

# 第八章 卤代烃

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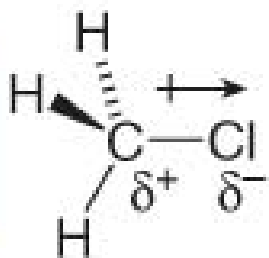
## Chapter 8 Alkyl Halides

主讲人：白 林

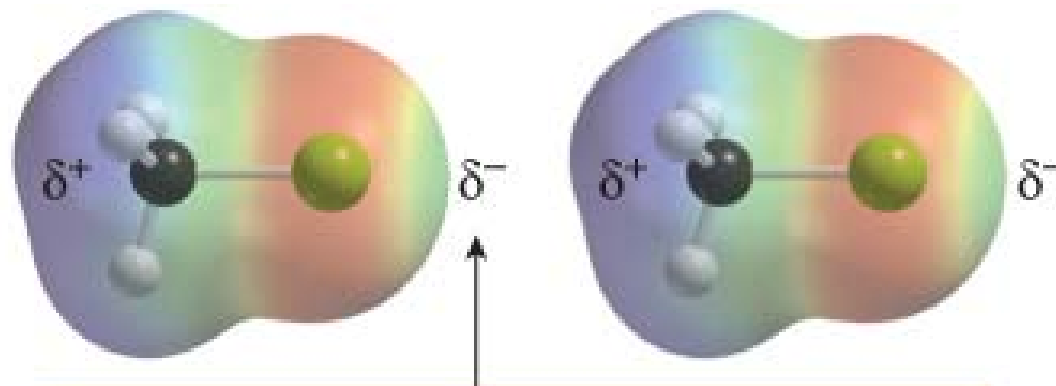
[bailin@lzcw.edu.cn](mailto:bailin@lzcw.edu.cn)

# Chapter 8 Alkyl Halides

Dipole-dipole interactions



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Opposite ends of the dipoles interact.

# 8.1 Introduction

分类：按所连烃基不同分类

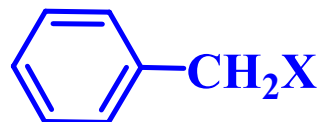
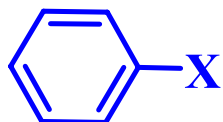
饱和卤代烃： $\text{CH}_3\text{CH}_2\text{CH}_2\text{X}$



不饱和：  
 $\text{RHC}=\text{CH}-\text{X}$  乙烯式  
 $\text{RHC}=\text{CH}-\text{CH}_2\text{X}$  烯丙式  
 $\text{RHC}=\text{CH}-\text{CH}_2\text{CH}_2\text{X}$  独立式

} 活性差别很大

卤代芳烃：



# 卤代烃：有机合成的桥梁物质

按所连的  
C原子数  
不同分类

一级卤代烃



二级



三级

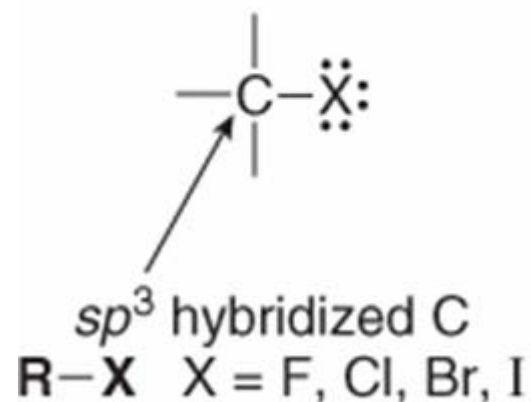


按所含卤原子数目分为

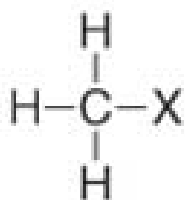
一卤代物：  $\text{R-X}$   
二卤代物：  $\text{CH}_2\text{X}_2$   
多卤代物：  $\text{CHX}_3, \text{CX}_4$

# RX are classified as shown below

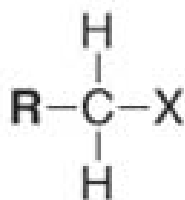
Alkyl halide



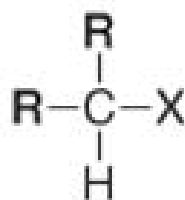
## Classification of alkyl halides



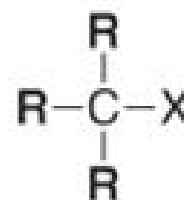
methyl halide



1°  
(one R group)



2°  
(two R groups)



3°  
(three R groups)

## 8.2 Nomenclature

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- Name the parent chain using rules previously learned.
- Number the carbons of the parent chain beginning at the end nearer the first substituent. Assign each carbon a number.



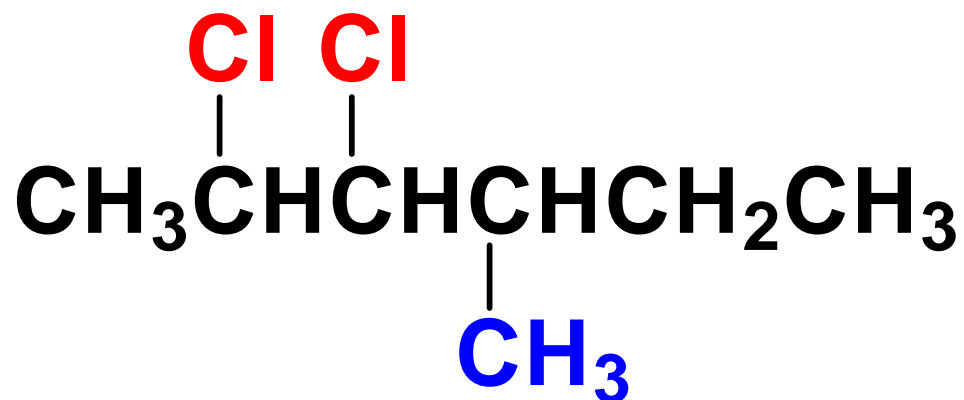




## Nomenclature

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- If more than one of the same kind of halogen is present, number each and use the prefixes di-, tri-, tetra-, and so on.

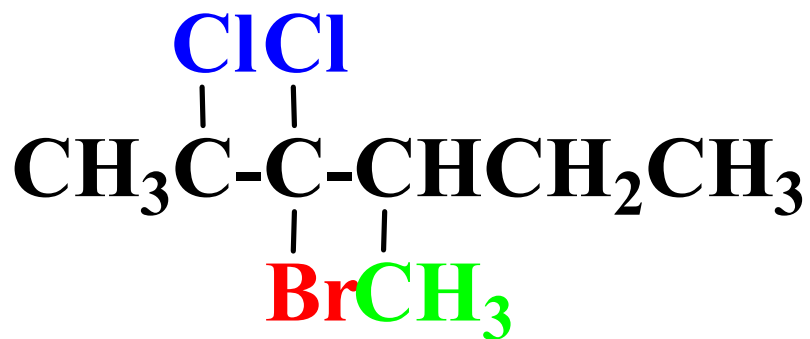


**2,3-dichloro-4-methylhexane**

# Nomenclature

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- If different halogens are present, number each according to its position on the chain, but list substituents alphabetically.

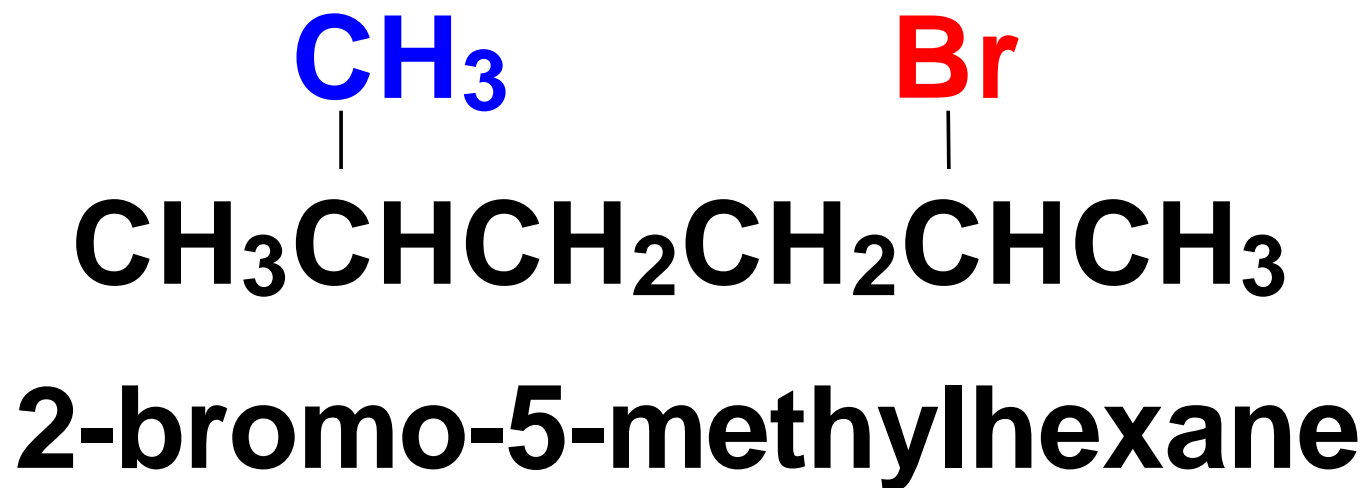


**3-bromo-2,3-dichloro-4-methylhexane**

## Nomenclature

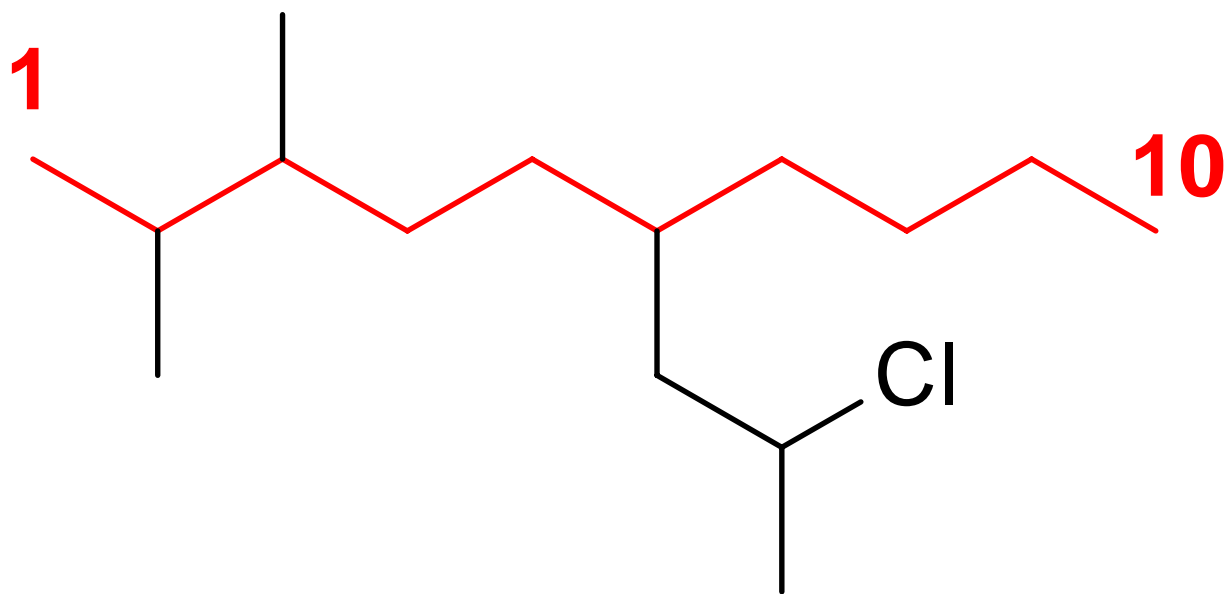
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- If the parent chain can be numbered properly from either end of the chain, begin at the end nearer the substituent that has alphabetical precedence.



# Nomenclature

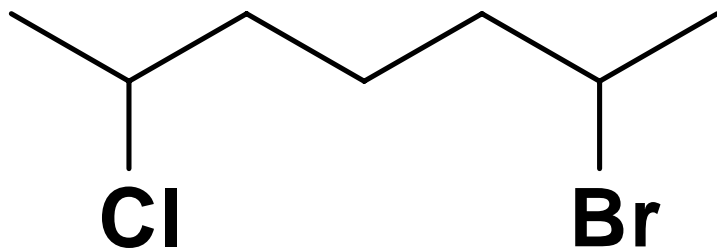
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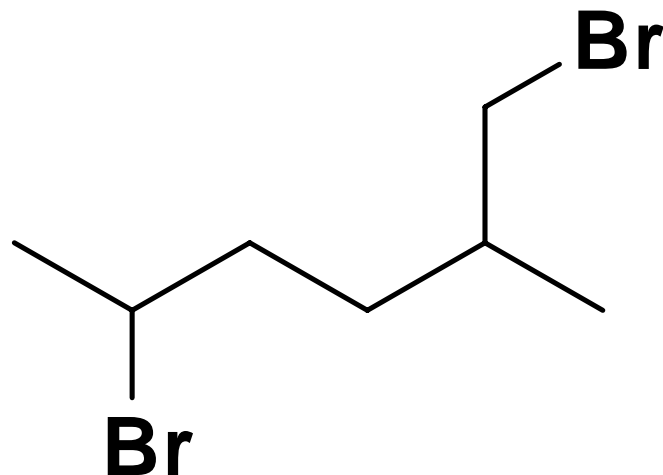
**6-(2-chloropropyl)-2,3-dimethyldecane**

# Nomenclature

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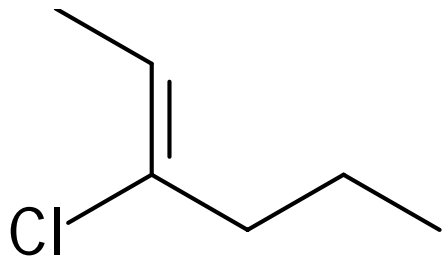
**2-bromo-6-chloroheptane**



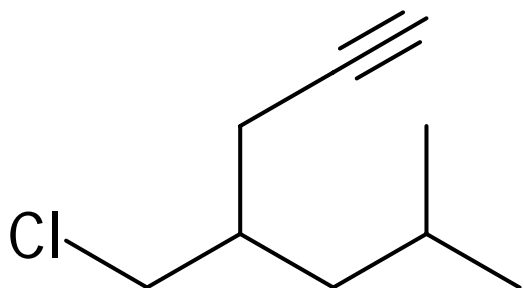
**1,5-dibromo-2-methylhexane**

# Nomenclature

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**(Z)-3-chloro-2-hexene**



**4-chloromethyl-6-methyl-1-heptyne**

## 8.3 Structure and physical properties

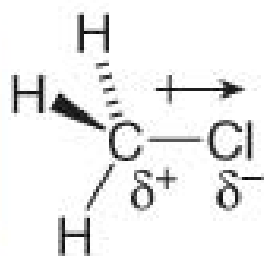
- C-X bond is longer as you go down periodic table
- C-X bond is weaker as you go down periodic table
- C-X bond is polarized with positive on carbon and negative on halogen

**TABLE 10.1** A Comparison of the Halomethanes

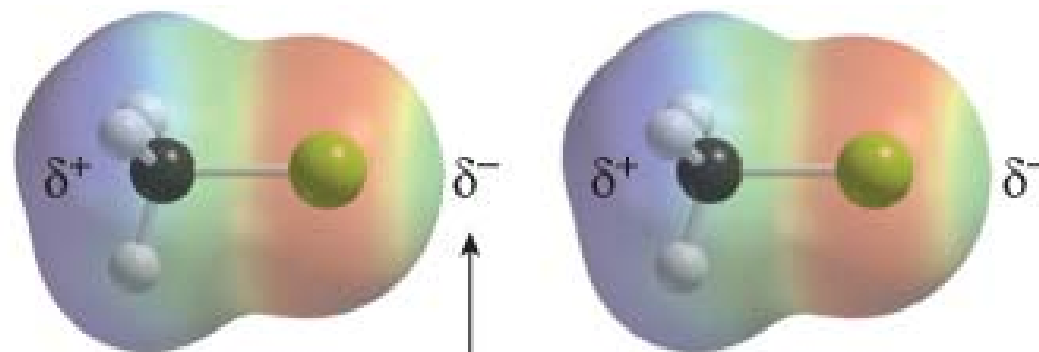
Halomethane	Bond length (pm)	Bond strength		Dipole moment (D)
		(kJ/mol)	(kcal/mol)	
CH <sub>3</sub> F	139	452	108	1.85
CH <sub>3</sub> Cl	178	351	84	1.87
CH <sub>3</sub> Br	193	293	70	1.81
CH <sub>3</sub> I	214	234	56	1.62

# The C-X bond is polarized

Dipole-dipole interactions



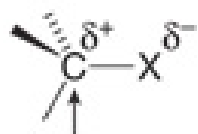
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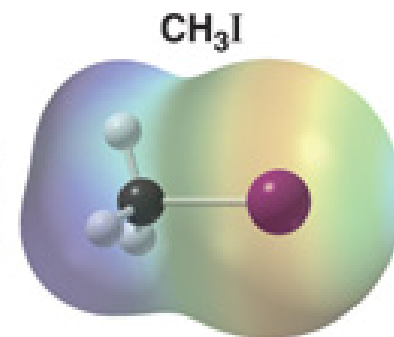
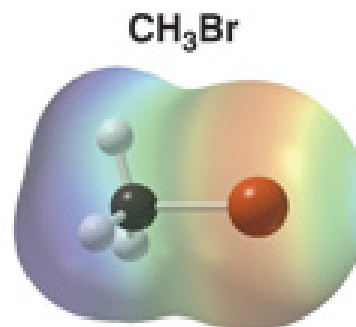
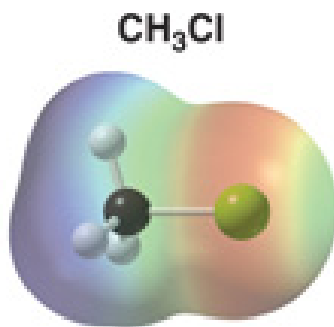
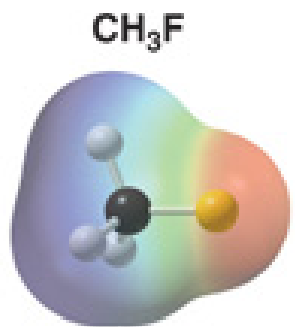
Opposite ends of the dipoles interact.



