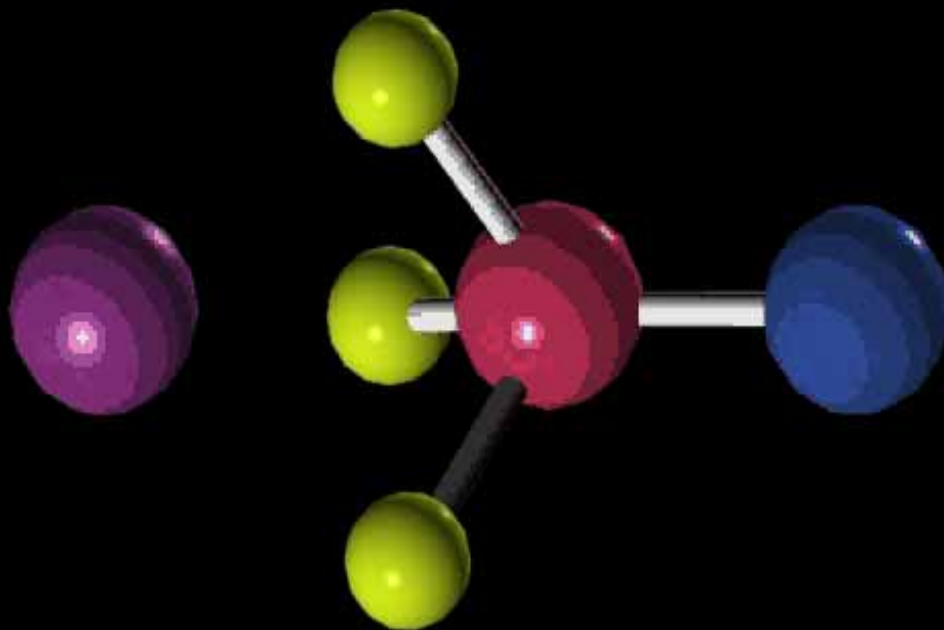
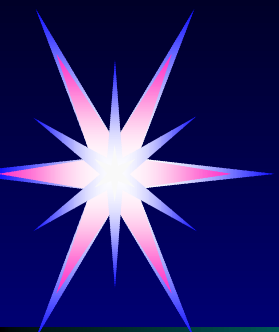


有机化学

(Organic Chemistry)

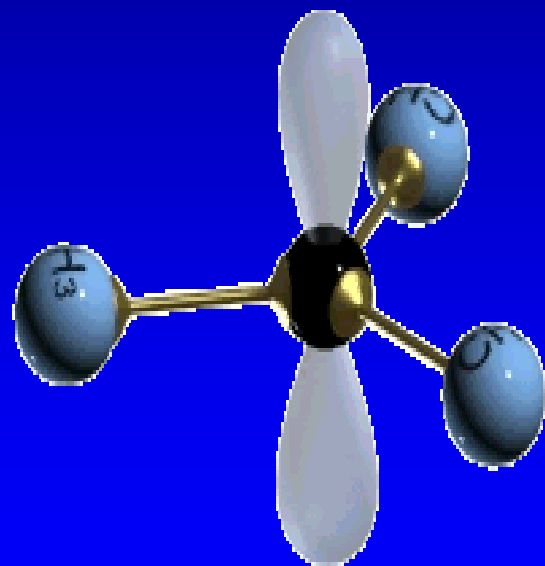


制作：付蕾 朱凤岗

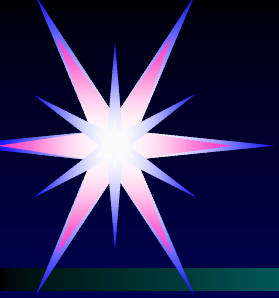


有机化学

(Organic Chemistry)



制作：付蕾 朱凤岗



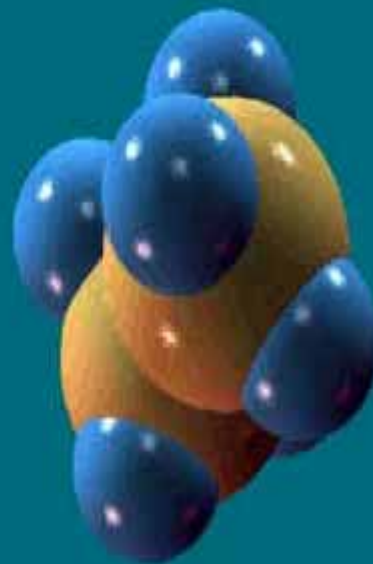
第七章

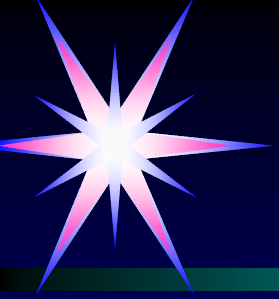
卤代烃 (Halohydrocarbons)

溴乙烷



乙烷

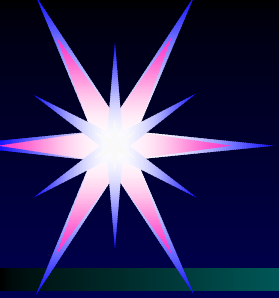




第七章

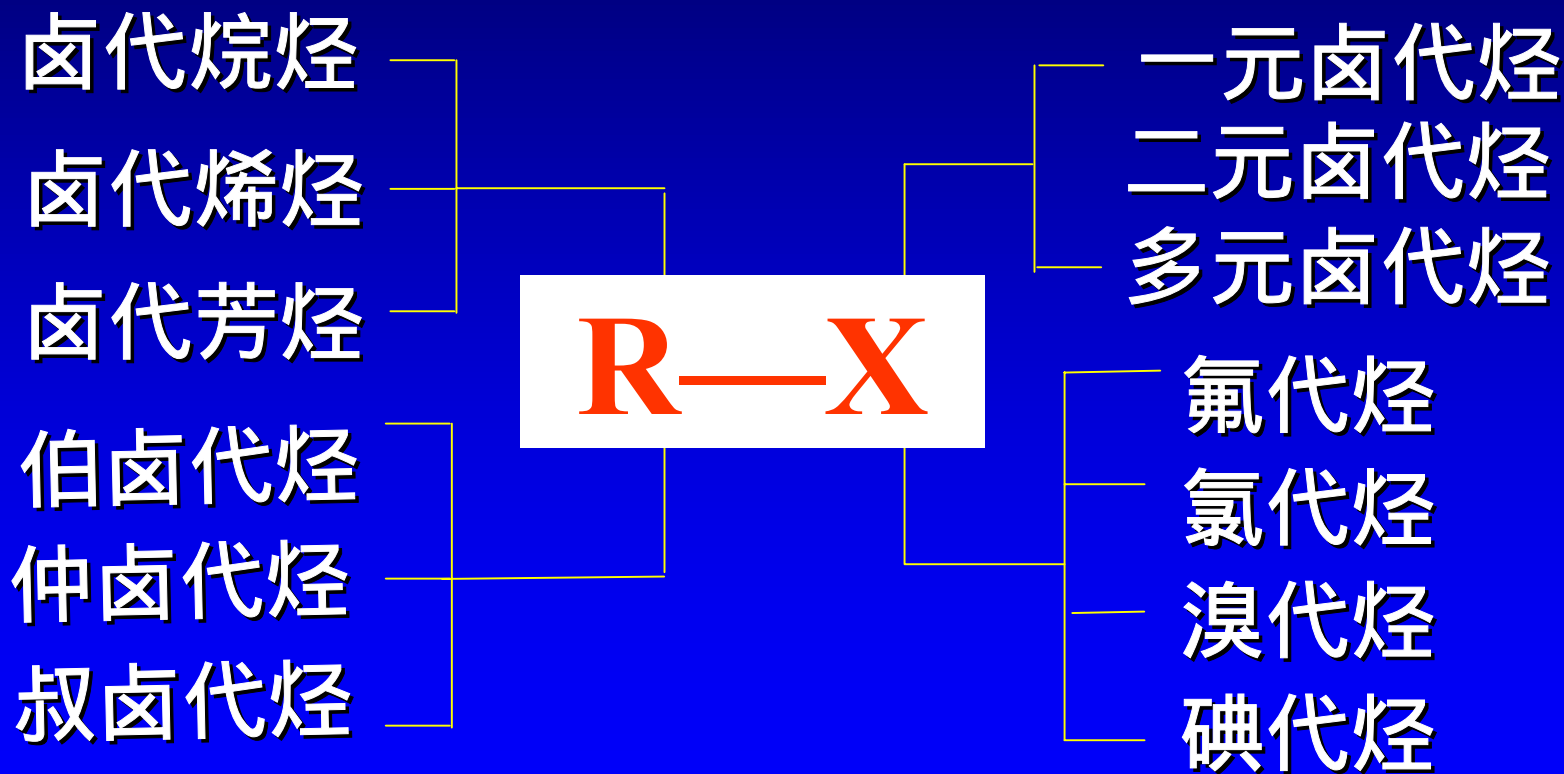
卤代烃 (Halohydrocarbons)

