction.

  ➡ Nucleophilicity is a measure of how readily an atom donates its electron pair to other atoms. It is characterized by a rate constant, $k$.

## Table 7.4    Common Nucleophiles in Organic Chemistry

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

$CH_3CH_2Cl$    and    $CH_3CH_2Br$ ← more polarizable halogen—higher mp and bp
mp = −136 °C      mp = −119 °C
bp = 12 °C       bp = 39 °C

Solubility
- RX is soluble in organic solvents.
- RX is insoluble in water.

# Mechanisms of Nucleophilic Substitution

In a nucleophilic substitution:



| Overall reaction | $R-X$ + $:Nu^-$ ⟶ $R-Nu$ + $X:^-$ |

This σ bond is broken.　　　This σ bond is formed.
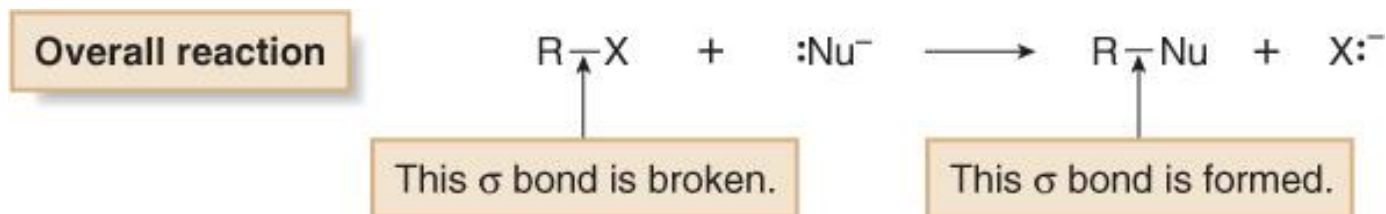
But what is the order of bond making and bond breaking? In theory, there are three possibilities.

**[1] Bond making and bond breaking occur at the same time.**



One-step mechanism:　$:Nu^-$ + $-C-X$ ⟶ $-C-Nu$ + $X:^-$

rate = $k[RX][:Nu^-]$
second-order rate equation

This bond is broken... **as** ...this bond is formed.
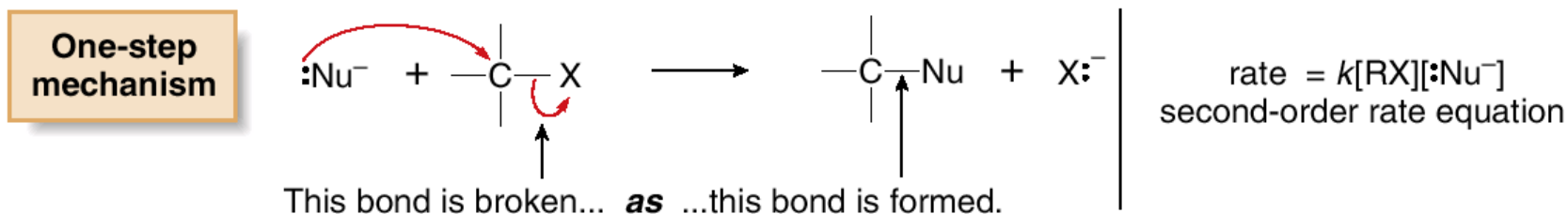
In this scenario, the mechanism is comprised of one step. In such a bimolecular reaction, the rate depends upon the concentration of both reactants, that is, the rate equation is second order.

# [2] Bond breaking occurs before bond making.

Two-step mechanism

$-\overset{|}{\underset{|}{C}}-X$ → $-\overset{|}{\underset{|}{C}}^+$ $\xrightarrow{:Nu^-}$ $-\overset{|}{\underset{|}{C}}-Nu$
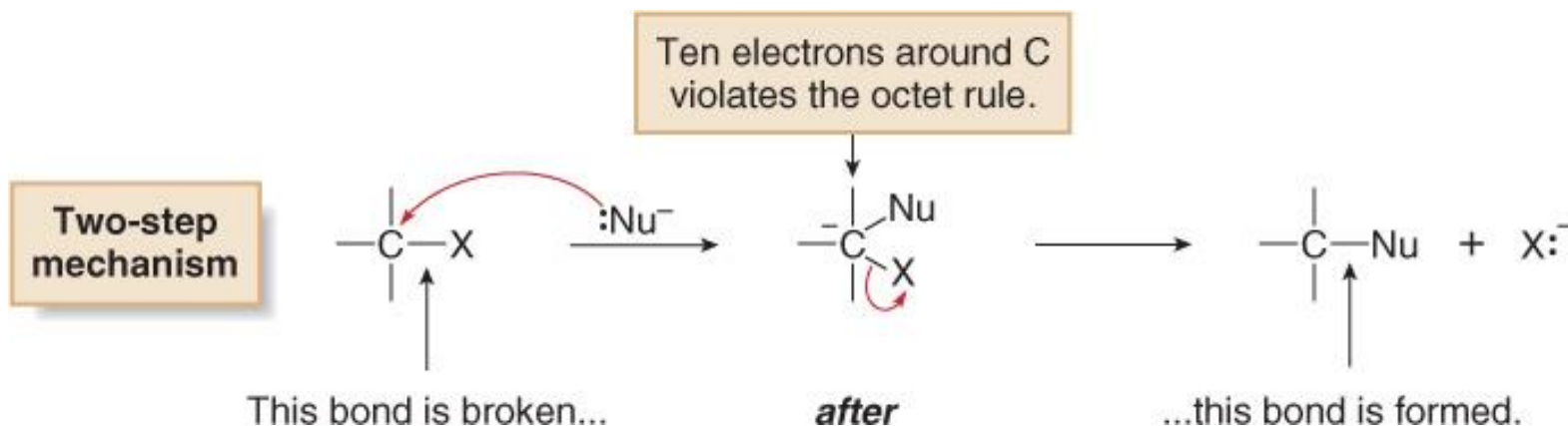
carbocation

