



# § 8. 卤代烃

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- 8.1 卤代烃的分类及命名
- 8.2 化学性质I --- 亲核取代反应
- 8.3 化学性质II --- 亲核取代反应机理
- 8.4 化学性质III - 消除反应
- 8.5 化学性质IV -- 与金属反应
- 8.6 化学性质V -- 还原反应
- 8.7 总结



## 8.1 卤代烃的分类及命名

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### 1、分类：

#### A. 按含卤原子的个数分类

- a. 单卤代                      b. 多卤代

#### B. 按卤原子所连的碳分类

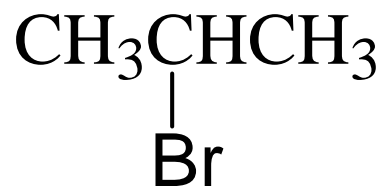
- a.  $1^\circ$  (伯) 卤代烷  
b.  $2^\circ$  (仲) 卤代烷  
c.  $3^\circ$  (叔) 卤代烷

## 2、命名：

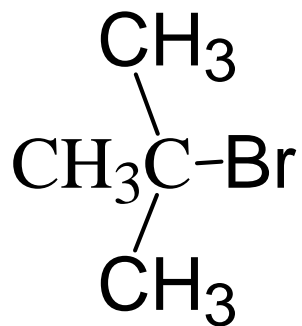
### A. 普通命名法：



(正) 丙基溴



异丙基溴



叔丁基溴

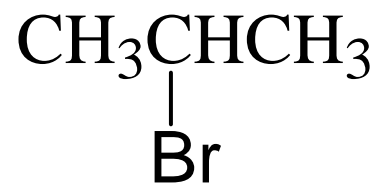


## B. 系统(IUPAC)命名法:

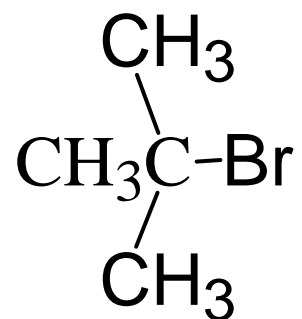
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1-溴丙烷



2-溴丙烷

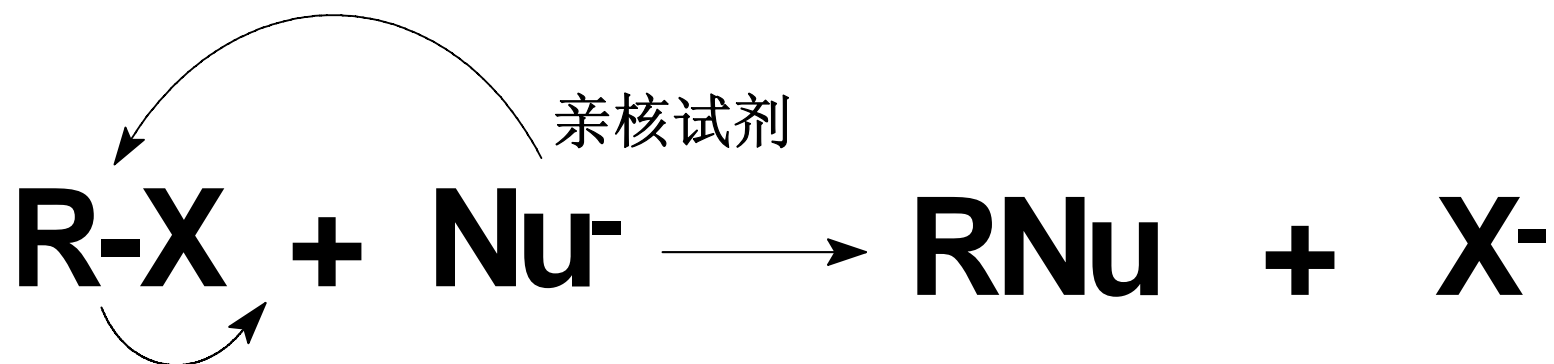


2-甲基-2-溴丙烷

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## 8.2 化学性质I --- 亲核取代反应

### ■ 1、亲核取代反应

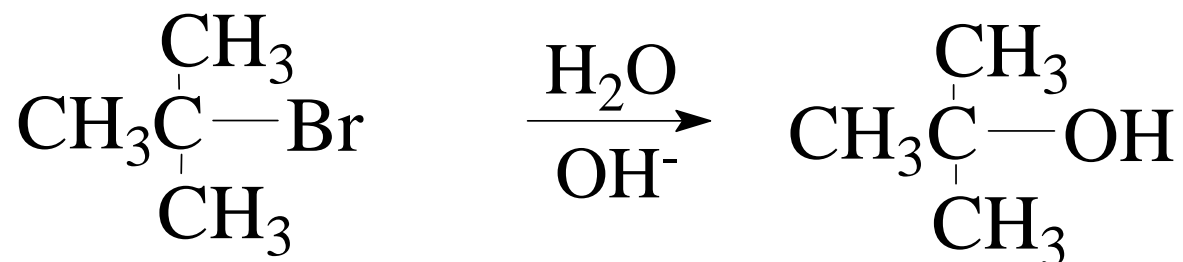
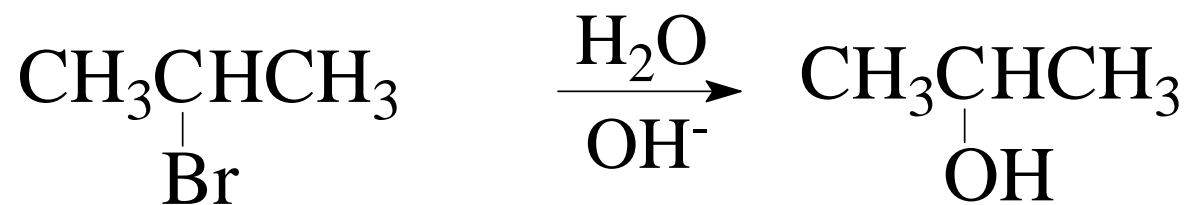
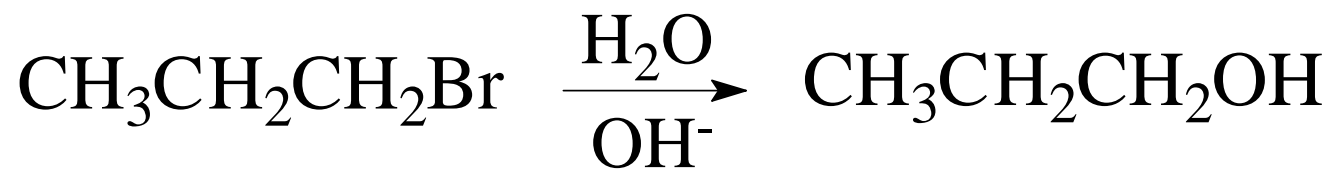


- A. 水解反应      B. 醇解反应  
C. 酸解反应      D. 氨解反应  
E. 氰解反应

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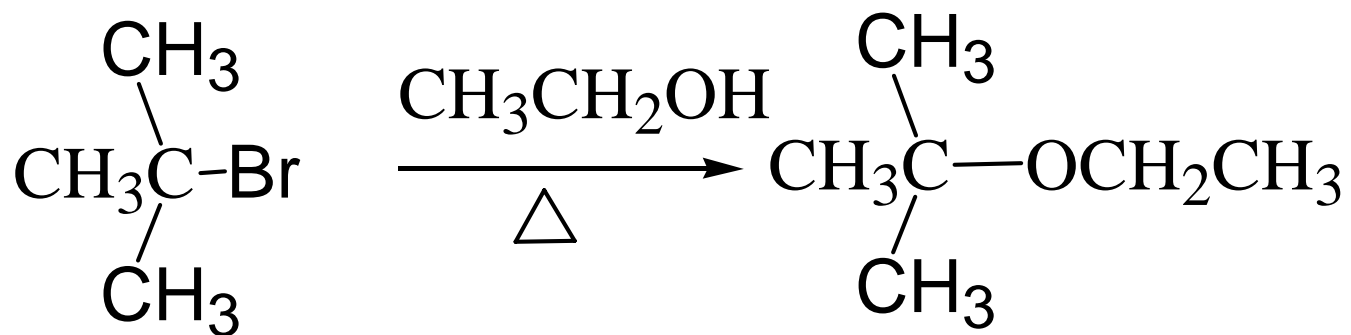
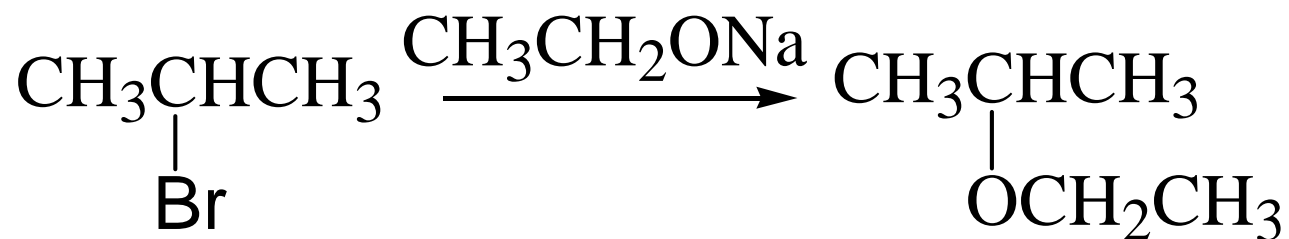
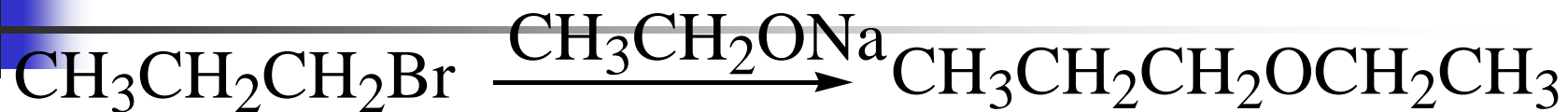