General structure



electron-deficient site  
electrophilic carbon



- The polar C–X bond makes the carbon atom *electron deficient* in each CH<sub>3</sub>X molecule.

## 8.3.2 Physical properties

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**形态:** R-Br (1C) R-Cl (1-2C) R-F (1-3C) 气体  
其他一般为液体, 高级为固体

**b.p. :** RI > RBr > RCl > RF > 支链

**比重:** RF、RCl < 1; RBr、RI、Ar-X > 1  
卤原子增加, d增大

**可极化性:** RI > RBr > RCl > RF

**溶解性:** 不溶于水 (虽有极性, 但不与水形成H-键)  
易溶于有机溶剂。

## 8.3.2 Physical properties

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- ◆ **沸点:** 一元卤烷的沸点随着碳原子数的增加而升高。  
相同烃基的卤烷沸点——碘烷 > 溴烷 > 氯烷。  
在卤烷同分异构体中，支链越多，沸点越低。
- ◆ **相对密度:** 一元卤烷的相对密度大于同碳数的烷烃。  
相同烃基的卤烷，相对密度碘烷 > 溴烷 > 氯烷。  
相同卤素的卤代烷，其相对密度随着烃基的相对分子量增加而减少。
- ◆ **溶解性:** 卤烷不溶于水，溶于醇、醚、烃等有机溶剂。
- ◆ **毒性:** 不少卤烷带有香味，但其蒸汽有毒(如碘烷)，应防止吸入。

## 8.4 Nucleophilic Substitution reactions

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General substitution reaction



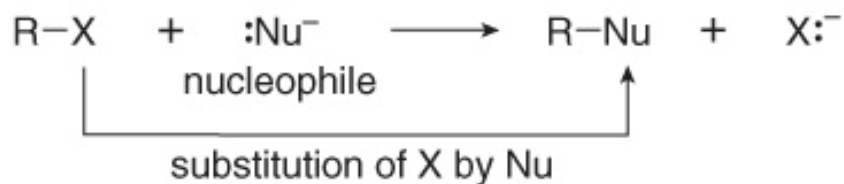
$sp^3$  hybridized C

nucleophile

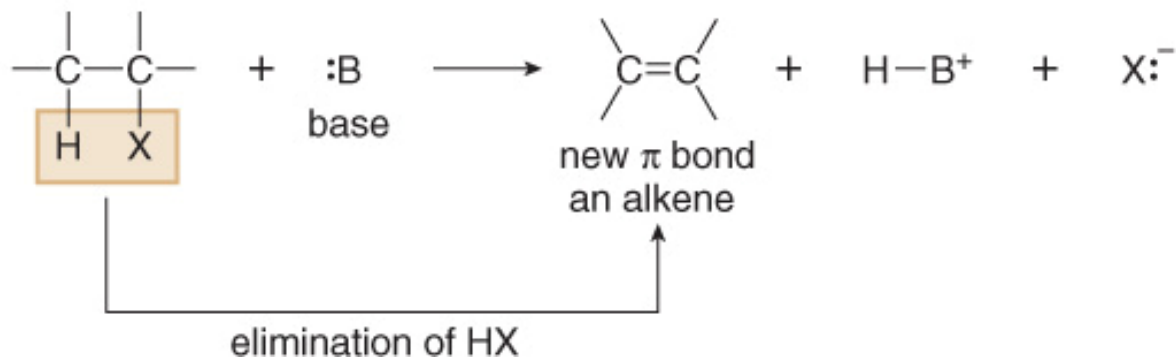
leaving group

# 8.4 Nucleophilic Substitution reactions

- ◆ Alkyl halides undergo substitution reactions with nucleophiles.



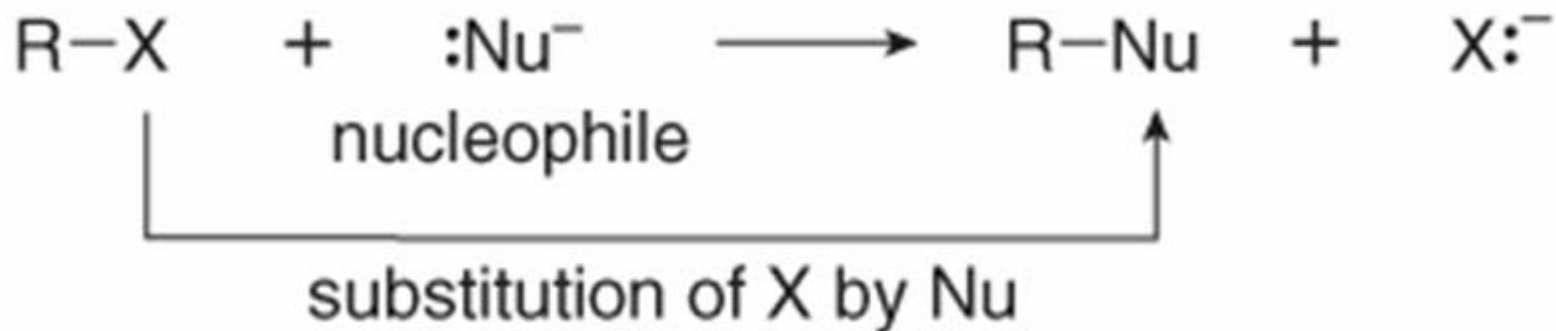
- ◆ Alkyl halides undergo elimination reactions with Brønsted-Lowry bases.



## 8.4 Nucleophilic Substitution reactions

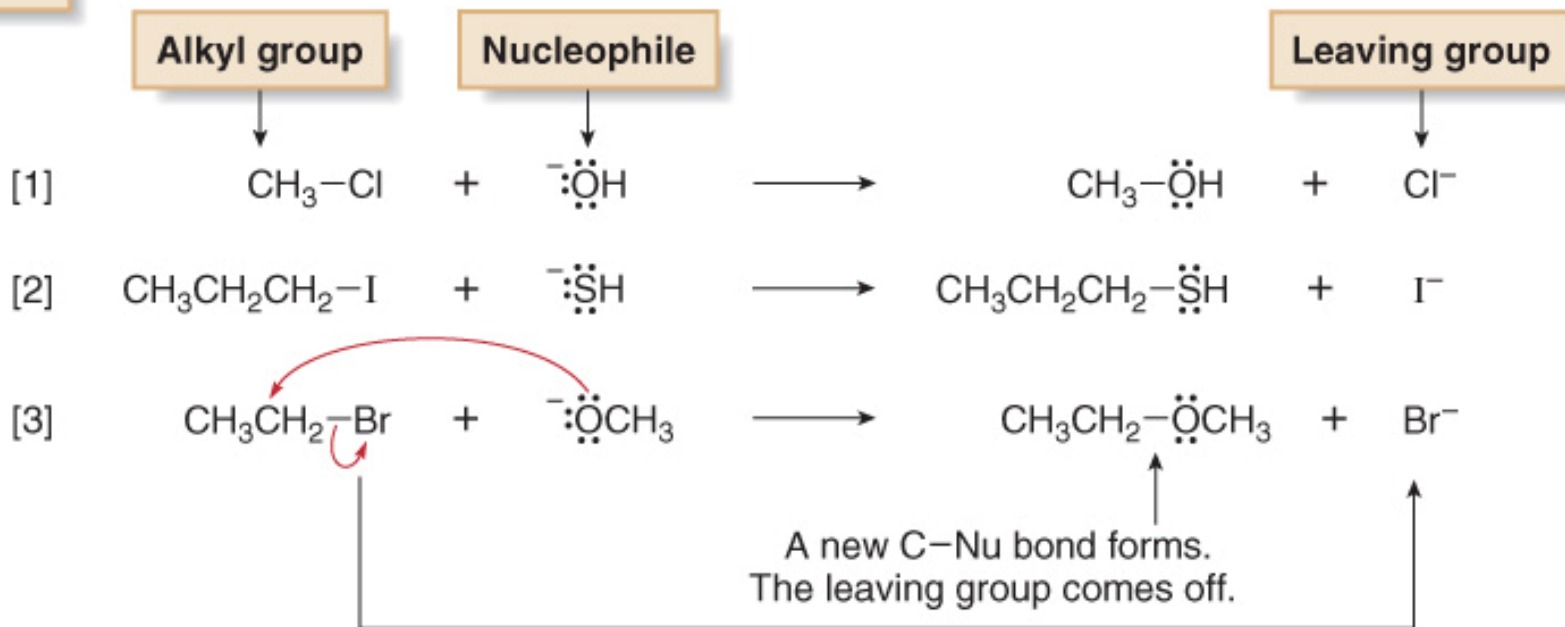
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Recall  $RX$  undergo a Nu substitution rxn due to the  $\delta+$  charge on the C of the C-X bond.

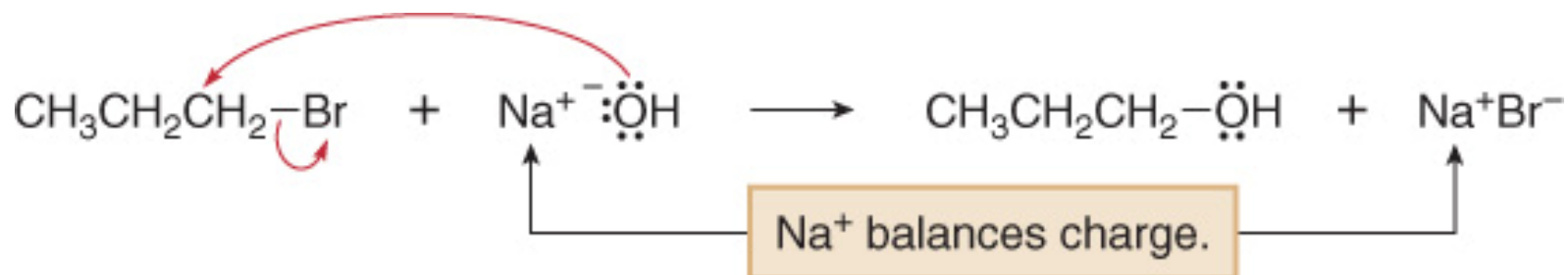


# 8.4 Nucleophilic Substitution reactions

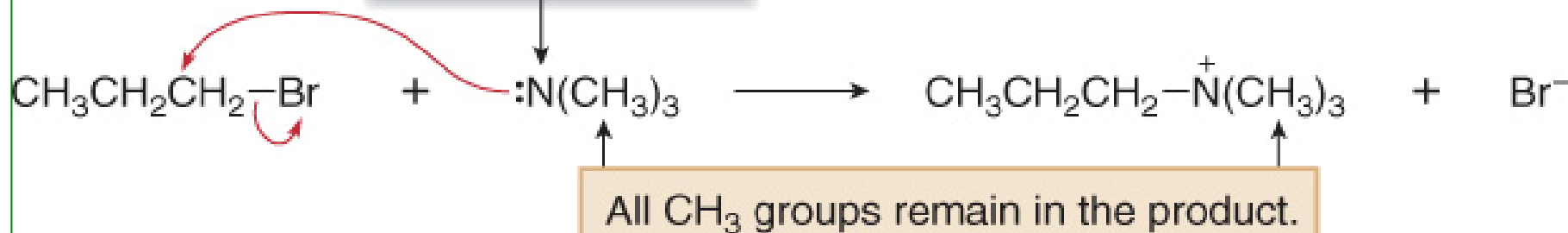
## Examples



## 8.4 Nucleophilic Substitution reactions

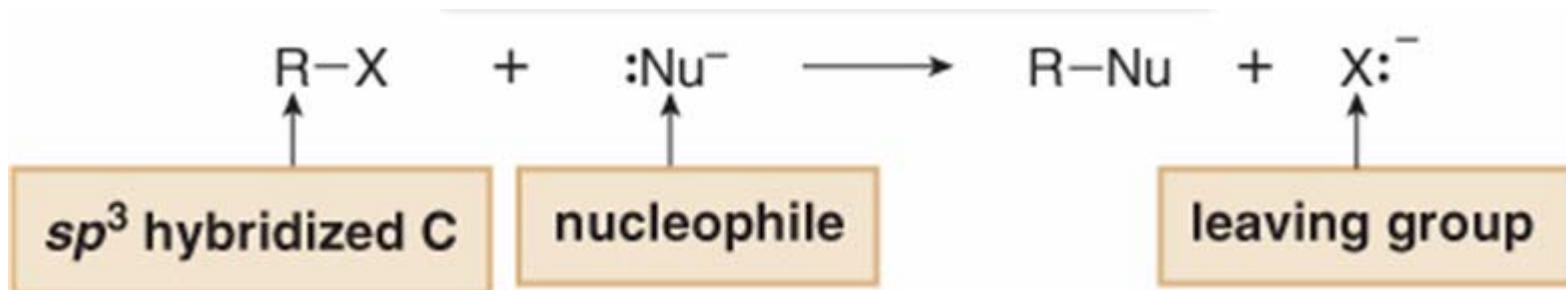


neutral nucleophile

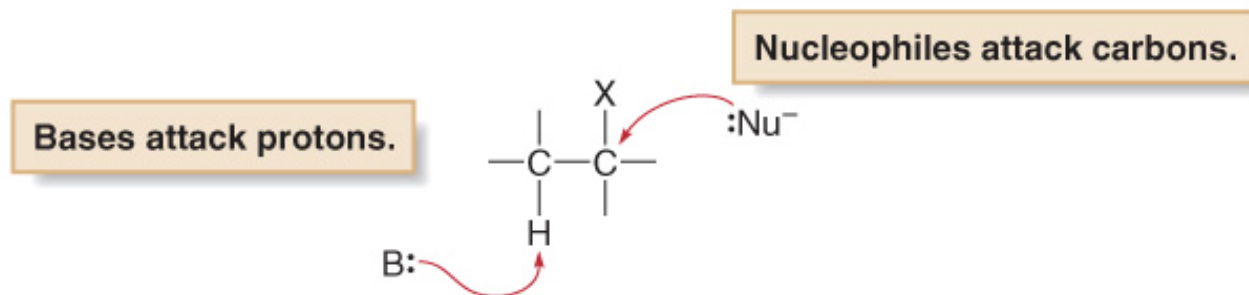




## 8.4.1 Nucleophile



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

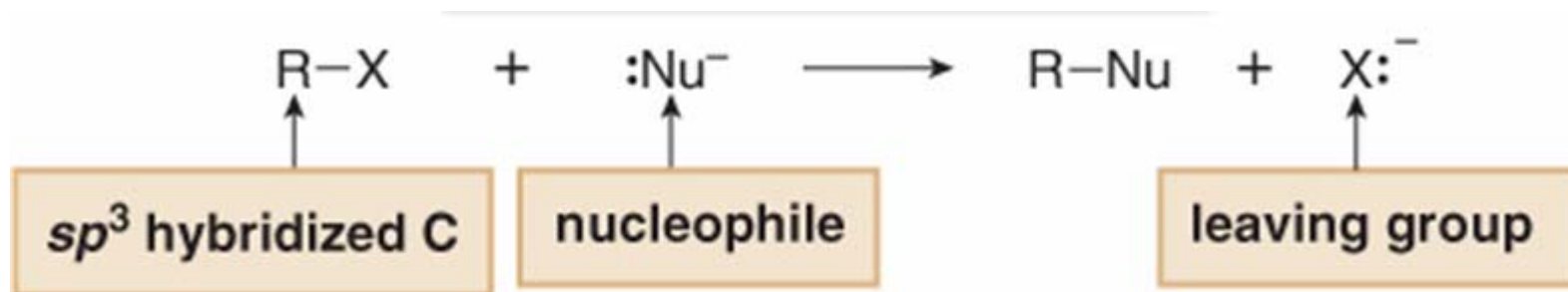


## 8.4.2 Leaving Group

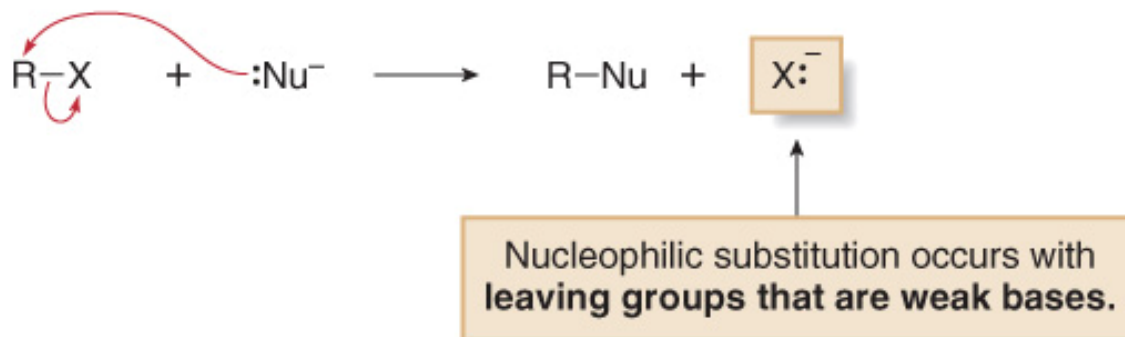
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Recall the leaving group is the negatively charge ion that separates from the carbon atom during  $S_N$

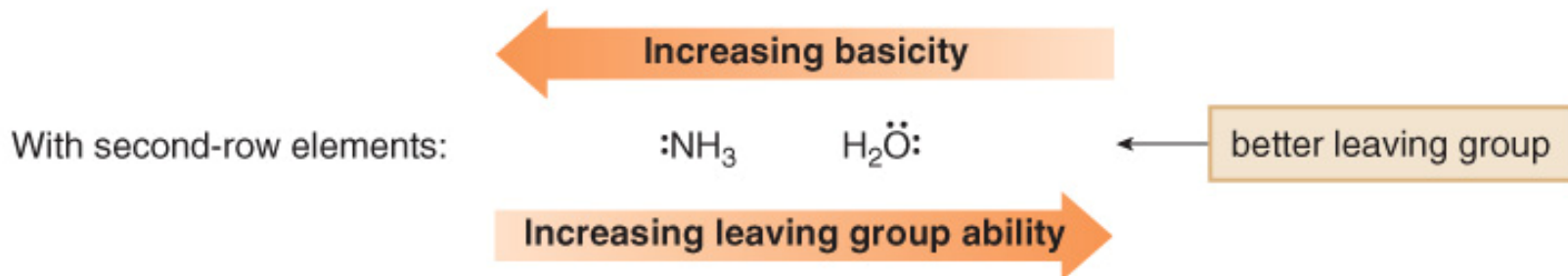
## 8.4.2 Leaving Group



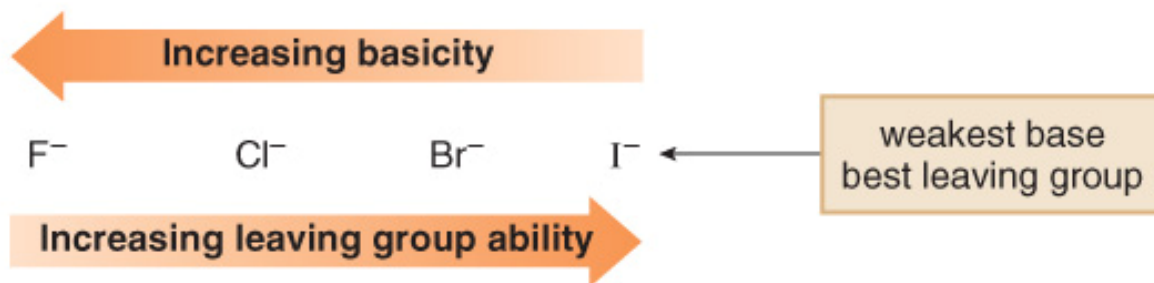
◆ In comparing two leaving groups, the better leaving group is the weaker base.