- 一、卤代烃的分类和命名
(Classification and nomenclature)
- 二、卤代烷的化学性质
(Properties of halohydrocarbons)
- 三、卤代烃化学结构与化学活性的关系



一、卤代烃的分类和命名

1. 分类 (Classification)





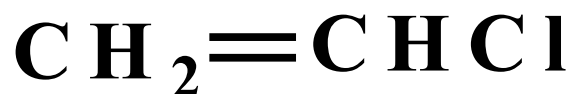
2. 命名 (Nomenclature)

Common name : “卤X 烃”或“X 基卤”



溴乙烷 (乙基溴)

bromoethane



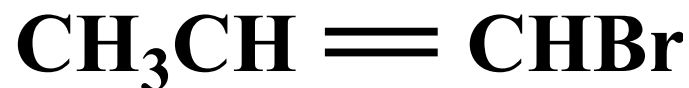
氯乙烯 (乙烯基氯)

chloroethen



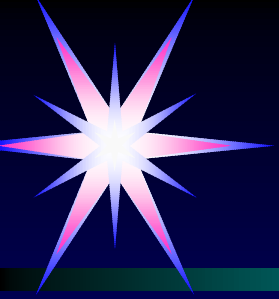
烯丙基氯

allyl chloride



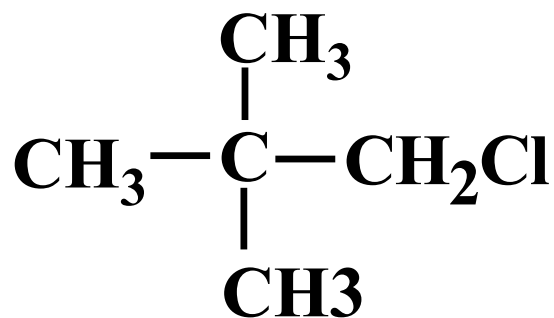
丙烯基溴

propenyl bromide



Systematic Name

选主链：含—X（官能团），—X 为取代基
编号：近取代基（官能团）端

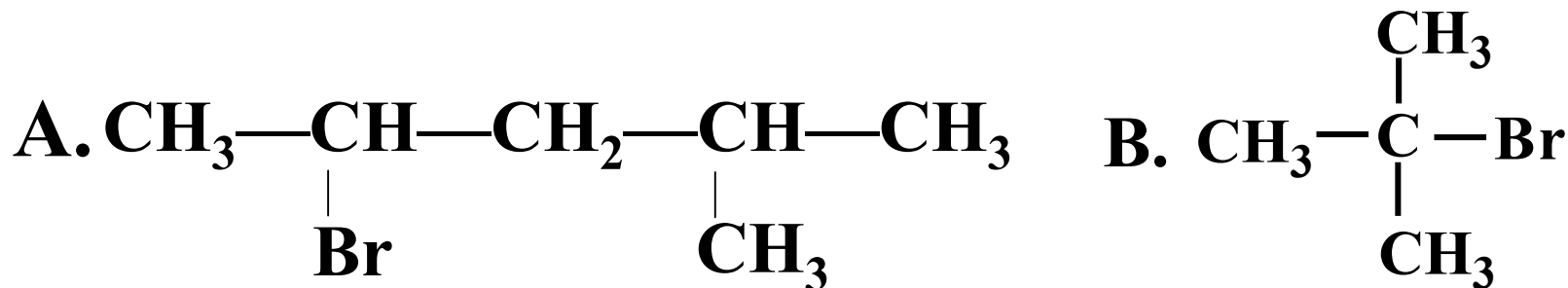


2,3-二甲基-1-氯丙烷（伯）

1-chloro-2,3-dimethylpropane



Alkyl halids



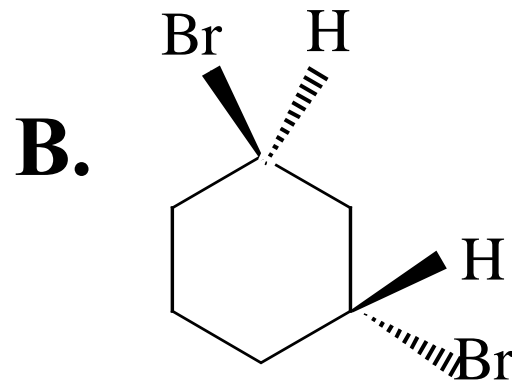
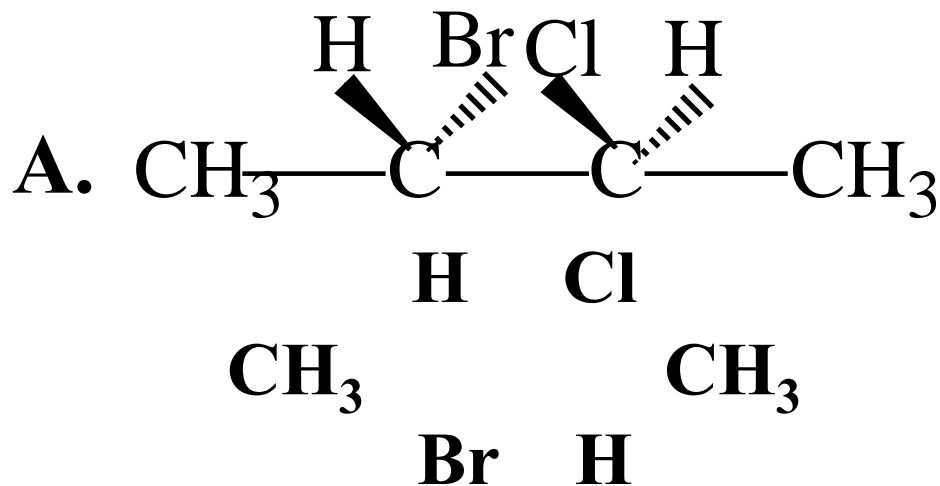
A. 2-甲基-4-溴戊烷 (仲)

2-bromo-4-methylpentane

B. 2-甲基-2-溴丙烷 (叔)

2-bromo-2-methylpropane

Alkyl halids



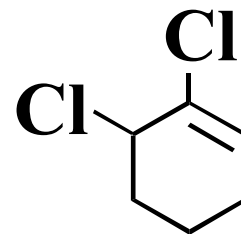
A. (2*S*,3*S*) - 2 - 氯 - 3 - 溴丁烷

B. (1*R*,3*R*) - 1, 3 - 二溴环己烷

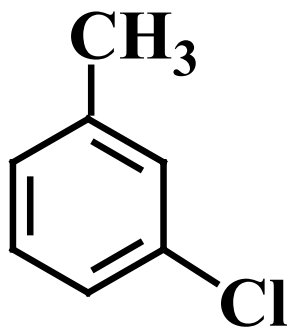
Allyl halid and aryl halid



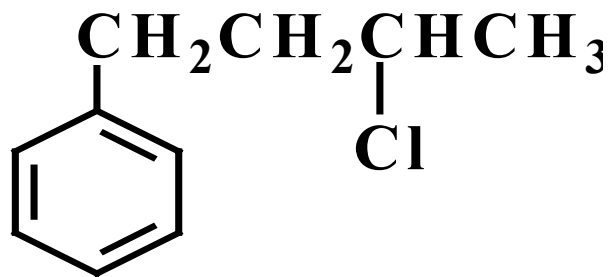
3-乙基-4-溴-1-丁烯



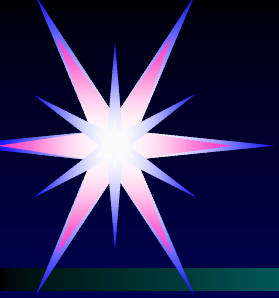
1,6-二氯环己烯



3-氯甲苯



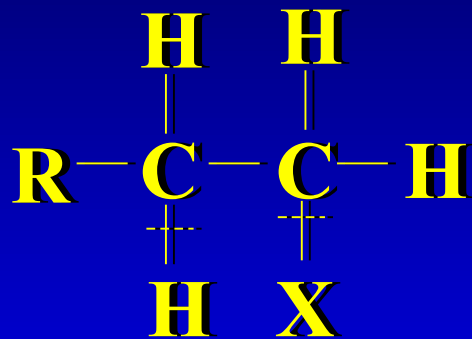
1-苯基-3-氯丁烷



二、卤代烷的化学性质

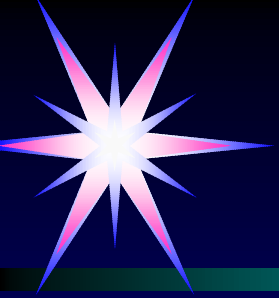
(Reactions of alcohols)