$+ \; X:^-$

This bond is broken... *before* ...this bond is formed.
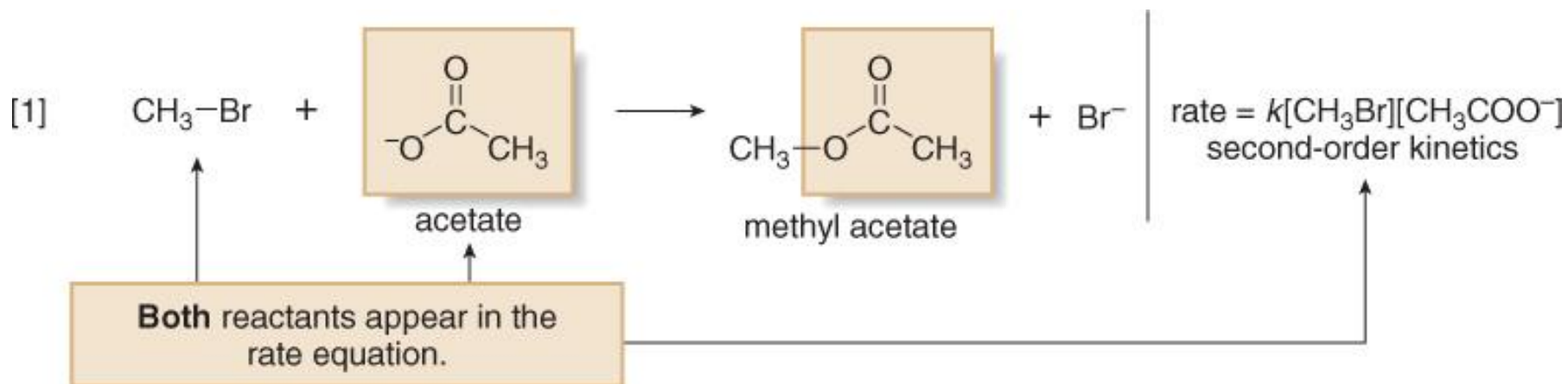
rate = $k$[RX]
first-order rate equation
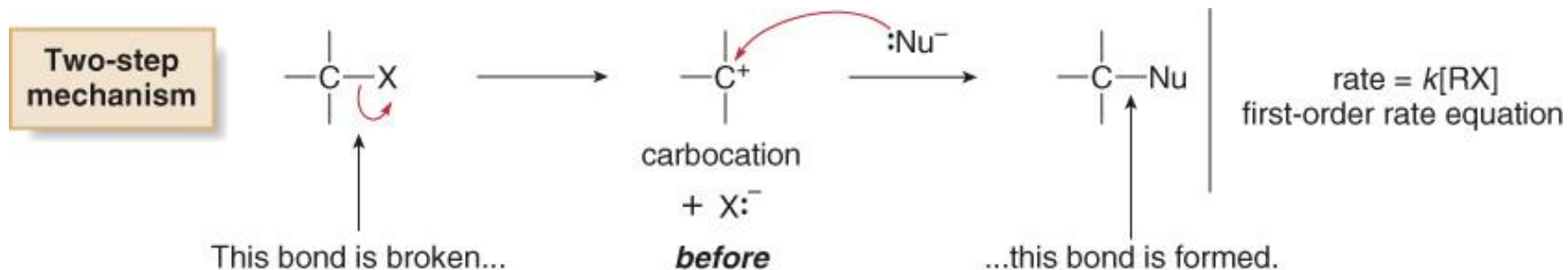
In this scenario, the mechanism has two steps and a carbocation is formed as an intermediate. Because the first step is rate-determining, the rate depends on the concentration of RX only; that is, the rate equation is first order.
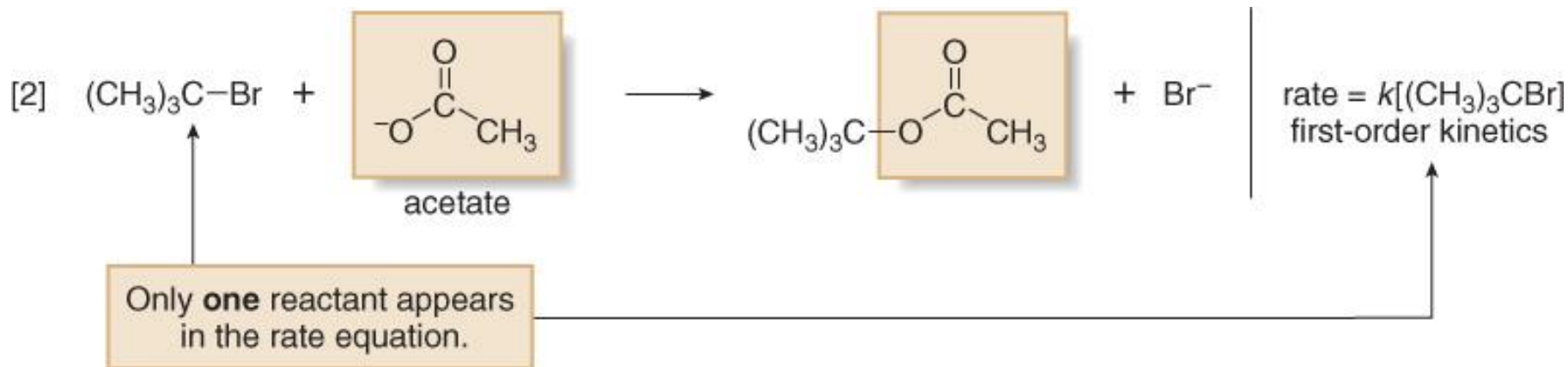
# [3] Bond making occurs before bond breaking.



This mechanism has an inherent problem. The intermediate generated in the first step has 10 electrons around carbon, violating the octet rule. Because two other mechanistic possibilities do not violate a fundamental rule, this last possibility can be disregarded.

Consider reaction [1] below:



[1]  $CH_3$—$Br$  +  acetate  $\longrightarrow$  methyl acetate  +  $Br^-$  | rate = $k[CH_3Br][CH_3COO^-]$
second-order kinetics

acetate

methyl acetate

**Both** reactants appear in the rate equation.

Kinetic data show that the rate of reaction [1] depends on the concentration of both reactants, which suggests a bimolecular reaction with a one-step mechanism. This is an example of an $S_N2$ (substitution nucleophilic bimolecular) mechanism.

Consider reaction [2] below:

[2]   $(CH_3)_3C{-}Br$  +



acetate

→

$(CH_3)_3C{-}O{-}$...$CH_3$

+ $Br^-$

rate = $k[(CH_3)_3CBr]$
first-order kinetics

Only **one** reactant appears in the rate equation.

Kinetic data show that the rate of reaction [2] depends on the concentration of only the alkyl halide. This suggests a two-step mechanism in which the rate-determining step involves the alkyl halide only. This is an example of an $S_N1$ (substitution nucleophilic unimolecular) mechanism.

# S$_N$2

The mechanism of an S$_N$2 reaction would be drawn as follows. Note the curved arrow notation that is used to show the flow of electrons.
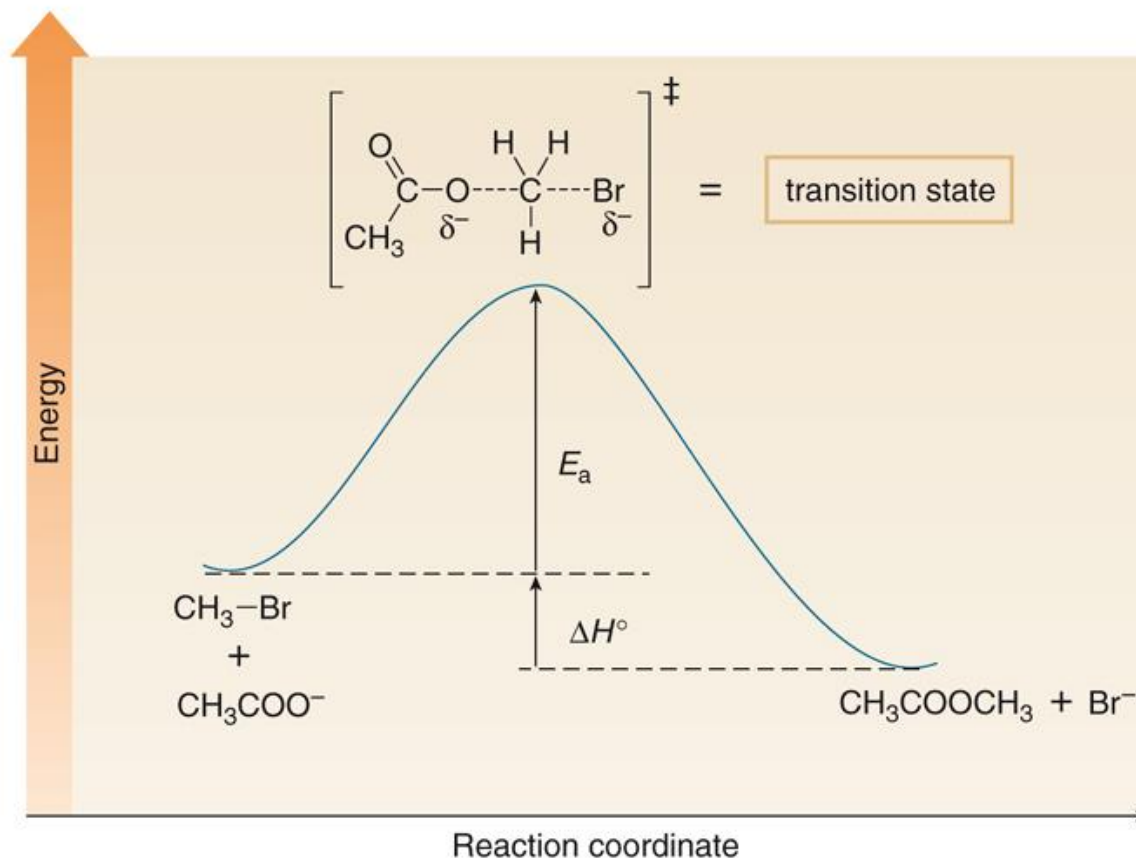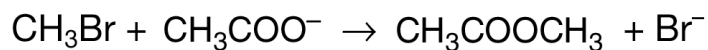


