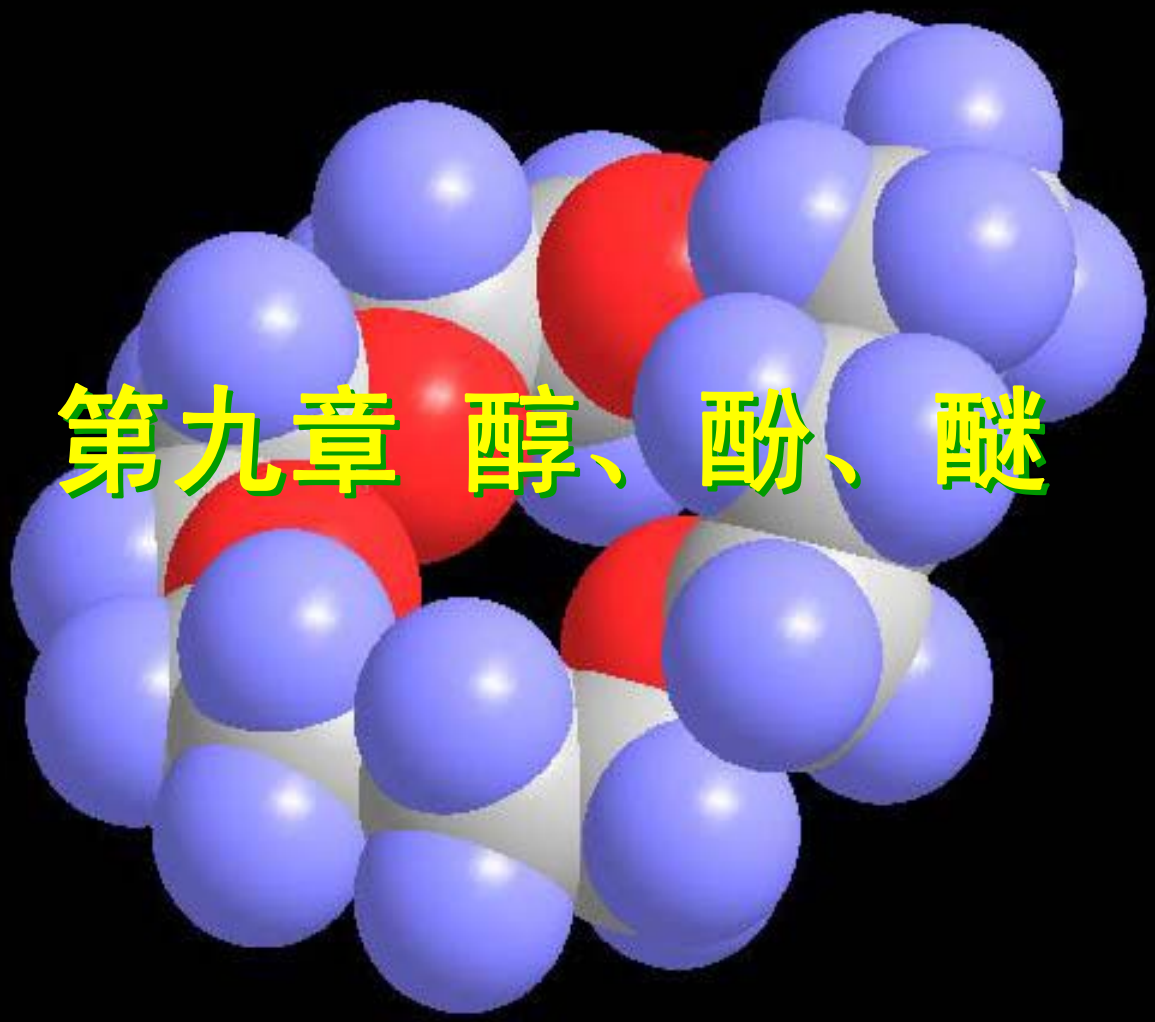
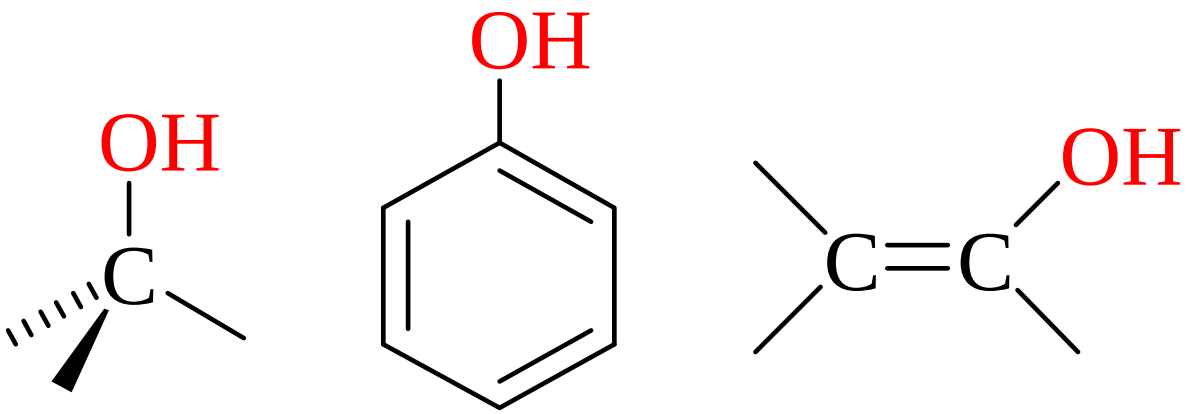


第九章 醇、酚、醚

8.1 醇

ROH 醇类

醇的官能团是羟基－OH



醇　　酚　　烯醇

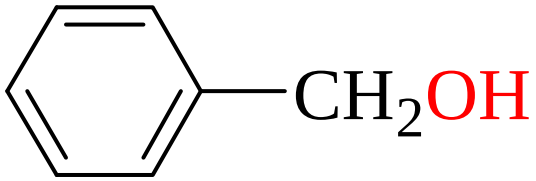
8.1.1 醇的分类和结构

1. 根据官能团所连烃基类型

$RCH_2—OH$	$R_2CH—OH$	$R_3C—OH$
伯醇	仲醇	叔醇
一级醇(1°)	二级醇(2°)	三级醇(3°)

2. 根据烃基结构

饱和醇　　不饱和醇　　芳香醇

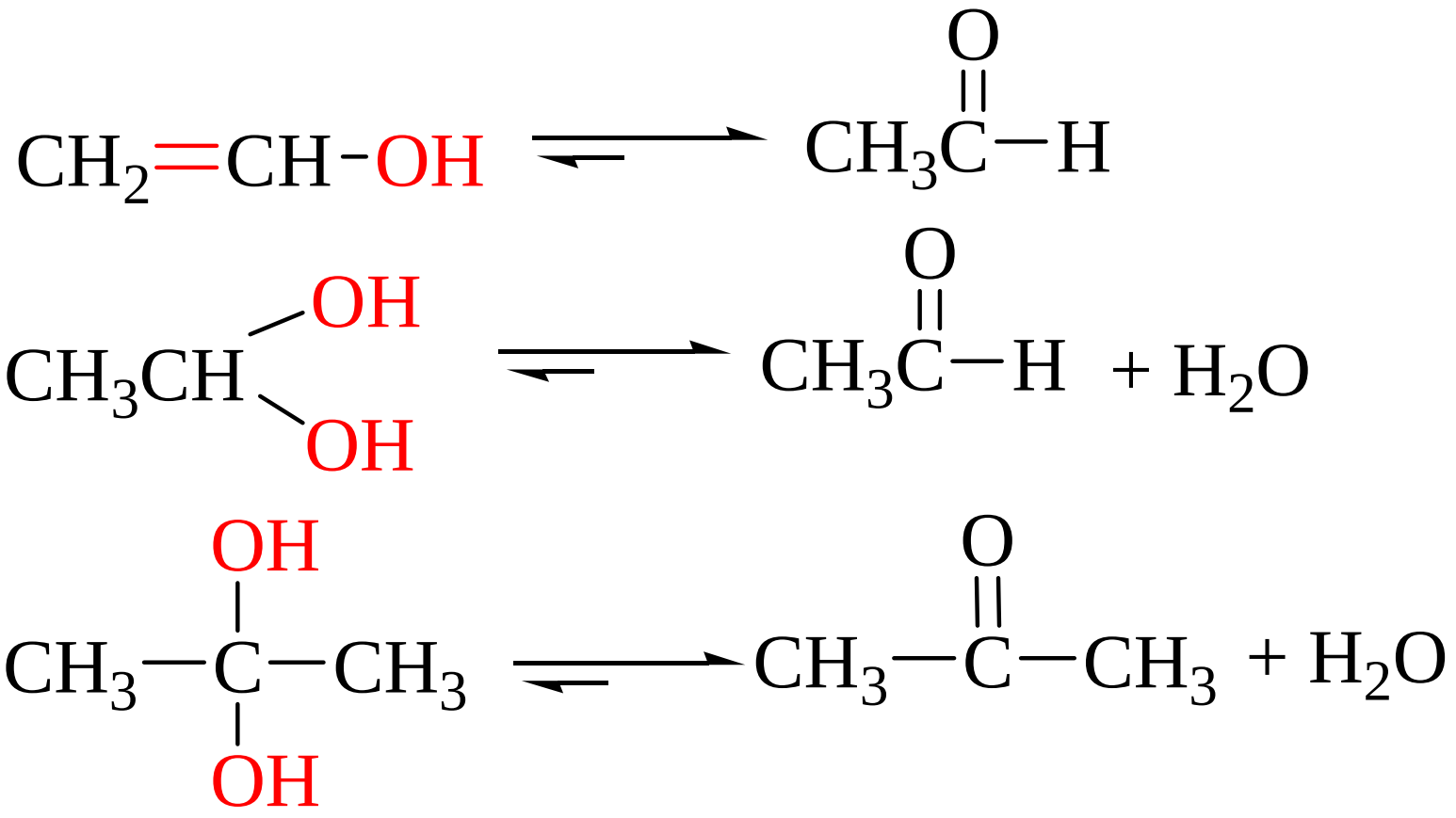
$CH_3CH_2CH_2OH$　　$CH_2{=}CHCH_2OH$　　 

3. 根据羟基数目

一元醇　　二元醇　　多元醇

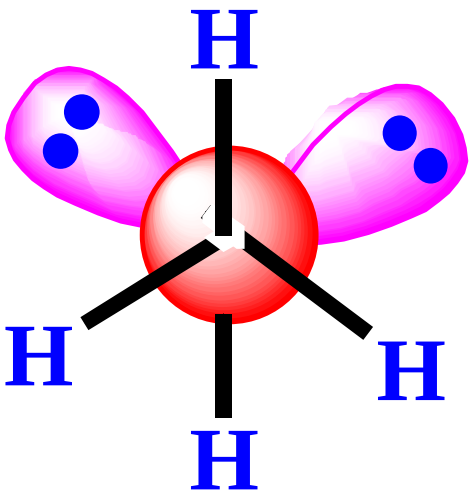
R—OH　　CH_2CH_2 (OH OH)　　CH_2CHCH_2 (OH OHOH)

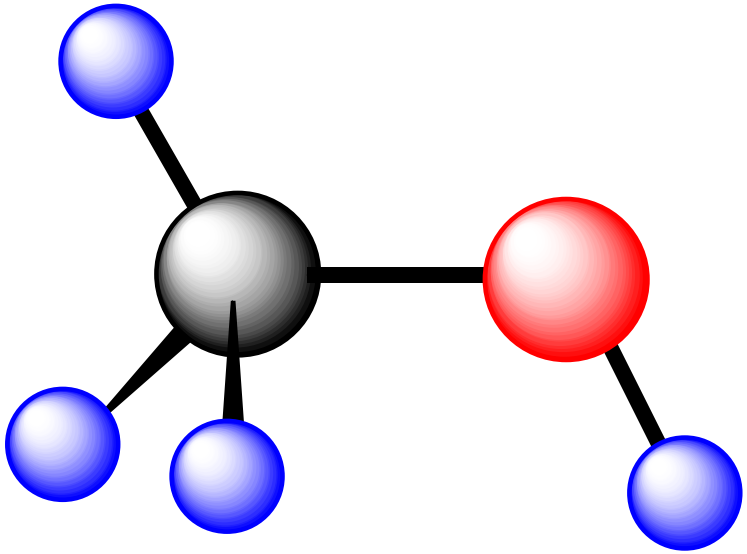
不稳定的醇



醇的结构

C，O都是sp^3杂化





8.1.2 醇的命名和物理性质

1. 普通命名

将相应烷烃名称中的烷→醇，

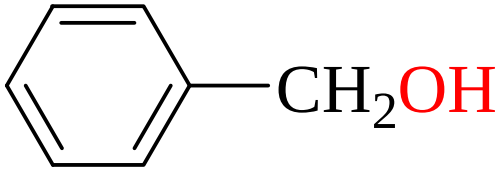
$CH_3CH_2CH_2CH_2OH$ 正丁醇 (1−丁醇)