结构分析:



$\delta^+ \quad \delta^-$
C X 键容易异裂

取代、消除、与金属作用

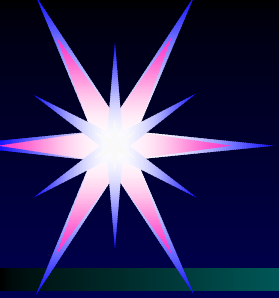


卤代烷的化学性质

$\begin{matrix} \delta^+ & \delta^- \\ \text{C} & \rightarrow & \text{X} \end{matrix}$	C—F	C—Cl	C—Br	C—I
键长 (nm)	0.139	0.176	0.194	0.214
键能 (kJ/mol)	456	351	293	243

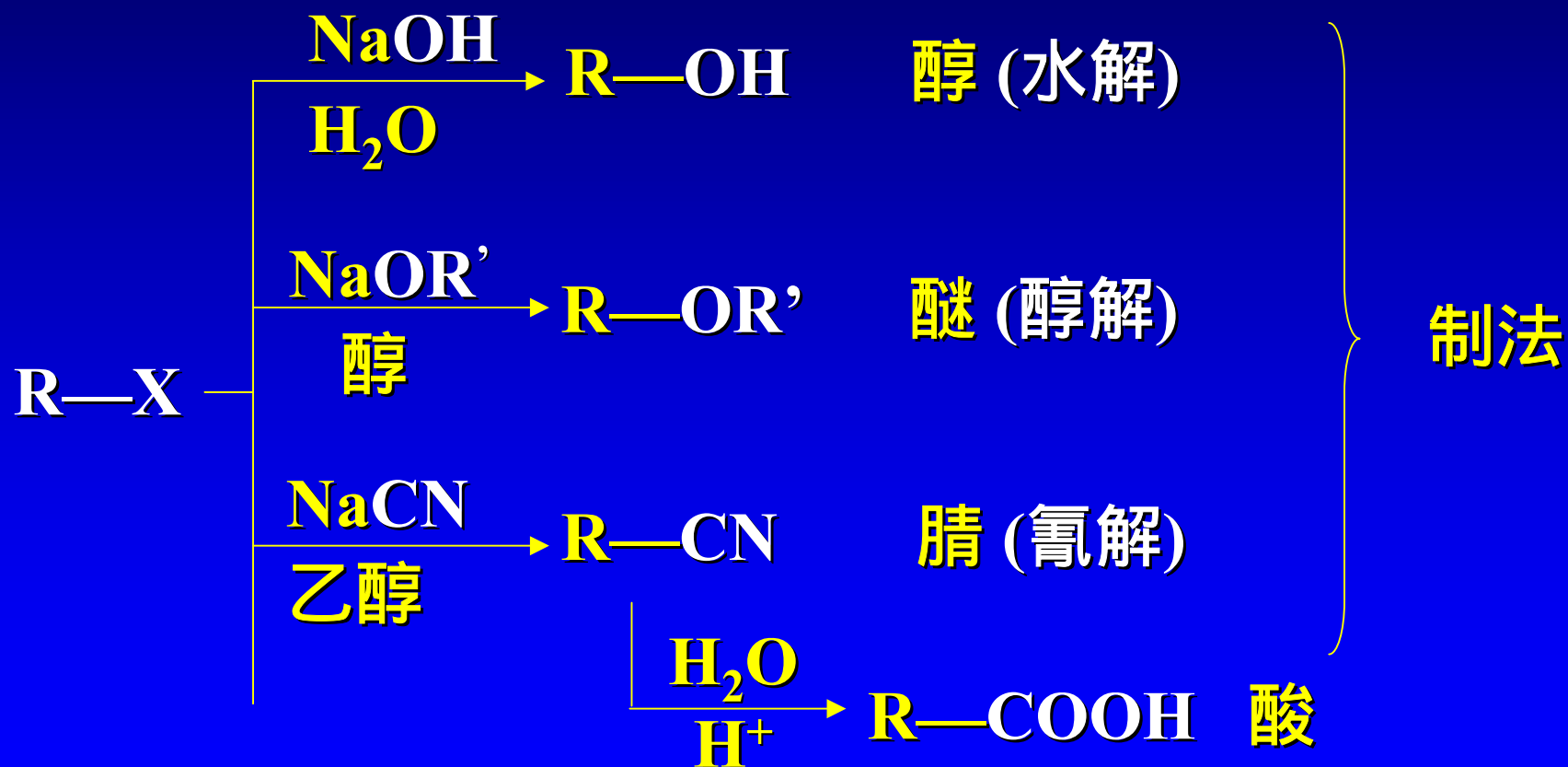
反应活性：

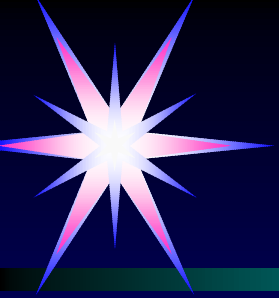




1. 亲核取代反应

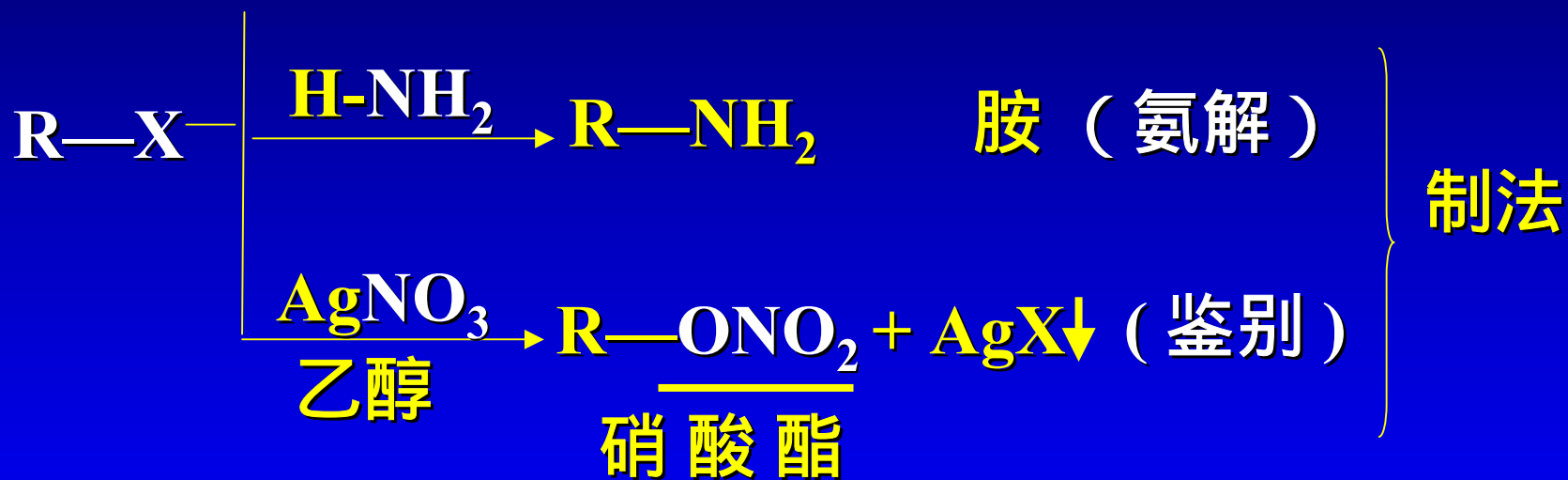
(Nucleophilic substitution reaction)

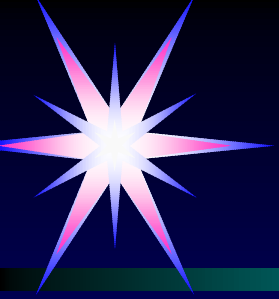




亲核取代反应

(nucleophilic substitution reaction)