Mechanism 7.1 The S$_N$2 Mechanism

One step The C–Br bond breaks as the C–O bond forms.

new C–O bond

# An energy diagram for the S$_N$2 reaction:

$$CH_3Br + CH_3COO^- \rightarrow CH_3COOCH_3 + Br^-$$



- 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.

# Stereochemistry:

- All $S_N2$ reactions proceed with backside attack of the nucleophile, resulting in *inversion of configuration* at a stereogenic center (Walden inversion).
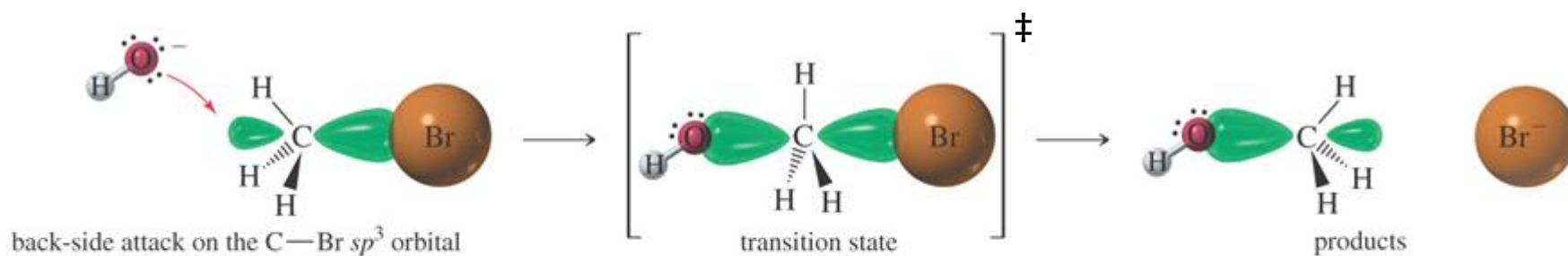
**Stereochemistry of the $S_N2$ reaction**



transition state
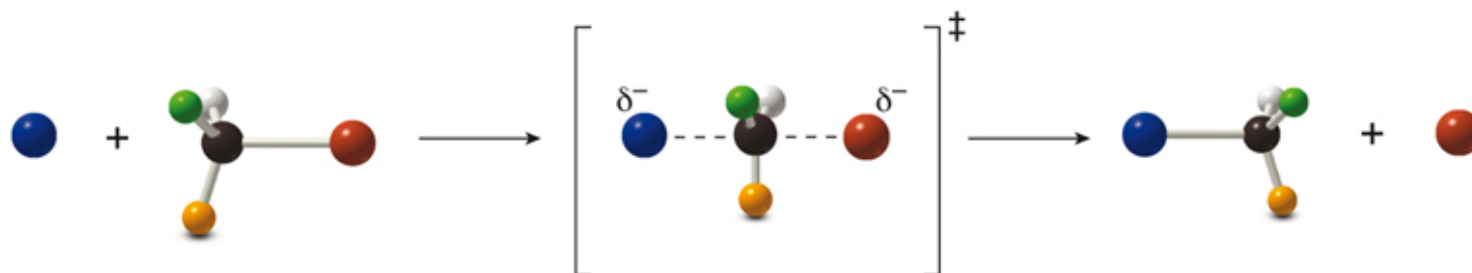
:Nu⁻ and Br⁻ are 180° away from each other, on either side of a plane containing R, H, and D.

## Walden inversion



back-side attack on the C—Br $sp^3$ orbital · transition state · products
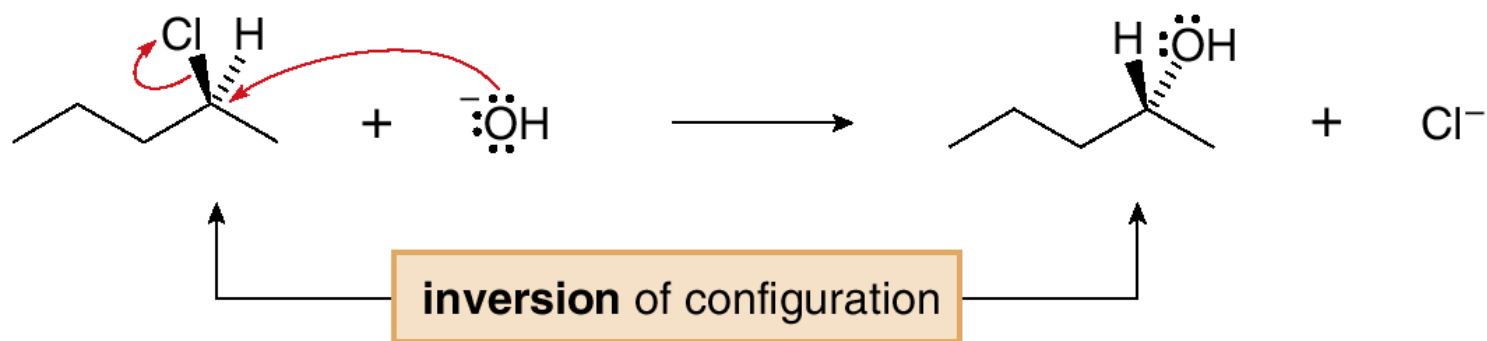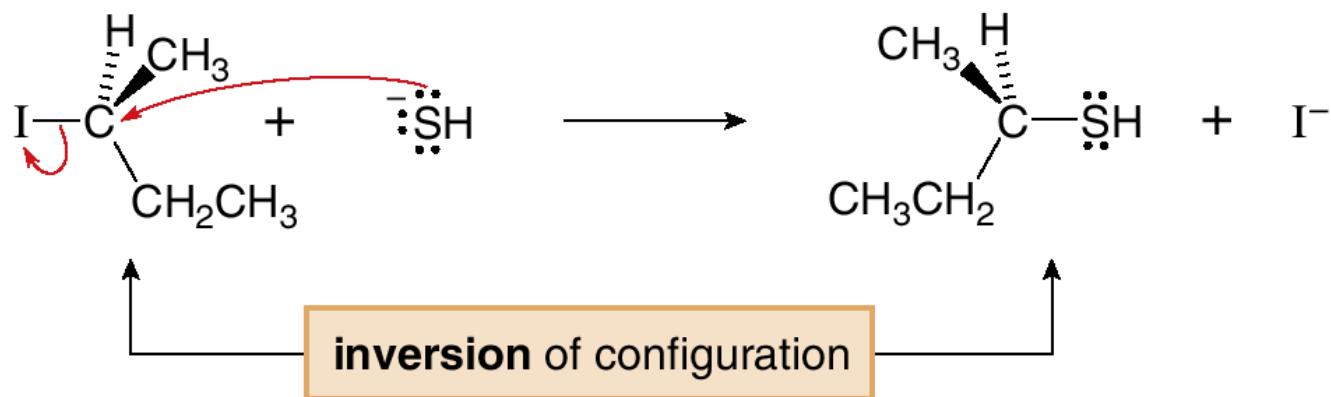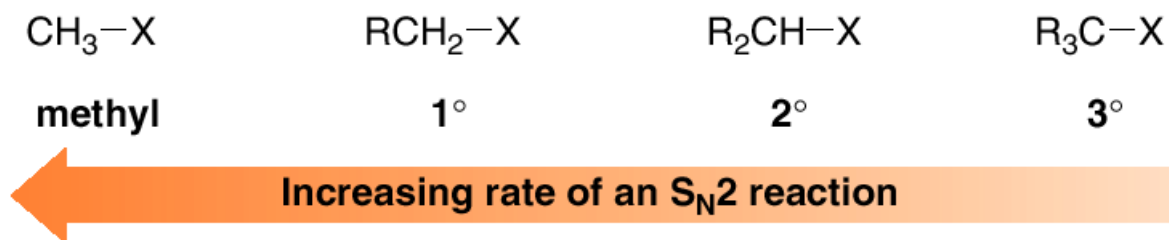
- The bond to the nucleophile in the product is always on the **opposite side** relative to the bond to the leaving group in the starting material.