## A. 水解反应

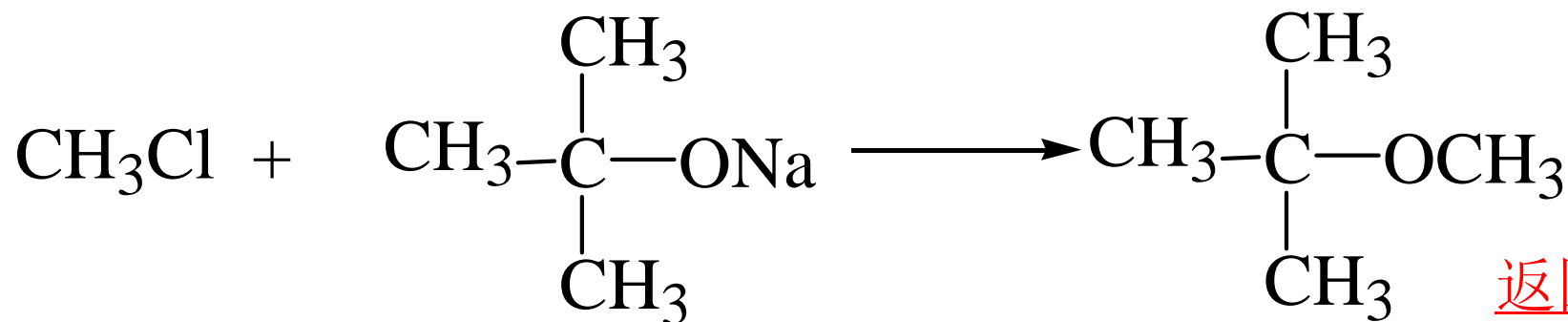
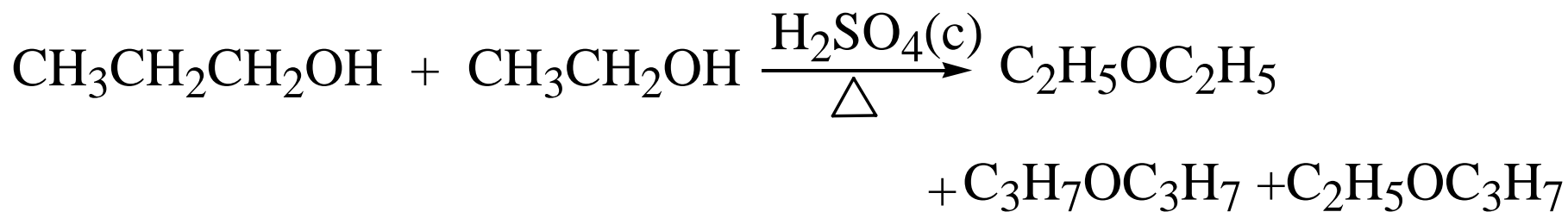
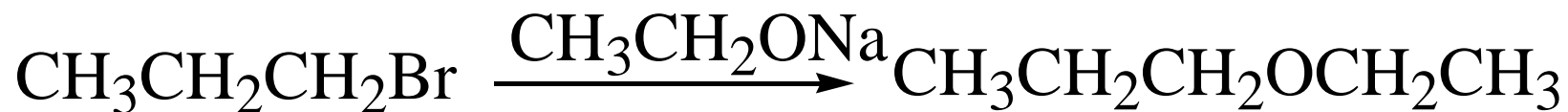


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## B. 醇解反应



## Willimenson法合成醚



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## C. 酸解反应

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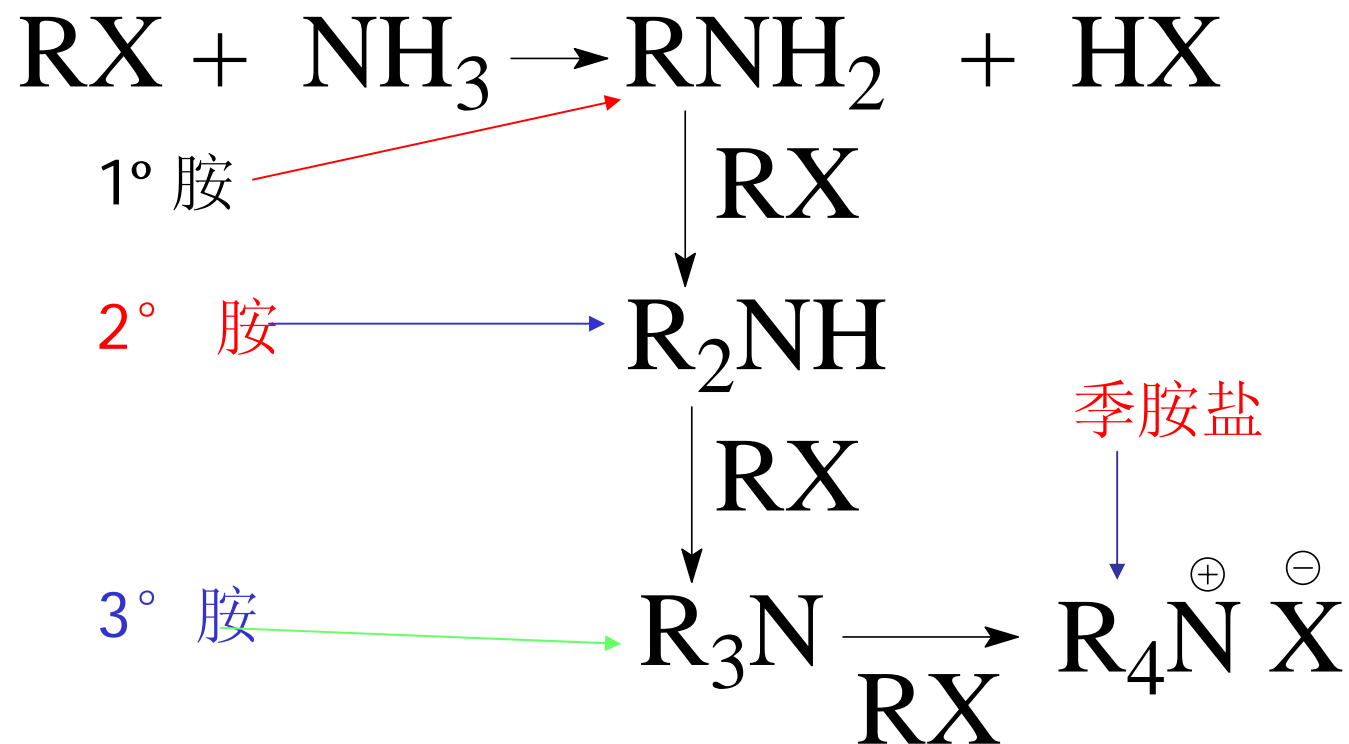


如：



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## D. 氨 (胺) 解反应



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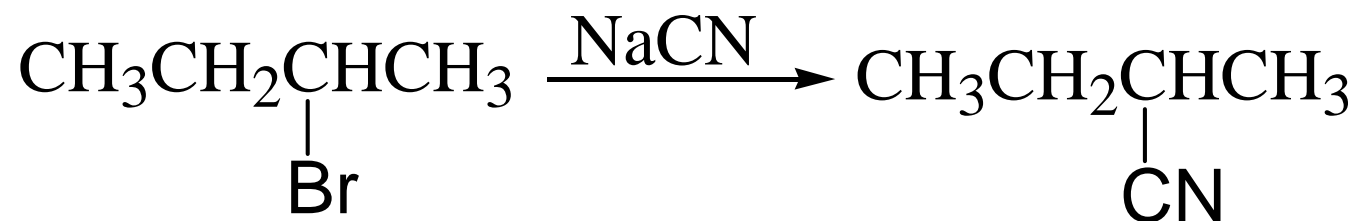


## E. 氰解反应

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如：

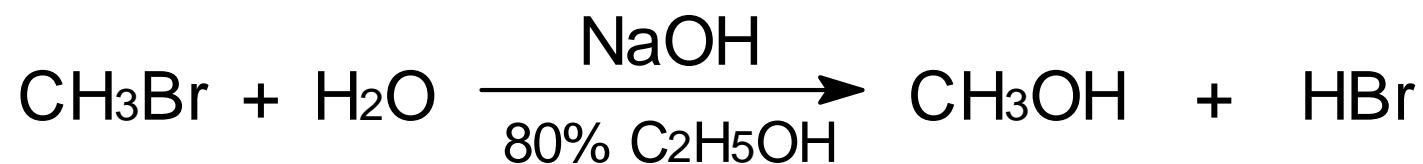


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## 8.3 化学性质II---亲核取代反应机理

### 动力学研究

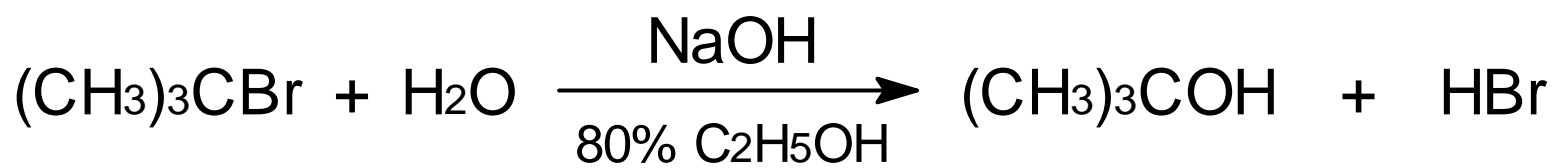
■ A



- 反应速率  $v = k[\text{CH}_3\text{Br}][\text{OH}^-]$
- a. 反应速率同时与两反应物浓度有关
- b. 双分子亲核取代机理,  $\text{S}_{\text{N}}2$