$(CH_3)_2CHCH_2OH$ 异丁醇 (2−甲基−1−丙醇)

$(CH_3)_3COH$ 叔丁醇 (2−甲基−2−丙醇)

$CH_3CH_2CH(CH_3)-OH$ 仲丁醇 (2−丁醇)

$CH_2=CHCH_2OH$ 烯丙醇 (2−丙烯−1−醇)



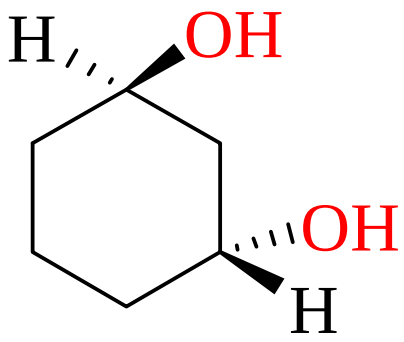
苄醇 (苯甲醇)

$HOCH_2CH_2OH$ $HOCH_2CHCH_2OH$ (OH) $ClCH_2CH_2OH$

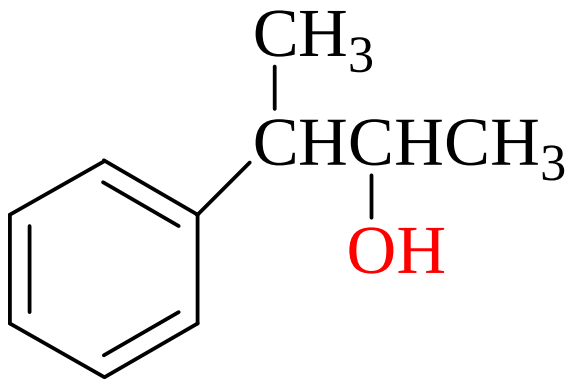
乙二醇 (甘醇) 丙三醇 (甘油) β–氯乙醇

(1,2–乙二醇) (1,2,3–丙三醇) (2–氯乙醇)

2. 系统命名



(1R,3R)–1,3–环己二醇

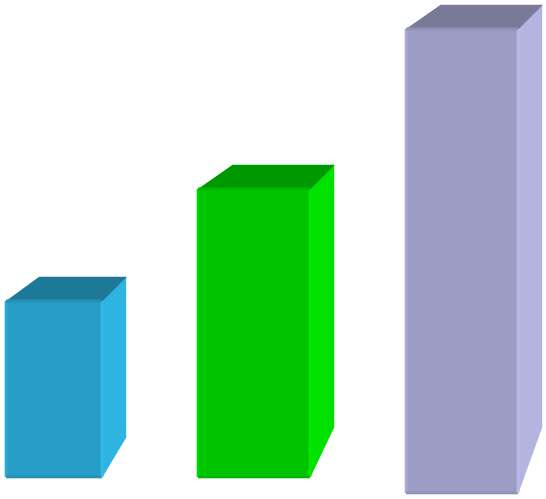


3–苯基–2–丁醇

3. 物理性质

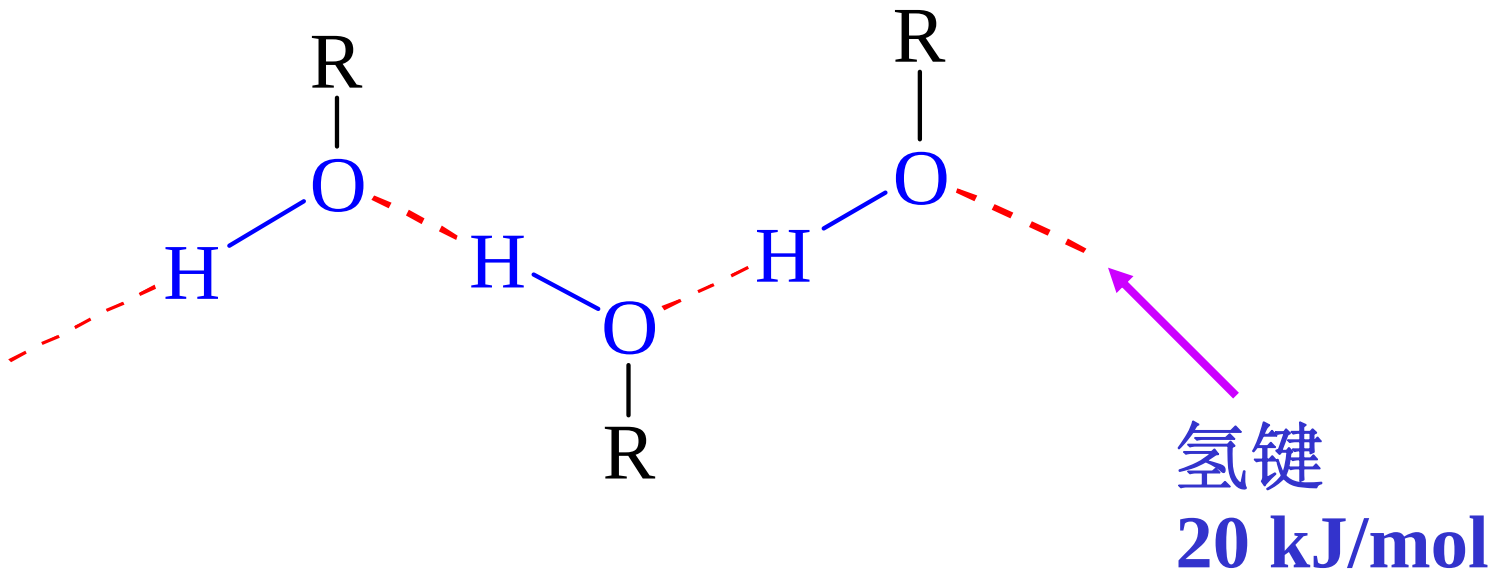
➢ (1) 沸点

比同碳原子数的烷烃、卤代烃高，也比分子量相近的烷烃高。



化合物	分子量	沸点(℃)
CH_3CH_2OH	46	78.5
CH_3CH_3	30	−98
$CH_3CH_2CH_3$	44	−42
CH_3CH_2Cl	64.5	12

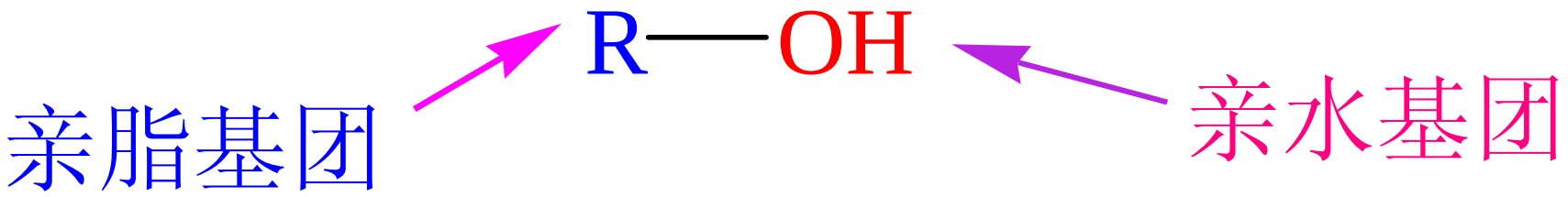
醇的分子间氢键



二元醇沸点大于一元醇（分子量相近）

(2) 溶解度

低级醇溶于水
随分子量增加溶解度降低



8.1.3 醇的制备和来源

- 由烯烃制备—— 水合，硼氢化-氧化
- 由羰基化合物制备—— **Grignard** 反应，与炔化物反应，还原.
- 由卤代烃水解

由烯烃制备

$$CH_2{=}CH_2 + H_2O \xrightarrow[300\ ℃,\ 10\ MPa]{H_3PO_4} CH_3CH_2OH$$

$$CH_3CH{=}CH_2 + H_2O \xrightarrow[300\ ℃,\ 10\ MPa]{H_3PO_4} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$$

$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 + H_2SO_4 \longrightarrow CH_3\underset{\displaystyle OSO_3H}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}CH_3$$

$$\xrightarrow[\triangle]{H_2O} CH_3\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}CH_3$$

可能发生重排

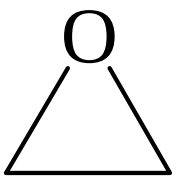
$$RCH{=}CH_2 \xrightarrow[(2)\ H_2O_2,\ OH^-]{(1)\ B_2H_6} RCH_2CH_2OH$$

由羰基化合物制备

$$CH_2O \xrightarrow[(2)\ H_3O^+]{(1)\ RMgX} RCH_2OH$$

$$CH_3CHO \xrightarrow[(2)\ H_3O^+]{(1)\ RMgX} RCH(OH)CH_3$$

$$CH_3COCH_3 \xrightarrow[(2)\ H_3O^+]{(1)\ RMgX} RC(OH)(CH_3)CH_3$$



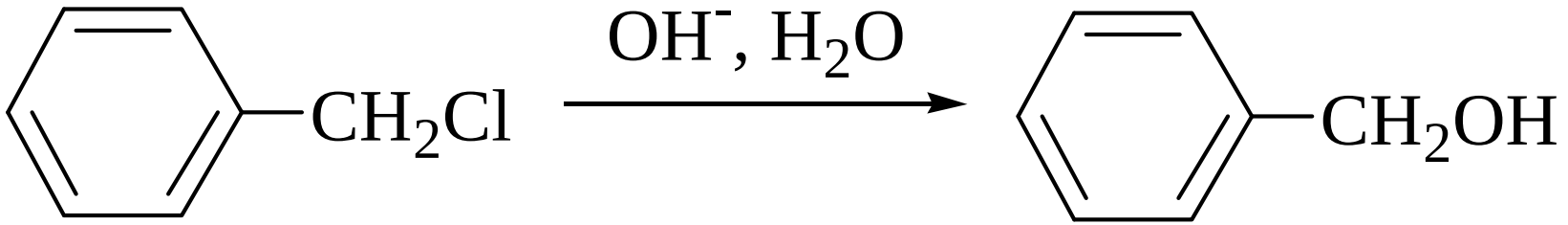
$$\xrightarrow[(2)\ H_3O^+]{(1)\ RMgX} RCH_2CH_2OH$$

由卤代烃水解

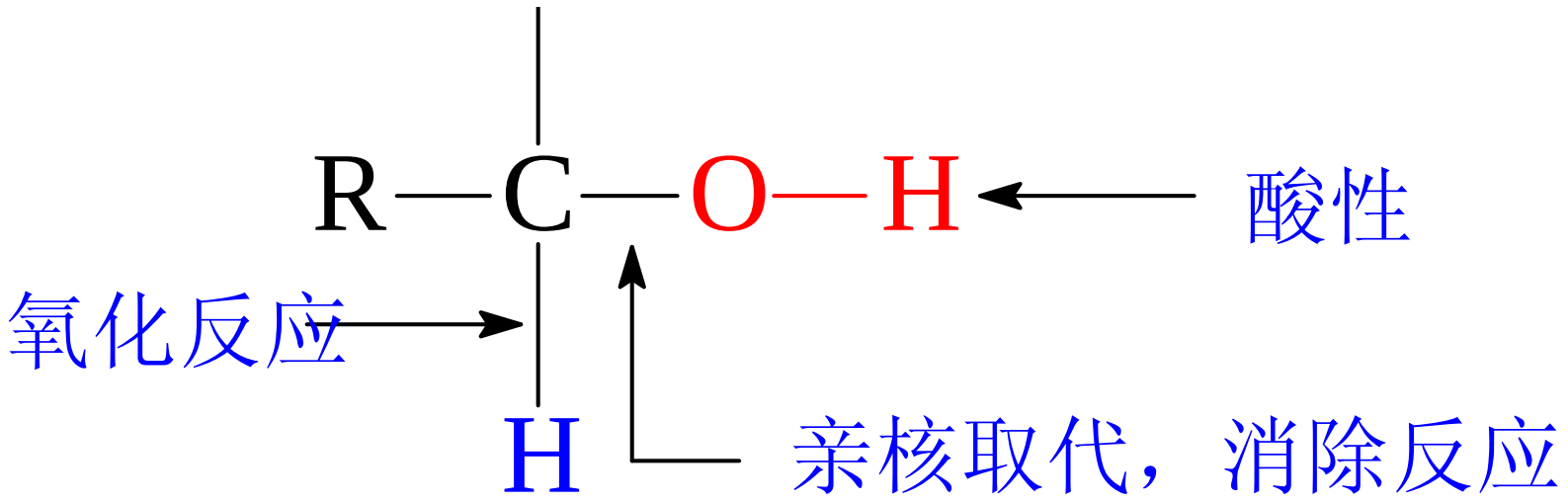
$$RX \xrightarrow{OH^-,\ H_2O} ROH$$ 不常用