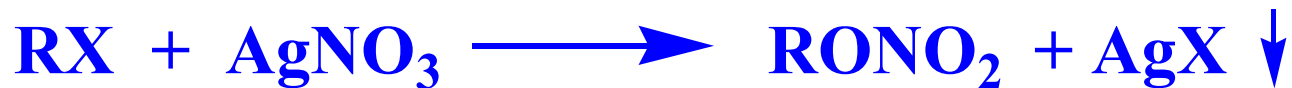


- ◆ Left-to-right across a row of the periodic table, basicity *decreases* so leaving group ability *increases*.



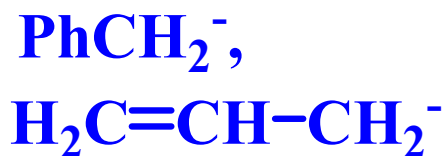
- ◆ Down a column of the periodic table, basicity *decreases* so leaving group ability *increases*.





不同类  
RX  
的  
别  
鉴

R



反应现象

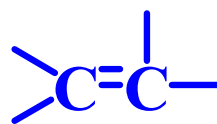
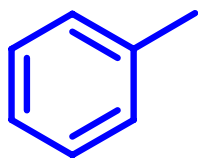
主要产生沉淀

2°

加热，产生沉淀

1°

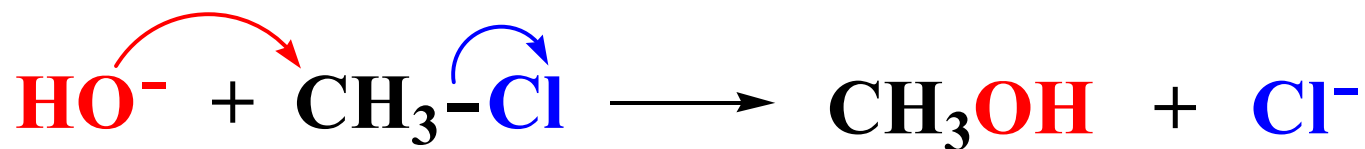
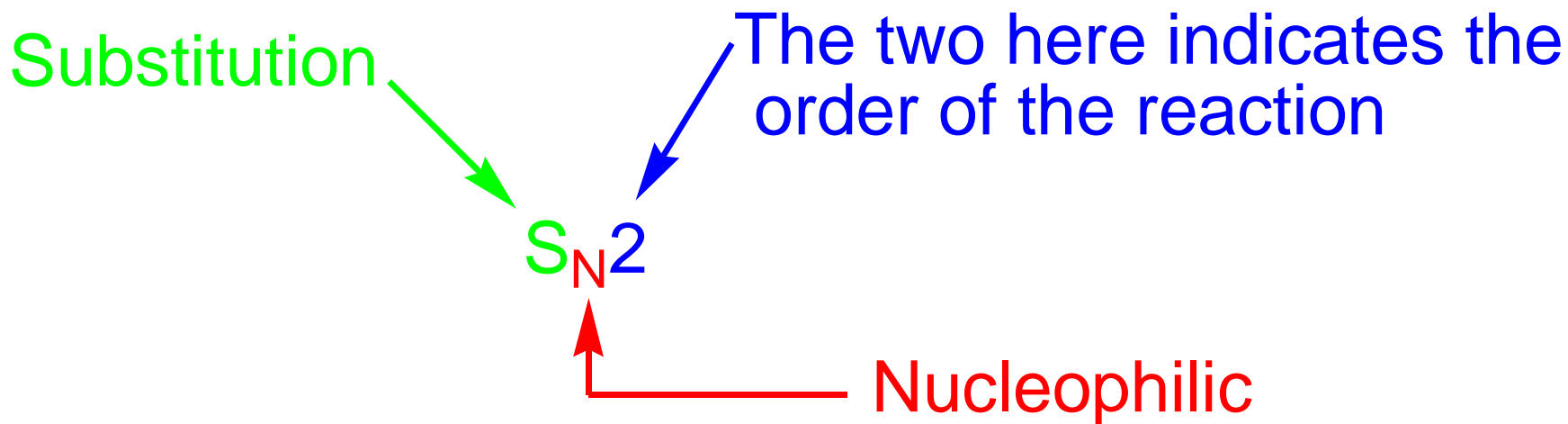
加热，等一段时间  
才产生沉淀



长时间加热，  
也不产生沉淀

# 8.5 The S<sub>N</sub>2 reaction

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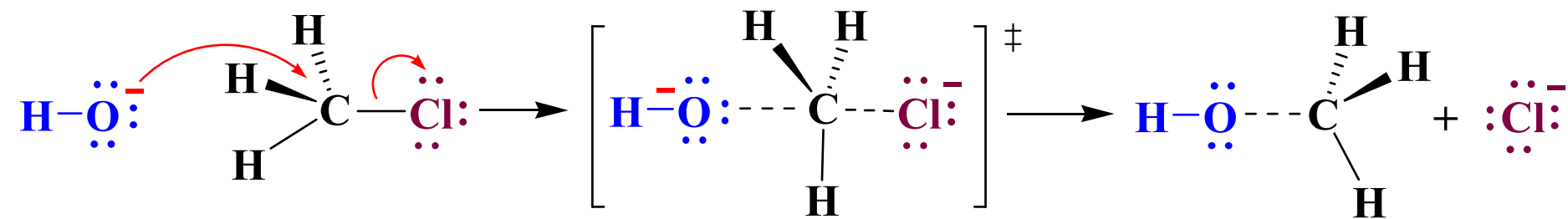
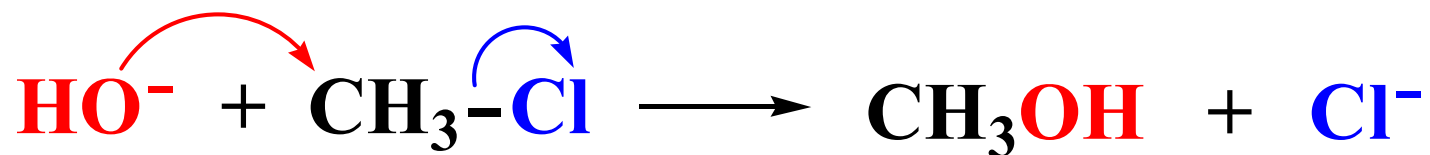
$$\text{Rate} = k [\text{CH}_3\text{Cl}] [\text{OH}^-]$$

*Second order overall*

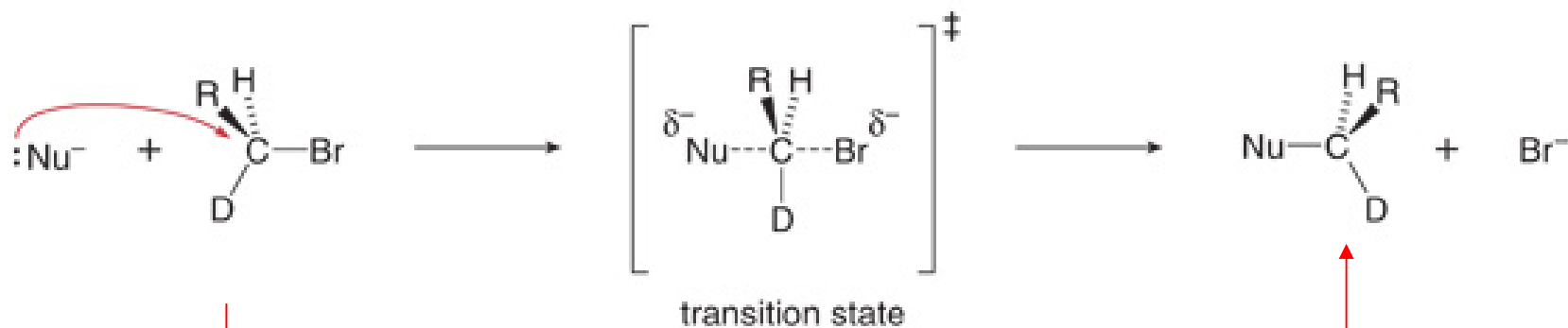
## 8.5.1 Mechanism of $S_N2$ reaction

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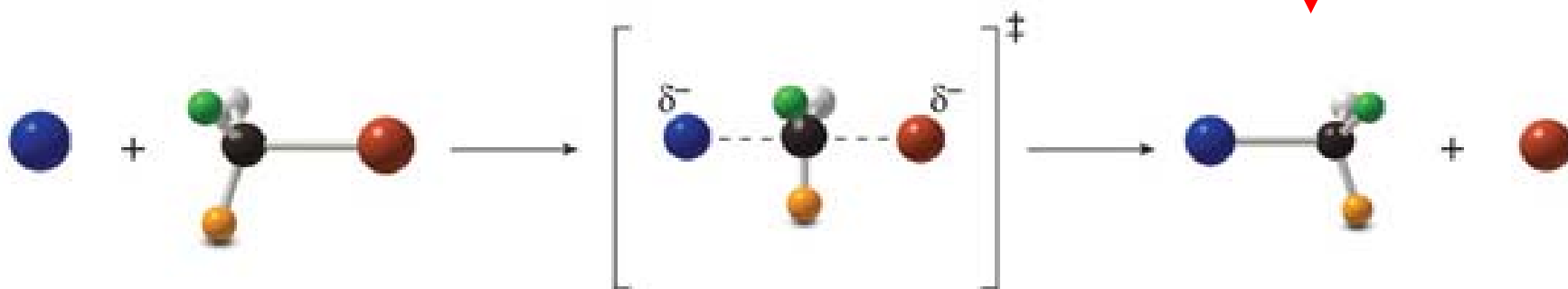
### Hughes-Ingold mechanism for $S_N2$ reaction



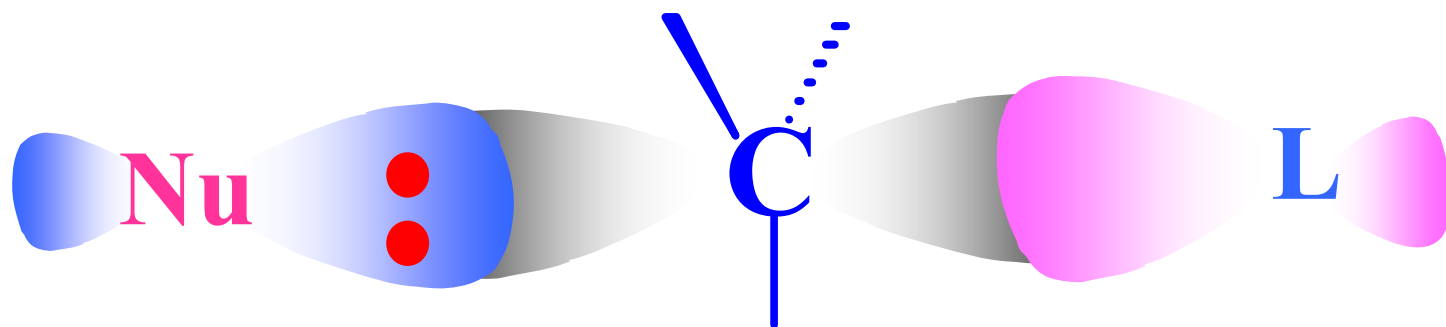
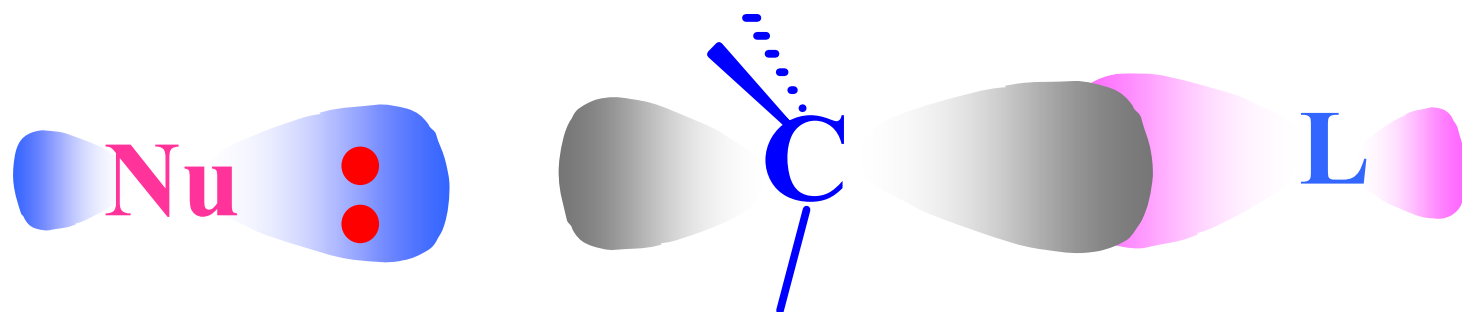
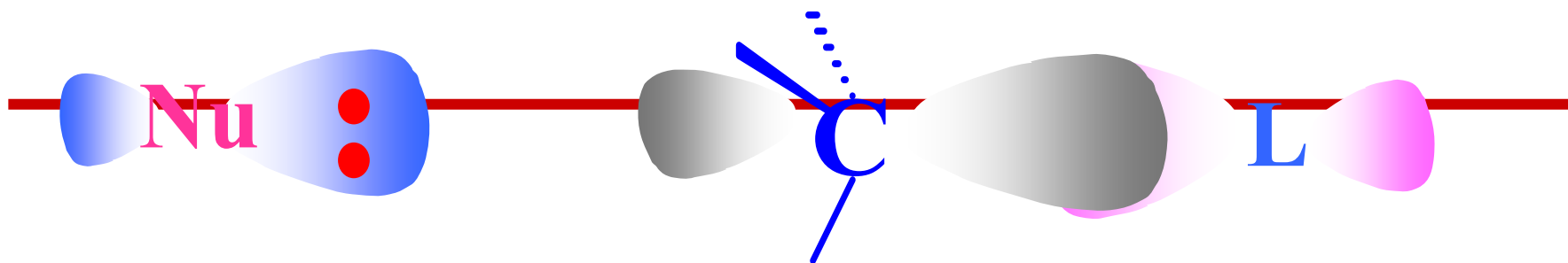
## 8.5.2 Stereochemistry of S<sub>N</sub>2 Reaction