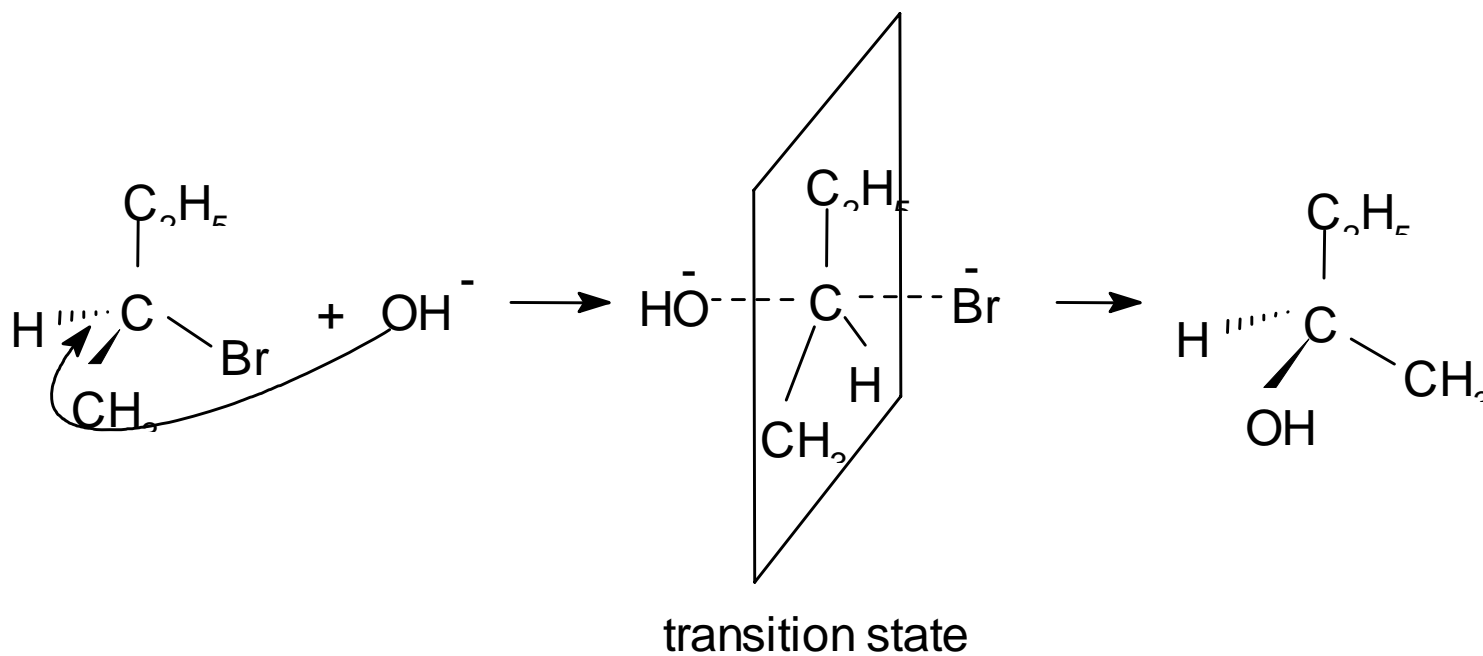


■ B



- 反应速率  $v = k[(\text{CH}_3)_3\text{CBr}]$
- a. 反应速率同时仅与反应物  $(\text{CH}_3)_3\text{CBr}$  浓度有关
- b. 单分子亲核取代机理,  $\text{S}_{\text{N}}1$

# $S_N2$ 反应历程

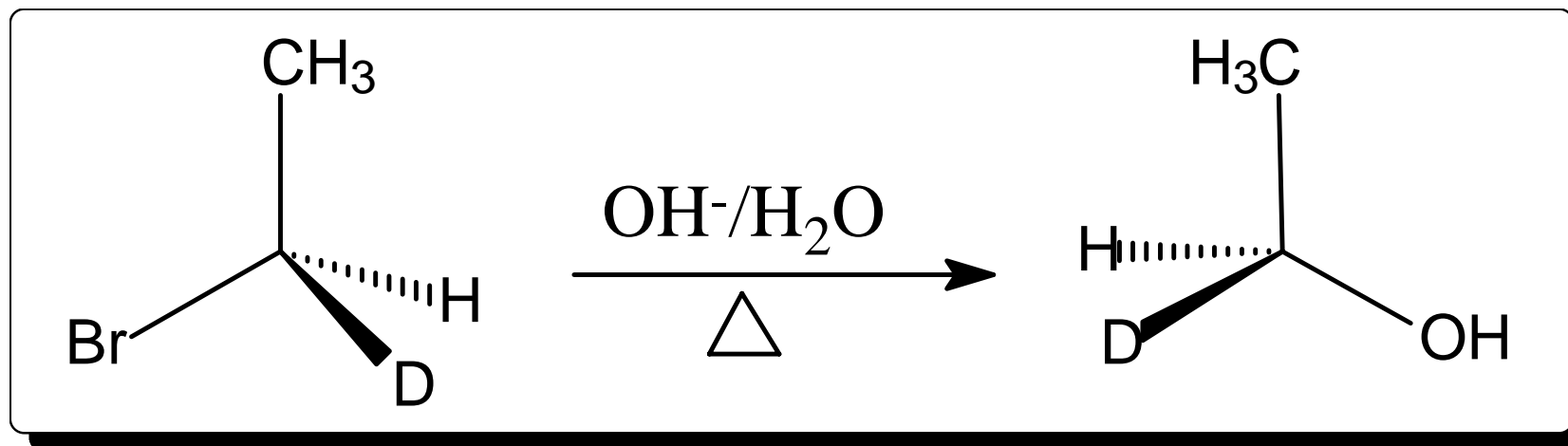




## SN2反应特点:

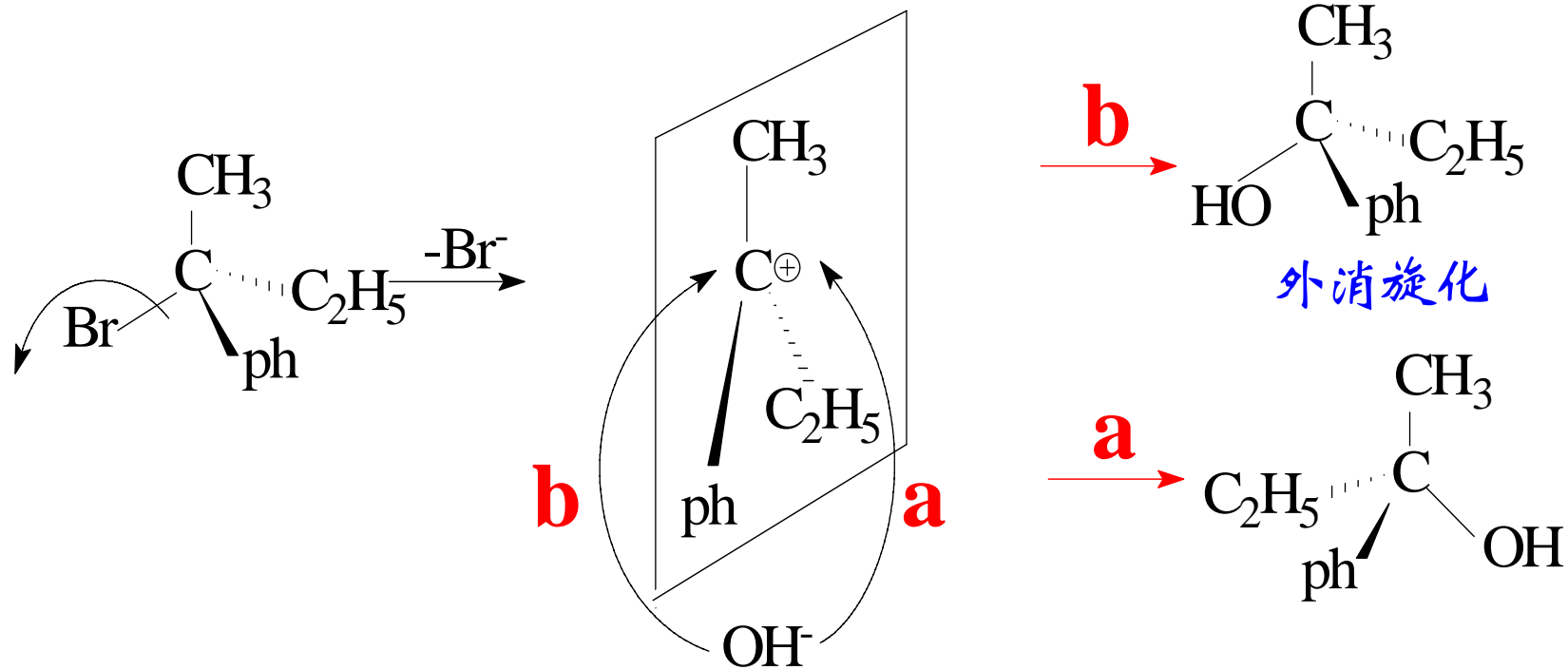
- a. 亲核试剂沿C-X键轴背面进攻，然后  
■ 后再断裂C-X键；
- b. 过渡态有五个基团，中心原子由  
■  $sp^3$ 杂化转化为 $sp^2$ 杂化；排斥力加  
■ 大，空间影响显著；
- c. 反应后构型发生翻转；
- d. 亲核试剂的亲核性强对反应有利。