**Two examples of inversion of configuration in the S$_N$2 reaction:**



**inversion** of configuration

**inversion** of configuration

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

| $CH_3-X$ | $RCH_2-X$ | $R_2CH-X$ | $R_3C-X$ |
| :---: | :---: | :---: | :---: |
| **methyl** | **1°** | **2°** | **3°** |

← **Increasing rate of an $S_N2$ reaction**

- 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. This order of reactivity can be explained by steric effects. Steric hindrance caused by bulky R groups makes nucleophilic attack from the backside more difficult, slowing the reaction rate.

Electrostatic potential maps illustrate the effects of steric hindrance around the carbon bearing the leaving group in a series of alkyl halides.
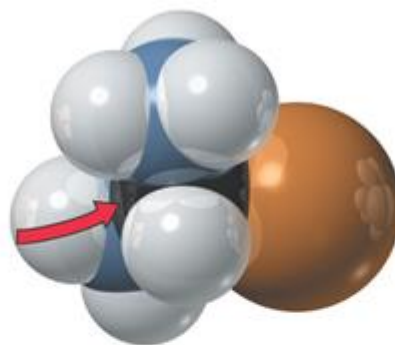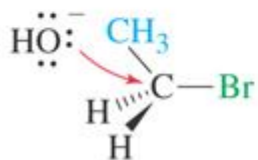
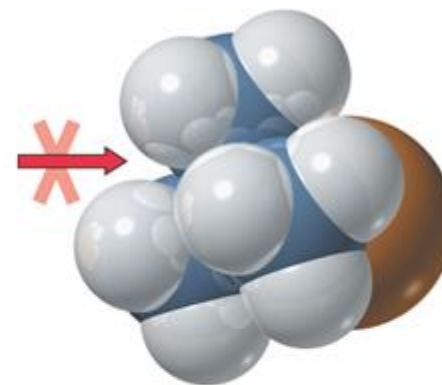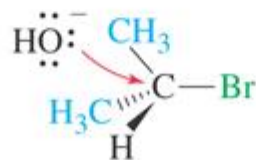**Steric effects in the $S_N2$ reaction:**
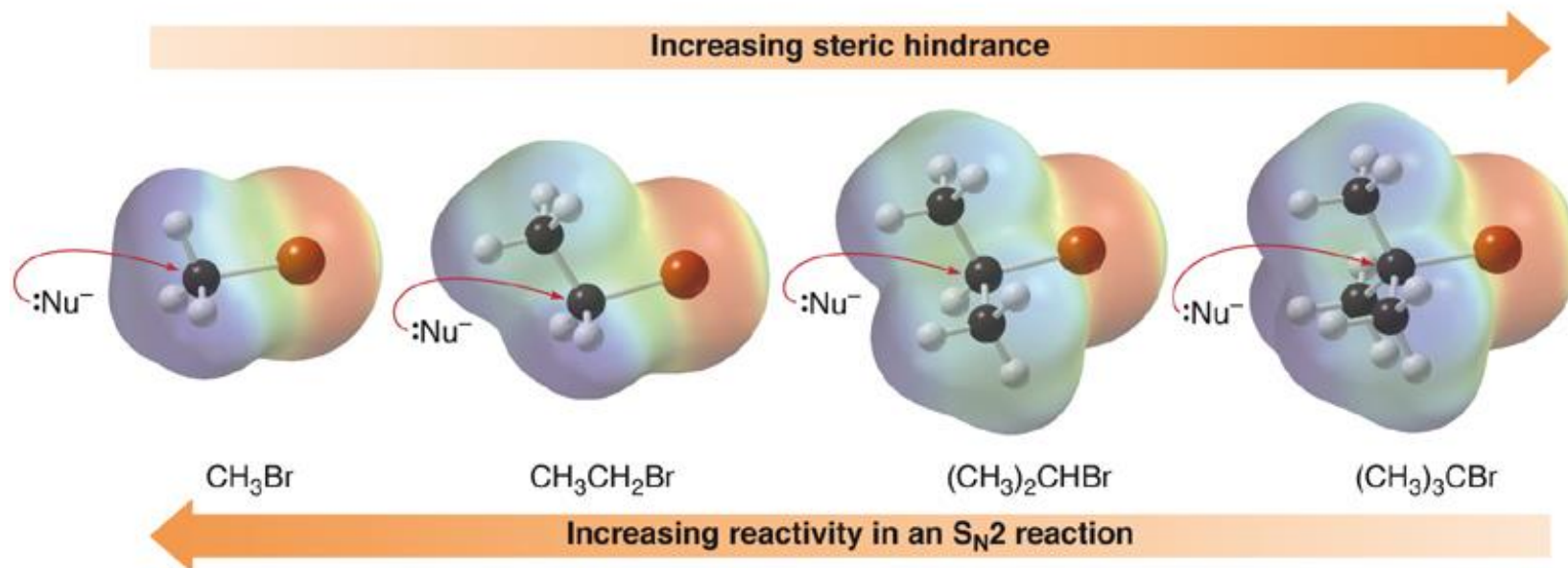
- As the number of R groups on the carbon with the leaving group *increases,* the rate of an $S_N2$ reaction *decreases.*