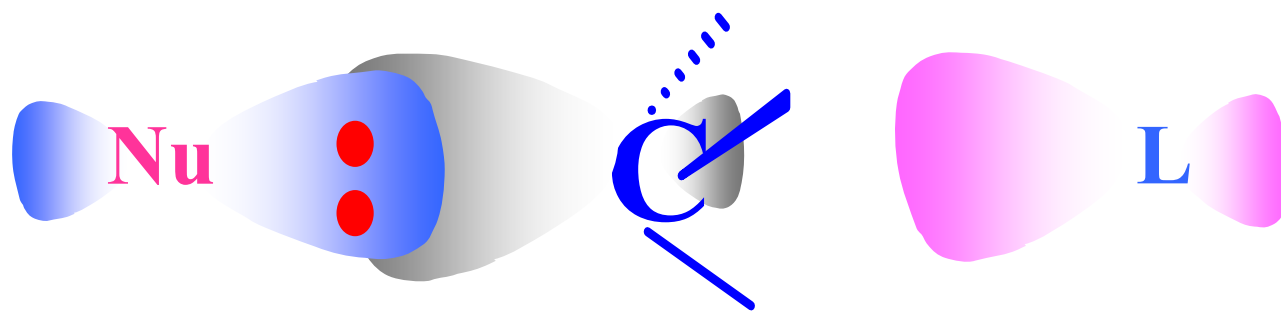
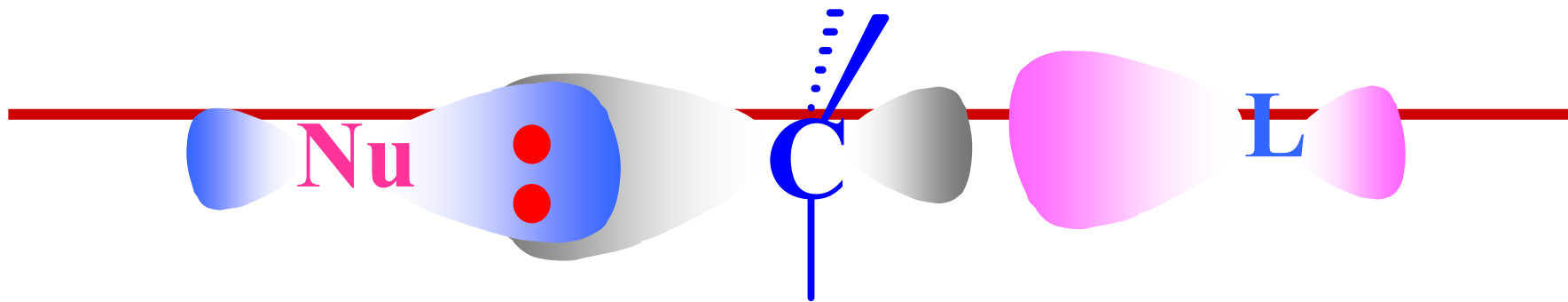


**An inversion of configuration**



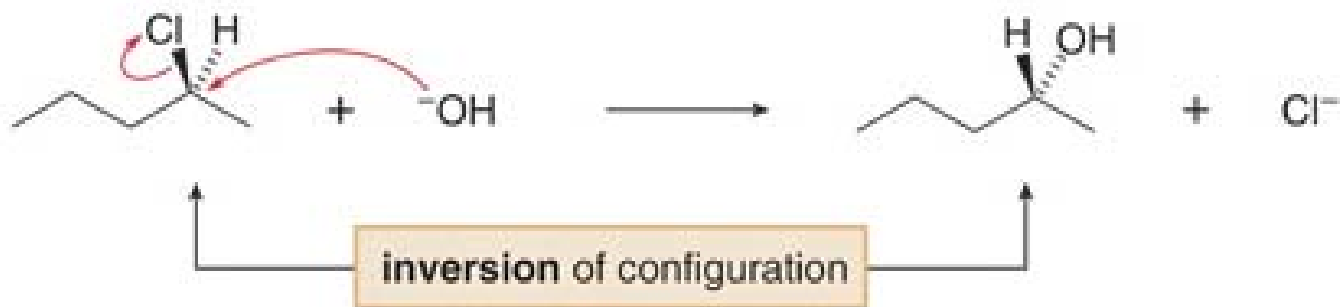
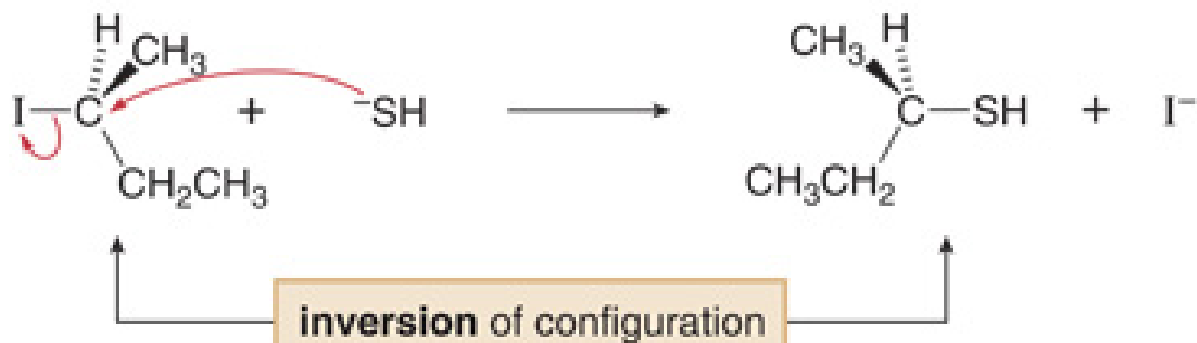




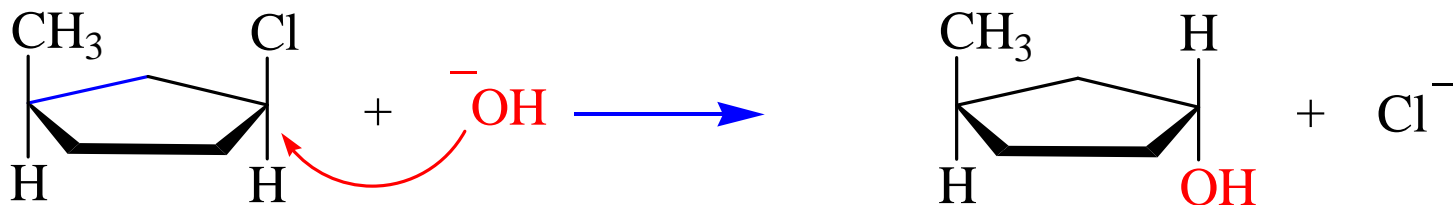


# Inversion of configuration is known as the

## Walden inversion

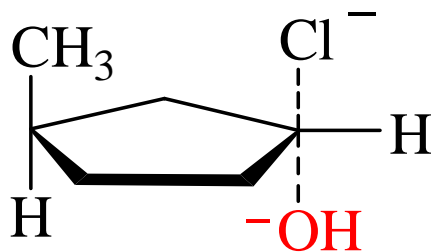


# Inversion of configuration ( **Walden inversion** )



*Cis*-1-chloro-3-methylcyclopentane

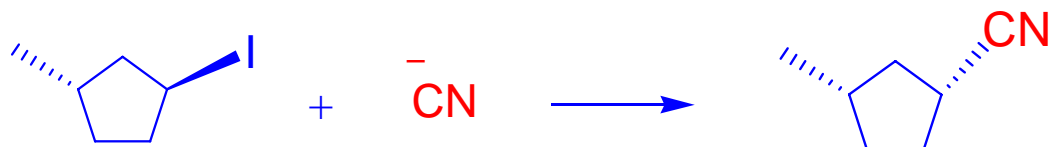
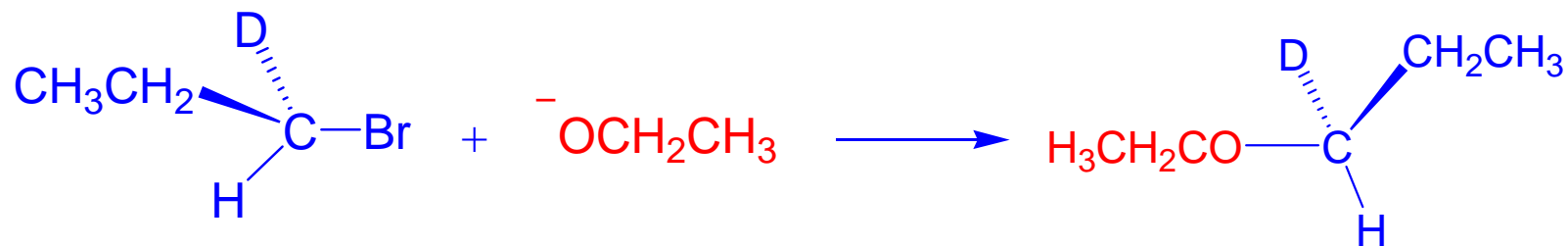
*trans*-1-chloro-3-methylcyclopentane



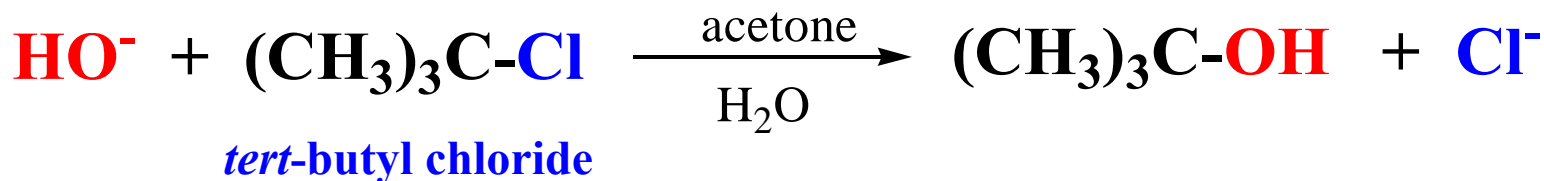
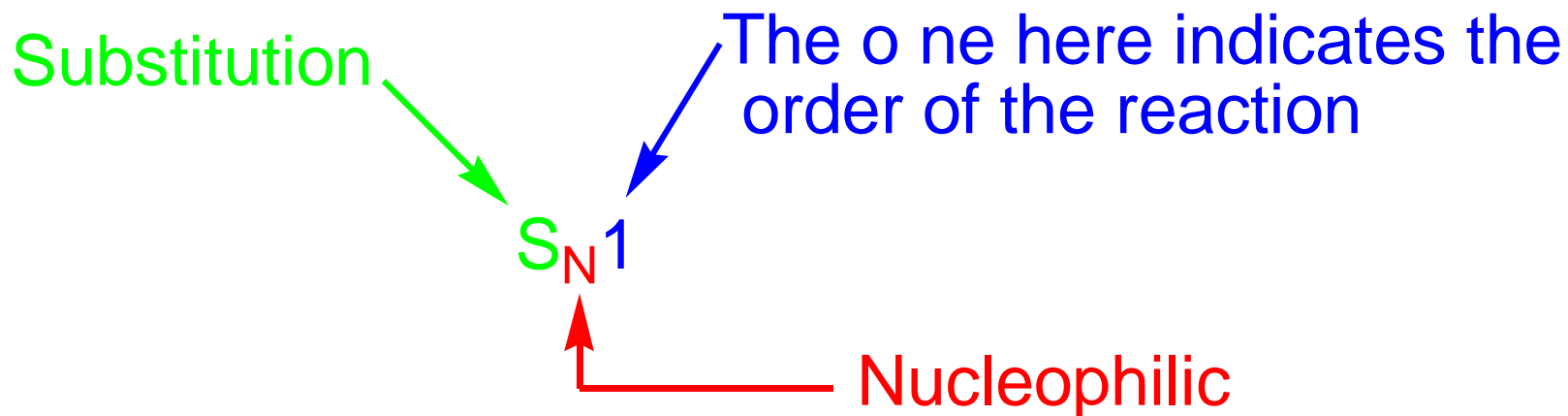
leaving group departs from the top side

nucleophile attacks from the bottom side

**Draw the product of each reaction to include the correct stereochemistry.**



## 8.6 The S<sub>N</sub>1 reaction



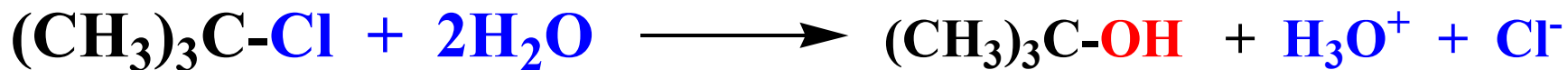
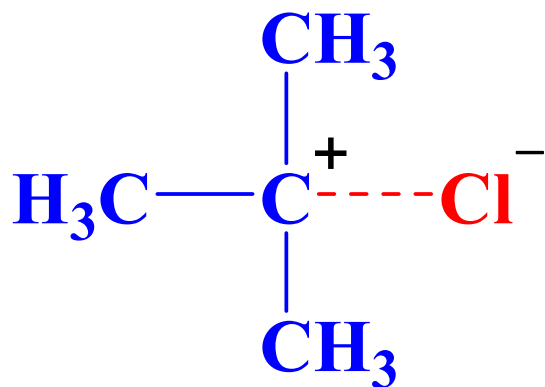
$$\text{Rate} = k [(\text{CH}_3)_3\text{CCl}]$$

*First order overall*



## 8.6.1 Mechanism for S<sub>N</sub>1 reaction

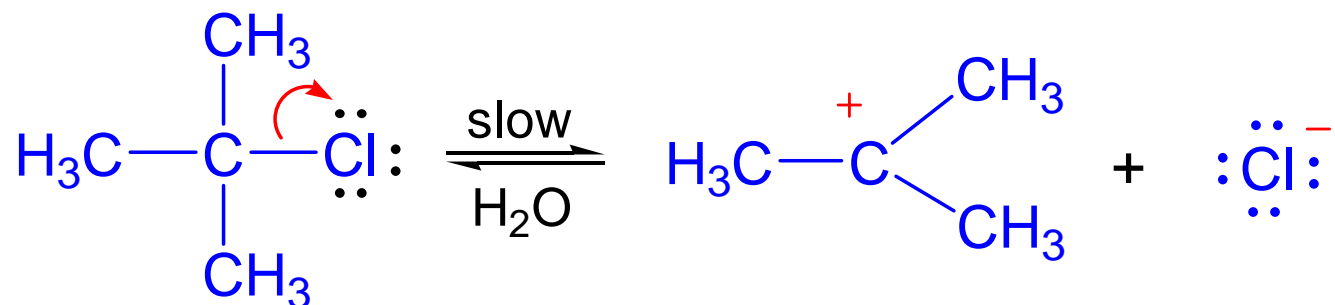
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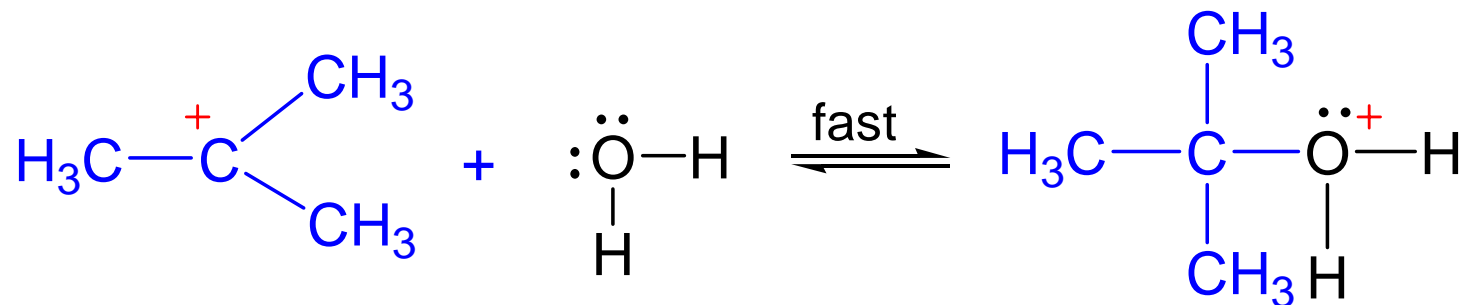


## 8.6.1 Mechanism for S<sub>N</sub>1 reaction

**Step [1]** The C-Cl bond is broken



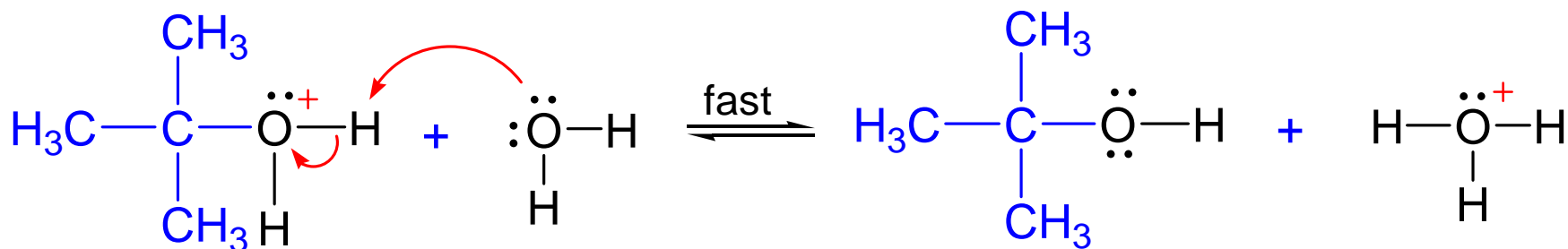
**Step [2]** The C-O bond is formed



## 8.6.1 Mechanism for S<sub>N</sub>1 reaction

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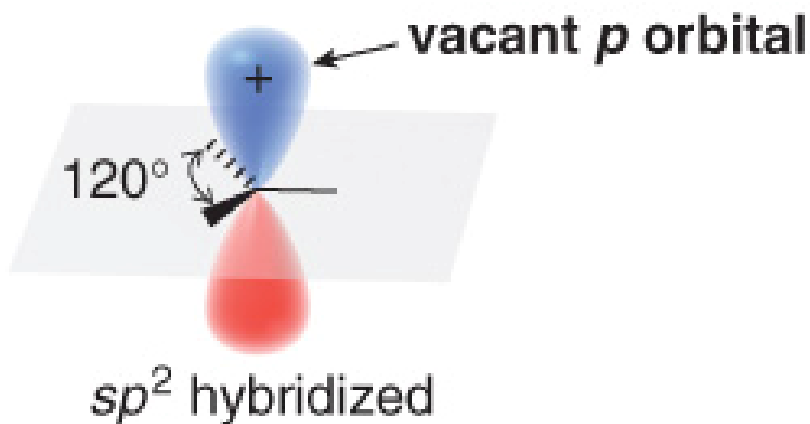
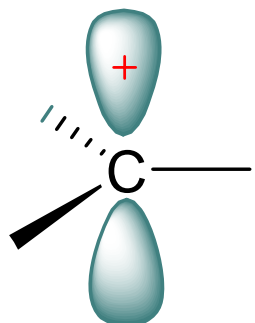
**Step [3]** The proton transfer to produce *tert*-butyl alcohol