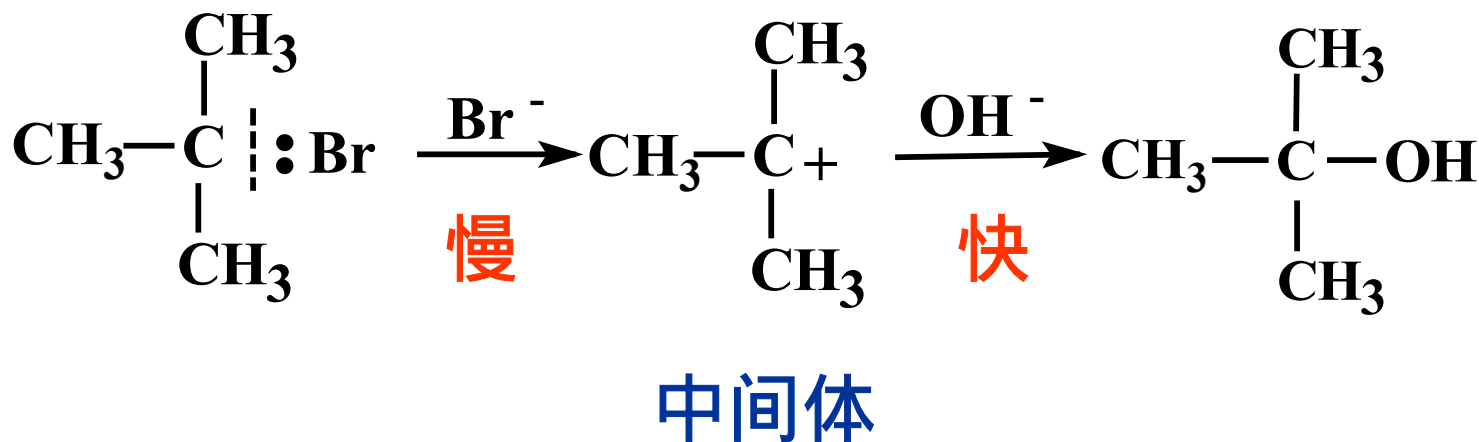


说明:

- (1) 亲核试剂:** (Nucleophilic reagent)
在反应中能提供电子对而成键的试剂。
- (2) 亲核取代反应:** (Nucleophilic substitution reaction)
由亲核试剂进攻而引起的 取代反应。
- (3) 亲核取代反应历程:** (Reaction mechanism of nucleophilic substitution)

单分子亲核取代反应历程 (S_N1)

Unimolecular Nucleophilic Substitution

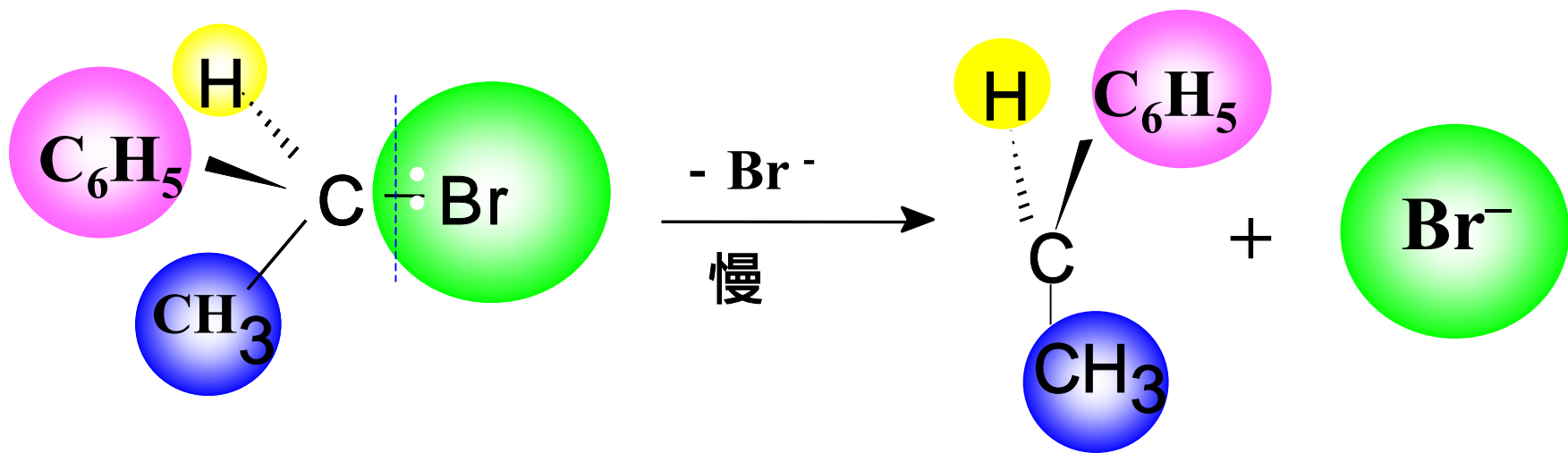


$$r = k c [(\text{CH}_3)_3\text{CBr}]$$

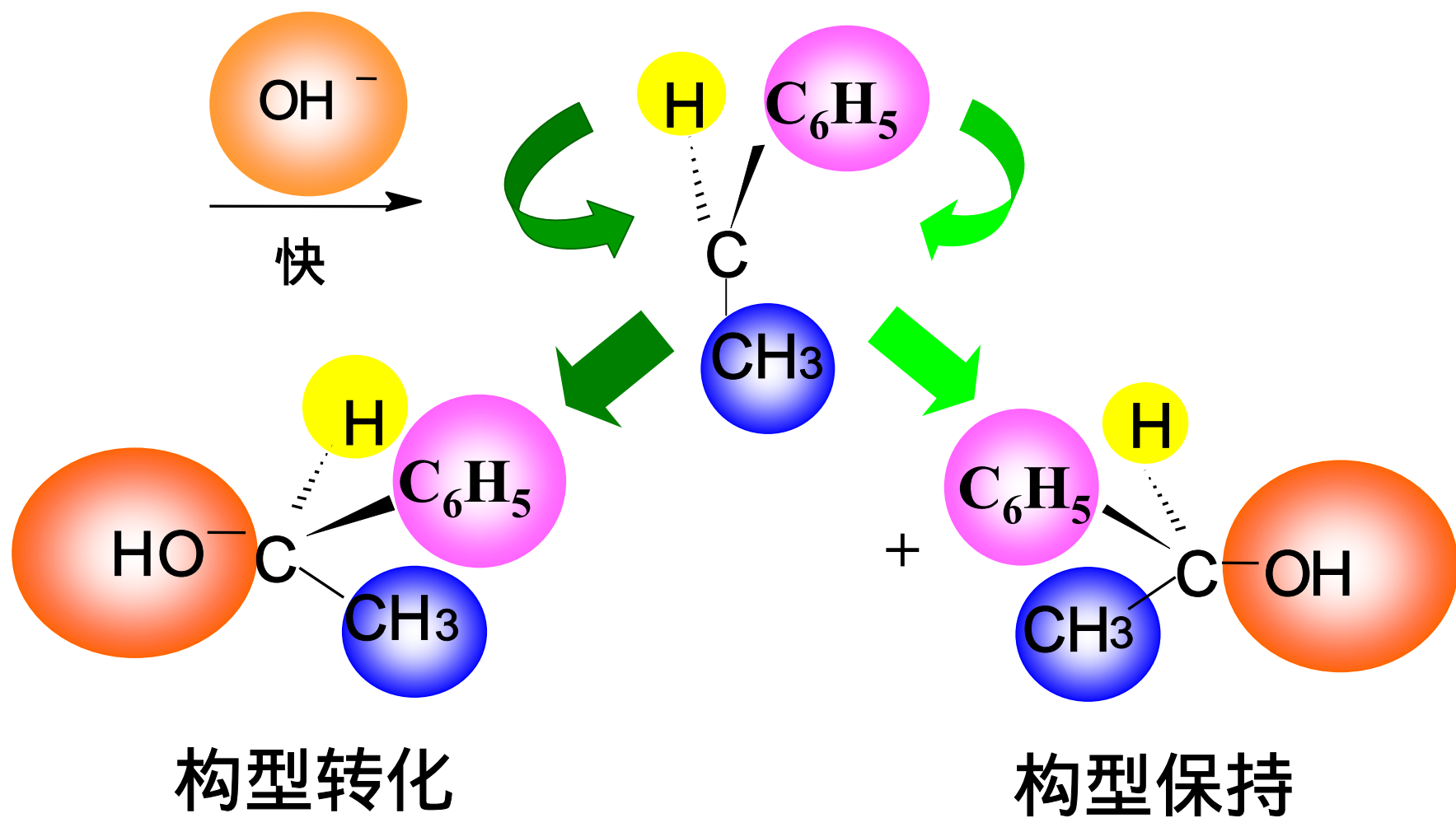
反应速率只决定于卤代烷的浓度 (单分子)

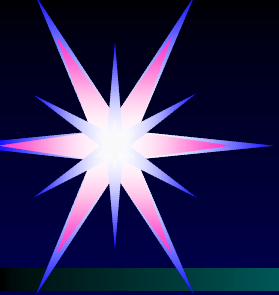
单分子亲核取代反应历程 (S_N1)