$$CH_3-X \qquad RCH_2-X \qquad R_2CH-X \qquad R_3C-X$$

methyl          1°          2°          3°

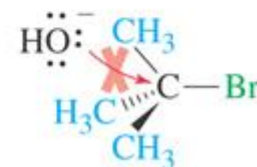← **Increasing rate of an $S_N2$ reaction**
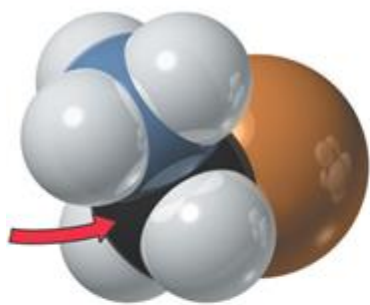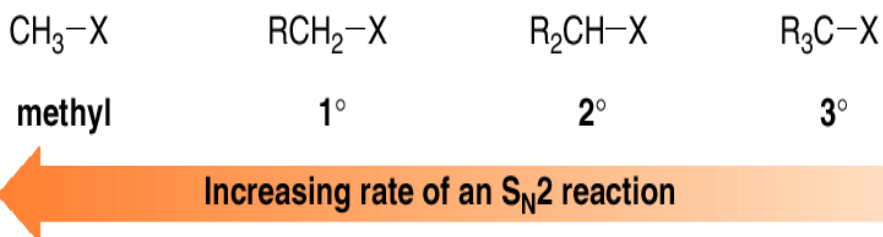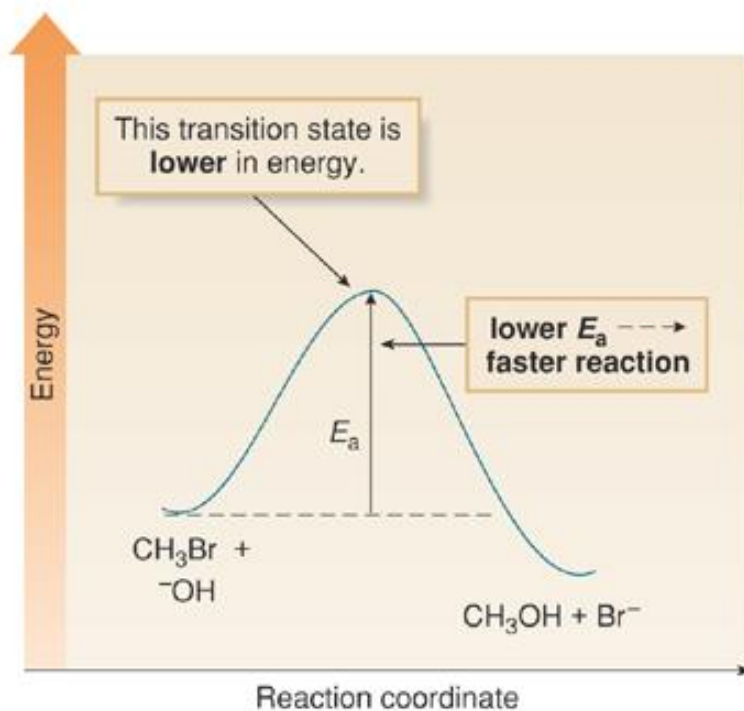


ethyl bromide (1°)
attack is easy

isopropyl bromide (2°)
attack is possible

*t*-butyl bromide (3°)
attack is impossible

- The higher the $E_a$, the slower the reaction rate. Thus, any factor that increases $E_a$ decreases the reaction rate ( lower $E_a$ means that a greater number of reacting molecules would reach the transition state).



a. $CH_3Br + {}^-OH \rightarrow CH_3OH + Br^-$

- $CH_3Br$ is an unhindered alkyl halide. The transition state in the $S_N2$ reaction is lower in energy, making $E_a$ lower and increasing the reaction rate.

b. $(CH_3)_2CHBr + {}^-OH \rightarrow (CH_3)_2CHOH + Br^-$
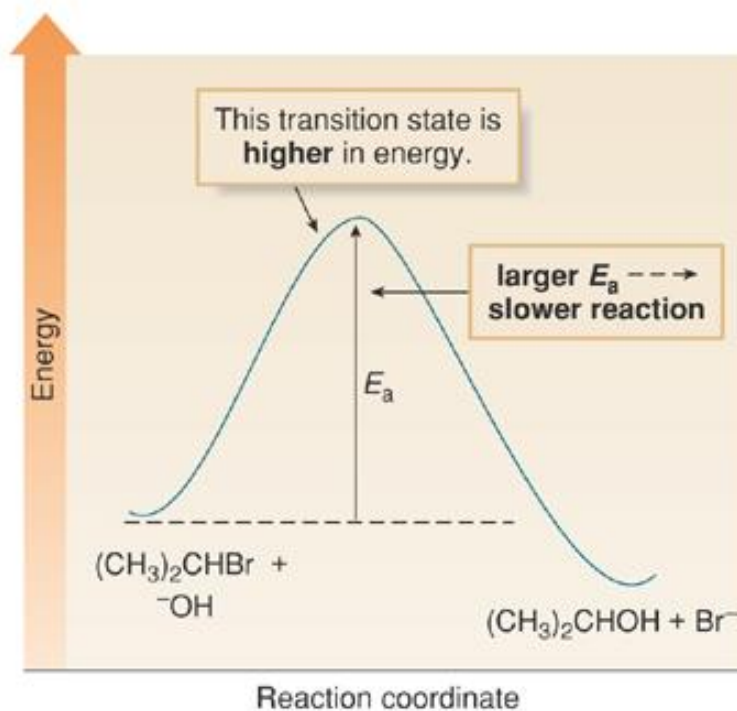
- $(CH_3)_2CHBr$ is a sterically hindered alkyl halide. The transition state in the $S_N2$ reaction is higher in energy, making $E_a$ higher and decreasing the reaction rate.

## Table 7.5 — Characteristics of the S$_N$2 Mechanism

| Characteristic | Result |
| --- | --- |
| Kinetics | • Second-order kinetics; rate = $k[RX][:Nu^-]$ |
| Mechanism | • One step |
| Stereochemistry | • Backside attack of the nucleophile<br>• Inversion of configuration at a stereogenic center |
| Identity of R | • Unhindered halides react fastest.<br>• Rate: $CH_3X > RCH_2X > R_2CHX > R_3CX$ |

The S$_N$2 reaction is a key step in the laboratory synthesis of many important drugs.

**Nucleophilic substitution in the synthesis of two useful drugs:**



ethambutol
(Trade name: Myambutol)

fluoxetine
(Trade name: Prozac)
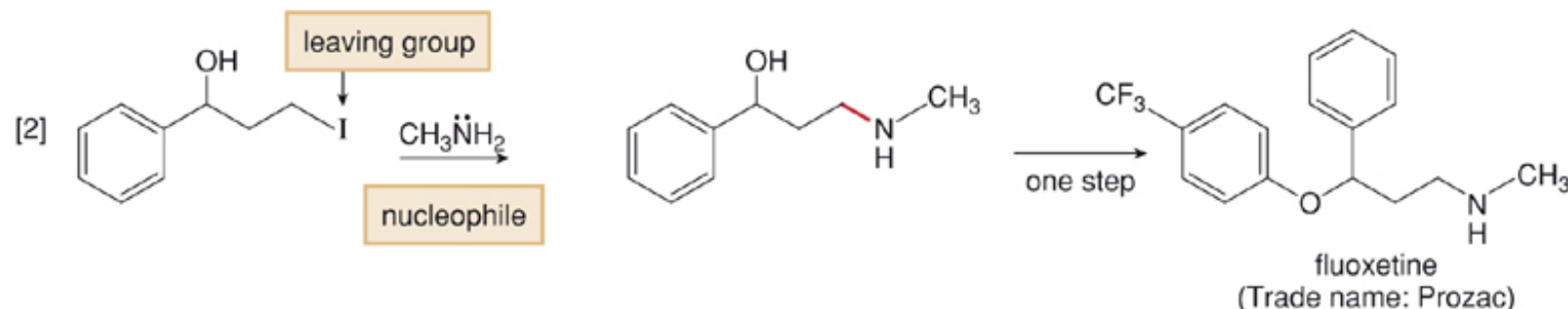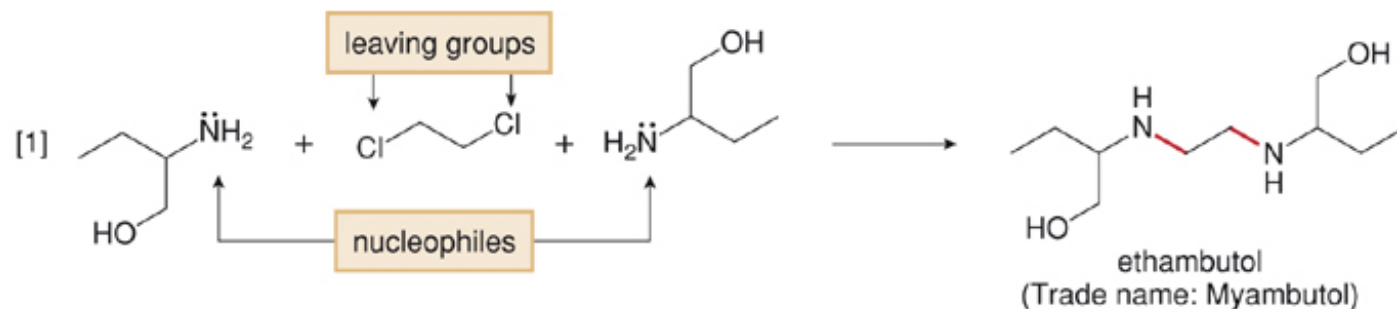
In both syntheses, the NH$_2$ group serves as a neutral nucleophile to displace halogen. The new bonds formed by nucleophilic substitution are drawn in red in the products.
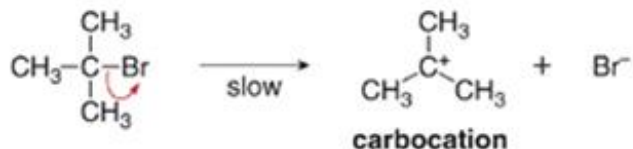
# S$_N$1