# $S_N2$ 反应立体化学: 构型翻转





# SN1 反应历程

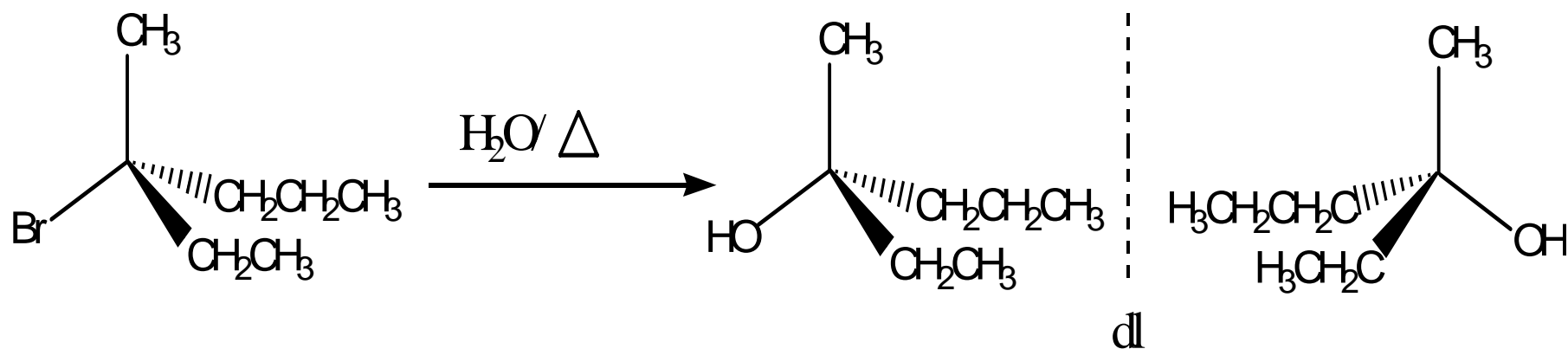




## SN1 反应特点:

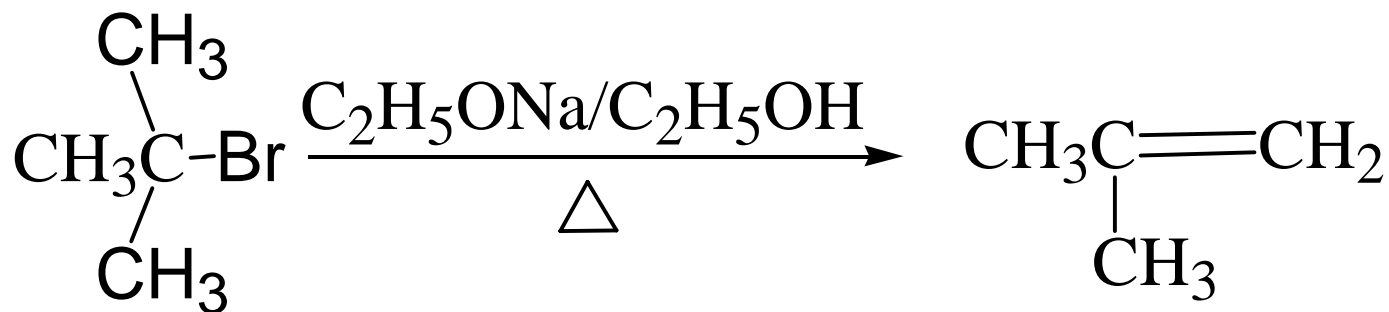
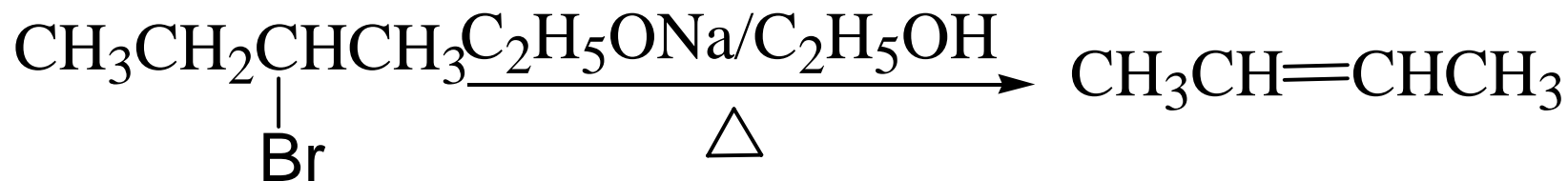
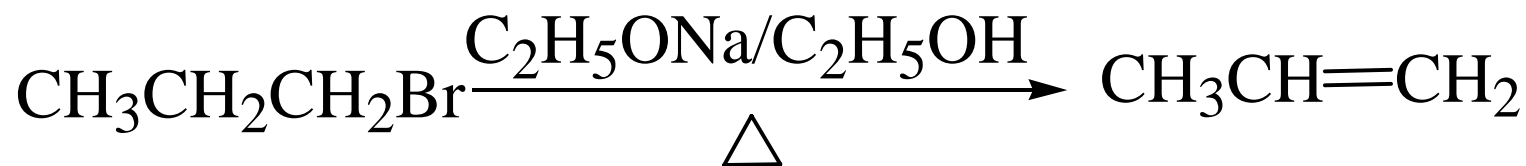
- a. C-X键首先断裂形成碳正离子;
- b. 过渡态为平面结构, 中心原子由 $sp^3$ 杂化转化为 $sp^2$ 杂化;
- c. 亲核试剂可以从碳正离子两侧与之结合, 生成等量的对映体, 即发生消旋化
- d. 与亲核试剂的亲核能力无关。

# SN1 反应立体化学：外消旋化



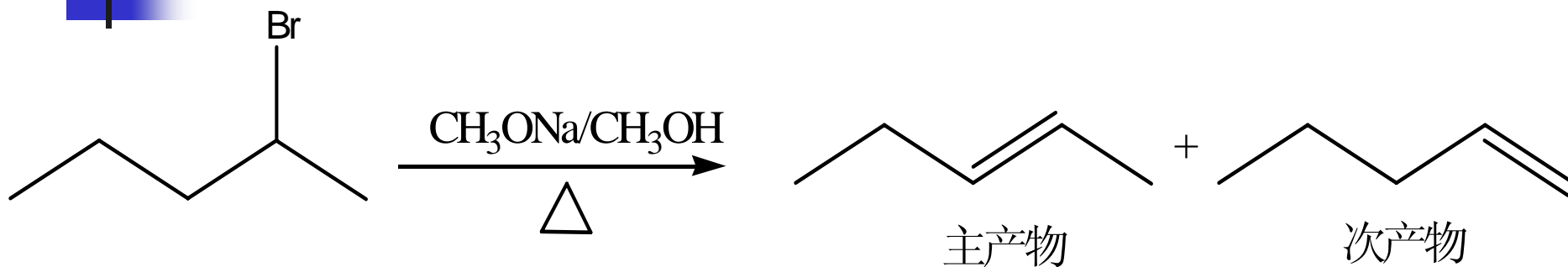
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## 8.4 化学性质III--消除反应

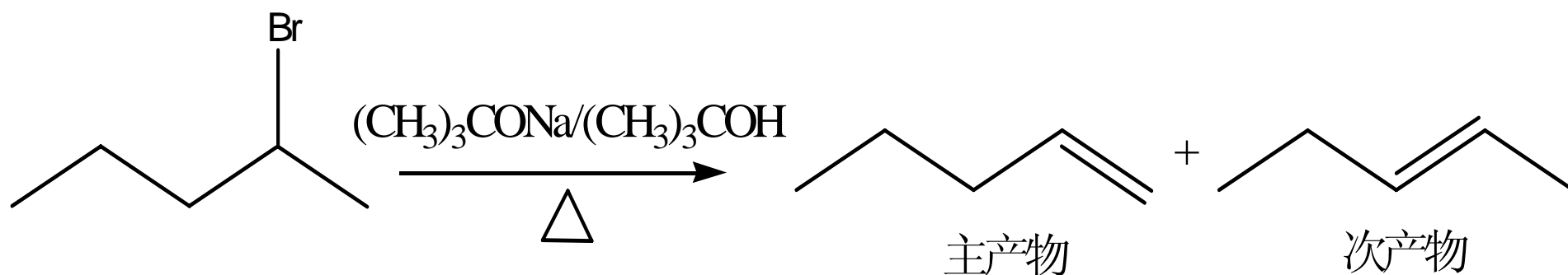


## A, 消除反应取向

Saytzerff规则：生成取代较多的烯烃

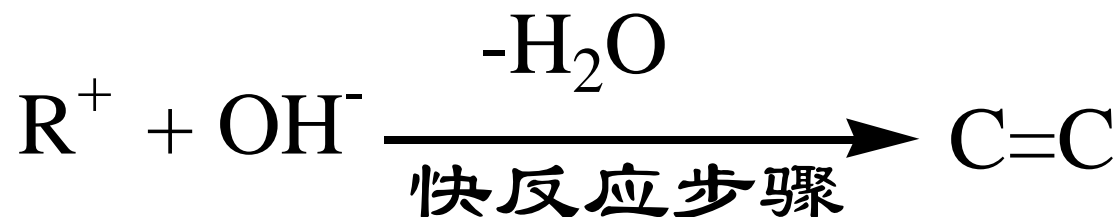
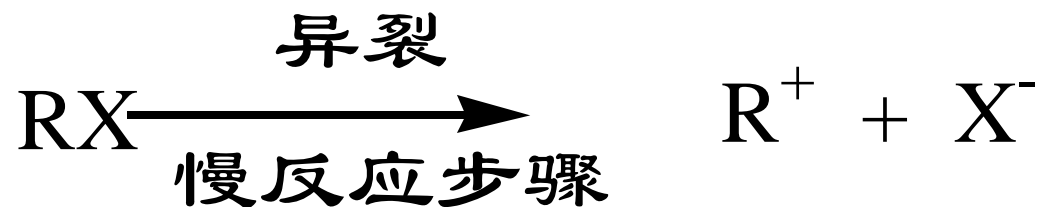