S_N1活泼性：



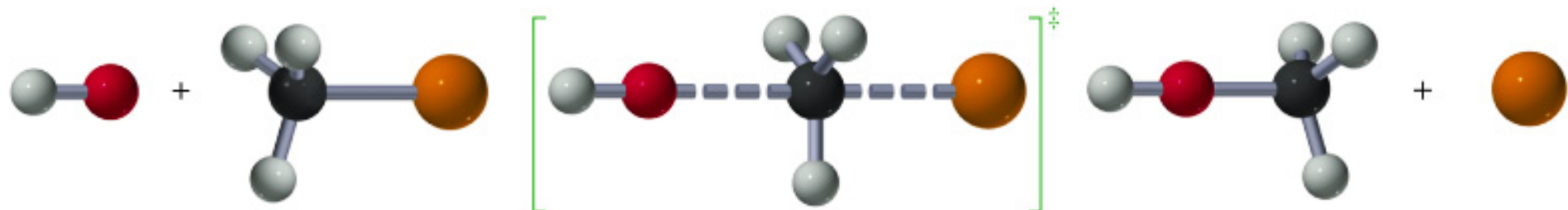
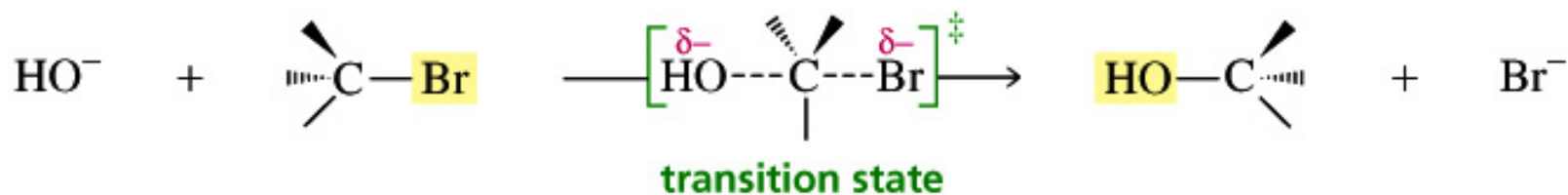
单分子亲核取代反应历程 (S_N1)





双分子亲核取代反应历程 (S_N2)

Bimolecular Nucleophilic Substitution

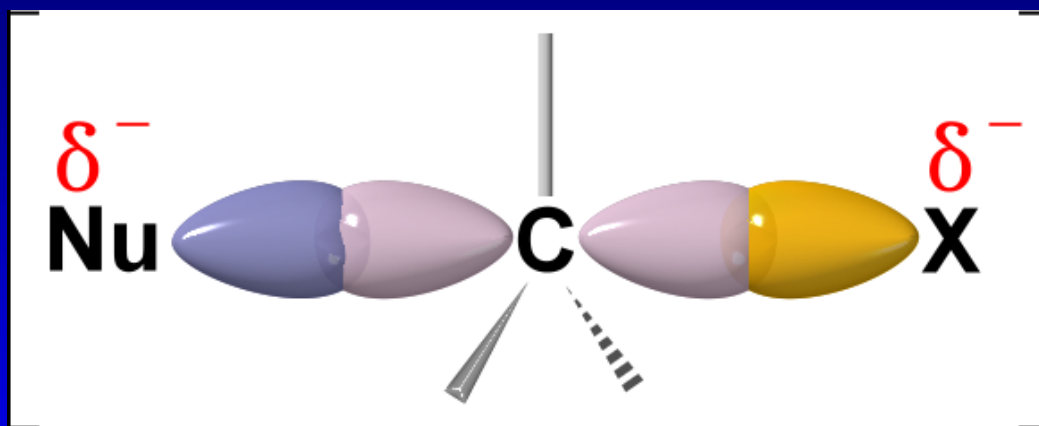


$$r = k c[\text{CH}_3\text{Br}] c[\text{OH}^-]$$

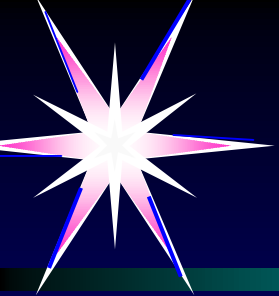
反应速率与卤代烷和OH⁻有关(双分子)

双分子亲核取代反应历程 (S_N2)

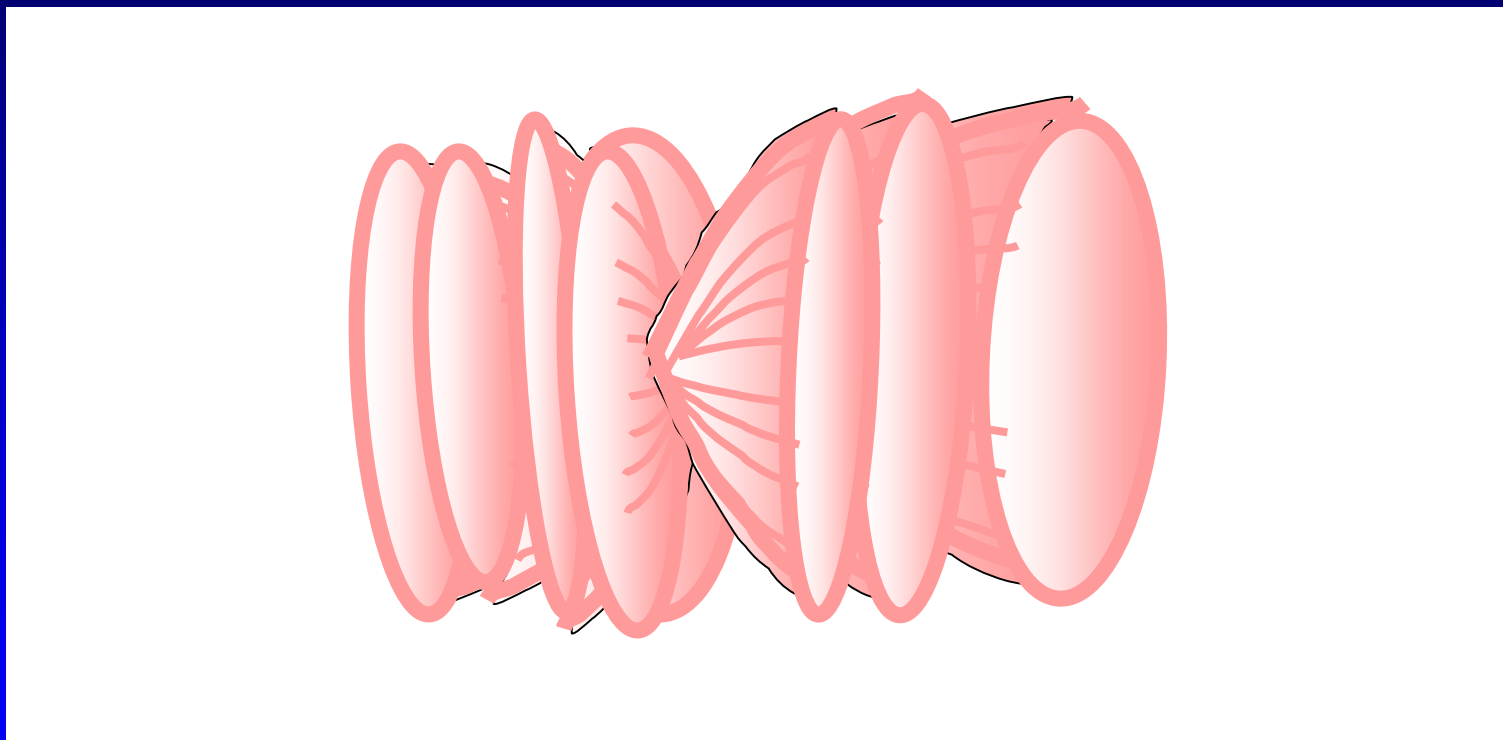
- S_N2 反应中过渡态结构：



- sp^2 杂化
- 新键已部分形成，旧键已部分断裂

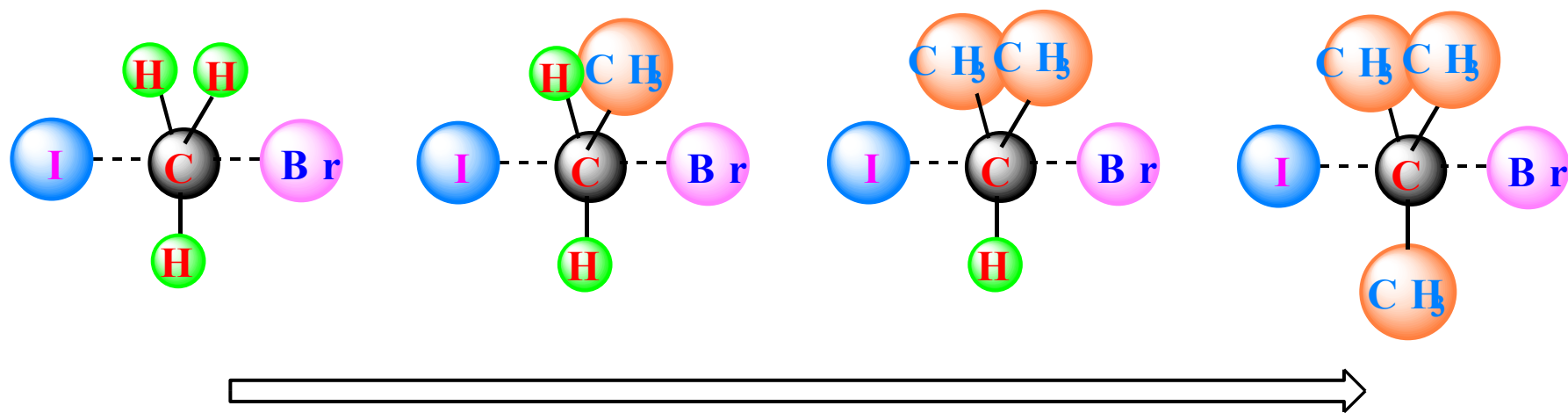


双分子亲核取代反应历程 (S_N2)