The mechanism of an S$_N$1 reaction would be drawn as follows: Note the curved arrow formalism that is used to show the flow of electrons.
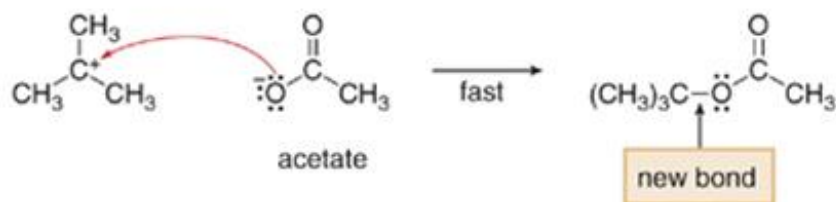


Mechanism 7.2 The S$_N$1 Mechanism

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.

Key features of the S$_N$1 mechanism are that it has two steps, and carbocations are formed as reactive intermediates.

**An energy diagram**
**for the $S_N1$ reaction**

$(CH_3)_3CBr + CH_3COO^- \rightarrow$
  $(CH_3)_3COCOCH_3 + Br^-$
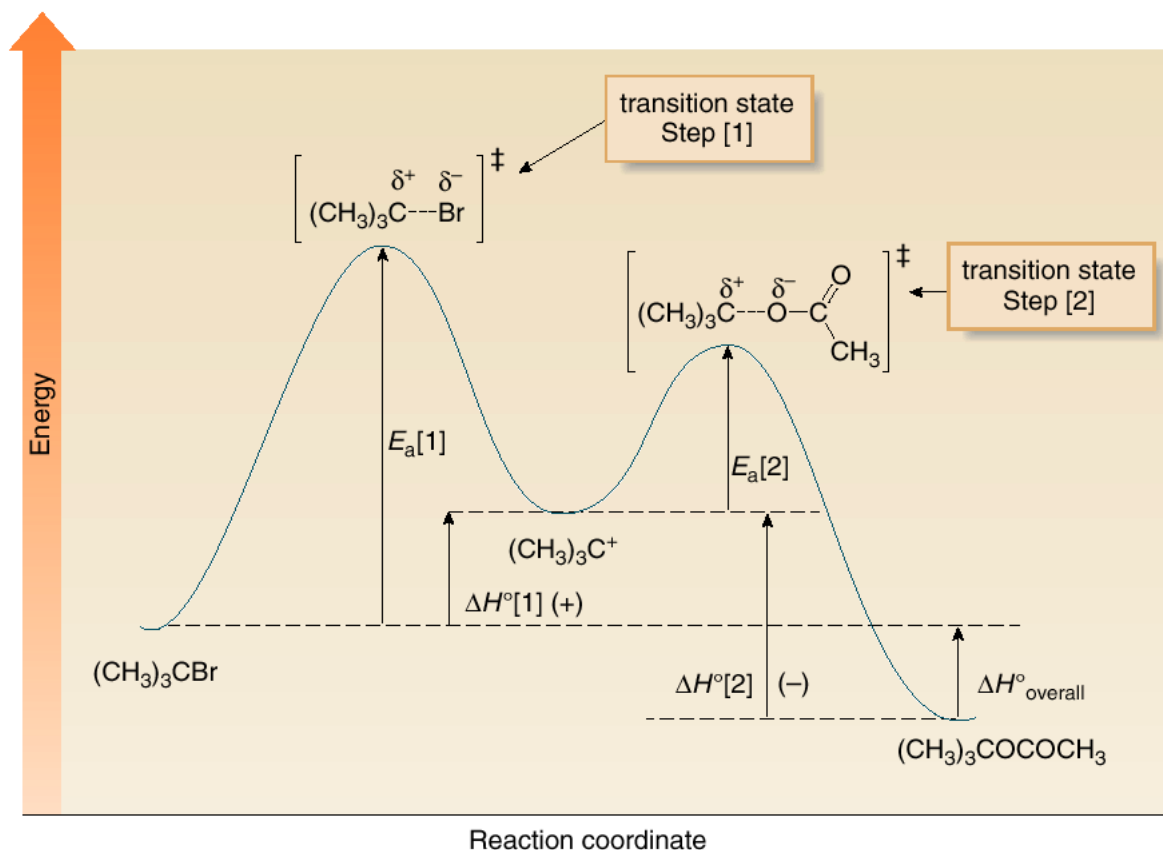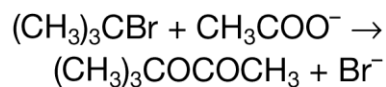


- Since the $S_N1$ mechanism has two steps, there are two energy barriers.
- $E_a[1] > E_a[2]$ since Step [1] involves bond breaking and Step [2] involves bond formation.
- In each step only one bond is broken or formed, so the transition state for each step has one partial bond.
- The reaction is drawn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

# Stereochemistry

To understand the stereochemistry of the $S_N1$ reaction, we must examine the geometry of the carbocation intermediate.



A trigonal planar carbocation

vacant *p* orbital

120°
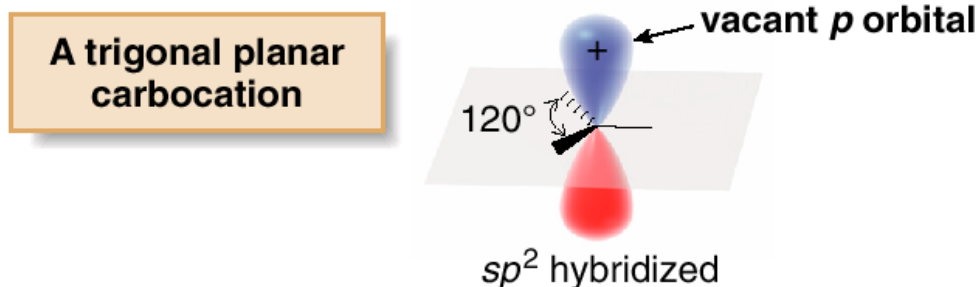
$sp^2$ hybridized

- A carbocation (with three groups around C) is $sp^2$ hybridized and trigonal planar, and contains a vacant *p* orbital extending above and below the plane.

- 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.