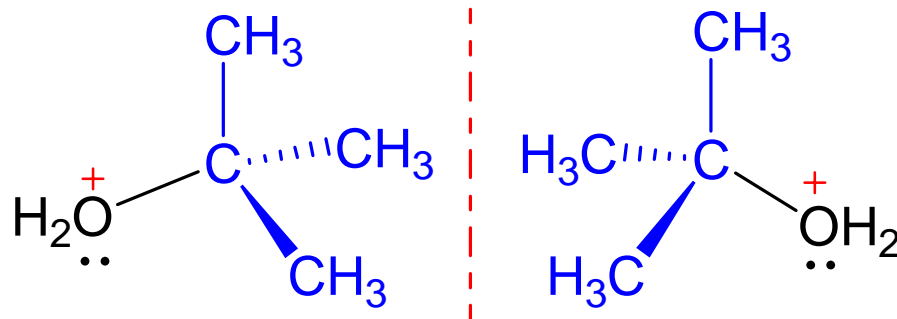
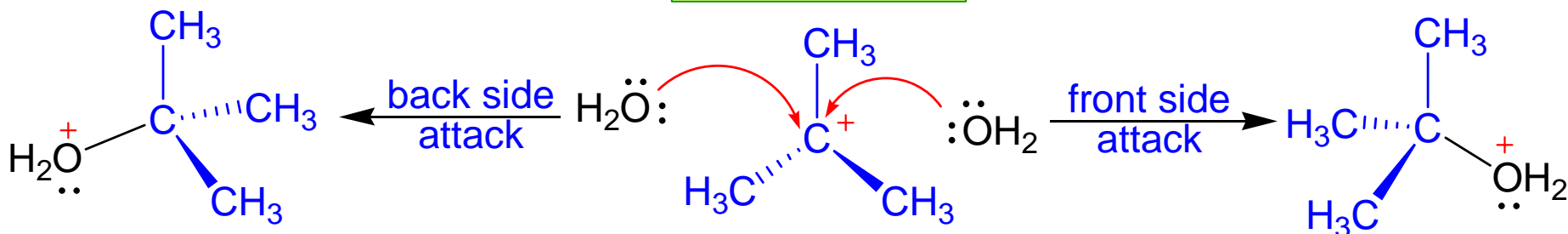
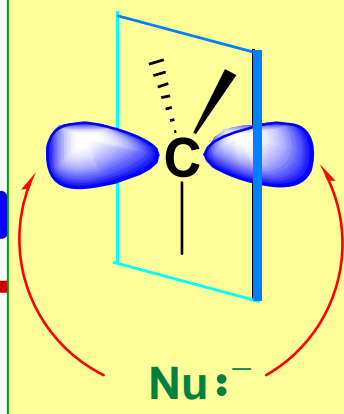
## 8.6.2 Stereochemistry of $S_N1$ reaction

The stereochemistry of  $S_N1$  is determined by the structure of the  $C^+$  intermediate.

A trigonal planar carbocation



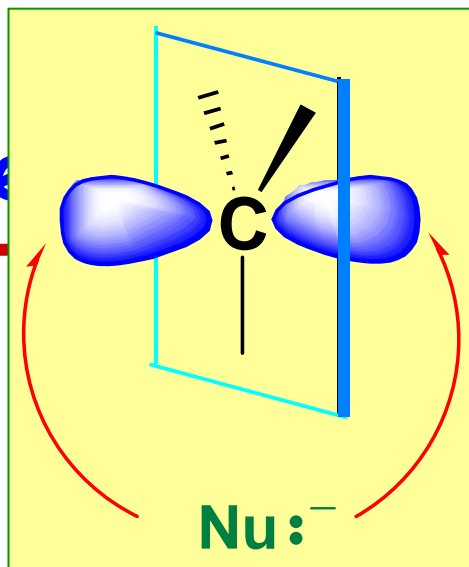
## 8.6.2 Stereochemistry of $S_N1$ reaction



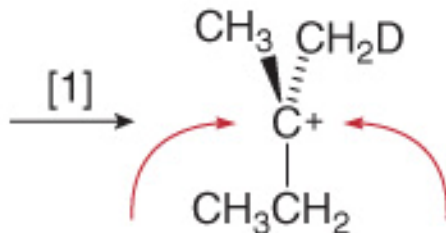
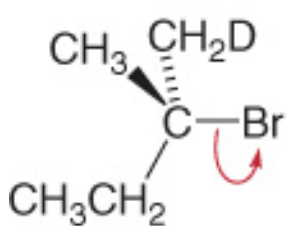
**Reactions that involve racemization**

# Stereochemistry

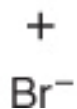
# S<sub>N</sub>1



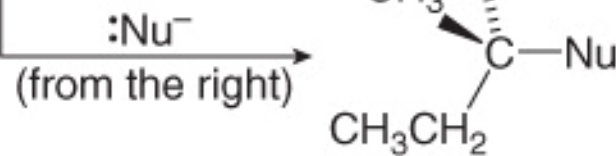
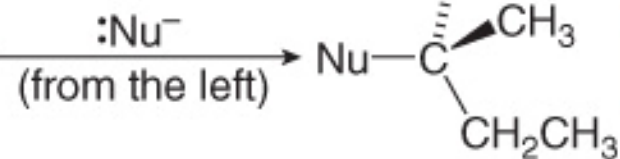
planar carbocation



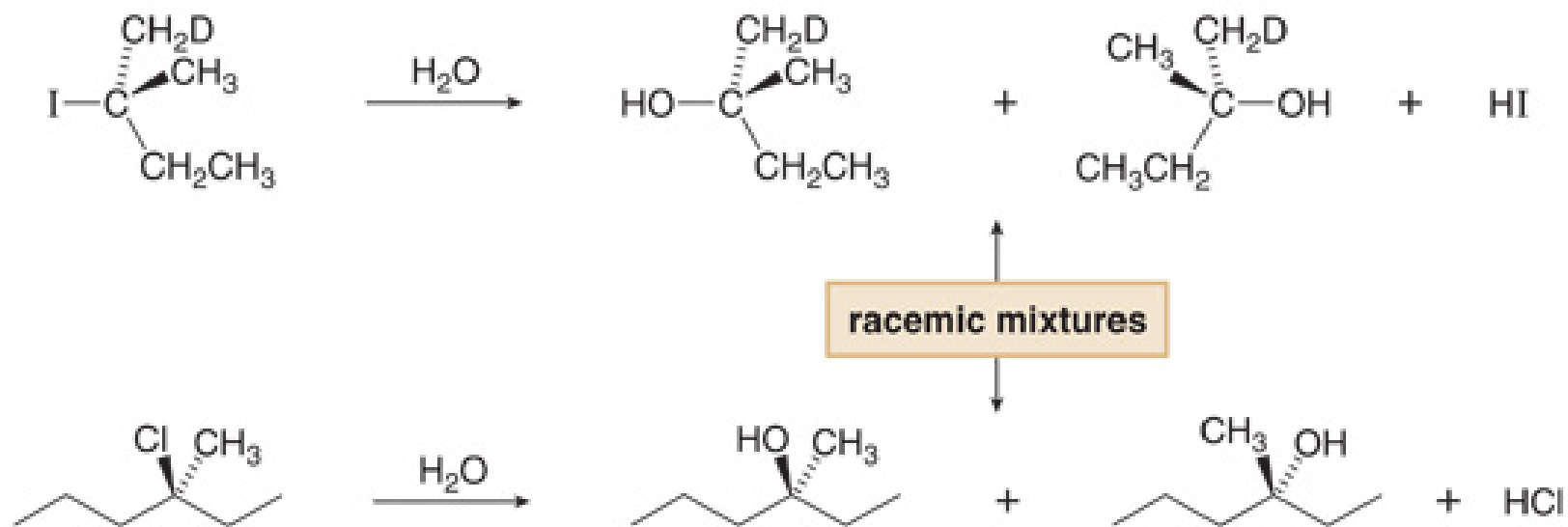
$\text{:Nu}^-$  can attack from either side.



[2]



# Examples of racemization in $S_N1$



## 8.7 Factors affecting the rates of $S_N1$ and $S_N2$ Reaction

---

Experiments have shown that a number of factors affect the relative rates of  $S_N1$  and  $S_N2$  Reaction. The most important factor are:

- ◆ The structure of substrate
- ◆ The concentration and reactivity of the nucleophile
- ◆ The effect of the solvent
- ◆ the nature of the leaving group

## 8.7.1 The effect of structure of substrate

### **S<sub>N</sub>2 reactions**

Larger R groups will decrease the rate constant of S<sub>N</sub>2



methyl



1°



2°



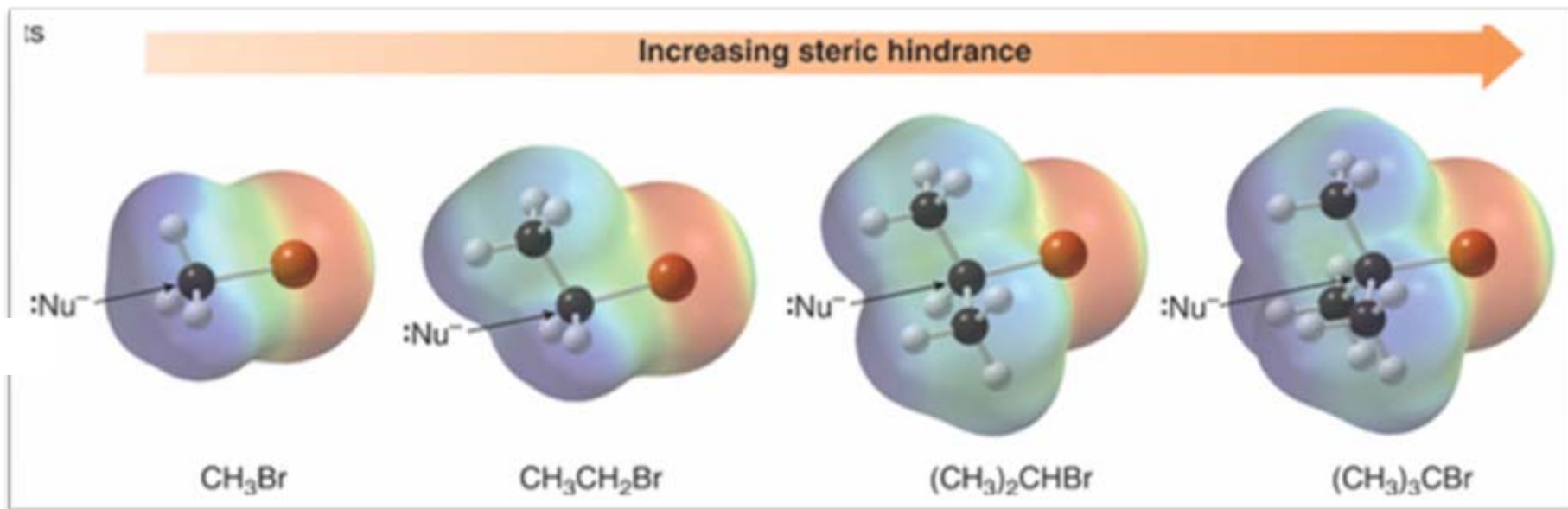
3°



Decreasing Rate Constant of S<sub>N</sub>2 Reaction

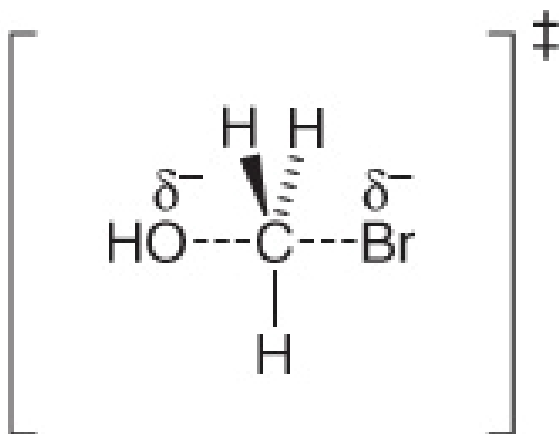


# $S_N2$ reactions



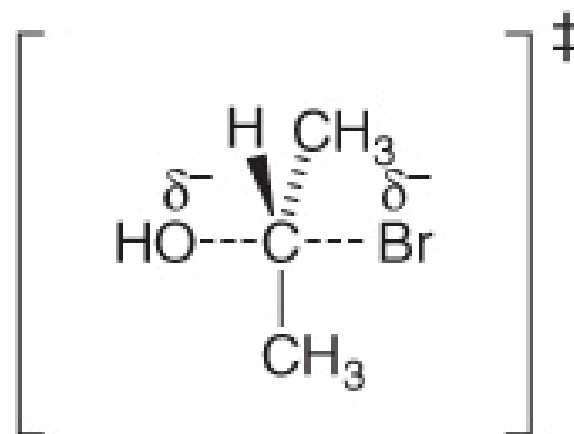
Decreasing Rate Constant of  $S_N2$  Reaction

# $S_N2$ reactions



less crowded transition state  
lower in energy

faster  $S_N2$  reaction

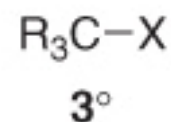
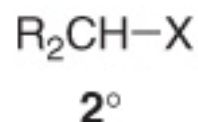
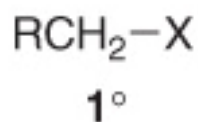
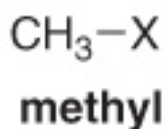


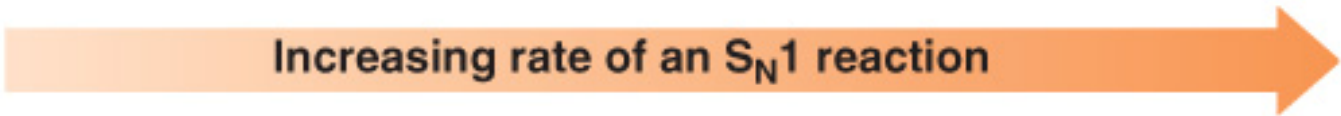
more crowded transition state  
higher in energy

slower  $S_N2$  reaction

# $S_N1$ reactions

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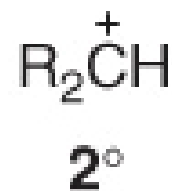
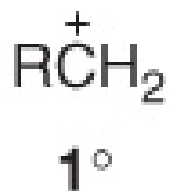
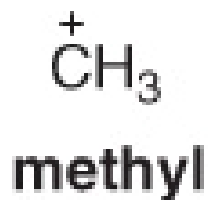
Increasing rate of an  $S_N1$  reaction 

**Note:** Methyl and primary  $\text{RX}$  do not undergo  $S_N1$  reaction

What is the explanation for this trend in  $S_N1$  reactivity among  $\text{RX}$ ?

## Carbocation stability affects

---



Increasing carbocation stability 

**Two questions:**

**(1) Why does the stability of  $\text{C}^+$  increase with more R groups?**

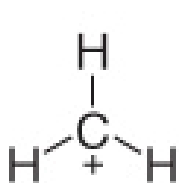
**(2) Why does the  $\text{C}^+$  affect the reaction?**

**Carbocation stability is determined by:**

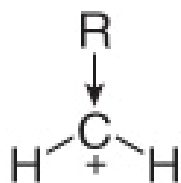
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**(1) inductive effects and (2) hyperconjugation**

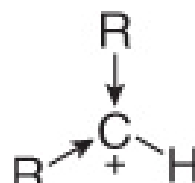
**Let's look at the inductive effect argument first**



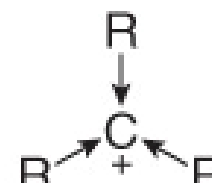
methyl



1°



2°



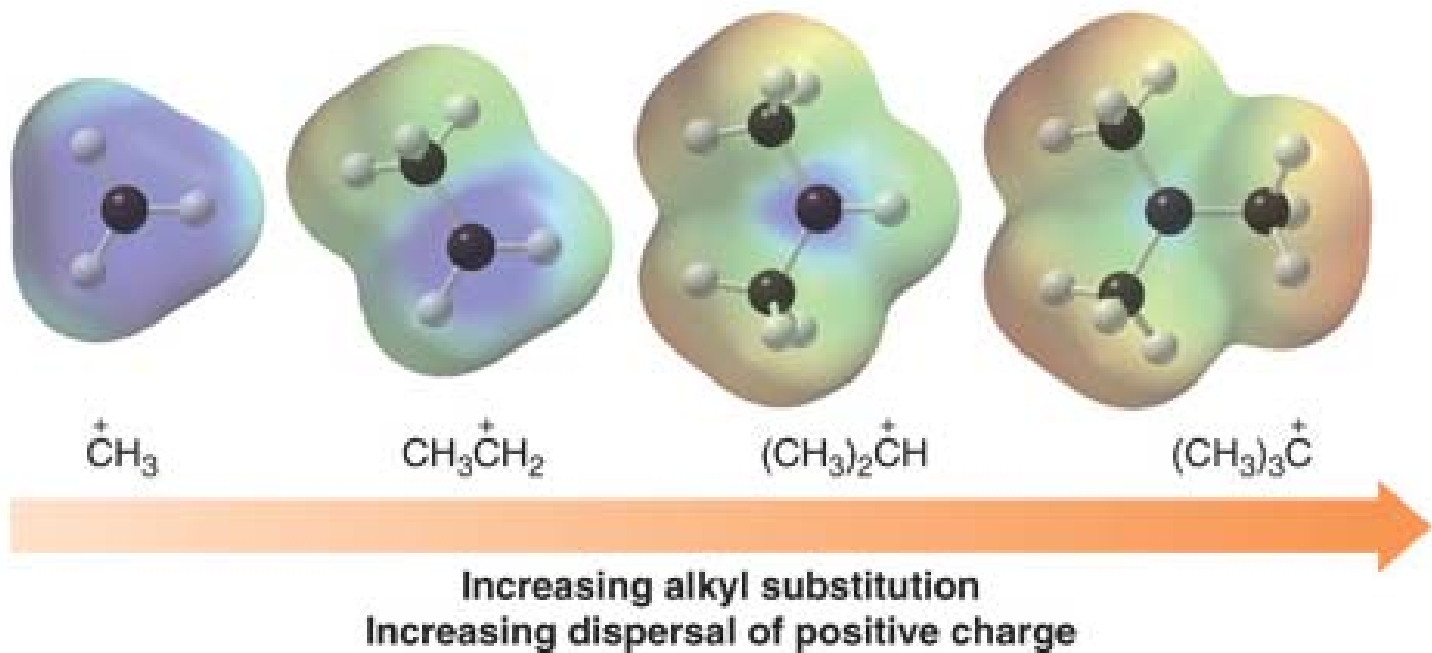
3°



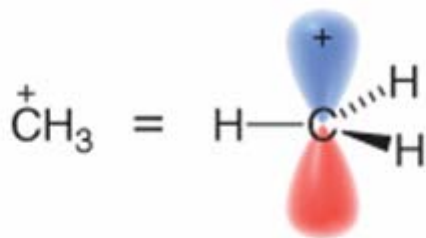
Increasing number of electron-donating R groups  
Increasing carbocation stability