Hoffmann规则：生成取代较少的烯烃

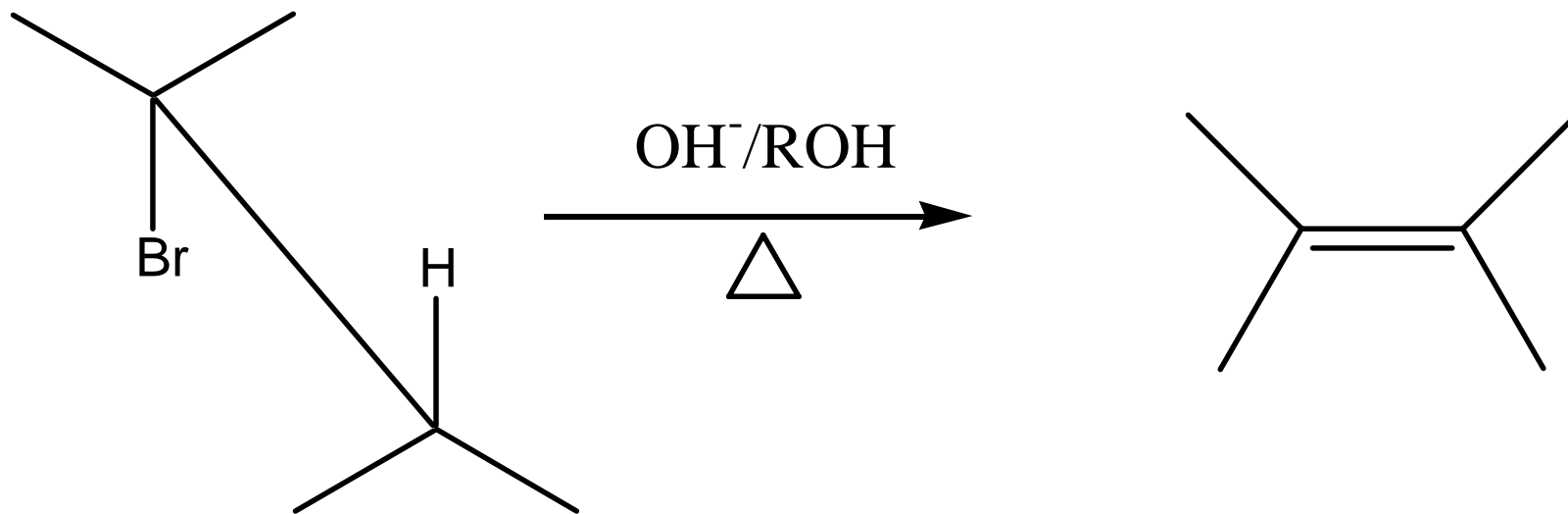


## 8. 消除反应机理及立体化学

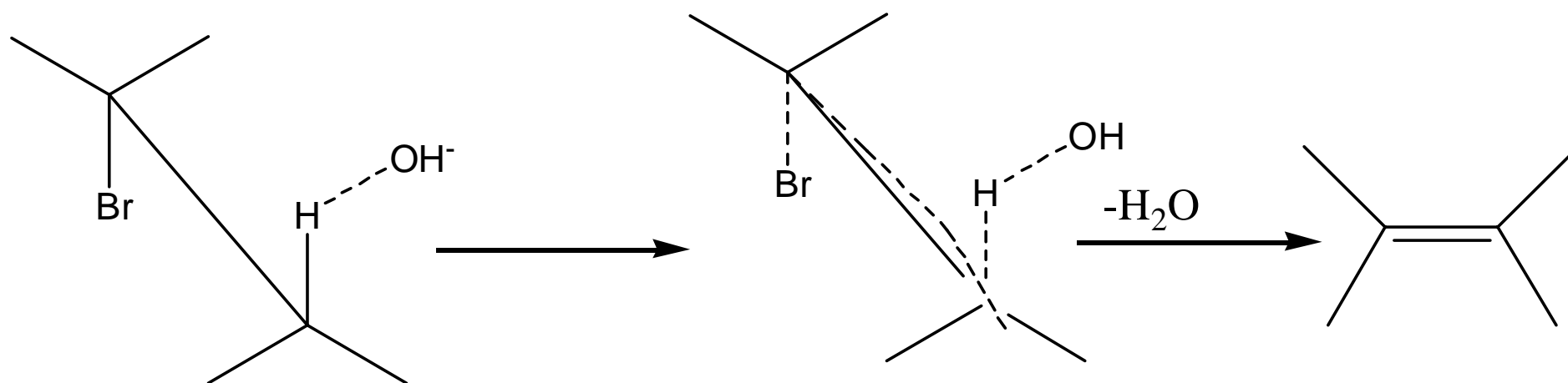
- 1. 消除反应机理
- E1: 消除反应(E)遵循一级反应动力学



# E2机理：遵循二级反应动力学

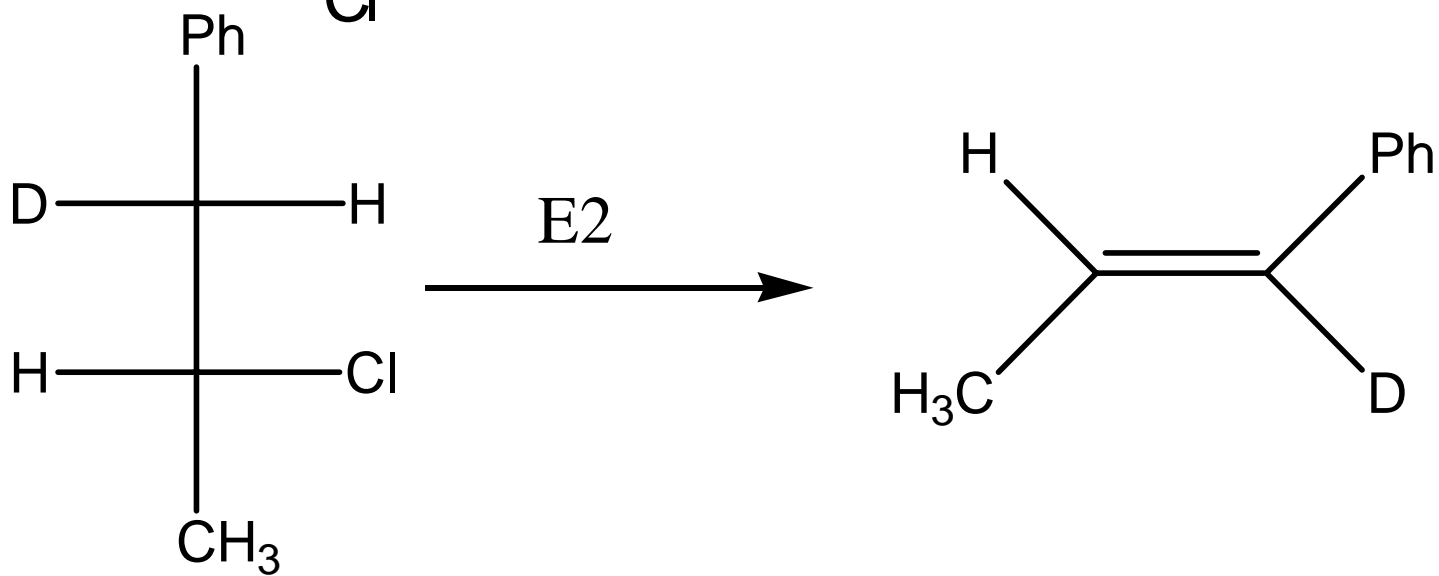
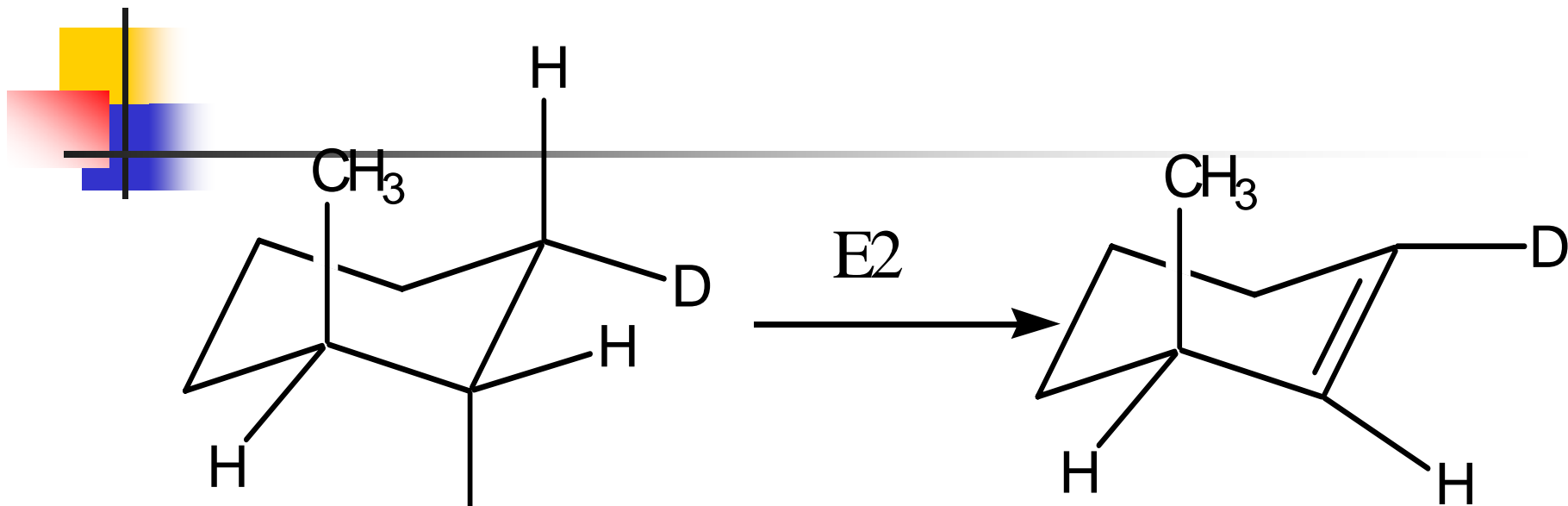


## 2, E2消除反应立体化学

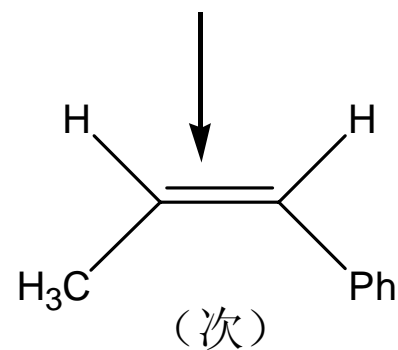
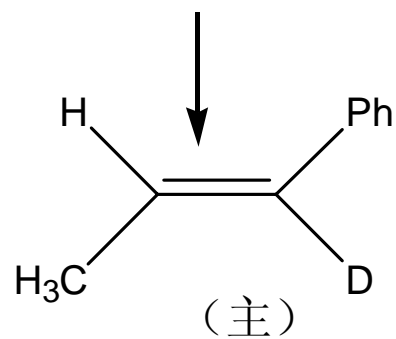
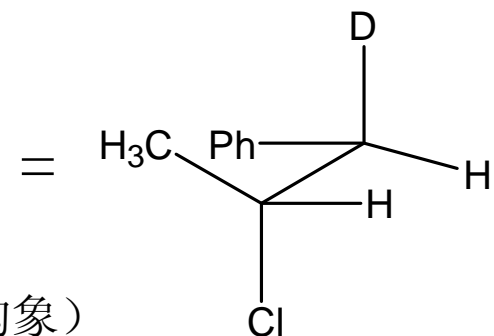
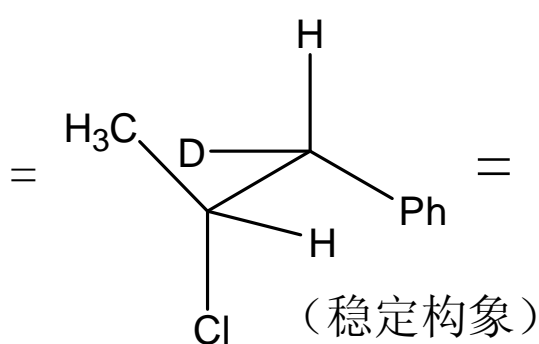
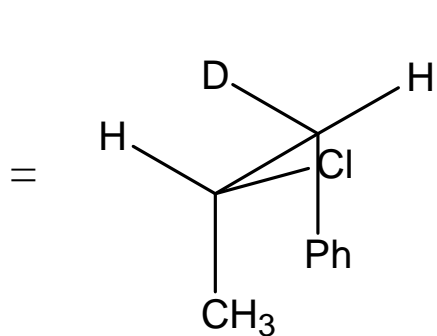
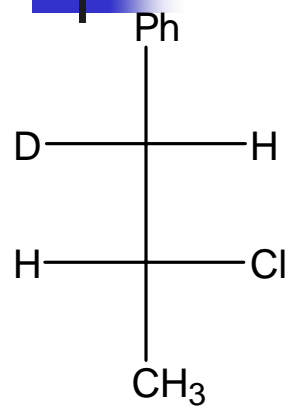