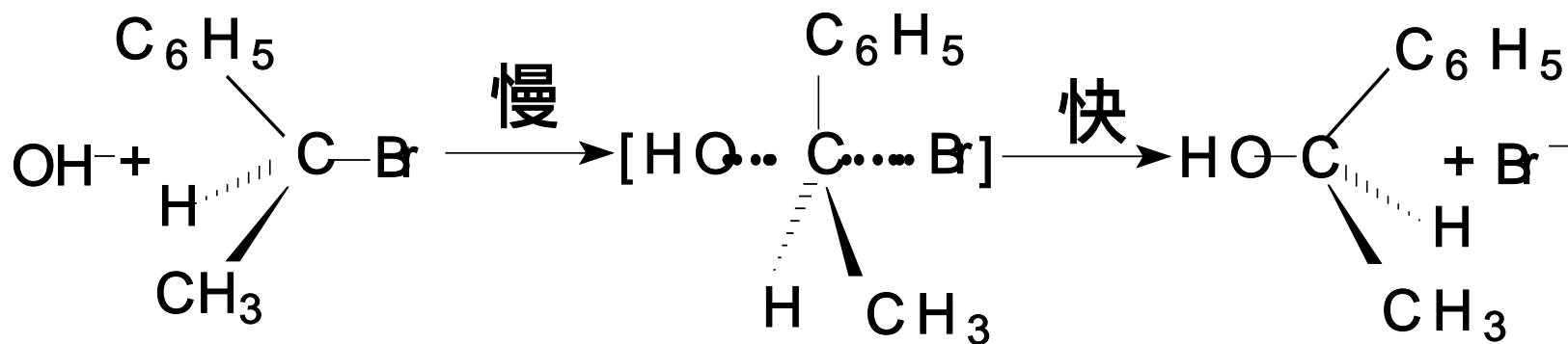


双分子亲核取代反应历程 (S_N2)

S_N2活泼性：



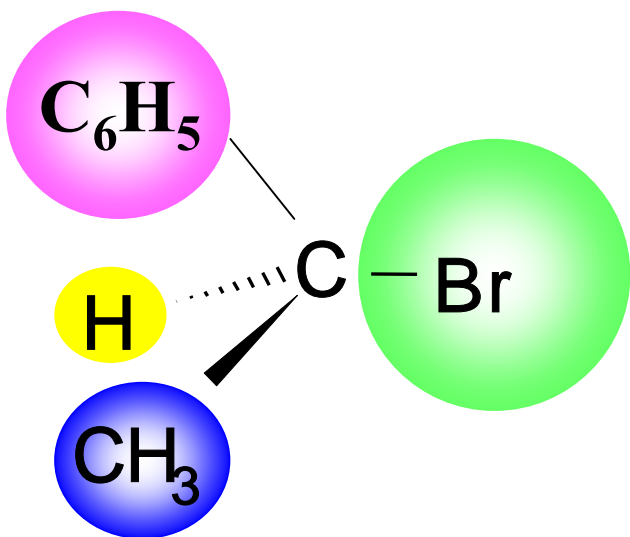
从左至右，随着烃基的增多，过渡状态的拥挤程度增大，反应速度降低。



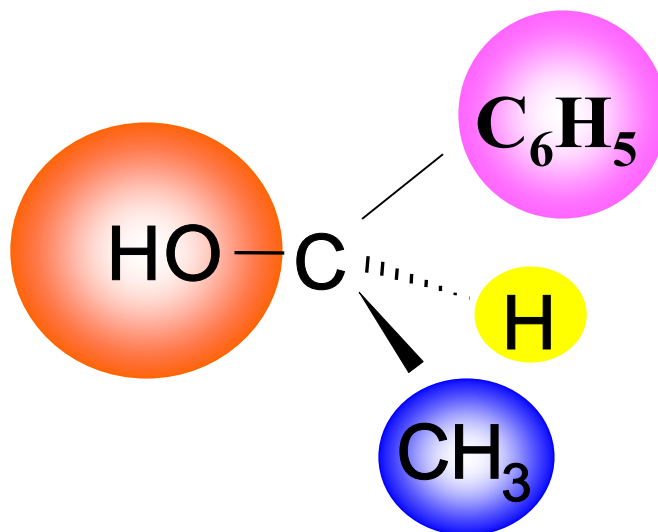
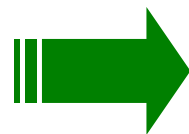
具C*反应物

过渡态

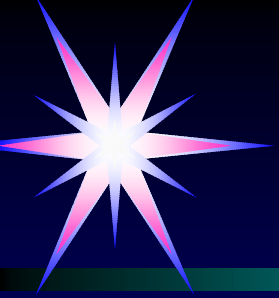
构型翻转



具C*反应物



构型翻转(瓦尔登)