(1) 副反应多　(2) 一般情况下醇比卤代烃易得

$$CH_2{=}CHCH_2Cl \xrightarrow{Na_2CO_3} CH_2{=}CHCH_2OH$$



8.1.4 醇的化学性质



1. 与金属钠反应

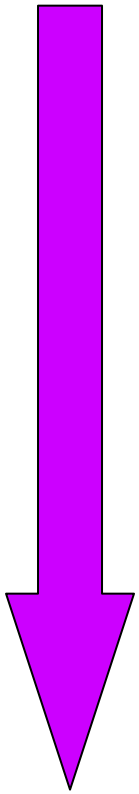
$$ROH + Na \longrightarrow RONa + H_2\uparrow$$

反应速度 $CH_3OH > CH_3CH_2OH > CH_3CH_2CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$

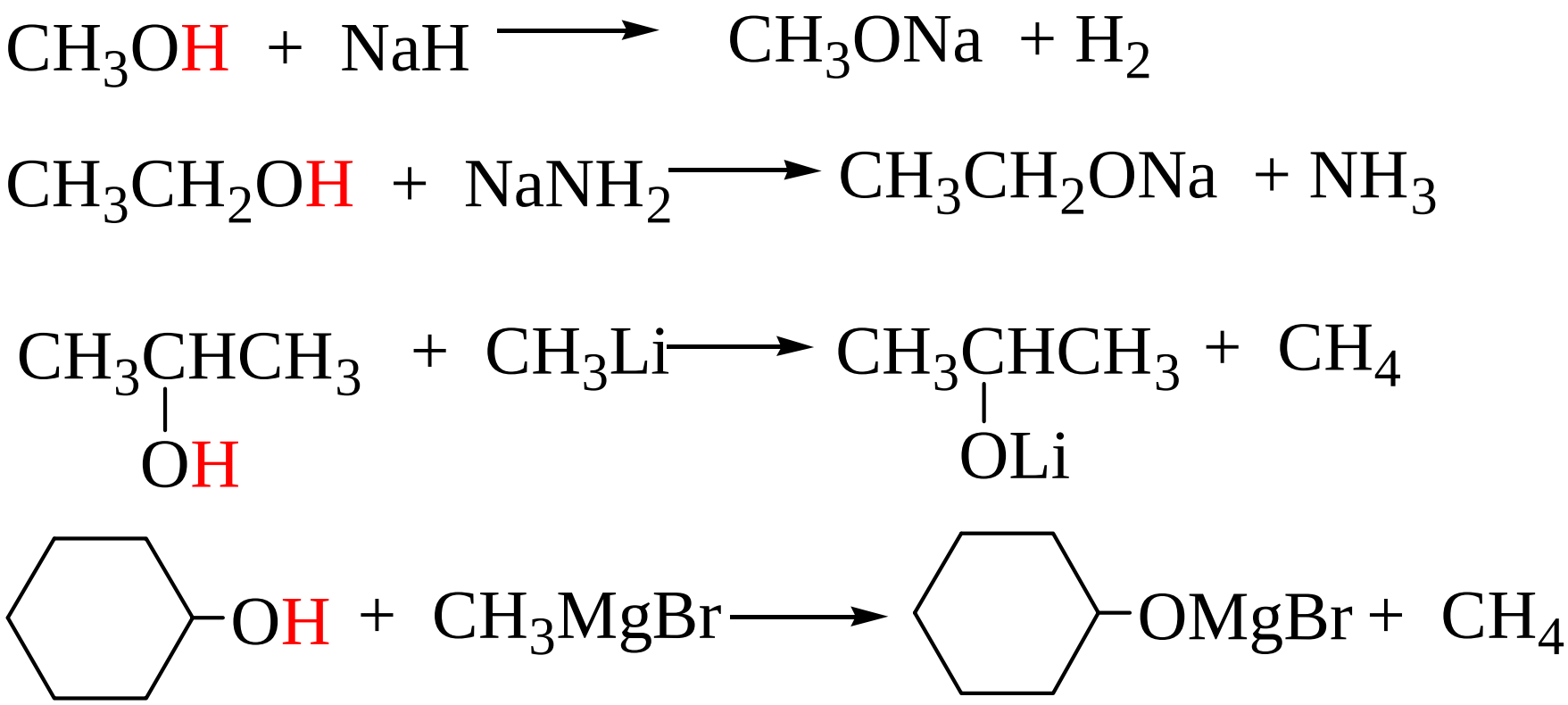
$$CH_3CH_2ONa + H_2O \rightleftharpoons CH_3CH_2OH + NaOH$$

醇是一种弱酸

化合物	pK_a
$(CH_3)_3COH$	18.00
CH_3CH_2OH	16.00
HOH	15.74
CH_3OH	15.54
CF_3CH_2OH	12.43
$(CF_3)_3COH$	5.4
HCl	−7.00



强酸


CH3OH + NaH → CH3ONa + H2
CH3CH2OH + NaNH2 → CH3CH2ONa + NH3
CH3CHCH3 + CH3Li → CH3CHCH3 + CH4
OH
OLi
OH + CH3MgBr → OMgBr + CH4

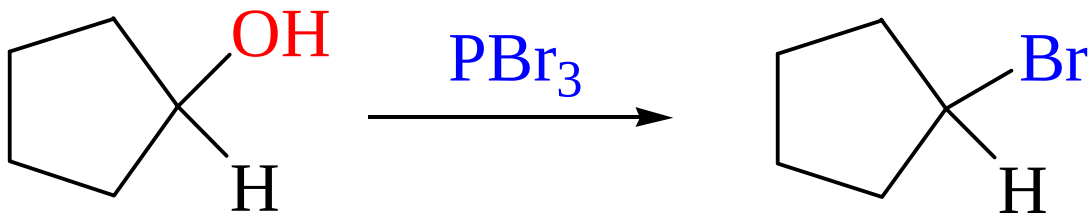
2. 与卤化磷和氯化亚砜的反应

$$3\ ROH + PX_3 \longrightarrow 3\ RX + P(OH)_3$$

或PX_5 或X_2, P

$$3\ CH_3CH_2OH + PBr_3 \longrightarrow 3\ CH_3CH_2Br + H_3PO_4$$

$$(CH_3)_2CHCH_2OH + PBr_3 \longrightarrow (CH_3)_2CHCH_2Br$$



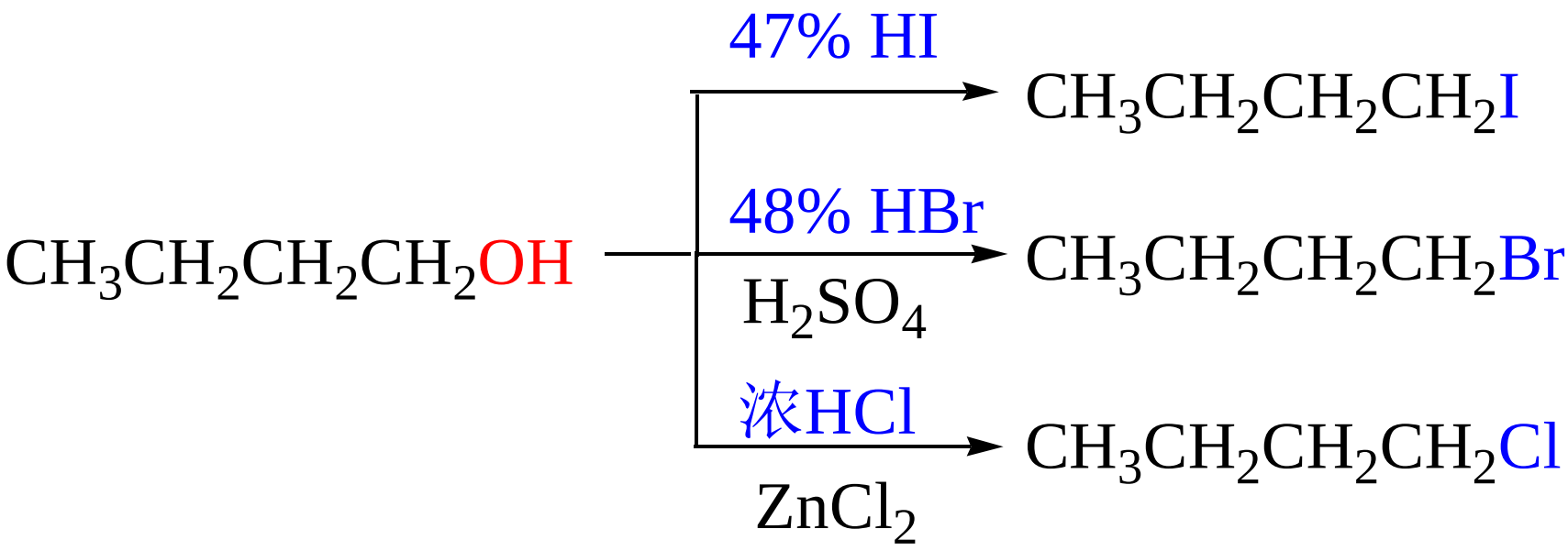
$$ROH + SOCl_2 \longrightarrow RCl + SO_2\uparrow + HCl\uparrow$$