■ 立体化学：反式共平面消除！

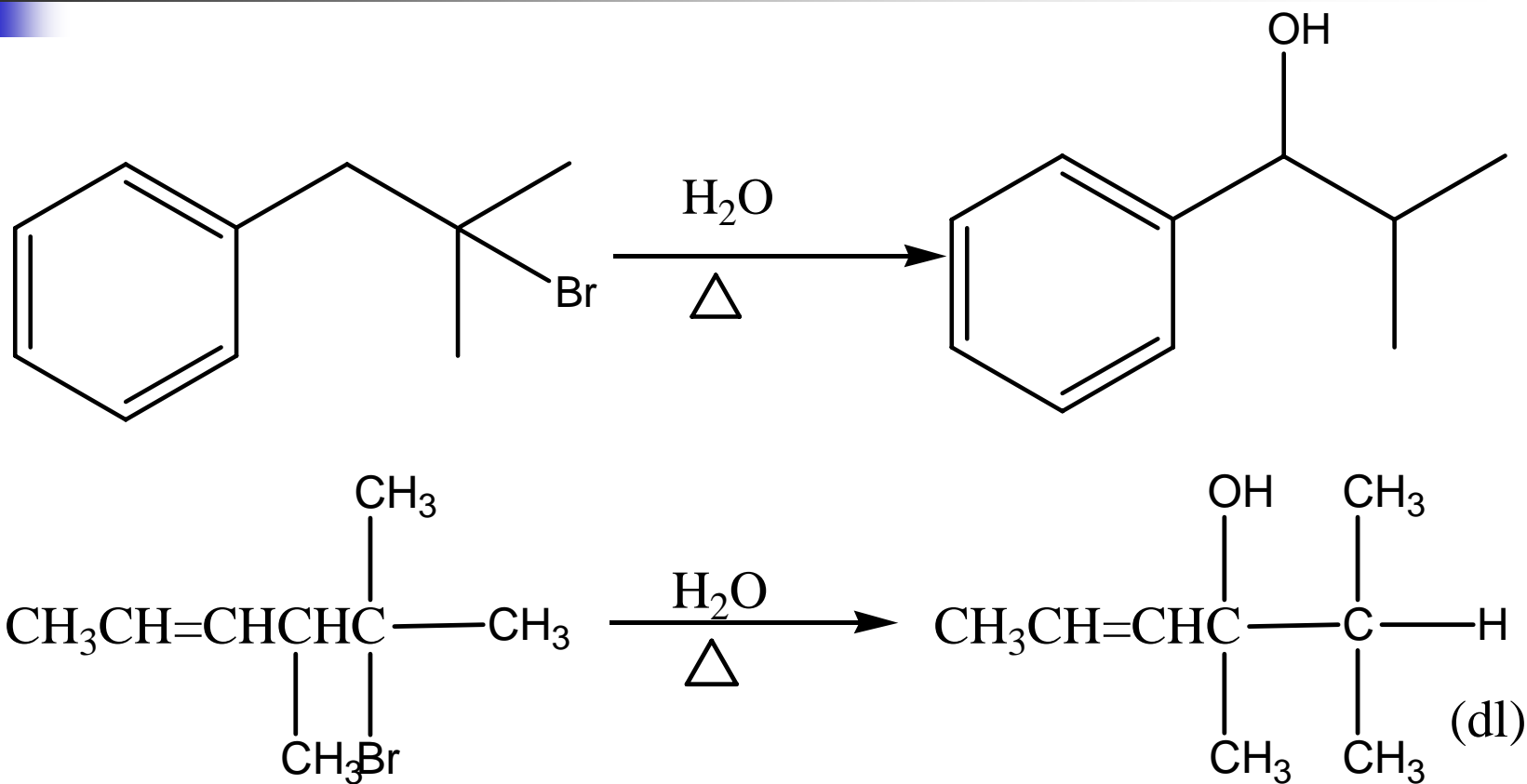


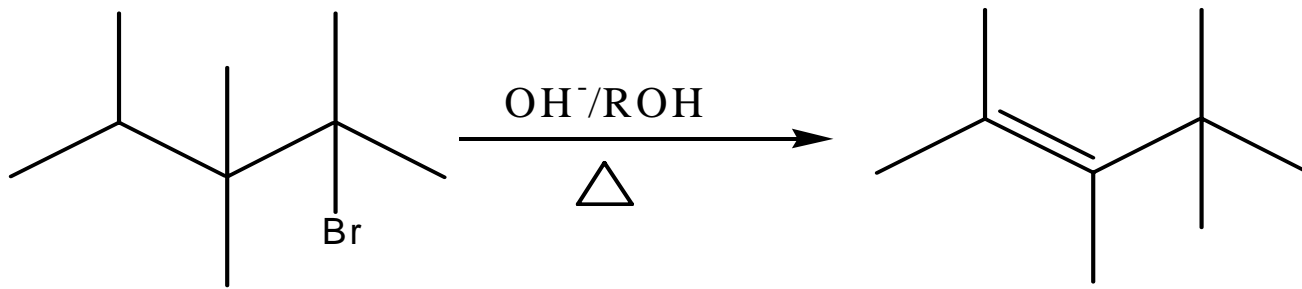
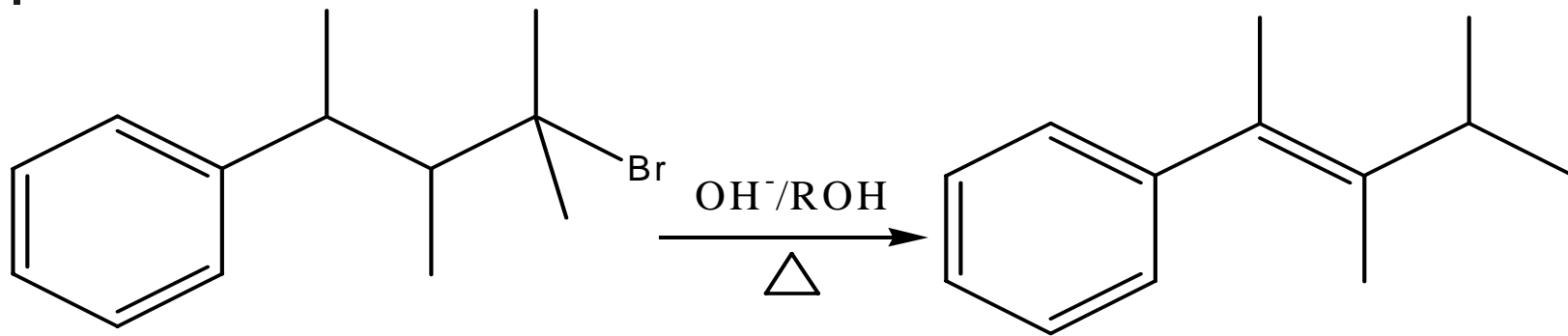
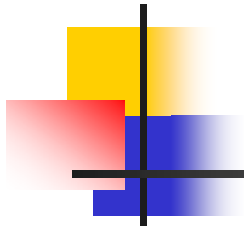


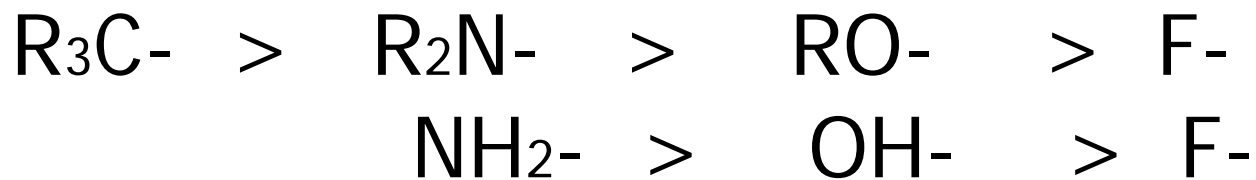
# 在稳定的构象中消除反式共平面的HX



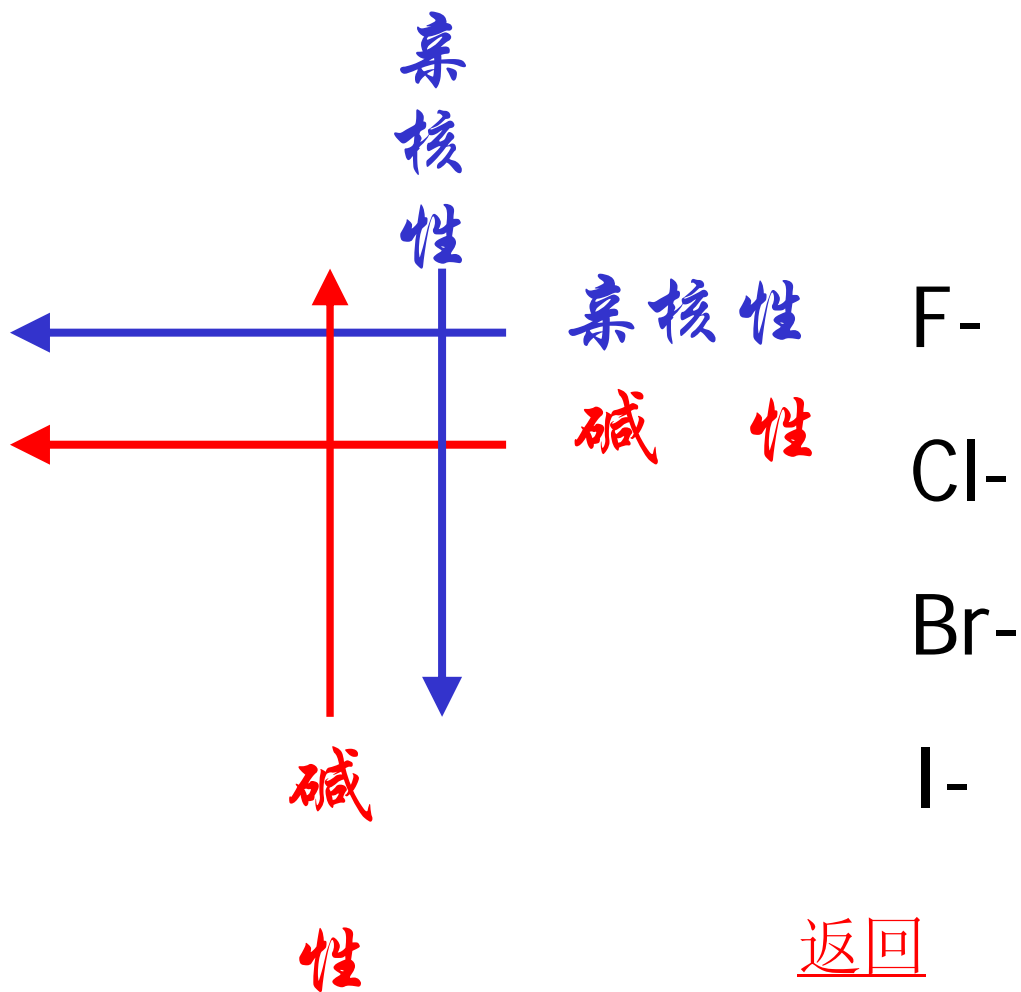
### 3, SN1及E1反应中正碳离子的重排







试剂的  
亲核性  
和碱性



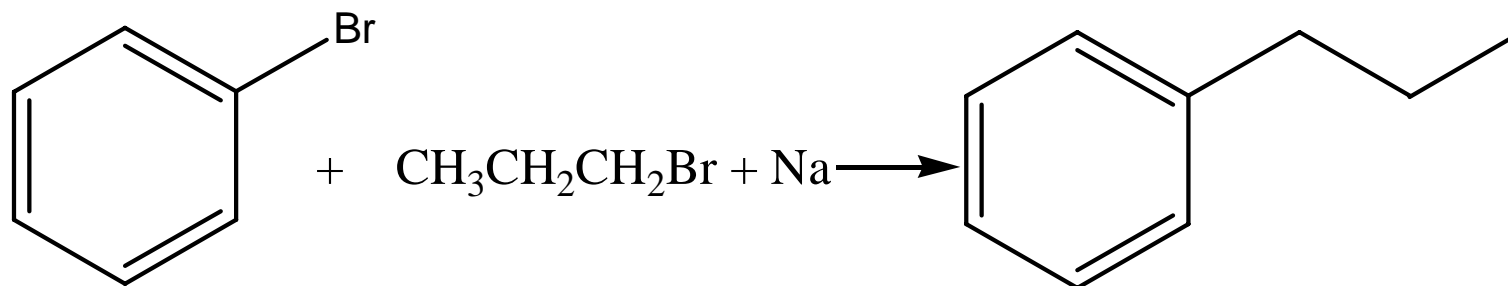
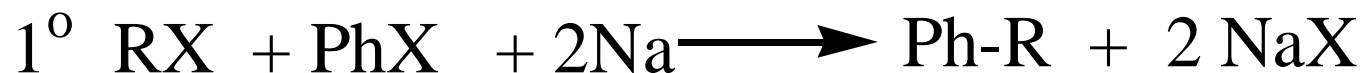
## 8.5 化学性质IV---与金属的反应