影响亲核取代反应的因素

A. 烃基结构：

一般叔 S_N1 ；仲 S_N1 、 S_N2 ；伯 S_N2

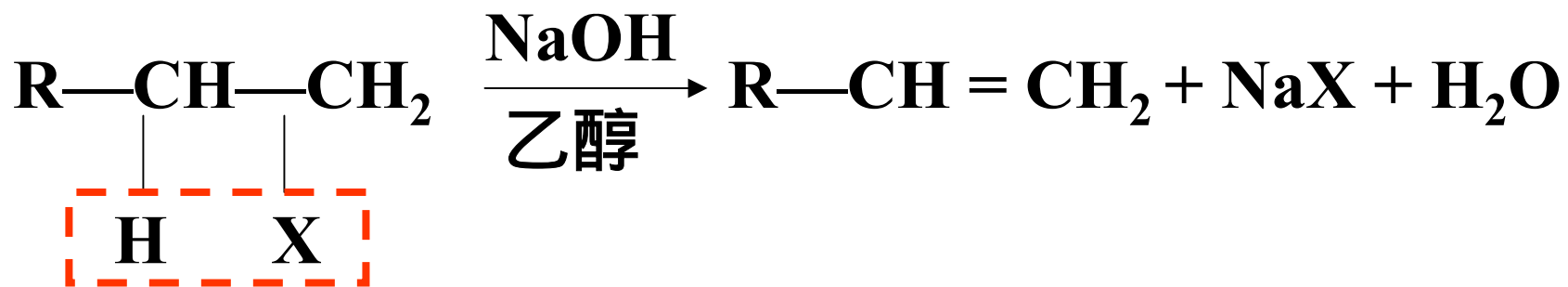
B. 卤素：

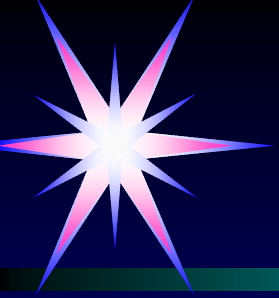
R - 相同时， $R - I > R - Br > R - Cl$



2. 消除反应

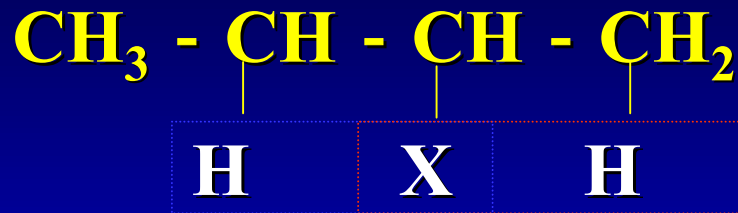
有机物分子中相邻两个碳上脱去一个小分子而形成双键的反应。





消除反应

取向：



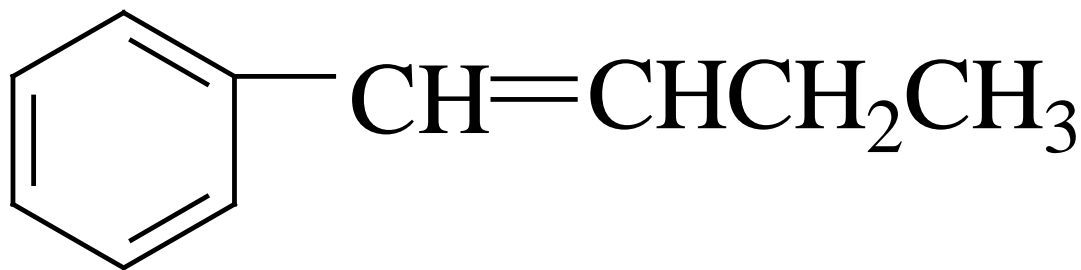
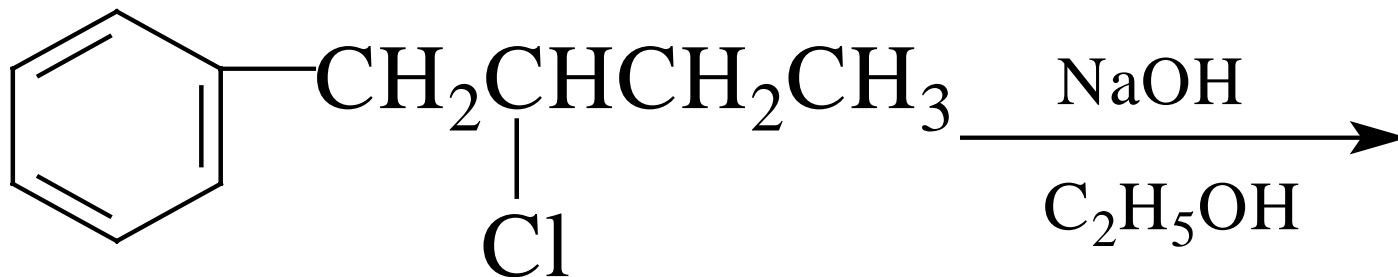
NaOH

乙醇

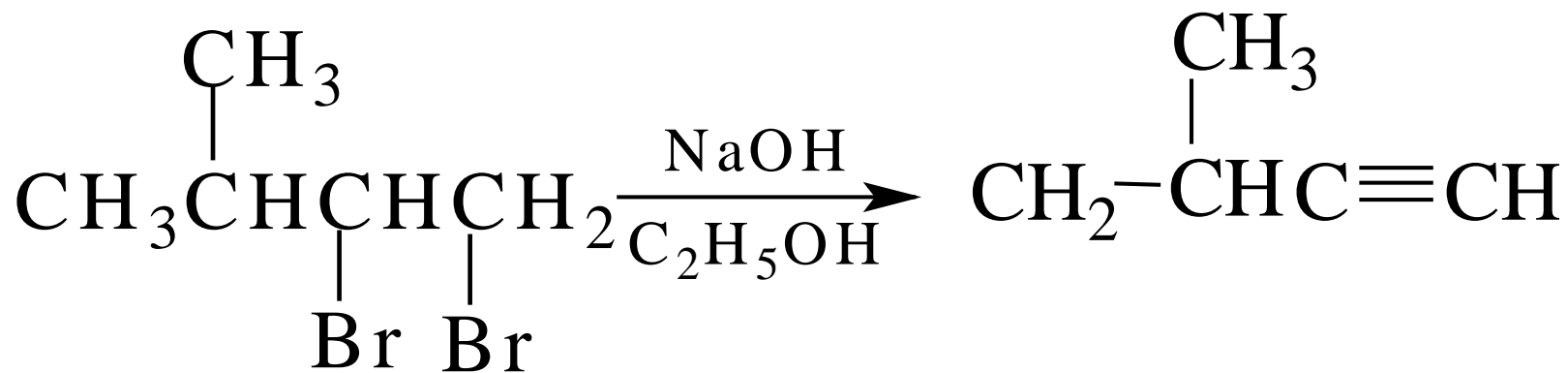
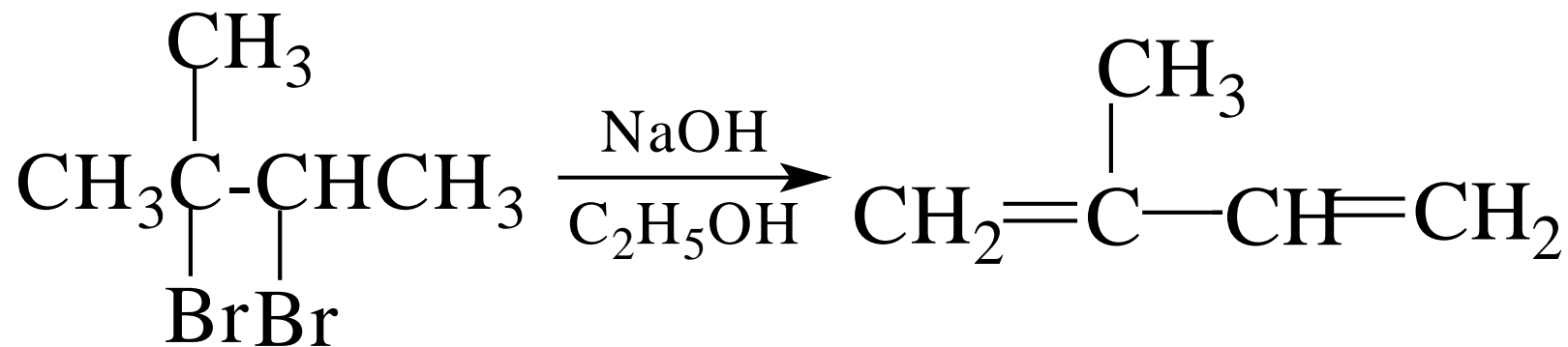


查依采夫规则：卤代烷在消除卤化氢时，卤原子主要与相邻含氢较少碳上的氢脱去卤化氢。

练习



练习





3. 与金属反应

(1) 与金属 Na



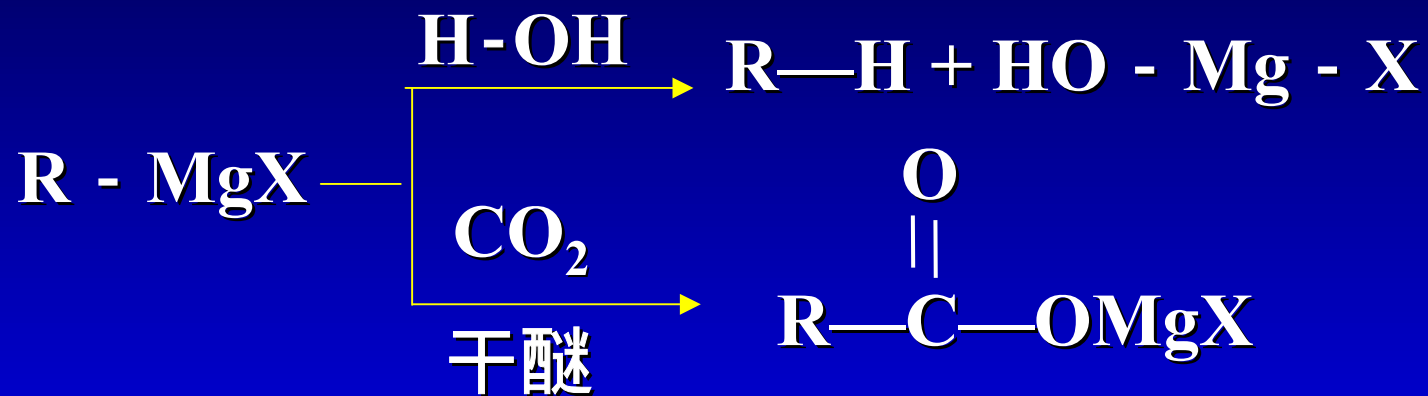
武慈反应适用于同种伯卤代烃

(2) 与金属 Mg



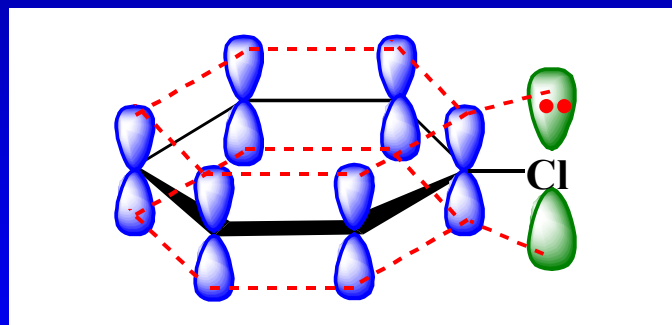
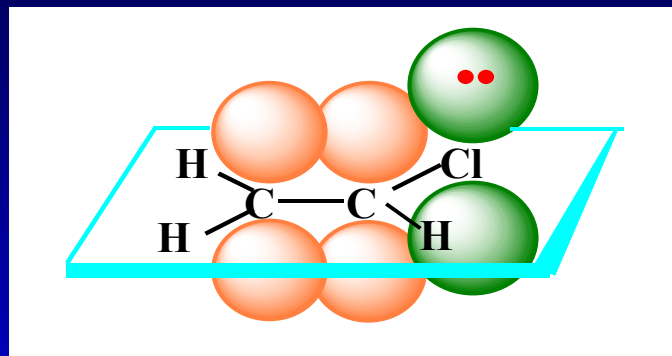
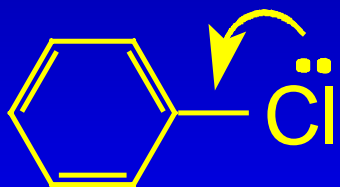