**More positive charge at  $C^+$  = a more unstable  $C^+$**

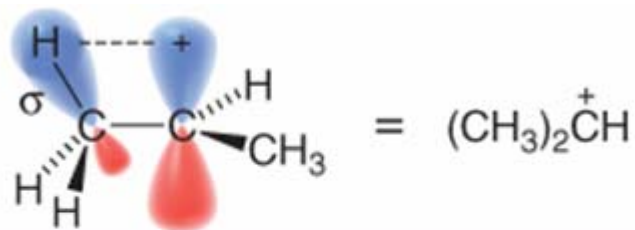
---



# Carbocation Stability and Hyperconjugation



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

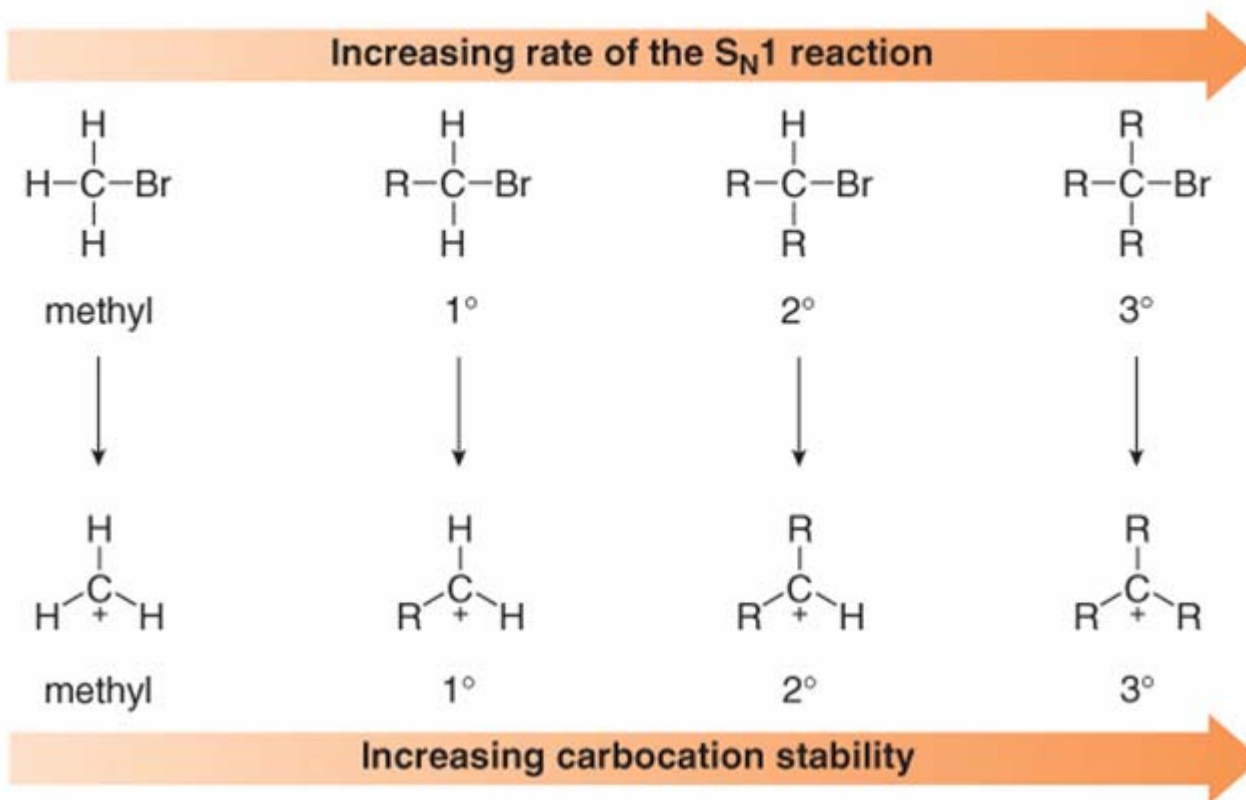


Overlap of the C—H  $\sigma$  bond with the adjacent vacant  $p$  orbital stabilizes the carbocation.

**Delocalization** of the **positive charge** on

**C<sup>+</sup> = increased carbocation stability**

# $S_N1$ reactions





## 8.7.2 The effect of the concentration and strength of the nucleophile

$S_N1$  速控步骤不涉及Nu  $\Rightarrow$  影响不大

$S_N2$  速控步骤涉及Nu  $\Rightarrow$  影响大

试剂亲核性的强弱对 $S_N1$ 反应不重要  
试剂亲核性越强，对 $S_N2$ 反应越有利

亲核性 — 与  $C^+$  的亲合力 } 都是提供一对电子与正离子成键的物质  
碱性 — 与  $H^+$  的亲合力 }

---

碱性：试剂对质子的亲合能力。

亲核性：一个试剂在形成过渡态时对碳原子的亲合能力。

亲核试剂的亲核性由两种因素决定  
试剂的给电子能力                  试剂的可极化性

给电子能力强，可极化性大，试剂亲核性强。

# Strength and basicity of the nucleophile

亲核试剂和碱性在多数场合一致，但有时不一致：

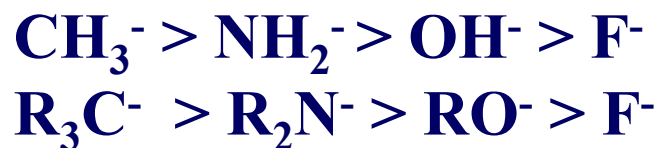
一致的情况：

① 试剂中的亲核原子相同：



碱性(亲核性) 大  $\longrightarrow$  小

② 同一周期的元素生成同类试剂



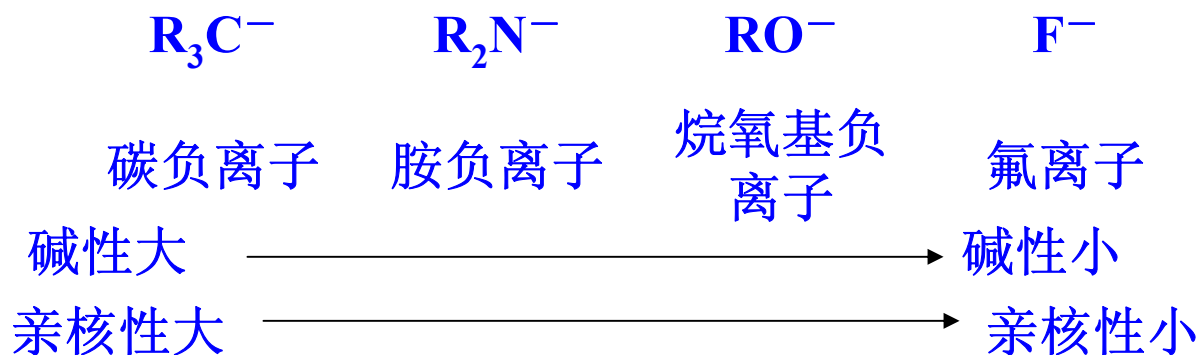
# 哪些因素决定了亲核性？

**碱性**（给出电子的能力）： 碱性越强，亲核性越强

- 中心原子相同时：亲核性与碱性顺序一致

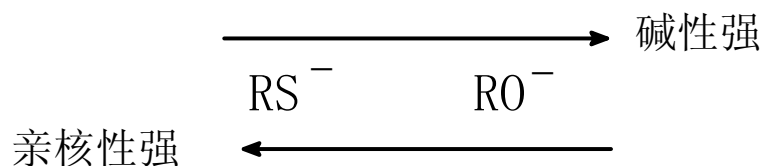
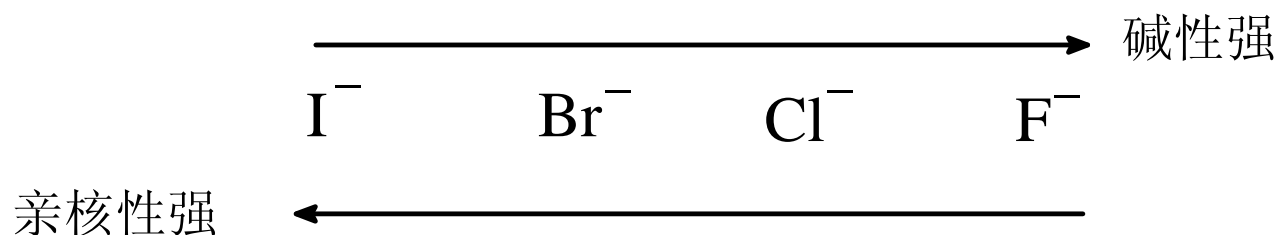
亲核性大小顺序  $\text{CH}_3\text{O}^- > \text{HO}^- > \text{PhO}^- > \text{CH}_3\text{COO}^- > \text{NO}^- > \text{CH}_3\text{OH}$   
共轭酸的pKa            15.9    15.7    9.89    4.8            -1.3    -1.7

- 中心原子不同，但同周期并有相同电荷时，亲核性与碱性顺序也一致



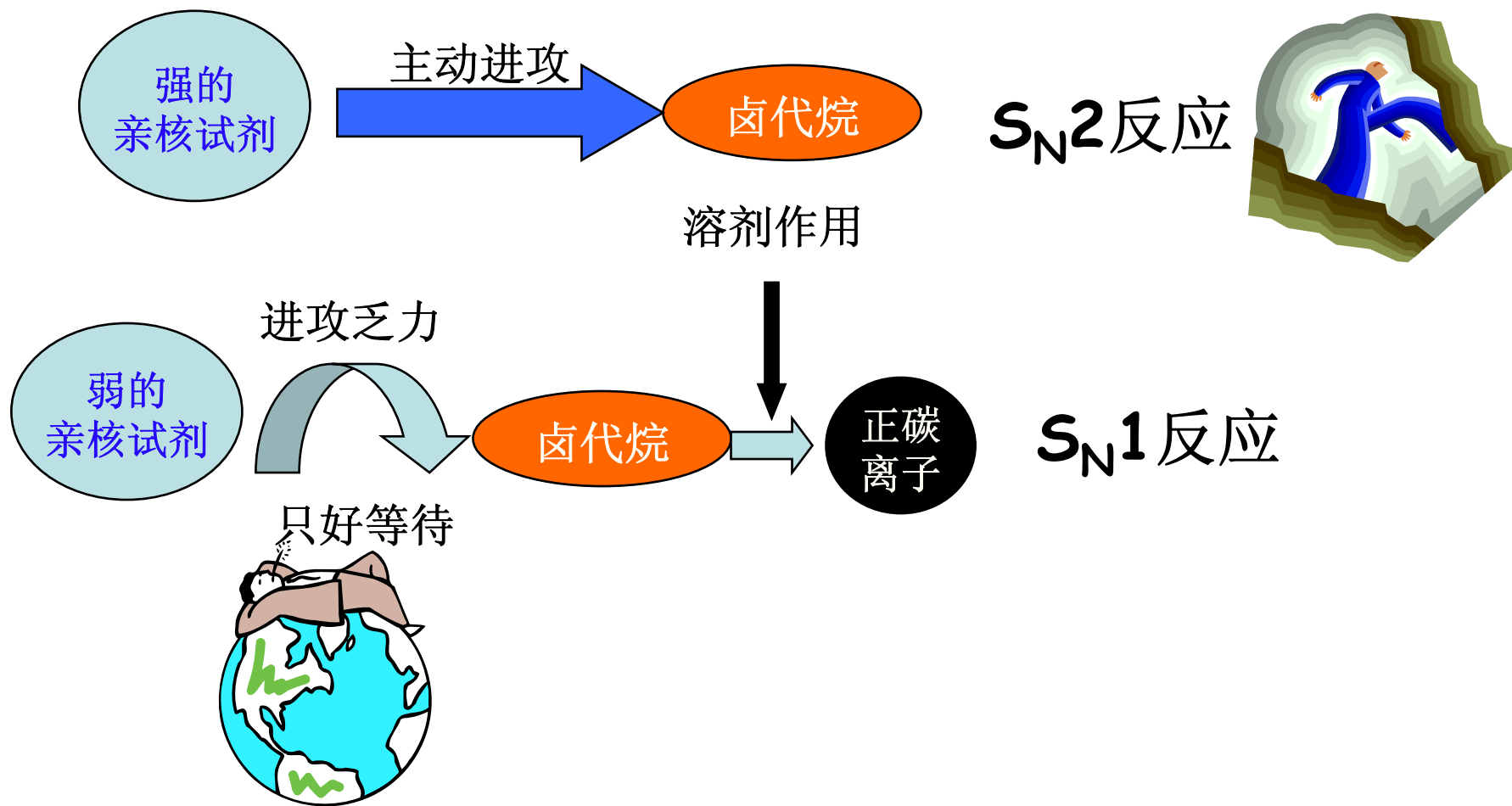
## 可极化性：可极化性越强，亲核性越强

- 中心原子不同，但处于周期表同一族时，亲核性和碱性强弱顺序相反



可极化性与溶剂的性质有关

亲核试剂亲核性的强弱，不仅影响 $S_N2$ 反应速率，而且对亲核取代反应的机理也有影响。

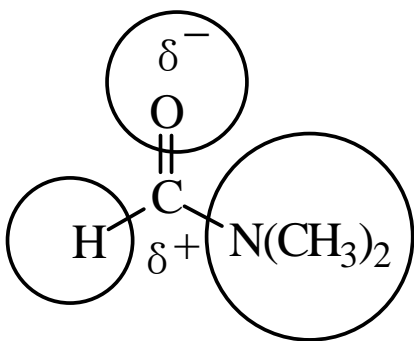


## 8.7.3 solvent effect: polar protic and aprotic solvents

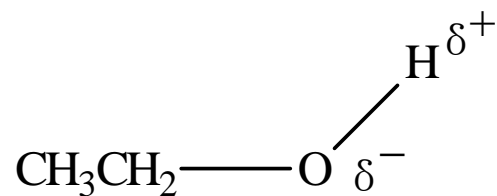
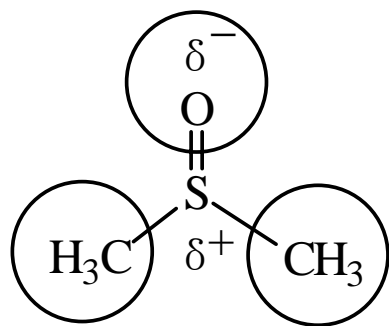
溶剂的分类：质子溶剂、偶极、非极性溶剂

质子性溶剂都是极性的溶剂

非质子性溶剂 { 极性（偶极）溶剂  
非极性溶剂

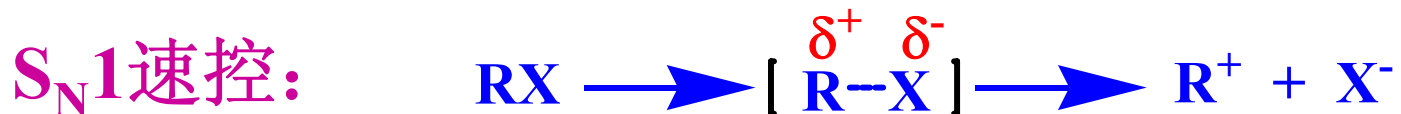


非质子性极性溶剂



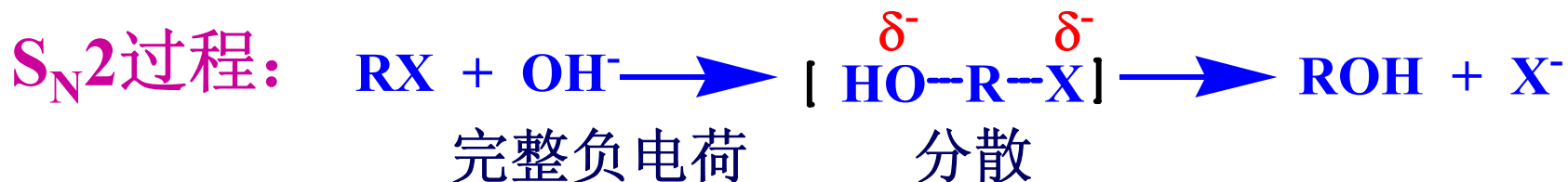
极性质子性溶剂

## 8.7.3 solvent effect: polar protic and aprotic solvents



过渡态比反应物电荷集中

极性溶剂对过渡态的溶剂化稳定作用比反应物大  
 $\Delta E_{\text{活化}} \downarrow \rightarrow$  反应加快



过渡态电荷分散，极性溶剂对过渡态溶剂化稳定作用比反应物小  $\rightarrow$  反应变慢。

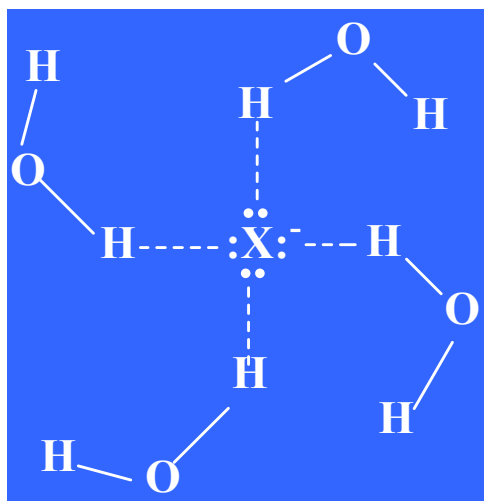


## 溶剂对反应影响的规律

▲ 极性溶剂对 $S_N1$ 反应有利，对 $S_N2$ 反应多数情况不利。

(因为 $S_N1$ 反应过渡态极性增大， $S_N2$ 反应过渡态极性减小)