- Because there is no preference for nucleophilic attack from either direction, an equal amount of the two enantiomers is formed—a racemic mixture. We say that racemization has occurred.
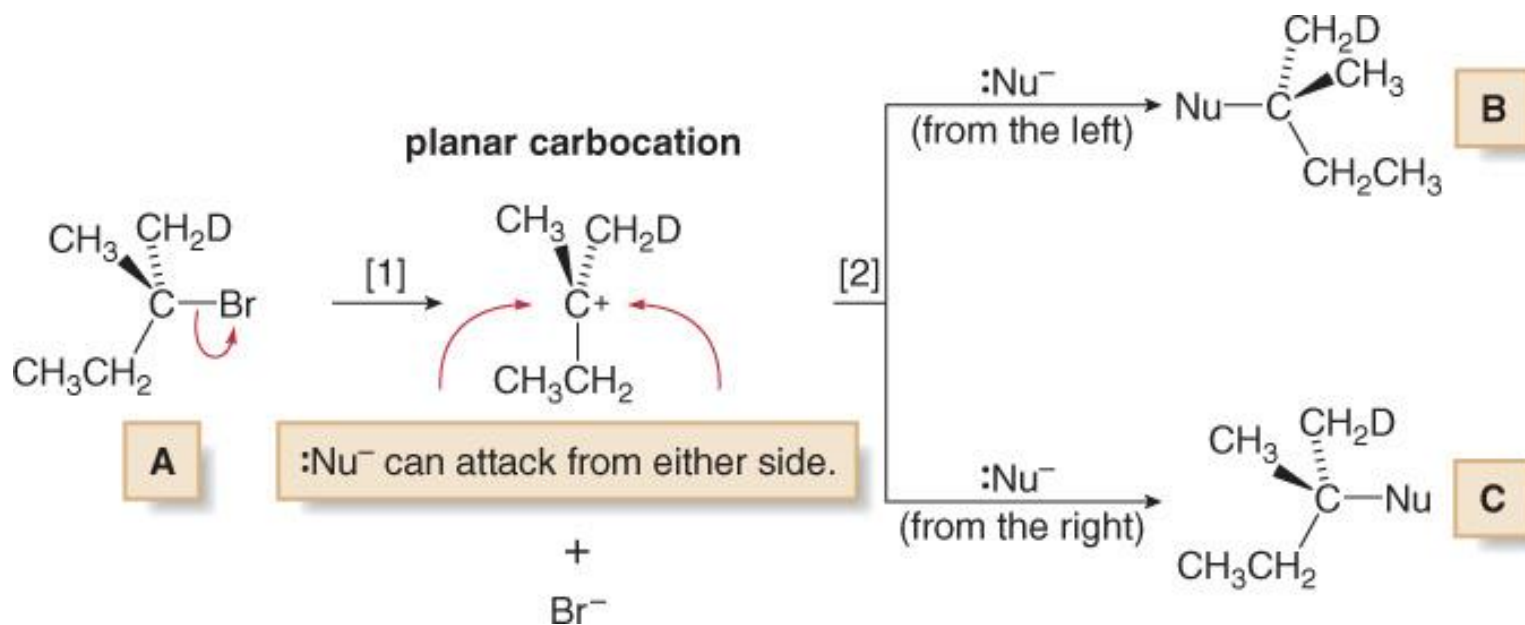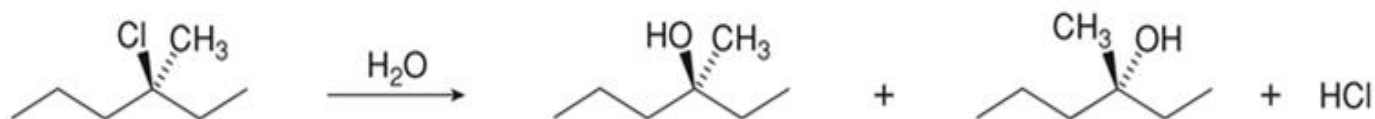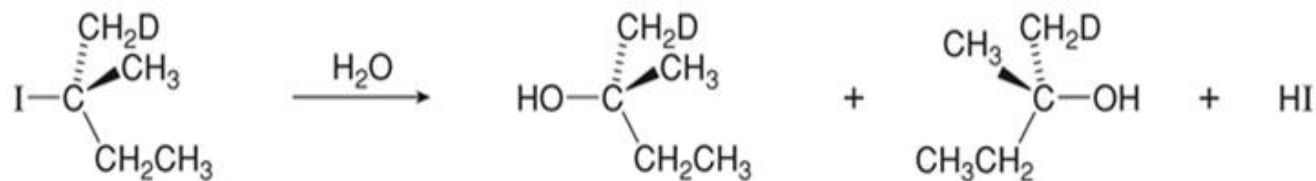
- Nucleophilic substitution of each starting material by an S$_N$1 mechanism forms a ---------------------- of two products.
- With H$_2$O, a neutral nucleophile, the initial product of nucleophilic substitution (ROH$_2^+$) loses a proton to form the final neutral product, ROH.
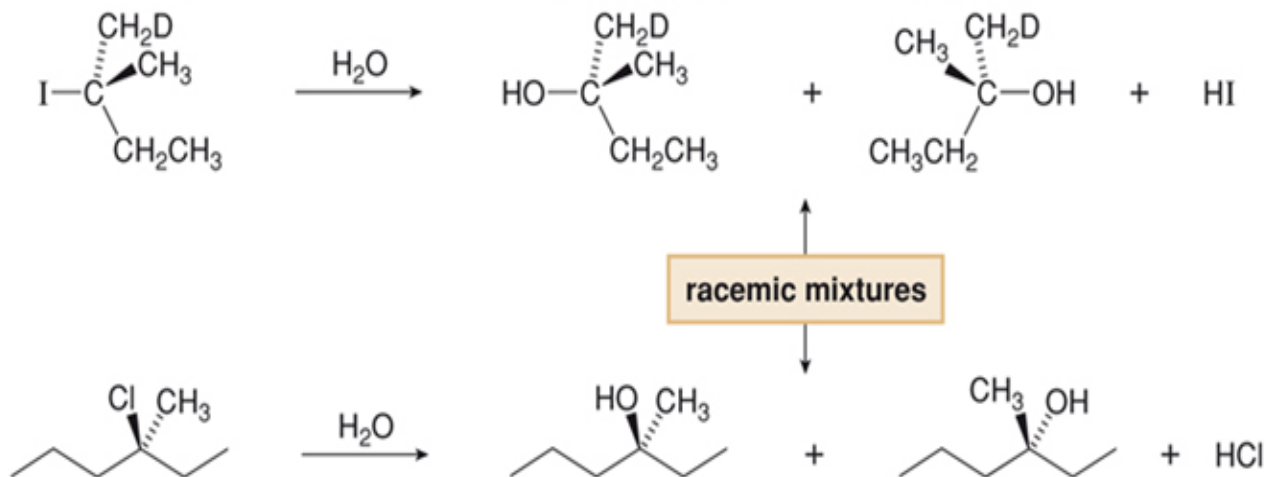
racemic mixtures

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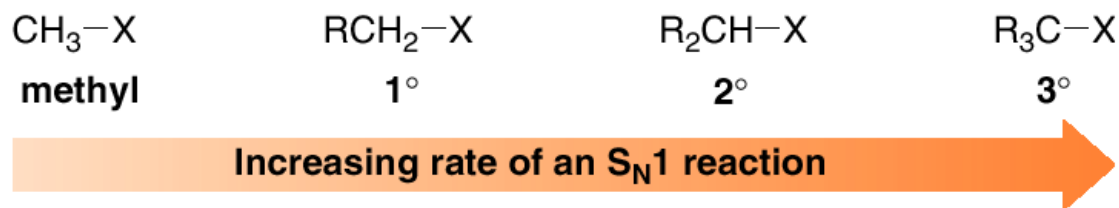
- The rate of an $S_N1$ reaction is affected by the type of alkyl halide involved.