### 1. 与Na的反应

A. Wurtz反应:

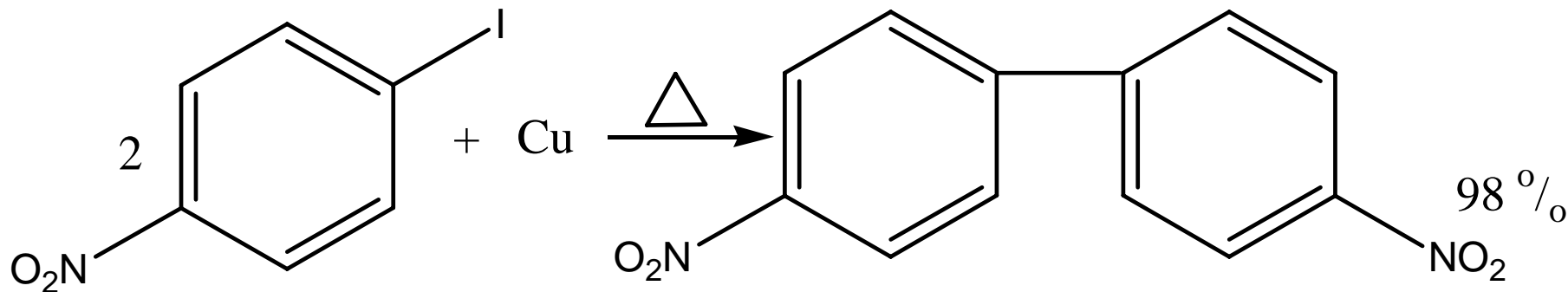
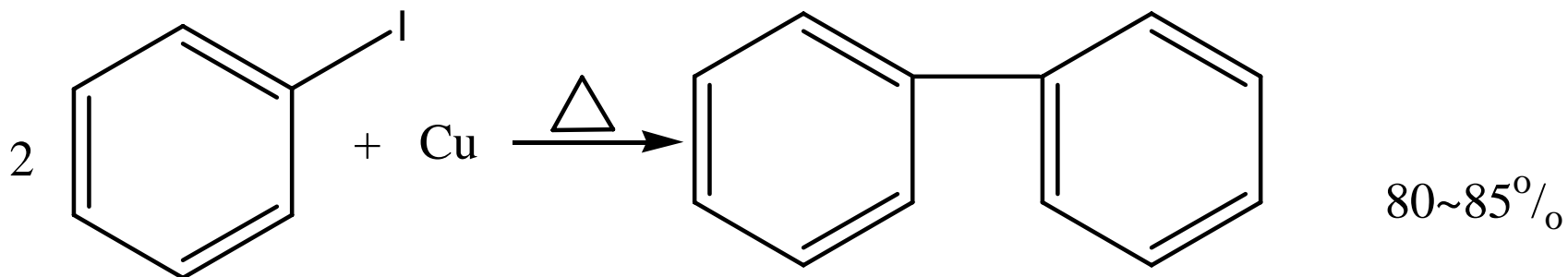
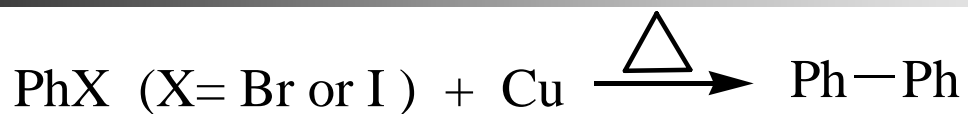


B. Wurtz-Fittig反应:



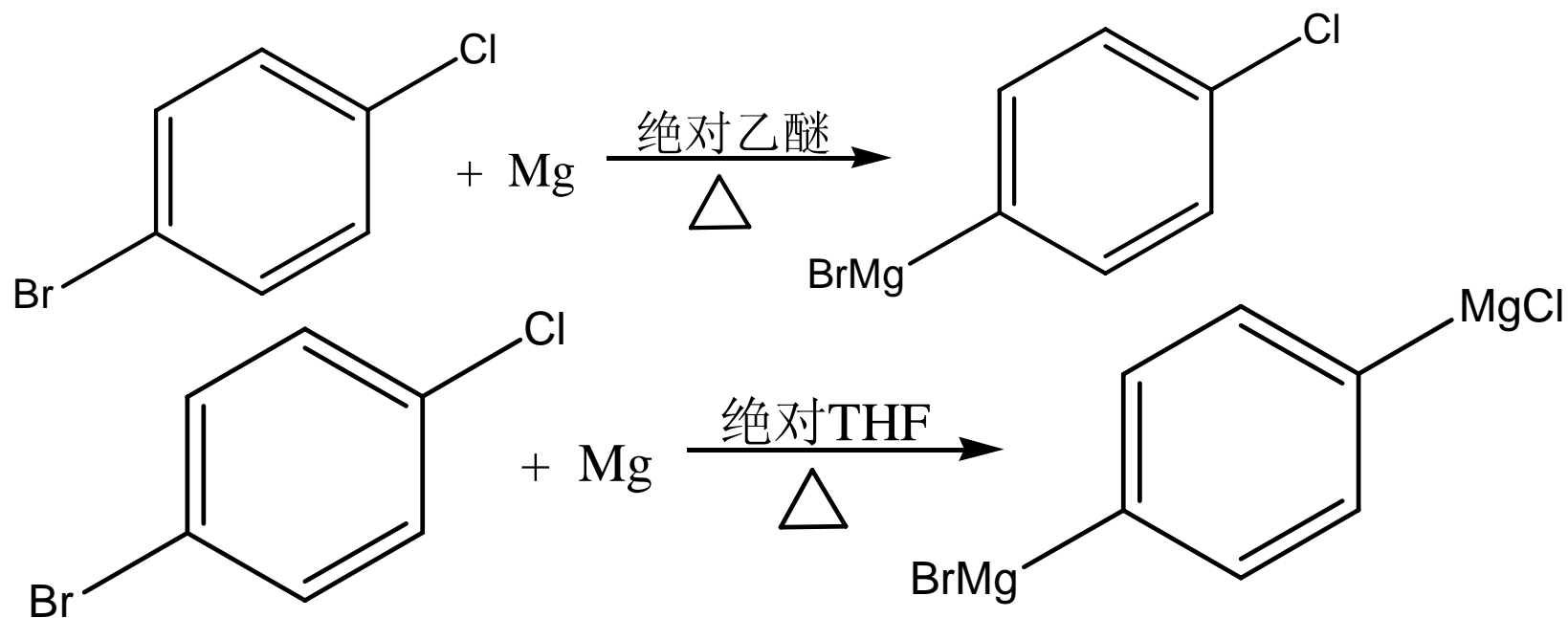
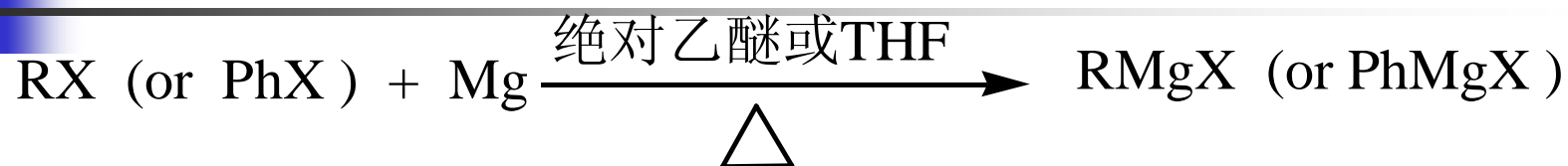
## 2. 与Cu的反应

### ■ 乌尔曼反应



### 3. 与Mg的反应

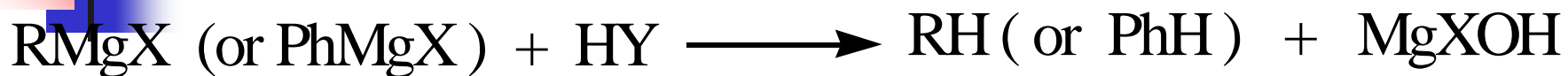
#### ■ A. 格氏试剂的制备:



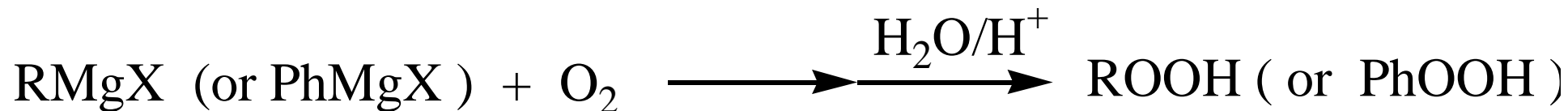
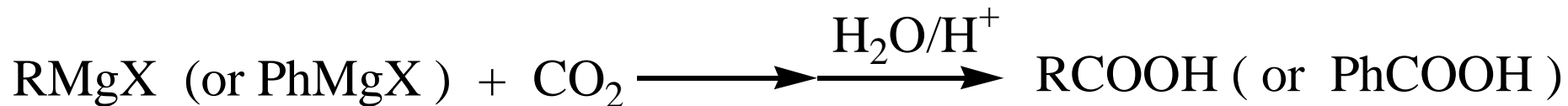