$S_N2$ 反应中，用质子性溶剂，使负离子亲核试剂溶剂化，降低试剂的亲核性，反应速率减慢。



卤负离子溶剂化程度： $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

卤负离子亲核性顺序： $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$

在质子性溶剂中，  
半径越小的离子越  
容易被溶剂化

## 溶剂化对反应影响的规律

---

凡使起始态稳定的溶剂化作用，将不利于反应；凡使过渡态稳定的溶剂化作用，将有利于反应；使起始态和过渡态同样稳定的溶剂化作用，对反应的影响不大。

### ▲ 使用非质子型极性溶剂有利于 $S_N2$ 反应

因为非质子性溶剂正电中心藏于分子内部，不能使作为亲核试剂的负离子溶剂化

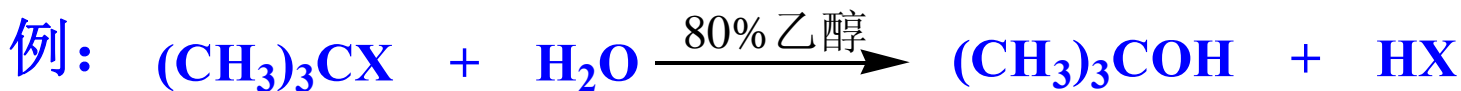
## 8.7.4 the nature of the leaving group

$S_N1$  速控步骤都涉及到C-L键断裂，L易离去对二者都有利  
 $S_N2$

对 $S_N1$ 影响 > 对 $S_N2$ 的影响（有Nu背面进攻的帮助）

✓HX（除HF）都是强酸， $X^-$ 弱碱—稳定，易离去。

离去难易： $I^- > Br^- > Cl^- > F^-$



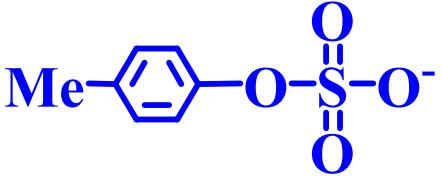
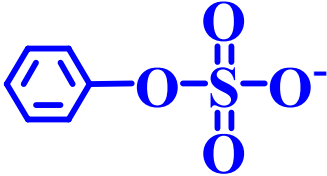
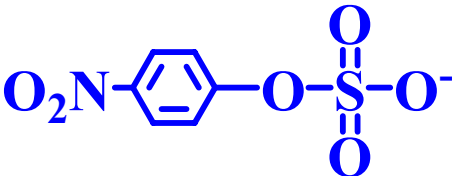
X:	F	Cl	Br	I	OTs
相对速度:	$10^{-5}$	1	39	99	$10^5$



# leaving group

下列基团在亲核取代反应中相对反应速度:

L:	F	ONO <sub>2</sub>	Cl	S(CH <sub>3</sub> ) <sub>2</sub>	Br	<sup>+</sup> OH <sub>2</sub>	I
相对速度:	10 <sup>-2</sup>	0.5	1	25	50	150	190

L:			
相对速度:	190	300	2800

# leaving group

---

不好的离去基团有

$F^-$ ,  $HO^-$ ,  $RO^-$ ,  $-NH_2$ ,  $-NHR$ ,  $-CN$

好的离去基团有

$Cl^-$   $Br^-$   $H_2O$   $I^-$   $^-OSO_2-C_6H_4-CH_3$   $^-OSO_2-C_6H_5$   $^-OSO_2-C_6H_4-NO_2$

离去基团的离去能力越强，对 $S_N1$ 和 $S_N2$ 反应越有利。

键能越弱，越易离去

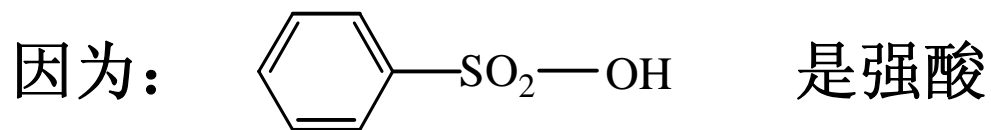
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卤代烷	CH <sub>3</sub> F	CH <sub>3</sub> Cl	CH <sub>3</sub> Br	CH <sub>3</sub> I
离解能 (kJ/mol)	1071.10	949.77	915	887.01

离去基团碱性越弱，越易离去

HF < HCl < HBr < HI,      碱性:      F<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup>

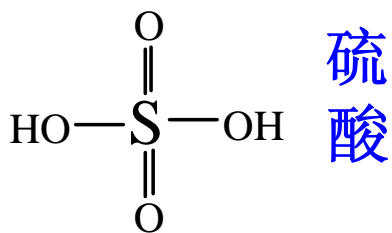
硫酸根、硫酸酯的酸根、磺酸根为什么是好的离去基团？



其共轭碱：**PhSO<sub>2</sub>O<sup>-</sup>**是一个极弱的碱——一个好的离去基团



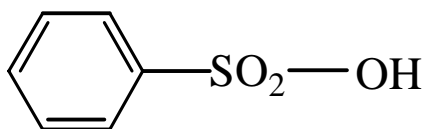
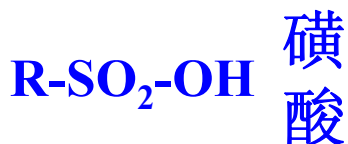
氧上的负电荷可以通过硫离域到整个酸根上，从而使负离子稳定，所以负离子易离去。



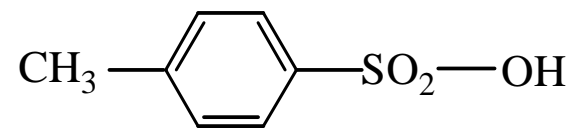
硫酸单甲酯



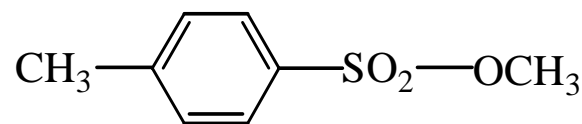
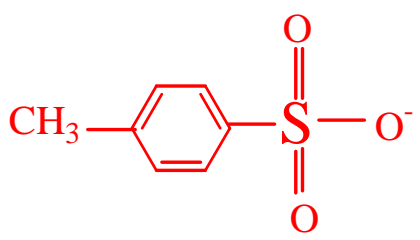
硫酸二甲酯



苯磺酸



对甲苯磺酸



对甲苯磺酸甲酯

## 8.7.5 summary: $S_N1$ versus $S_N2$

---

### Key Characteristics of the $S_N2$ Mechanism

1. A one step  $2^\circ$  order reaction
2. Nucleophile attacks from the opposite side of the leaving group
3. Reactant undergoes inversion of configuration
4. Mechanism affected by steric hindrance
5. Mechanism is best in polar aprotic solvents

## Key Characteristics of the S<sub>N</sub>2 Mechanism

---

**TABLE 7.5** Characteristics of the S<sub>N</sub>2 Mechanism

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

---

# Key Characteristics of the S<sub>N</sub>1 Mechanism

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1. A multistep **1° order** reaction
2. Nu attacks from the **top and bottom sides of the C<sup>+</sup> intermediate**
3. Reactant undergoes **racemization**
4. Mechanism favored by **stable carbocations**
5. Mechanism is best in **polar protic solvents**

# Key Characteristics of the S<sub>N</sub>1 Mechanism

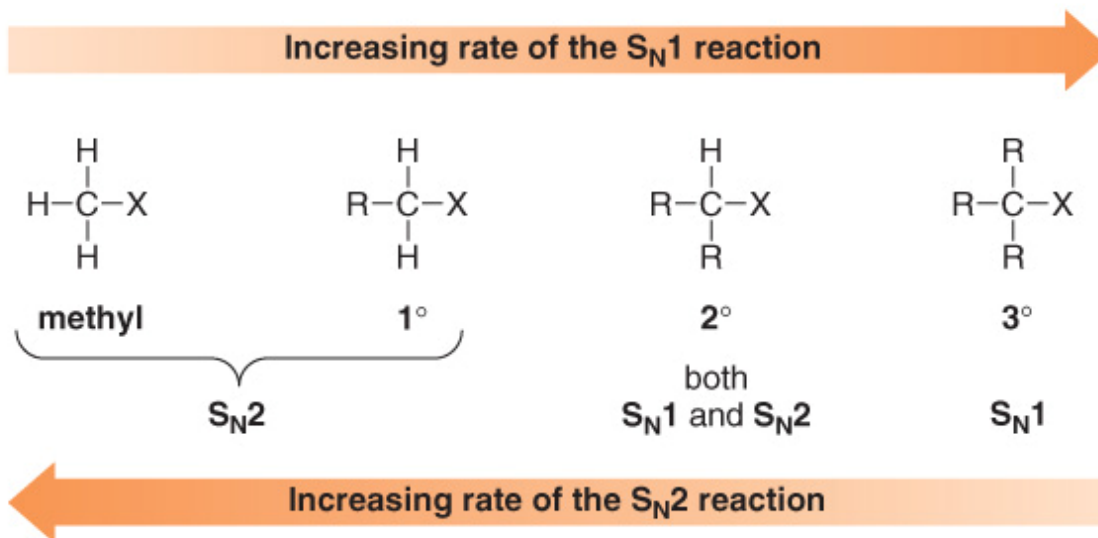
**TABLE 7.6** Characteristics of the S<sub>N</sub>1 Mechanism

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

# Predicting the Likely Mechanism of a Substitution Reaction

- Four factors are relevant in predicting whether a given reaction is likely to proceed by an  $S_N1$  or an  $S_N2$  reaction—The most important is the identity of the alkyl halide.

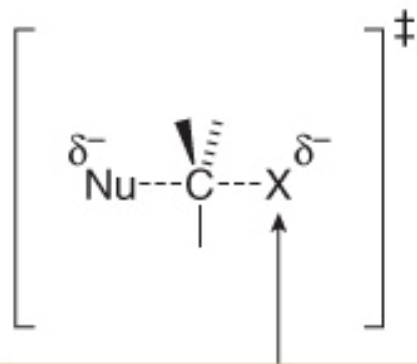
- ◆ Increasing alkyl substitution favors  $S_N1$ .
- ◆ Decreasing alkyl substitution favors  $S_N2$ .



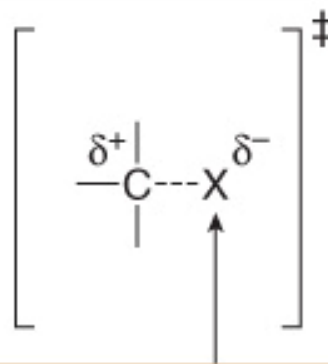
- ◆ Methyl and  $1^\circ$  halides ( $\text{CH}_3\text{X}$  and  $\text{RCH}_2\text{X}$ ) undergo  $S_N2$  reactions only.
- ◆  $3^\circ$  Alkyl halides ( $\text{R}_3\text{CX}$ ) undergo  $S_N1$  reactions only.
- ◆  $2^\circ$  Alkyl halides ( $\text{R}_2\text{CHX}$ ) undergo both  $S_N1$  and  $S_N2$  reactions. Other factors determine the mechanism.

**A better leaving group increases the rate of both  $S_N1$  and  $S_N2$  reactions.**

Transition state of the  $S_N2$  mechanism



Transition state of the rate-determining step of the  $S_N1$  mechanism



A better leaving group is more able to accept the negative charge.

R-F

R-Cl

R-Br

R-I



Increasing leaving group ability  
Increasing rate of  $S_N1$  and  $S_N2$  reactions

# Predicting the Likely Mechanism of a Substitution Reaction

**TABLE 7.7** Summary of Factors that Determine the  $S_N1$  or  $S_N2$  Mechanism

Alkyl halide	Mechanism	Other factors
$CH_3X$ $RCH_2X$ ( $1^\circ$ )	$S_N2$	Favored by <ul style="list-style-type: none"><li>• <b>strong nucleophiles</b> (usually a net negative charge)</li><li>• polar <b>aprotic</b> solvents</li></ul>
$R_3CX$ ( $3^\circ$ )	$S_N1$	Favored by <ul style="list-style-type: none"><li>• <b>weak nucleophiles</b> (usually neutral)</li><li>• polar <b>protic</b> solvents</li></ul>
$R_2CHX$ ( $2^\circ$ )	$S_N1$ or $S_N2$	The mechanism depends on the conditions. <ul style="list-style-type: none"><li>• <b>Strong nucleophiles favor the <math>S_N2</math> mechanism over the <math>S_N1</math> mechanism.</b> For example, <math>RO^-</math> is a stronger nucleophile than <math>ROH</math>, so <math>RO^-</math> favors the <math>S_N2</math> reaction and <math>ROH</math> favors the <math>S_N1</math> reaction.</li><li>• <b>Protic solvents favor the <math>S_N1</math> mechanism and aprotic solvents favor the <math>S_N2</math> mechanism.</b> For example, <math>H_2O</math> and <math>CH_3OH</math> are polar protic solvents that favor the <math>S_N1</math> mechanism, whereas acetone [<math>(CH_3)_2C=O</math>] and DMSO [<math>(CH_3)_2S=O</math>] are polar aprotic solvents that favor the <math>S_N2</math> mechanism.</li></ul>



**TABLE 7.8 Molecules Synthesized from R–X by the S<sub>N</sub>2 Reaction**

	Nucleophile (:Nu <sup>-</sup> )	Product	Name
Oxygen compounds	<sup>-</sup> OH	R–OH	alcohol
	<sup>-</sup> OR'	R–OR'	ether
	$\begin{array}{c} \text{O} \\    \\ \text{O}^- - \text{C} - \text{R}' \end{array}$	$\begin{array}{c} \text{O} \\    \\ \text{R} - \text{O} - \text{C} - \text{R}' \end{array}$	ester
Carbon compounds	<sup>-</sup> CN	R–CN	nitrile
	<sup>-</sup> :C≡C–H	R–C≡C–H	alkyne
Nitrogen compounds	N <sub>3</sub> <sup>-</sup>	R–N <sub>3</sub>	azide
	:NH <sub>3</sub>	R–NH <sub>2</sub>	amine
Sulfur compounds	<sup>-</sup> SH	R–SH	thiol
	<sup>-</sup> SR'	R–SR'	sulfide

↑  
the products of nucleophilic substitution

## (二) 消除反应

## (Elimination reaction)

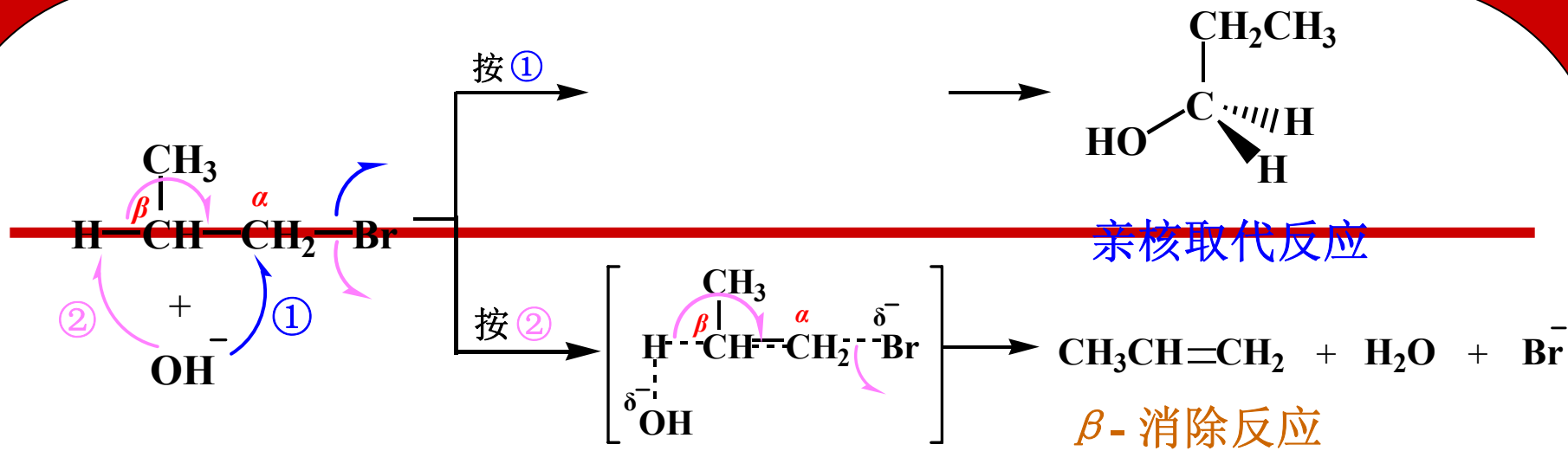
定义：卤代烷失去一分子卤化氢，生成稀烃的反应称为卤代烷的消除反应。



1. 消除反应机理：

(1) 双分子消除反应(E2)