氯化亚砜
亚硫酰氯

$$CH_3CH(CH_2)_5CH_3 + SOCl_2 \xrightarrow{\text{吡啶}} CH_3CH(CH_2)_5CH_3$$

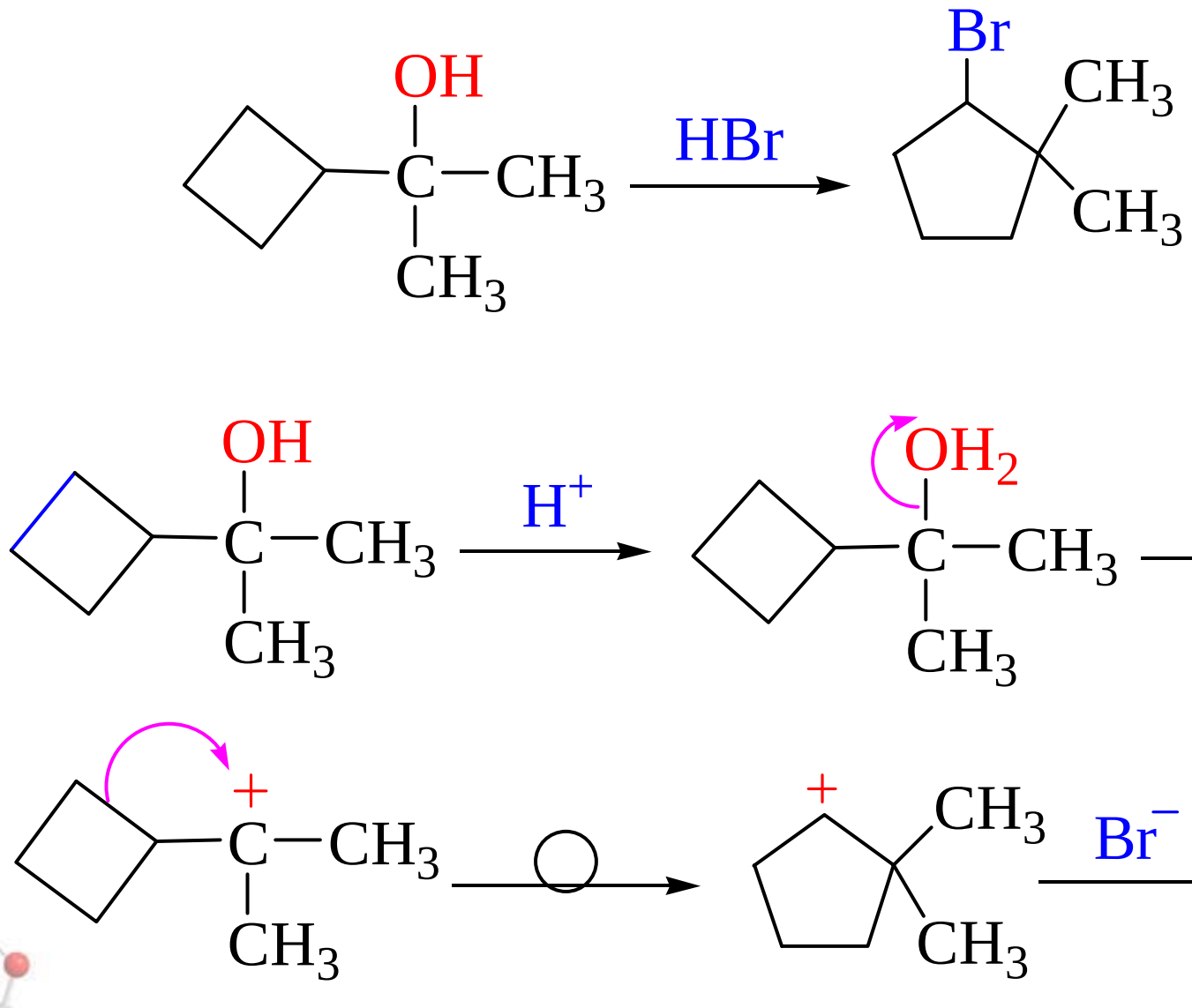
OH　　Cl

3. 与氢卤酸反应

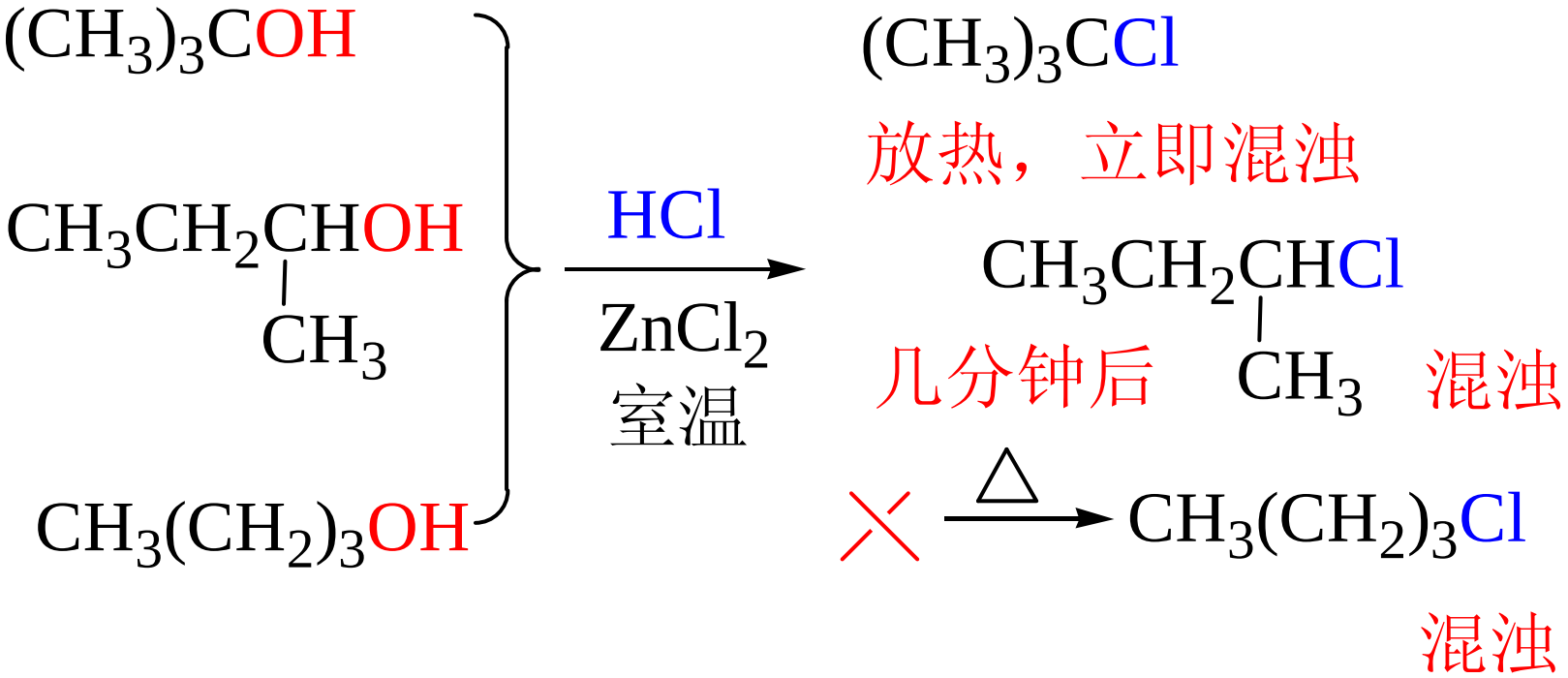


反应活性：**HI > HBr > HCl**

叔醇 > 仲醇 > 伯醇


OH
C
CH3
CH3
HBr
Br
CH3
CH3
OH
C
CH3
CH3
H+
OH2
C
CH3
CH3
−H2O
+
C
CH3
CH3
CH3
+
CH3
CH3
Br−
Br
CH3
CH3

Lucas 试剂(浓HCl/$ZnCl_2$)



用于伯、仲、叔醇的鉴别。
适用于C6以下的醇

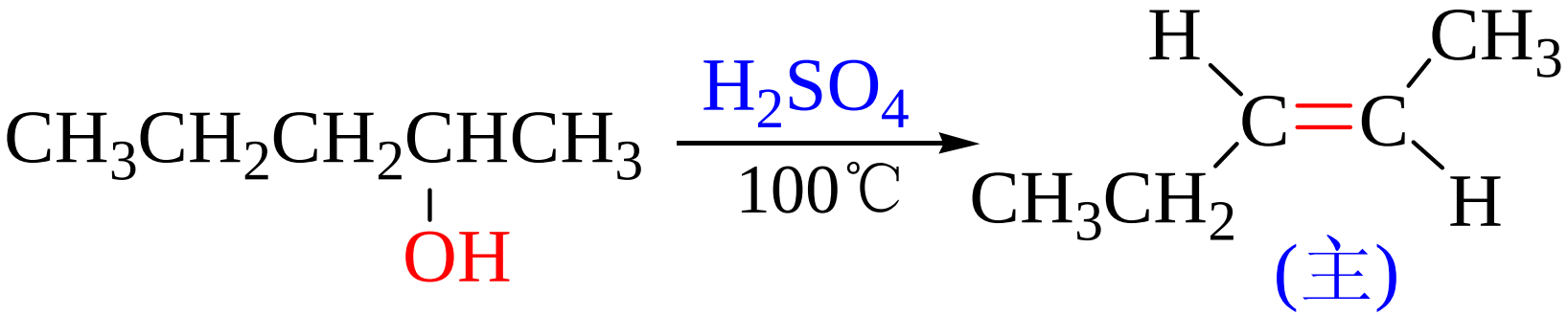
4. 脱水反应

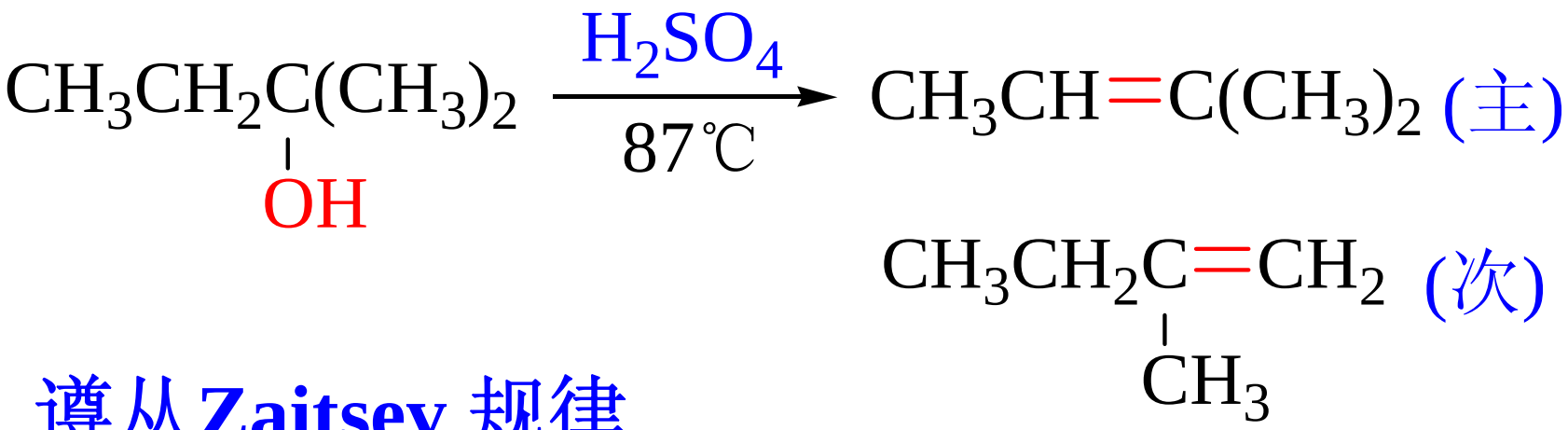
(1) 分子内脱水

$$RCH_2CH_2OH \xrightarrow[\triangle]{H^+} RCH{=}CH_2 + H_2O$$

$$CH_3CH_2OH \xrightarrow[170℃]{H_2SO_4} CH_2{=}CH_2 + H_2O$$

常用催化剂：**H_2SO_4, H_3PO_4, Al_2O_3**





遵从Zaitsev 规律

(2) 分子间脱水

$$2\,ROH \xrightarrow[\triangle]{H^+} R-O-R + H_2O$$

$$2\,CH_3CH_2OH \xrightarrow[140℃]{H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$$

$$2CH_2CH(CH_3)OH \xrightarrow[\triangle]{H_2SO_4} (CH_3)_2CHOCH(CH_3)_2 + H_2O$$