## 3. 格氏试剂的反应:

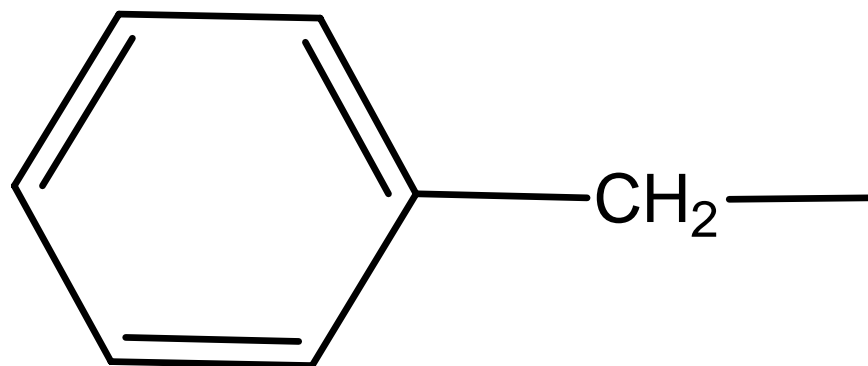
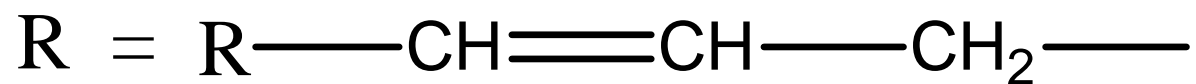
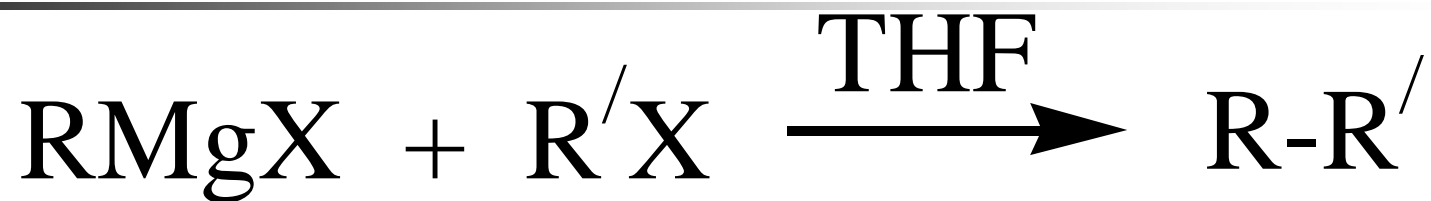
### ■ a. 与活泼氢的反应



### ■ b. 与CO<sub>2</sub>或O<sub>2</sub>的反应

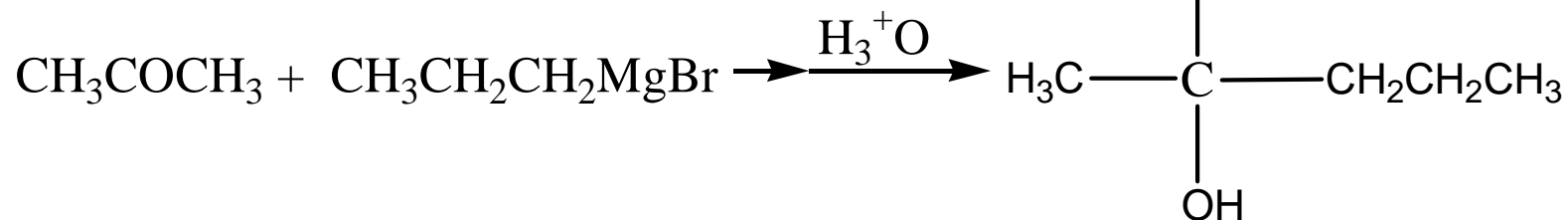
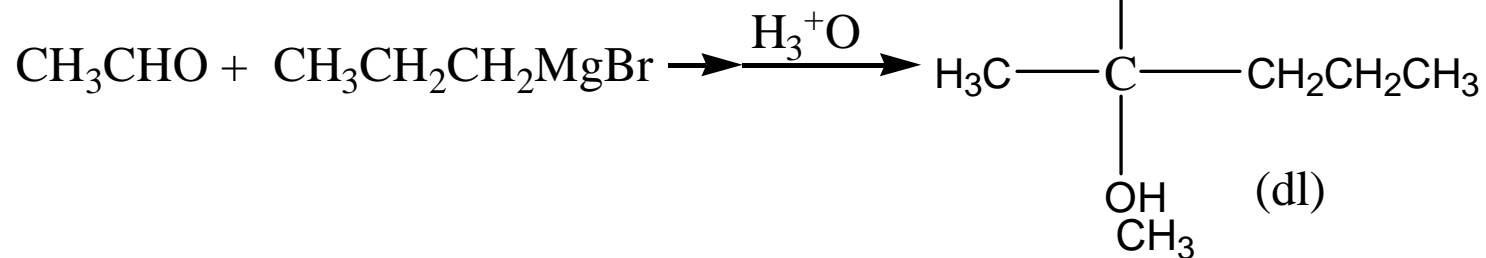
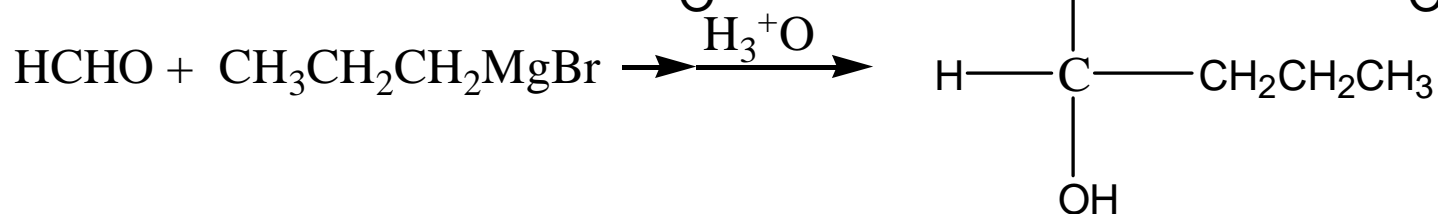
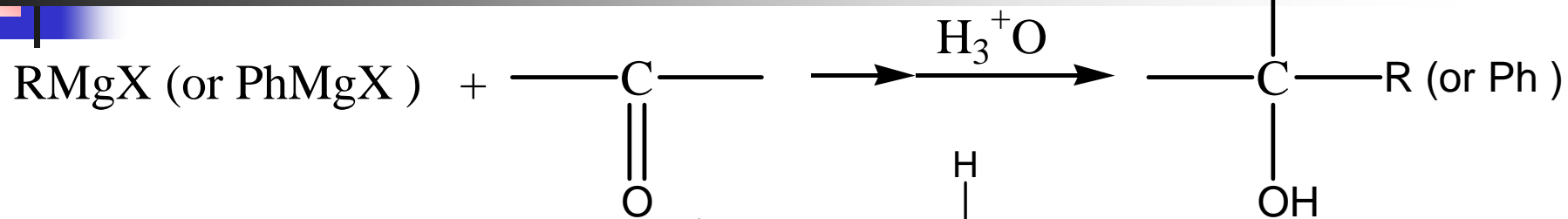


c. 与活泼卤代烃的偶联反应



3° R-

## d. 与醛或酮的加成反应---合成醇

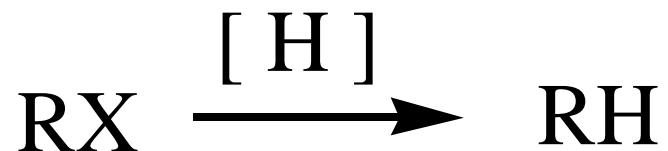


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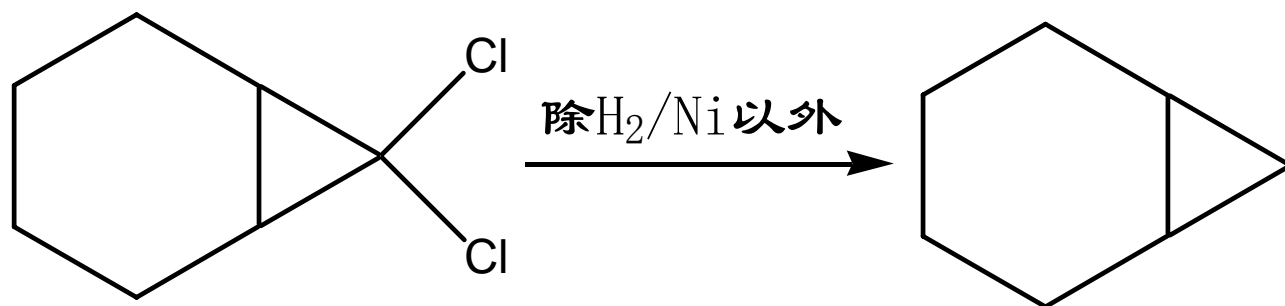
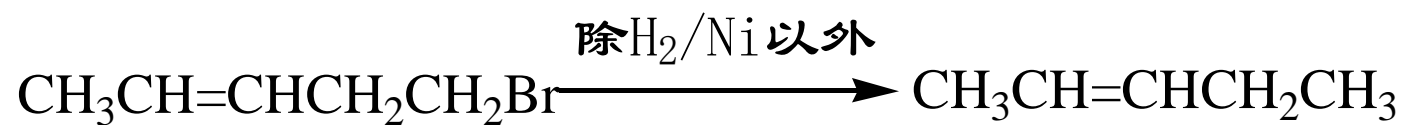
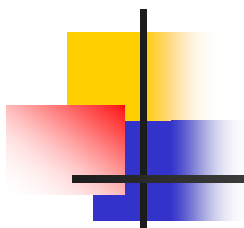
## 8.6 化学性质V --- 还原反应

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$[\text{H}] = \text{H}_2/\text{Ni}$  or  $\text{Pd}$  or  $\text{Pt}$ ;  $\text{Fe}$  or  $\text{Zn}$  or  $\text{Sn}/\text{H}^+$ ;

$\text{Na}$  or  $\text{K}$  or  $\text{Li}/\text{ROH}$ ;  $\text{NaBH}_4$ ;  $\text{LiAlH}_4$



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# 总结

- 1. 伯卤代烃易发生取代反应，叔卤代烃易发生消除反应；
- 2. 一级卤代烃，烯丙基(苄基)卤代烃按照 $S_N2$ 机理；三级卤代烃，烯丙基(苄基)卤代烃按照 $S_N1$ 机理；
- 3.  $S_N2$ 构型反转； $S_N1$ 外消旋化；
- 4. 格氏试剂用于合成各种醇。

2004年5月