以 $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ 为例：

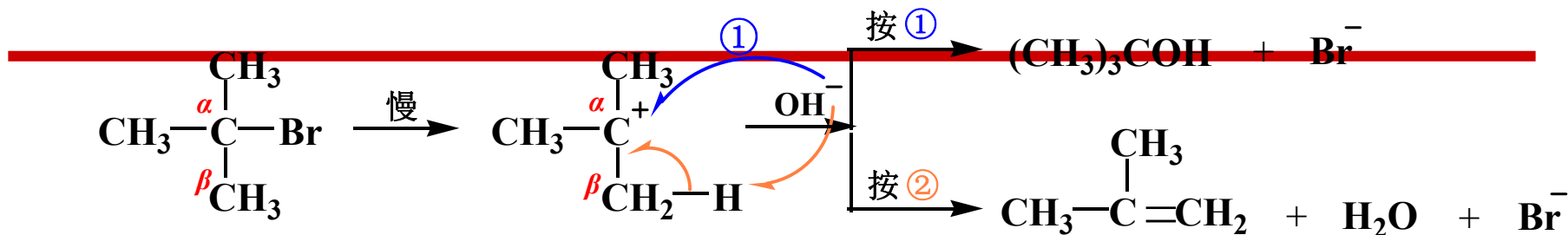


上述反应的本质差别在于：按①进行反应，碱进攻的是  $\alpha$ -C，发生的是亲核取代反应；按②进行反应，碱进攻的是  $\beta$ -H，发生的是消除反应。

由反应历程可见，卤代烷的双分子消除反应也是一步完成的反应，反应的动力学方程为：

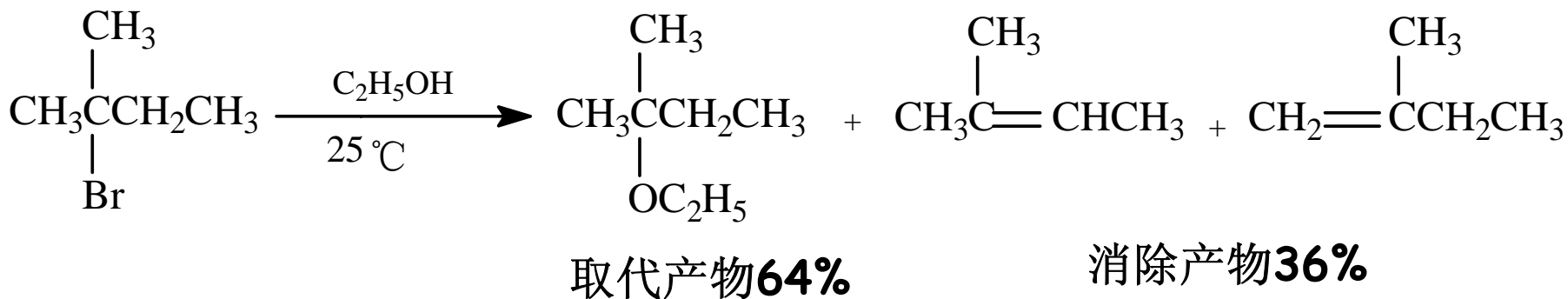
$$v = k [\text{RX}] [\text{碱}] \quad \text{碱} = \text{HO}^-, \text{RO}^- \text{ 等。}$$

## (2) 单分子消除反应(E1)以 $(\text{CH}_3)_3\text{CBr}$ 为例:



由此可见: a. 反应也是分步进行的; b. 反应速度只与RX有关, 其动力学方程为:  $v = k[\text{RX}]$

总之, 亲核取代反应和消除反应是相互竞争, 伴随发生的。

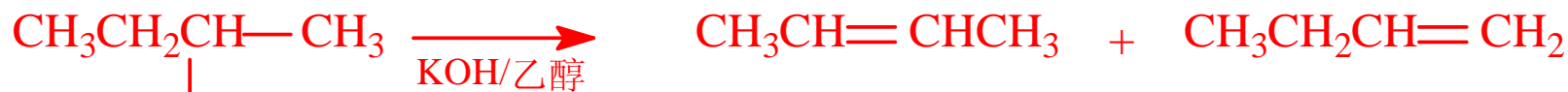


## 2. 消除反应的取向

当卤代烷分子含有两个或两个以上不同的  $\beta$ -H 原子可供消除时，生成的烯烃也就不止一种结构，那么，究竟优先消除哪一个  $\beta$ -H 原子，这就是取向问题。

实践表明：卤代烷的  $\beta$ -消除反应，一是 **Saytzeff** (查依采夫) 取向，另一个是 **Hofmann** (霍夫曼) 取向。

通常情况下将遵循 **Saytzeff** 规则——生成连有取代基较多的烯烃。



2-溴丁烷

2-丁烯 (81%)

1-丁烯 (19%)



2-甲基-2-溴丁烷

2-甲基-2-丁烯 (70%)

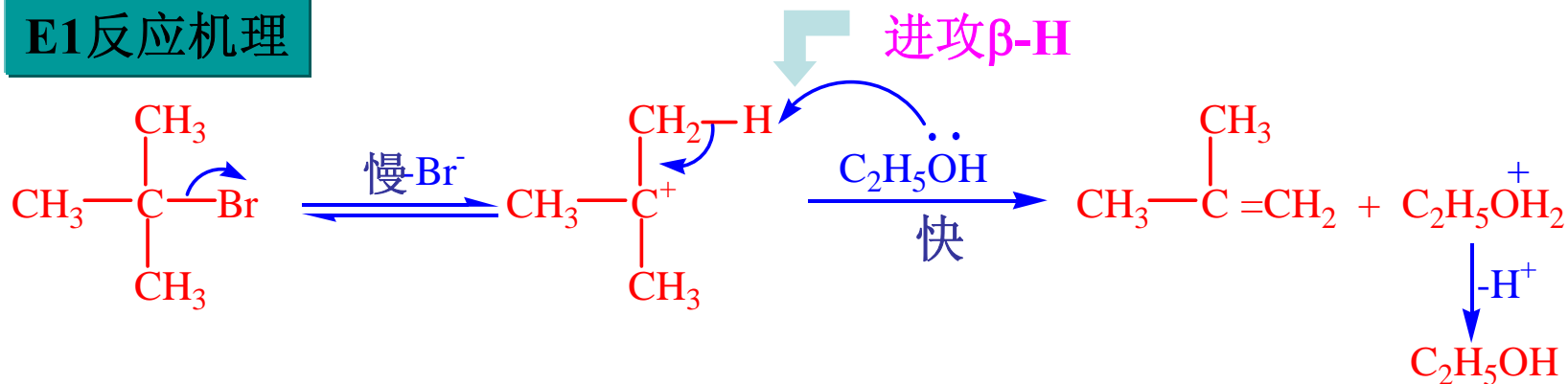
2-甲基-1-丁烯 (30%)

消除反应的这种取向的规律与烯烃的稳定性有关。其规律是：在消除反应中，优先生成热力学稳定的烯烃。

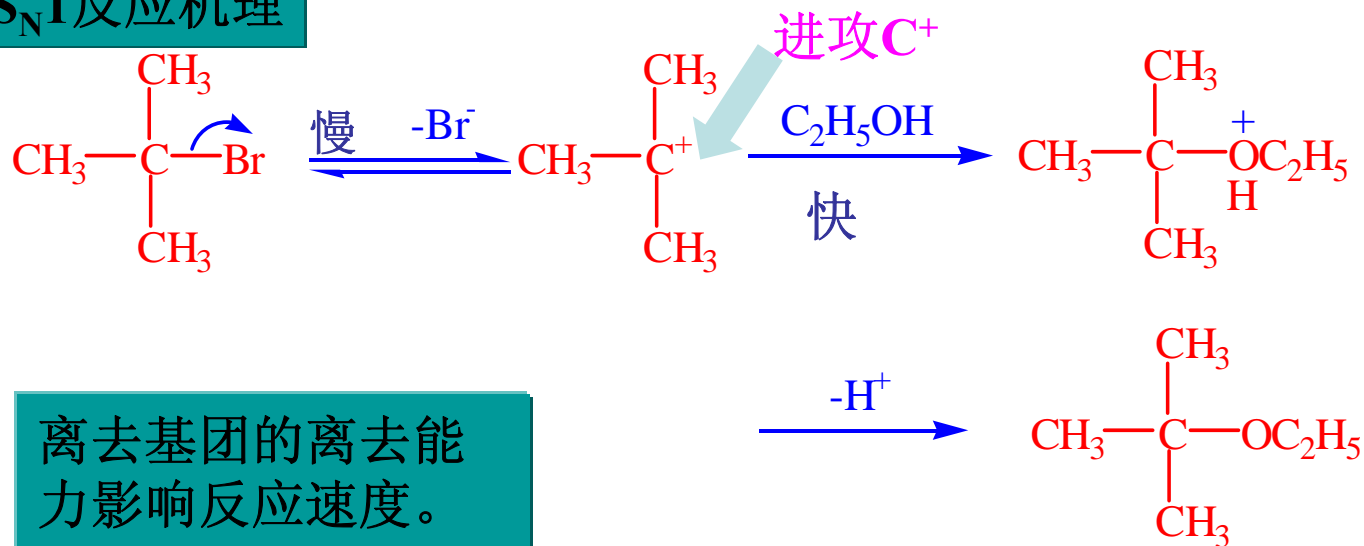
在双键碳原子上连有的烷基越多烯烃就越稳定

# E1反应机理和S<sub>N</sub>1反应机理的比较

## E1反应机理



## S<sub>N</sub>1反应机理



离去基团的离去能力影响反应速度。

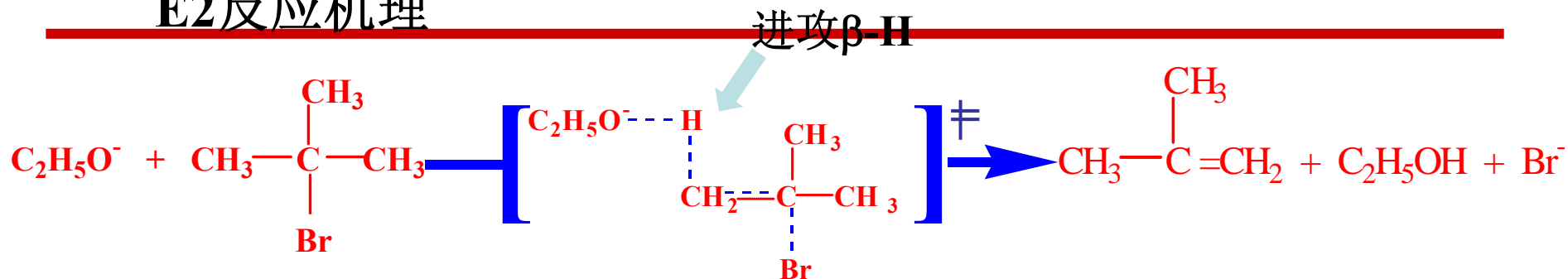
试剂亲核性强弱影响产物比例。

碱性强，升温对E1有利。

中性极性溶剂对S<sub>N</sub>1有利。

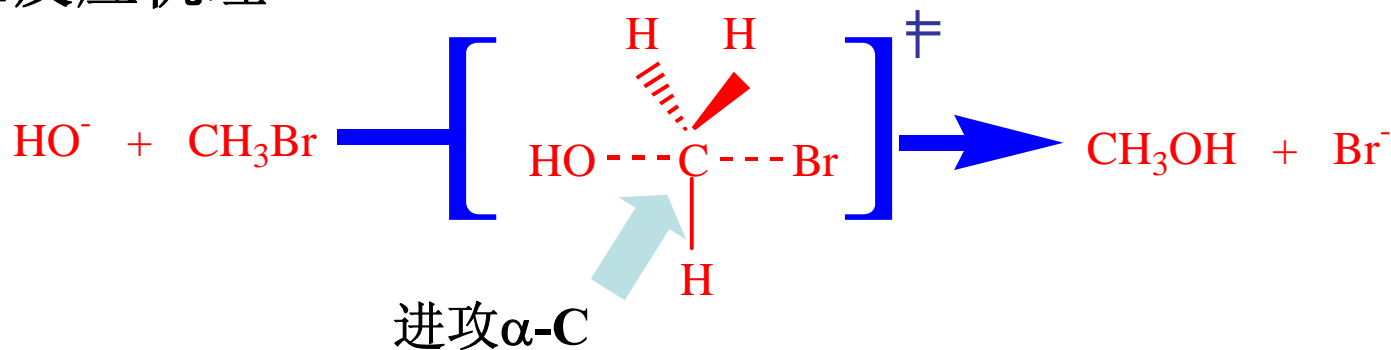
# E2反应机理和S<sub>N</sub>2反应机理的比较

## E2反应机理



试剂亲核性强，碱性弱，体积小，利于S<sub>N</sub>2。试剂碱性 strong，浓度大，体积大，升温利于E2。

## S<sub>N</sub>2反应机理



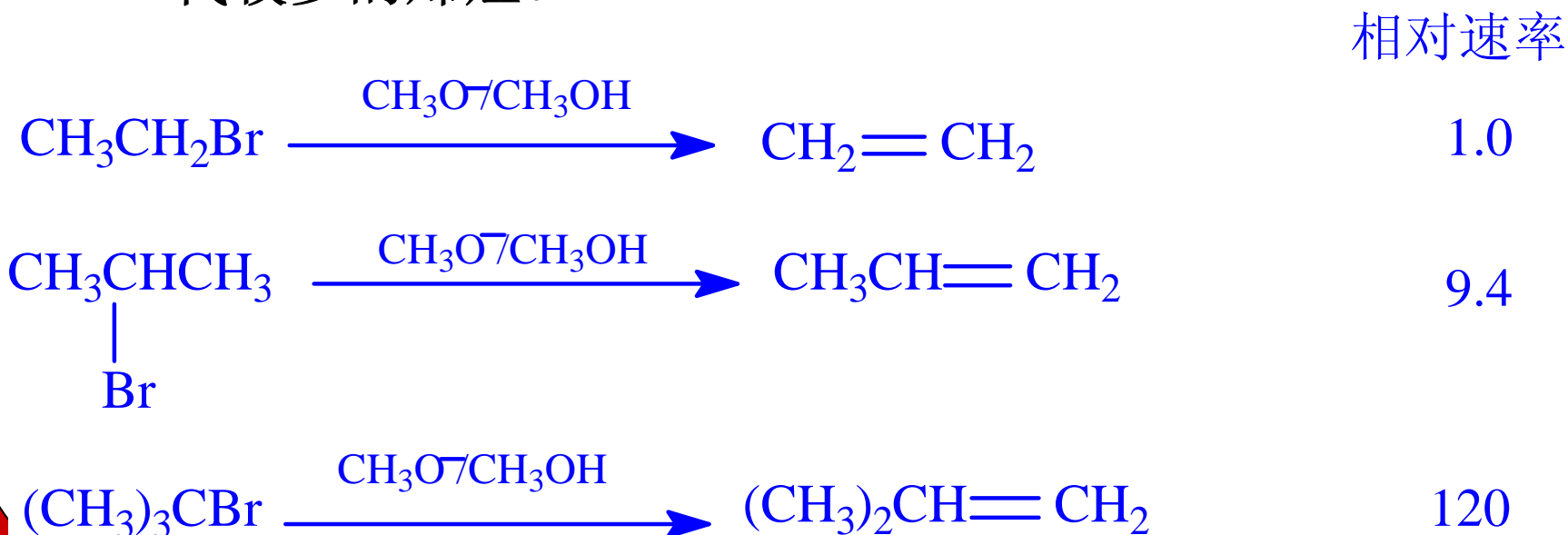


### 3. 消除反应中卤代烷的活性

无论对于E1还是E2的机理卤代烷消除反应的活性顺序均为  
叔 > 仲 > 伯

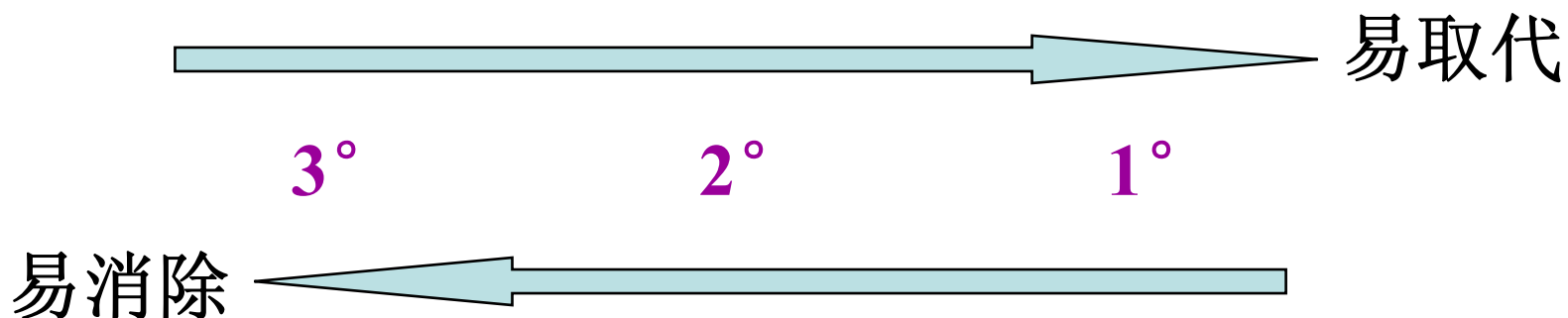
对于E1反应，是因为叔卤代烷产生的碳正离子最稳定，因此其活性最高。

对于E2反应，是由于叔卤代烷消除后更易生成烷基取代较多的烯烃。



## 4. 取代反应与消除反应的活性比较

不考虑具体的反应历程，只考虑一个卤代烷的结构对取代或消除反应的影响。结论为：



伯卤代烷主要发生取代反应，而叔卤代烷主要发生消除反应。