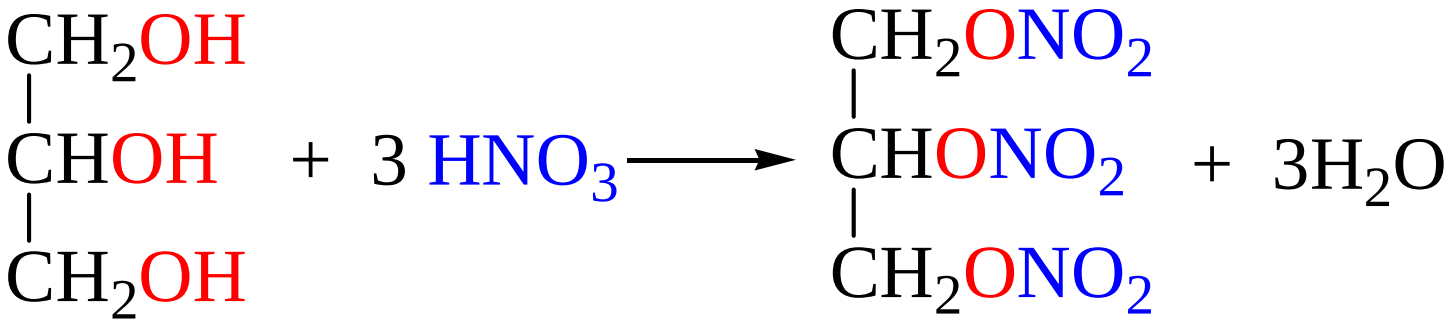
主要副反应：分子内脱水。
不适用于叔醇

5. 成酯反应

$$RCO_2H + R'OH \underset{}{\overset{H^+}{\rightleftharpoons}} RCO_2R' + H_2O$$

$$CH_3OH + H_2SO_4 \longrightarrow CH_3OSO_3H + H_2O$$

硫酸氢甲酯

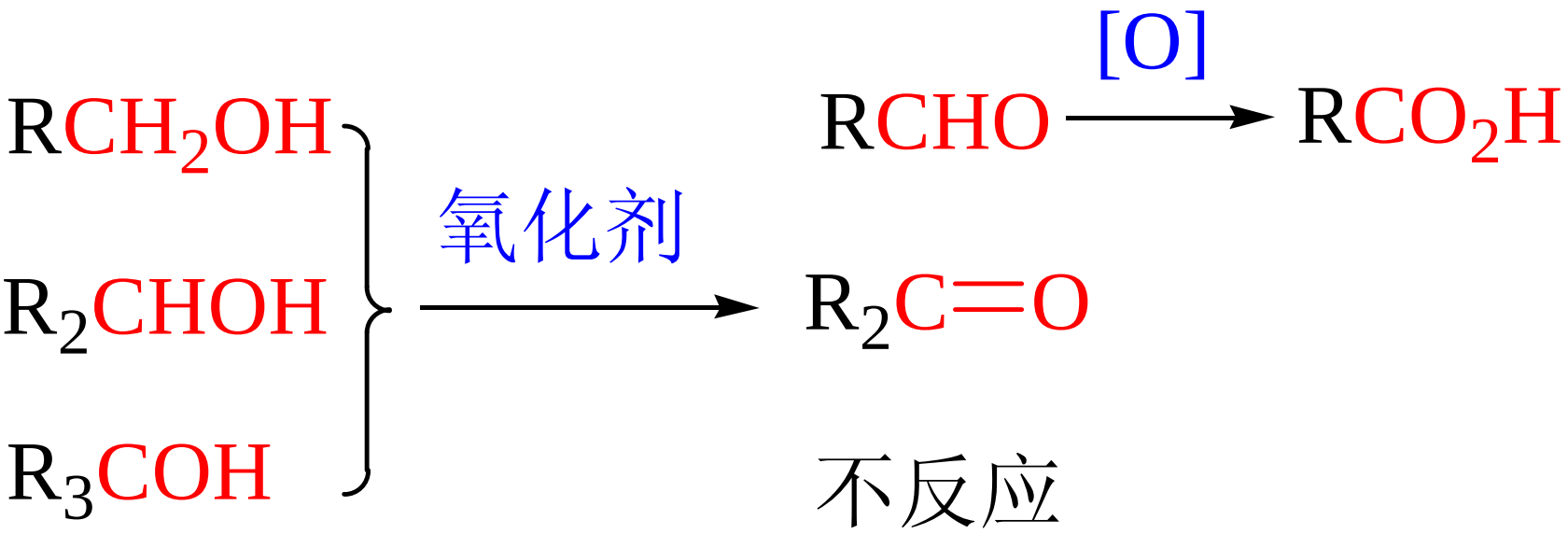


甘油

甘油三硝酸酯
硝化甘油

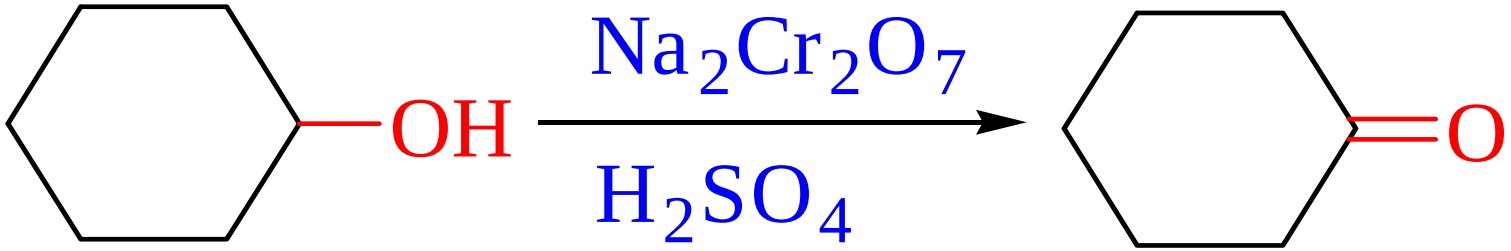
6. 氧化与脱氢

(1) 氧化剂氧化



氧化剂：$KMnO_4$, H_2CrO_4, $K_2Cr_2O_7/H_2SO_4$
$Na_2Cr_2O_7/H_2SO_4$, CrO_3/H_2SO_4

$$CH_3CH_2OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3CO_2H$$

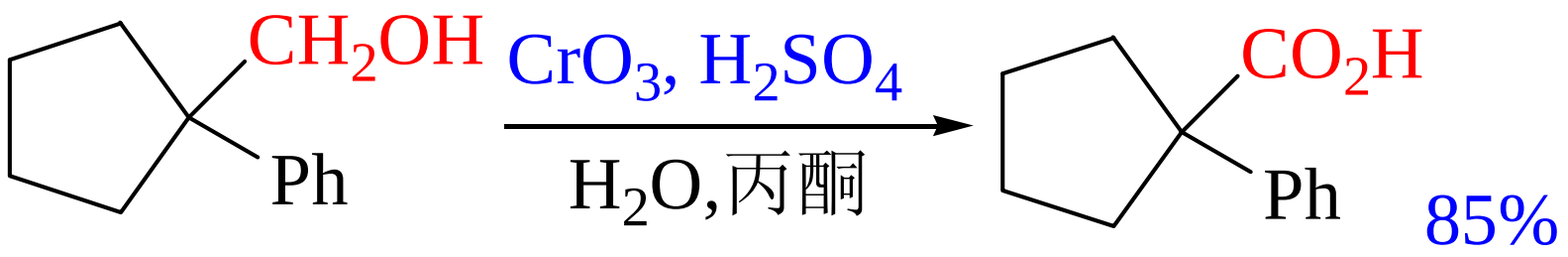


$$CH_3OH \xrightarrow{KMnO_4} HCO_2H \xrightarrow{KMnO_4} H_2CO_3$$

$$\longrightarrow H_2O + CO_2$$

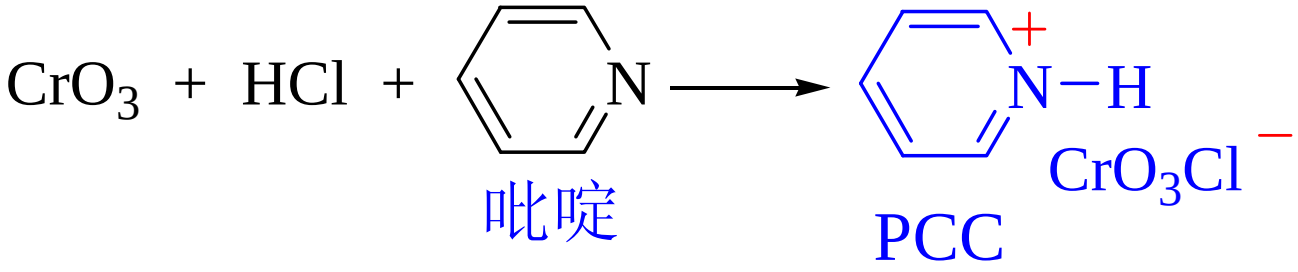
Jones'试剂 —— CrO_3 / H_2SO_4

$$CH_3(CH_2)_8CH_2OH \xrightarrow[H_2O,\text{丙酮}]{CrO_3,\ H_2SO_4} CH_3(CH_2)_8CO_2H \quad 93\%$$