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

$$CH_3-X \qquad RCH_2-X \qquad R_2CH-X \qquad R_3C-X$$

methyl     1°     2°     3°

**Increasing rate of an $S_N1$ reaction**

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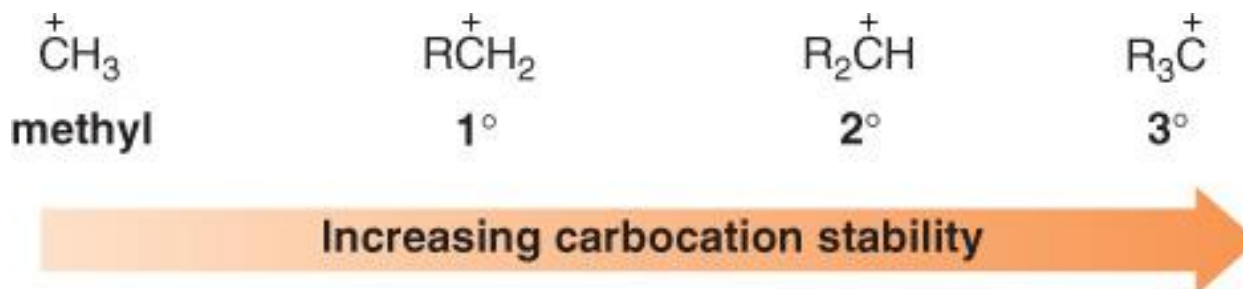- Methyl and 1° alkyl halides do *not* undergo $S_N1$ reactions.

- This trend is exactly opposite to that observed in $S_N2$ reactions.

## Table 7.6 — Characteristics of the $S_N1$ Mechanism

| Characteristic | Result |
|---|---|
| Kinetics | • First-order kinetics; rate = $k[RX]$ |
| Mechanism | • Two steps |
| Stereochemistry | • Trigonal planar carbocation intermediate<br>• Racemization at a single stereogenic center |
| Identity of R | • More substituted halides react fastest.<br>• Rate: $R_3CX > R_2CHX > RCH_2X > CH_3X$ |

- The effect of the type of alkyl halide on $S_N1$ reaction rates can be explained by considering carbocation stability.

- Carbocations are classified as primary (1°), secondary (2°), or tertiary (3°), based on the number of R groups bonded to the charged carbon atom. As the number of R groups increases, carbocation stability increases.

$$\overset{+}{C}H_3 \qquad R\overset{+}{C}H_2 \qquad R_2\overset{+}{C}H \qquad R_3\overset{+}{C}$$

methyl          1°              2°              3°

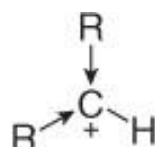**Increasing carbocation stability** →

- The order of carbocation stability can be rationalized through **inductive effects** and **hyperconjugation**.

- **Inductive effects** are electronic effects that occur through $\sigma$ **bonds**. Specifically, the inductive effect is the pull of electron density through $\sigma$ bonds caused by electronegativity differences between atoms.

- Alkyl groups are **electron donating** groups that stabilize a positive charge. 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.

- In general, the greater the number of alkyl groups attached to a carbon with a positive charge, the more stable will be the cation.
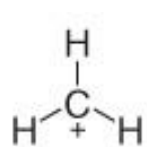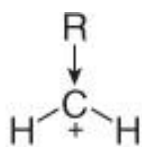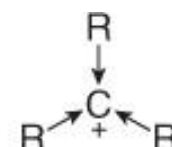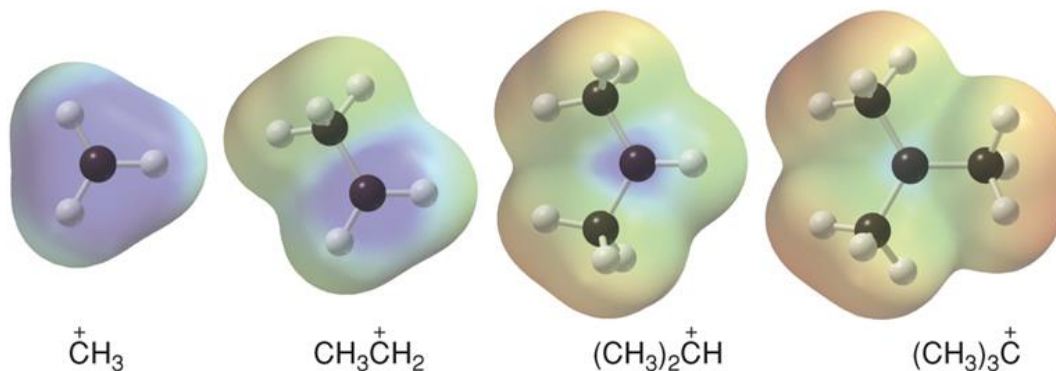
Increasing number of electron-donating R groups
Increasing carbocation stability

**Electrostatic potential maps for different carbocation**



Increasing alkyl substitution
Increasing dispersal of positive charge

- Dark blue areas in electrostatic potential plots indicate regions low in electron density. As alkyl substitution increases, the region of positive charge is less concentrated on carbon.

- The order of carbocation stability is also a consequence of hyperconjugation.

- **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 $(CH_3)_2CH^+$ can.



$\overset{+}{C}H_3$ = 
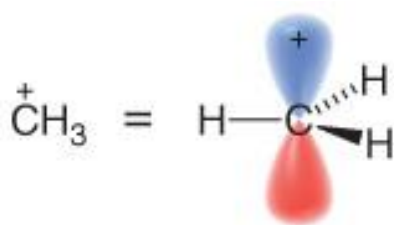
This carbocation has no opportunity for orbital overlap with the vacant *p* orbital.

$(CH_3)_2\overset{+}{C}H$
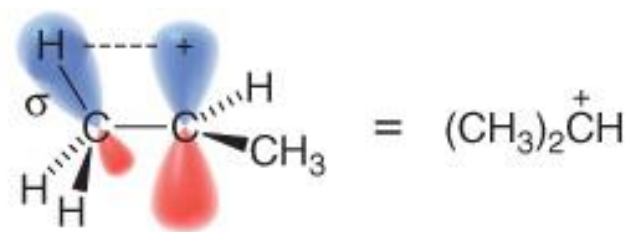
Overlap of the C–H σ bond with the adjacent vacant *p* orbital stabilizes the carbocation.

# Summary of SN² Reaction

| Table 7.5 | Characteristics of the $S_N2$ Mechanism |
|---|---|
| **Characteristic** | **Result** |
| Kinetics | • Second-order kinetics; rate = $k$[RX][:Nu⁻] |
| Mechanism | • One step |
| Stereochemistry | • Backside attack of the nucleophile<br>• Inversion of configuration at a stereogenic center |
| Identity of R | • Unhindered halides react fastest.<br>• Rate: $CH_3X > RCH_2X > R_2CHX > R_3CX$ |

# Summary of SN$^1$ Reaction

| Table 7.6 | Characteristics of the S$_N$1 Mechanism |
|---|---|
| **Characteristic** | **Result** |
| Kinetics | • First-order kinetics; rate = $k$[RX] |
| Mechanism | • Two steps |
| Stereochemistry | • Trigonal planar carbocation intermediate <br> • Racemization at a single stereogenic center |
| Identity of R | • More substituted halides react fastest. <br> • Rate: $R_3CX > R_2CHX > RCH_2X > CH_3X$ |