与金属 Mg 反应



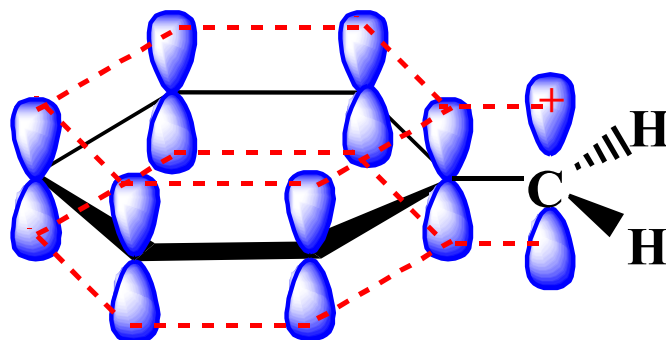
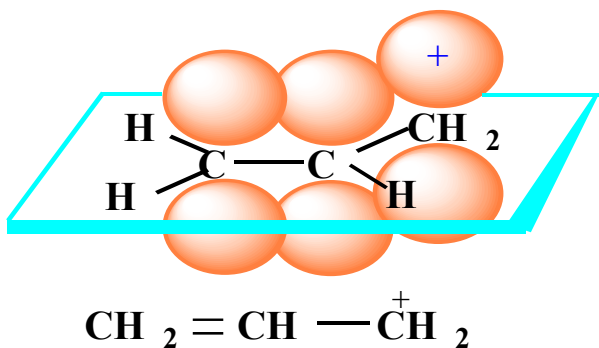
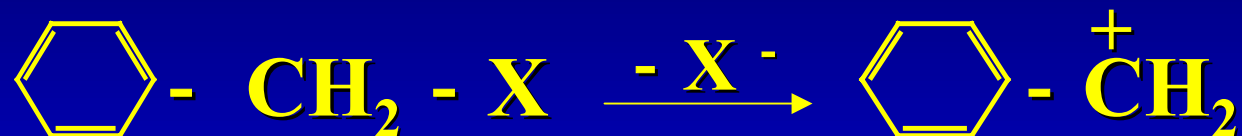
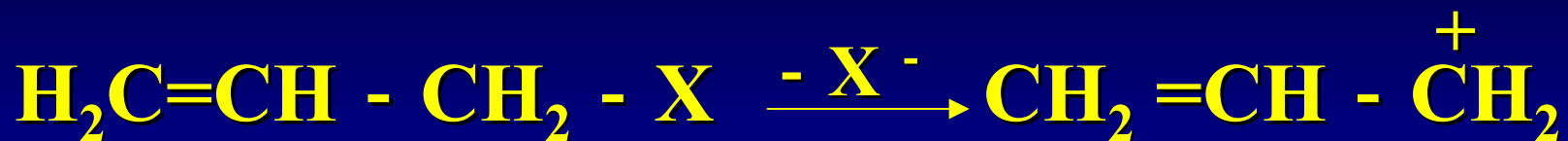
三、卤代烃化学结构与化学活性的关系

1. 乙烯型和芳基型

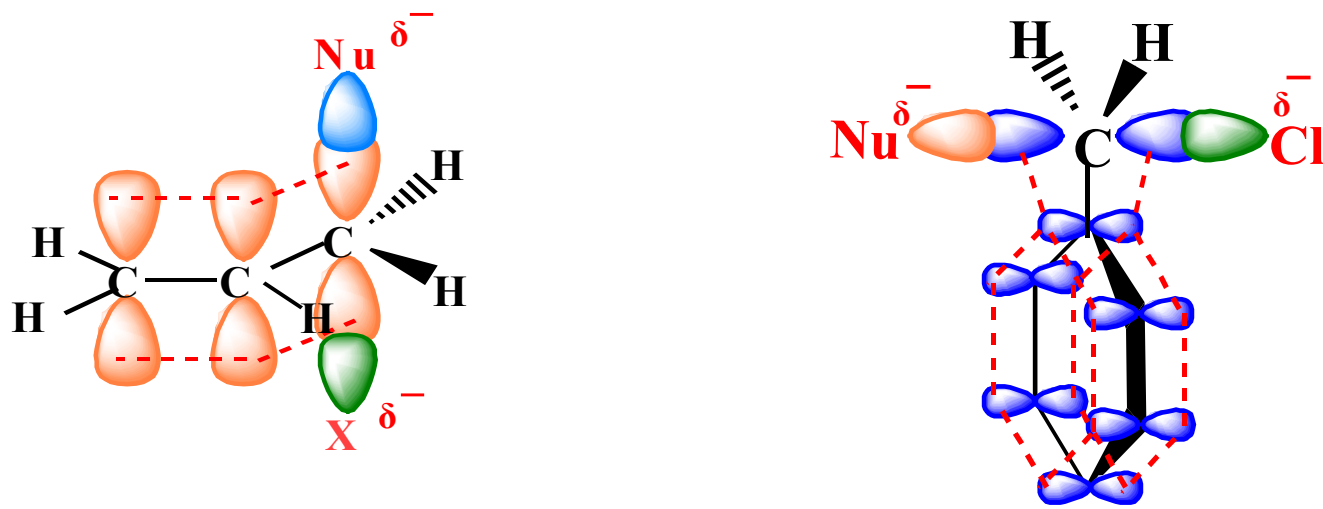


不活泼：一般不发生取代反应，加成仍遵守马氏规则。

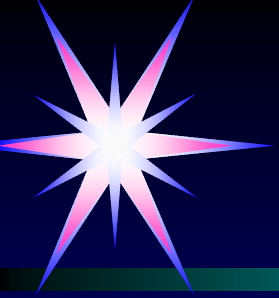
2. 烯丙基型和苄基型



S_N2



非常活泼：很容易发生取代反应，加成仍遵守马氏规则。

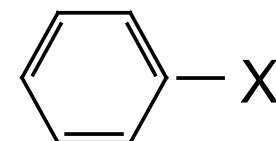
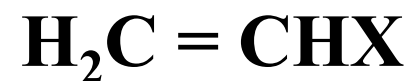
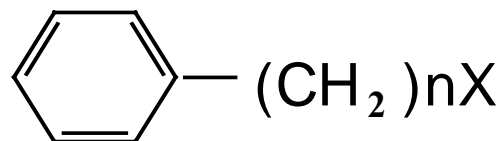
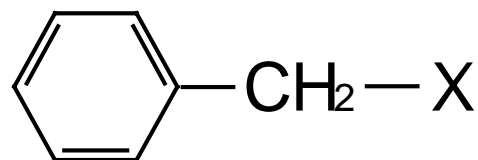


3. 隔离型卤代烯和卤代芳烃



活性同相应的烯烃与卤代烷烃

不同卤代烃活性次序

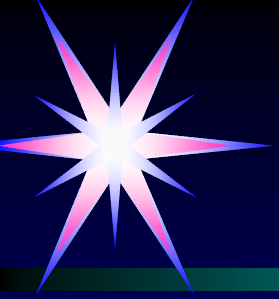


$\text{AgNO}_3/\text{乙醇}$

立即

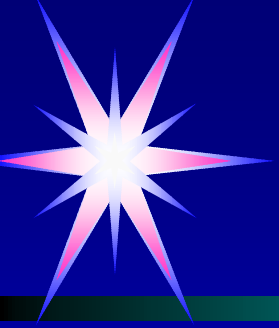
×

烯丙基型和苄基型 > 隔离型 > 乙烯型和芳基型



第七章 重点讲解问题

1. 卤代烃的命名和异构现象
2. 卤代烃的化学性质
3. 卤代烃化学结构与化学活性的关系



再见
Good-bye