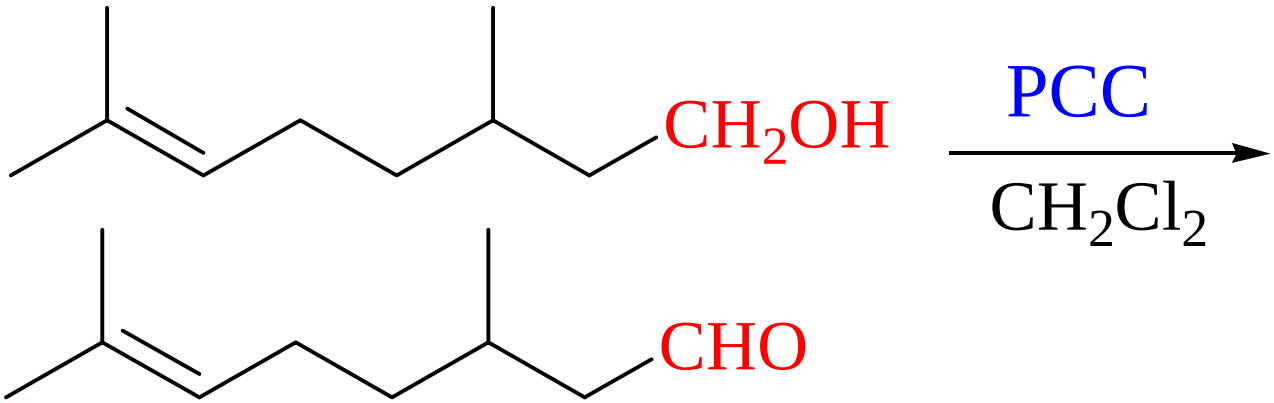


选择性氧化

CrO_3/吡啶 或 PCC氧化剂



$$CH_3(CH_2)_5CH_2OH \xrightarrow{CrO_3/\text{吡啶}} CH_3(CH_2)_5CHO$$

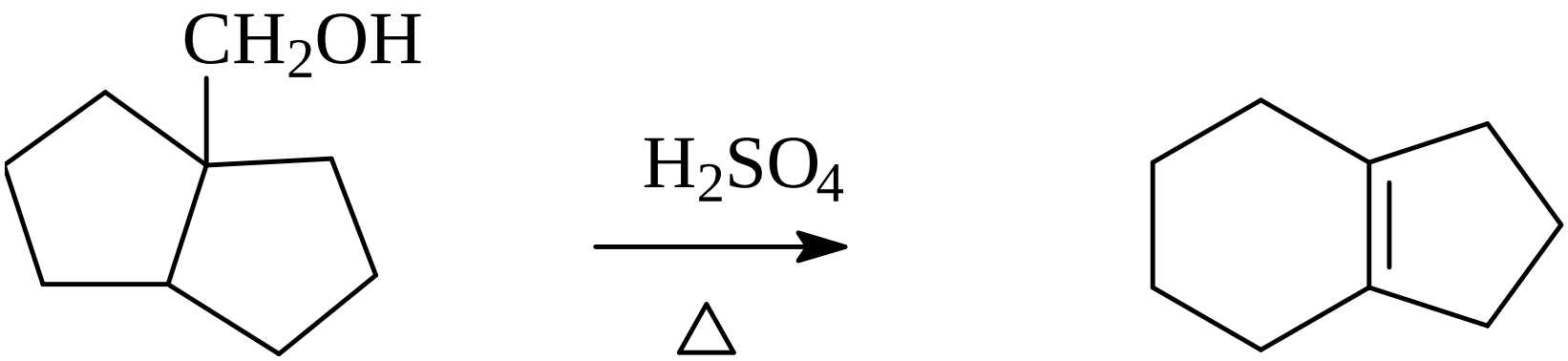


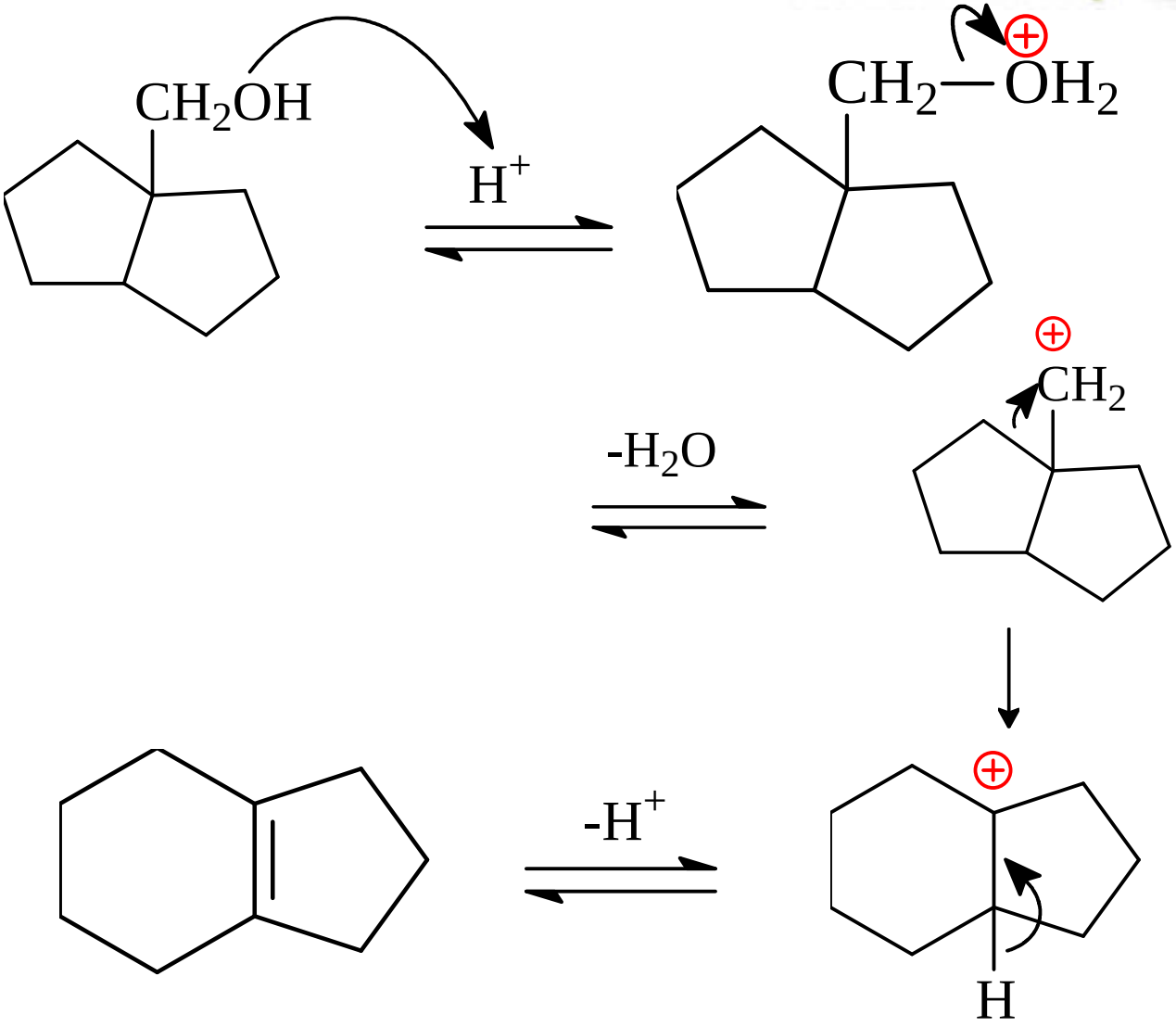
(2) 催化脱氢

$$CH_3CH_2OH \xrightarrow[550℃]{O_2,\ Cu\ or\ Ag} CH_3CHO + H_2O$$

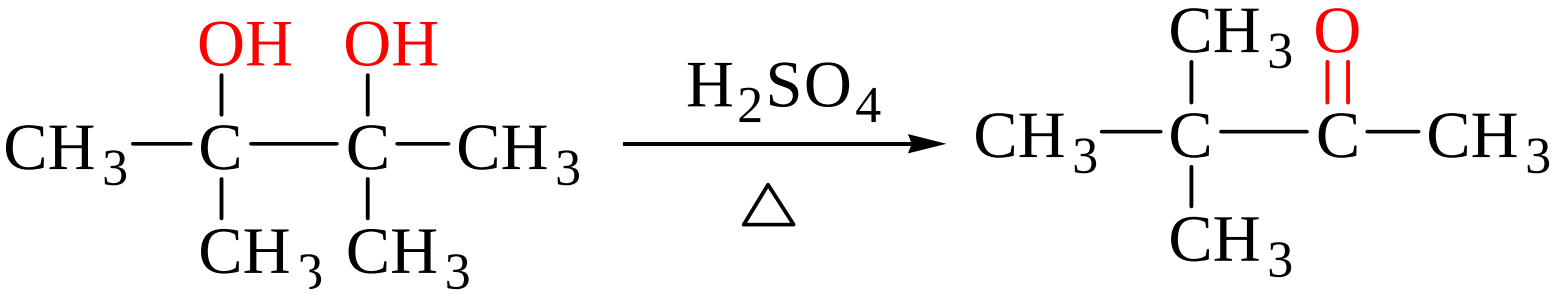
$$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 \xrightarrow[380℃]{ZnO} CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_3 + H_2O$$

课堂练习：
用反应机理解释如下反应

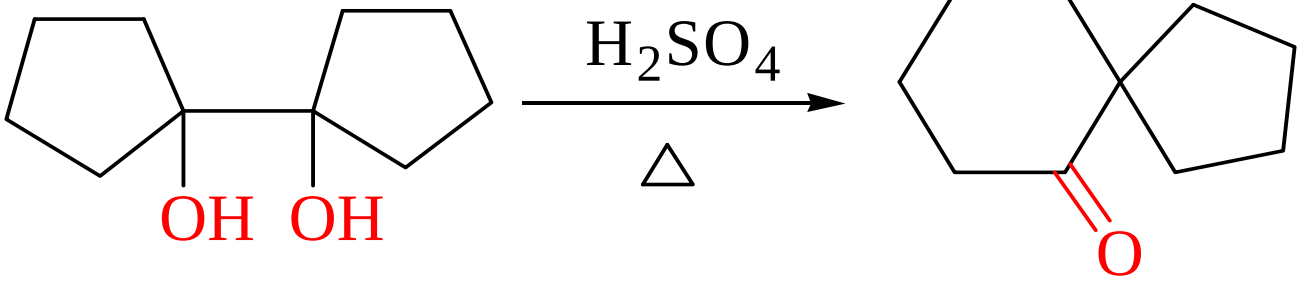


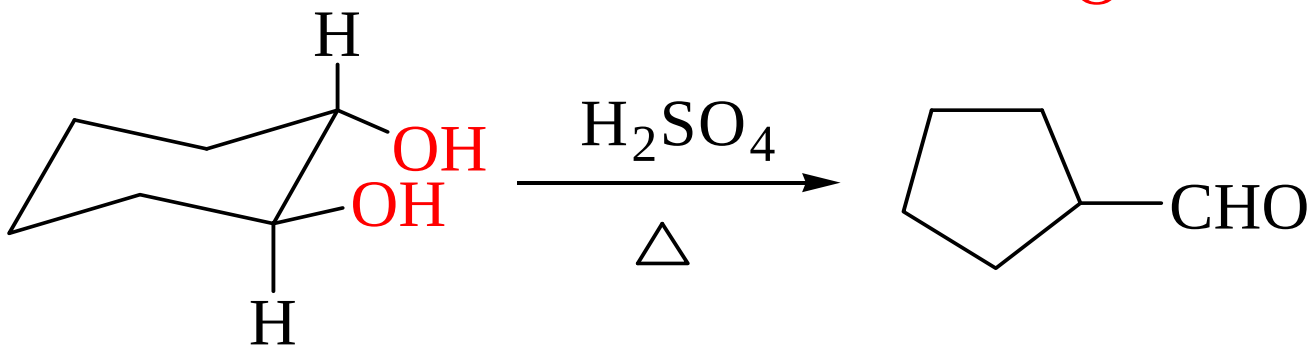

CH2OH
H+
CH2—OH2
-H2O
CH2
-H+
H

Pinacol rearrangement(频哪醇重排)

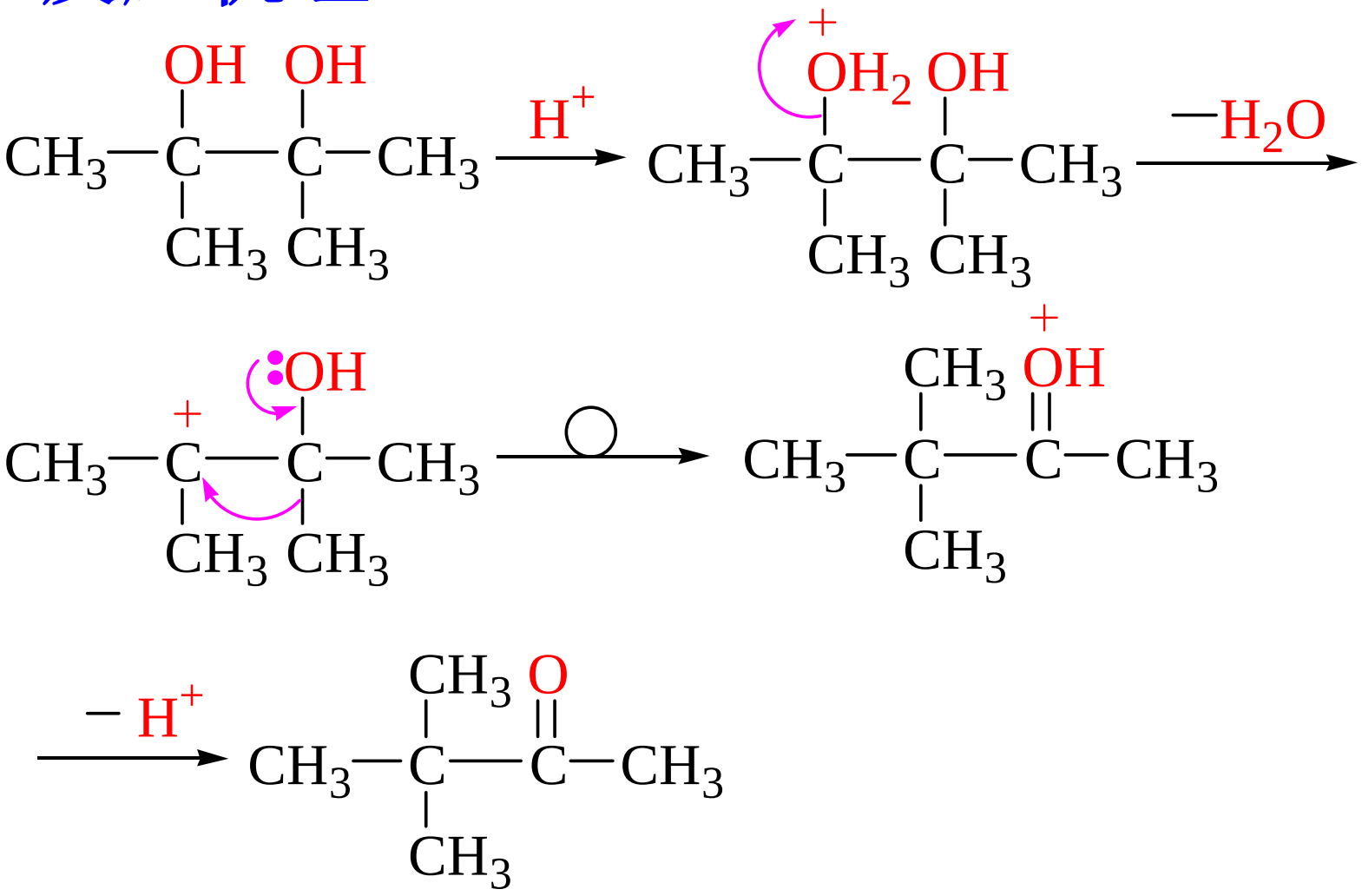


Pinacolone





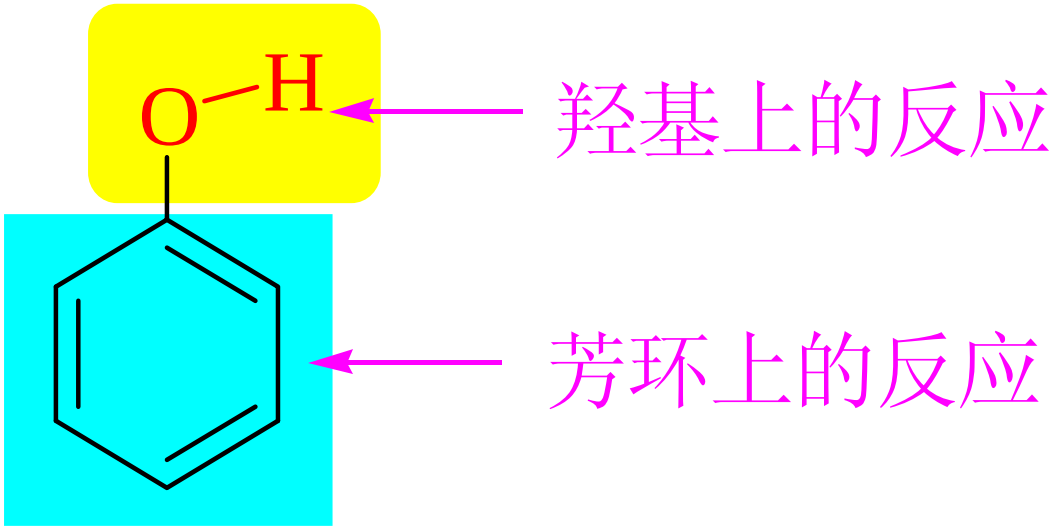
反应机理


OH OH
CH3—C—C—CH3
CH3 CH3
H+
+
OH2 OH
CH3—C—C—CH3
CH3 CH3
—H2O
OH
+
CH3—C—C—CH3
CH3 CH3
CH3 OH
+
CH3—C—C—CH3
CH3
− H+
CH3 O
CH3—C—C—CH3
CH3

8.2 酚

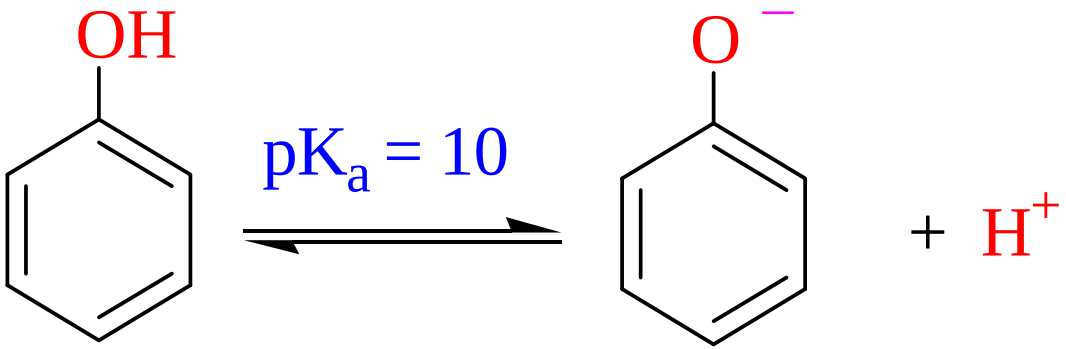
8.2.1 酚的结构、分类、命名和物理性质（自学）

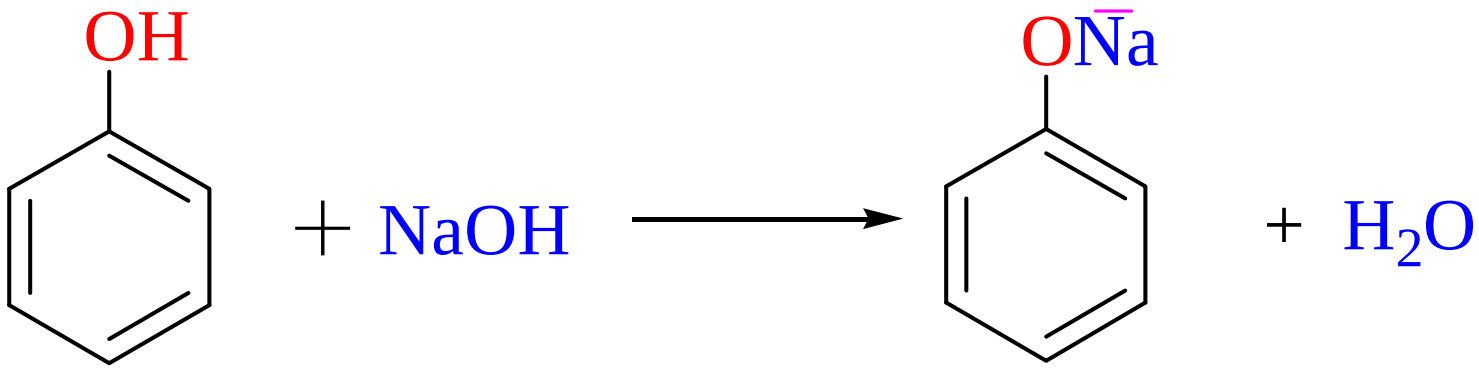
8.2.2 一元酚的反应



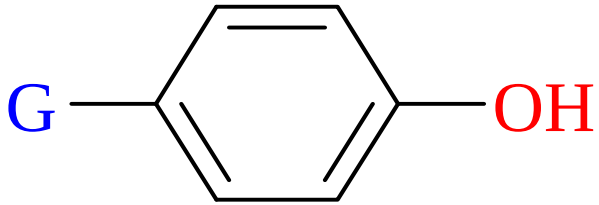
1. 羟基上的反应

(1) 酸性





取代酚的酸性

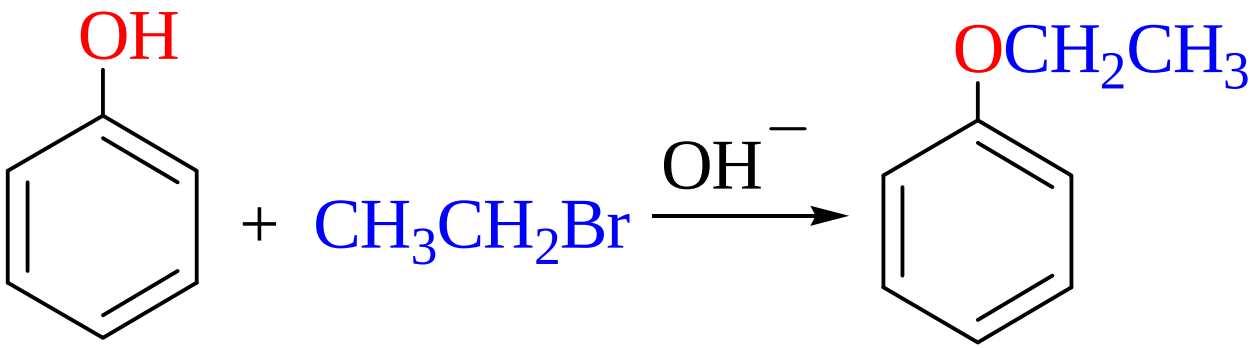


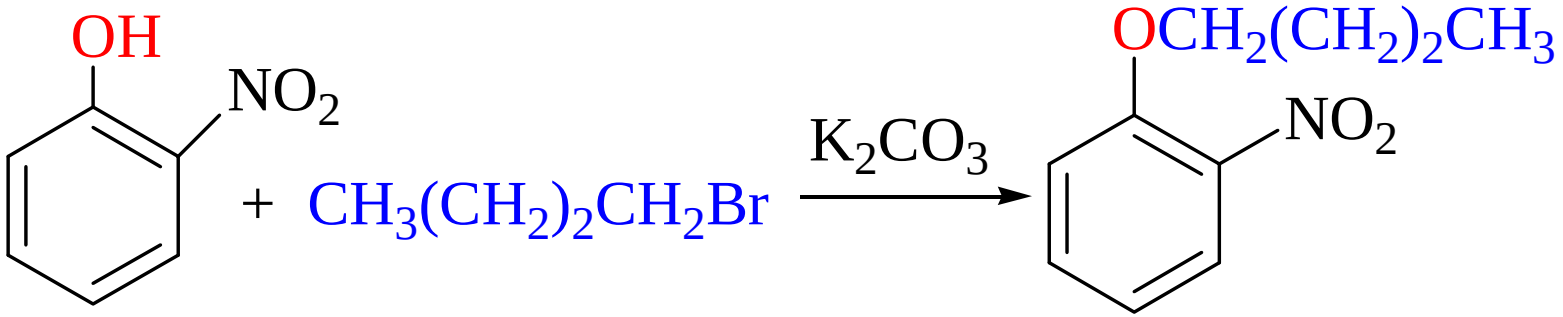
G	NH_2	CH_3	CH_3O	**H**	Cl	Br	I	NO_2
pK_a	10.46	10.26	10.21	10.0	9.38	9.35	9.30	7.16

苯环上连有吸电子基，酸性增强

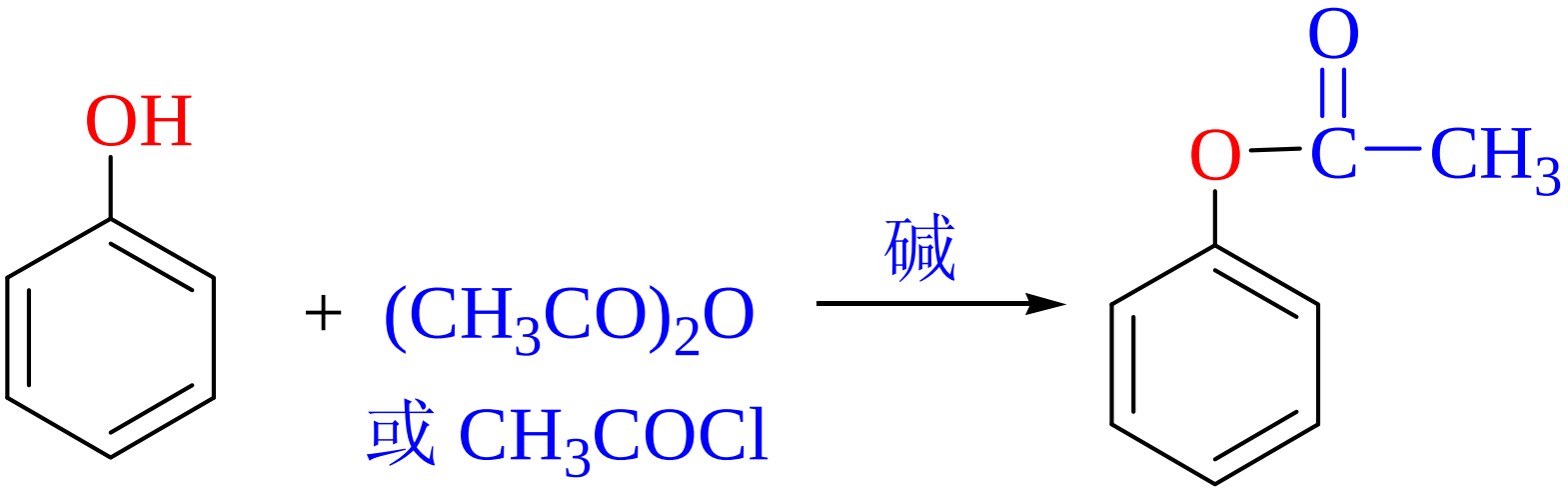
苯环上连有给电子基，酸性减弱

(2) 烃基化反应


OH
+ CH3CH2Br
OH−
OCH2CH3

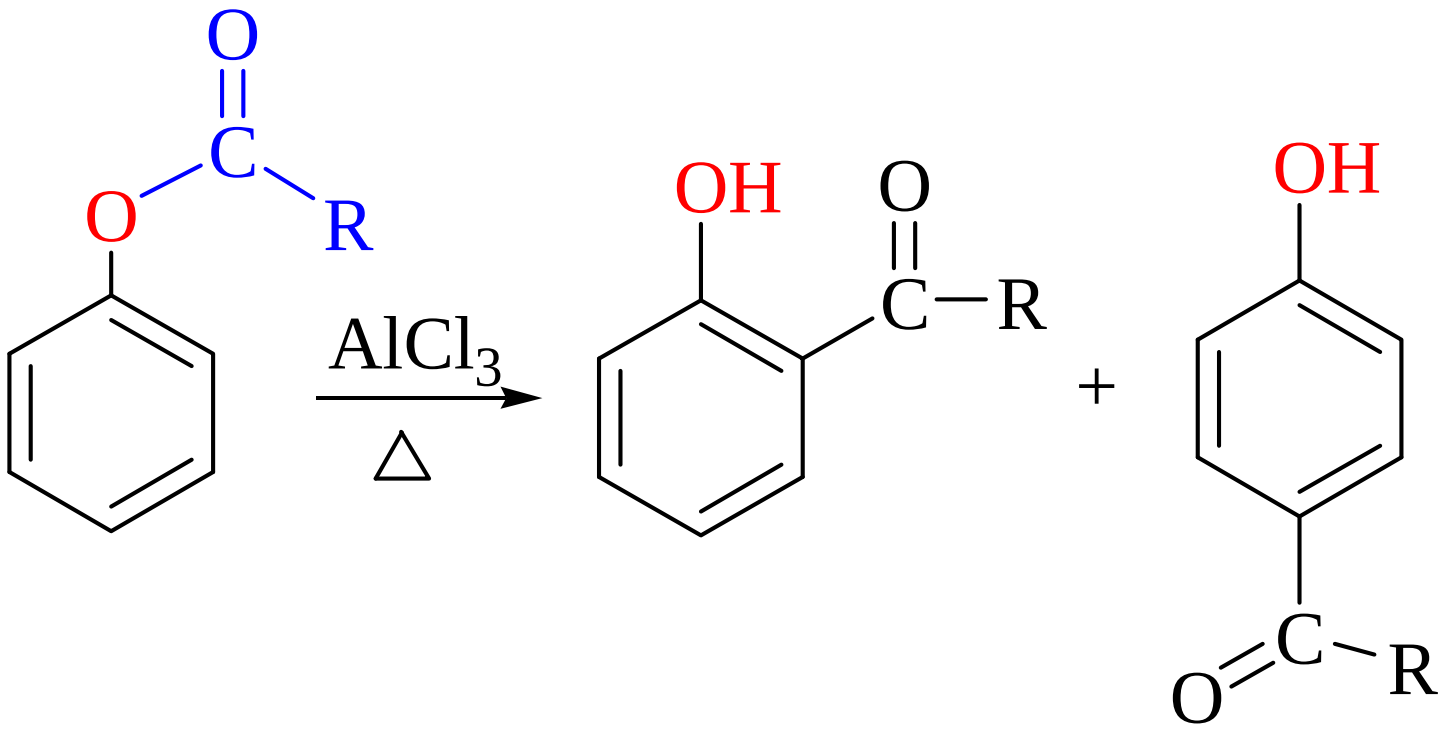

OH
NO2
+ CH3(CH2)2CH2Br
K2CO3
OCH2(CH2)2CH3
NO2

(3) 酰基化反应及Fries重排



碱：吡啶，NaOH，Na_2CO_3, NaOAc

Fries重排反应



高温下产物以邻位为主
较低温度下产物以对位为主

(1) 与三氯化铁的显色反应

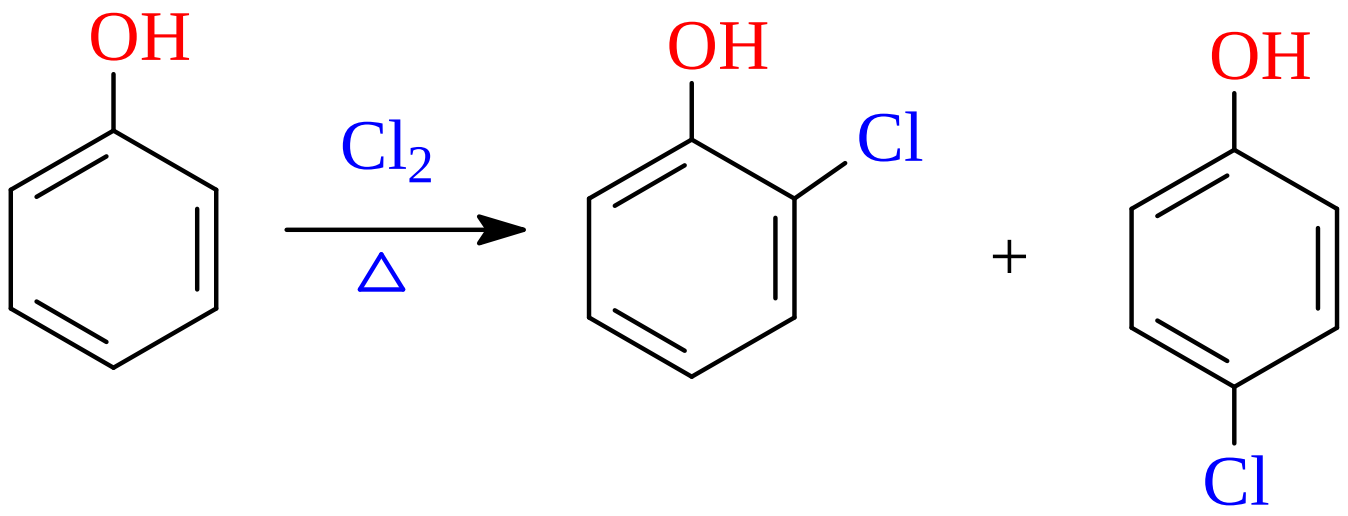
$$6\,C_6H_5OH + FeCl_3 \longrightarrow H_3[Fe(OC_6H_5)_6] + H_2O$$

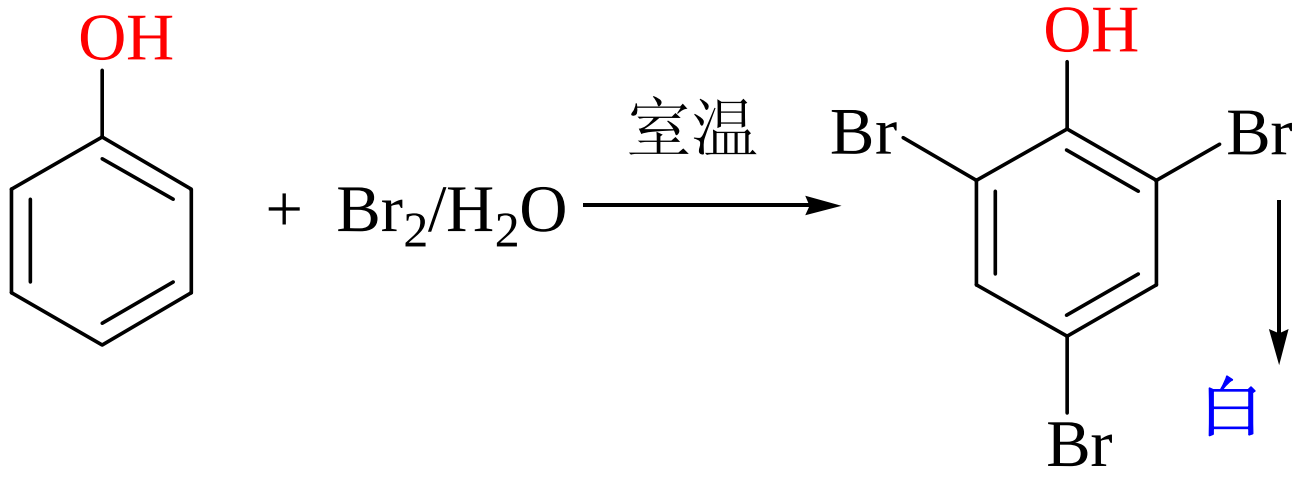
蓝紫色

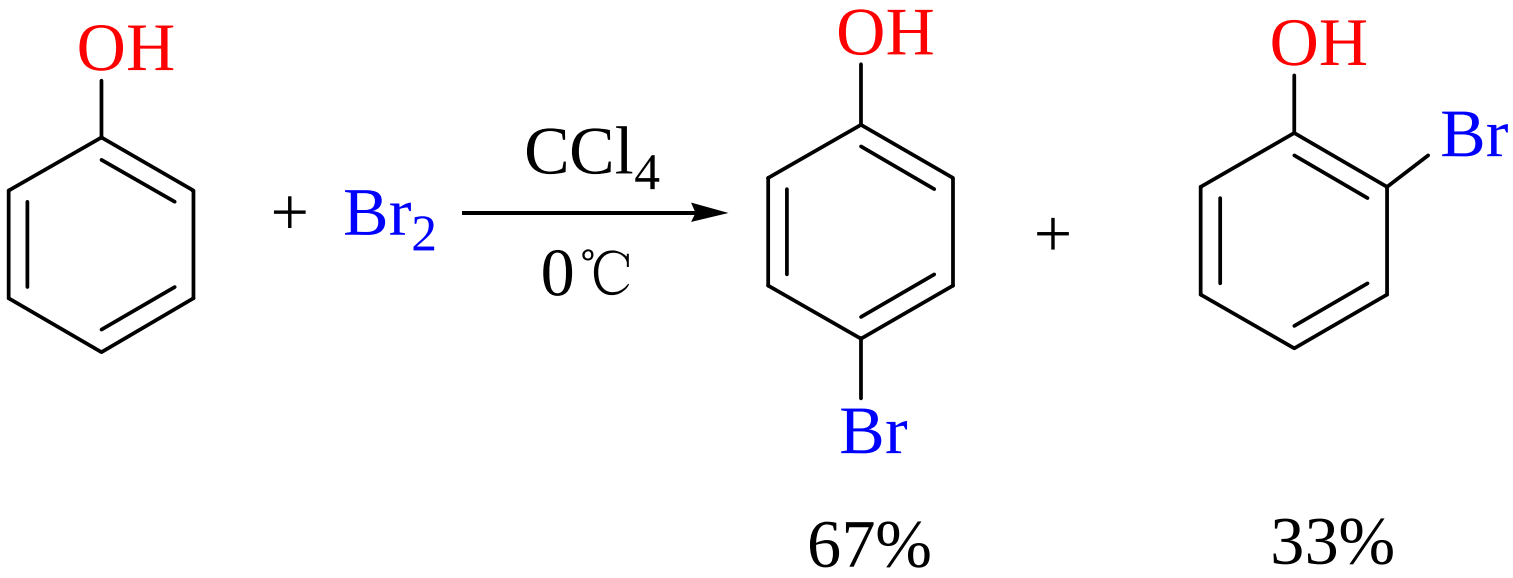
烯醇式结构的化合物大多能使三氯化铁显色

2. 芳环上的反应

(1) 卤化反应

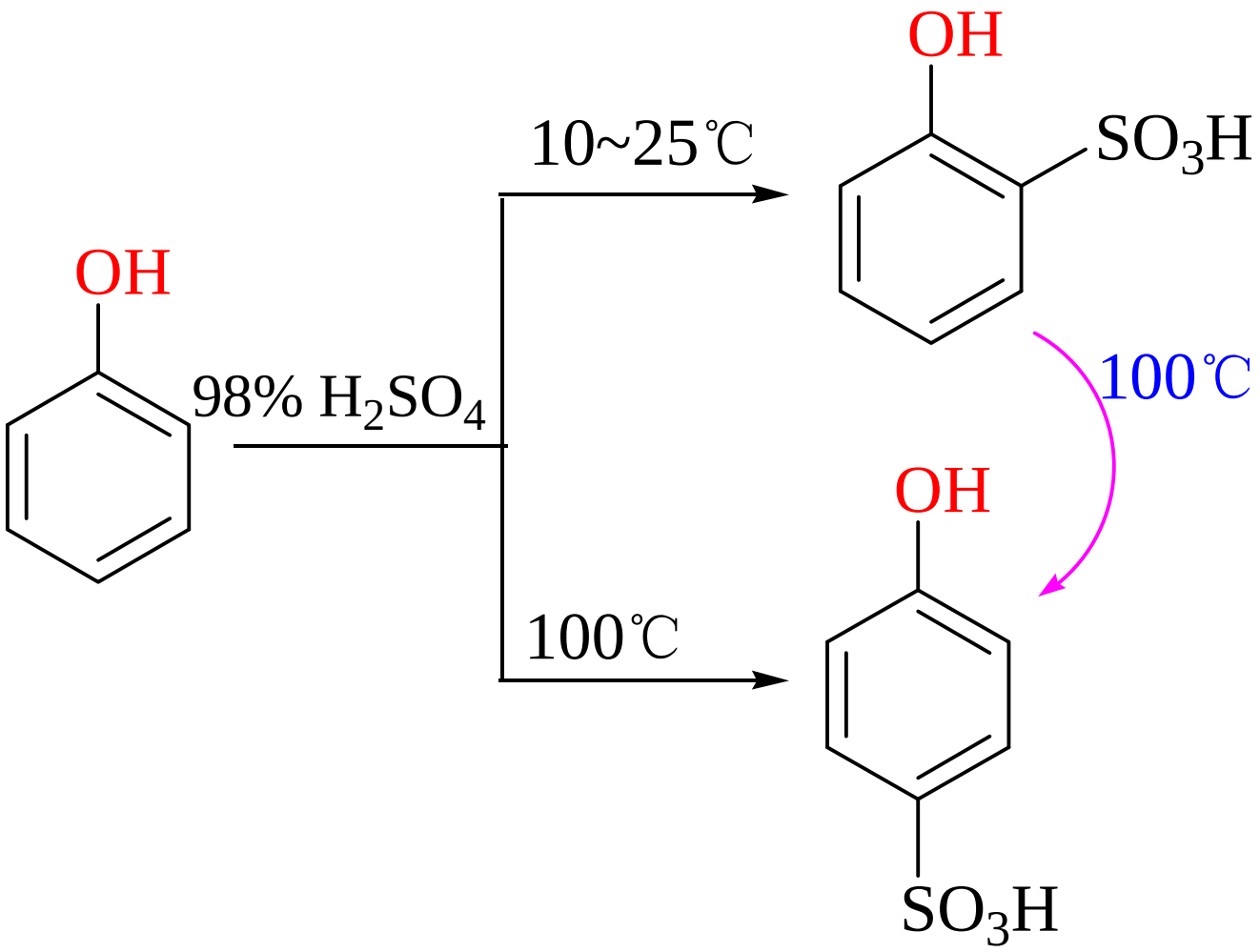




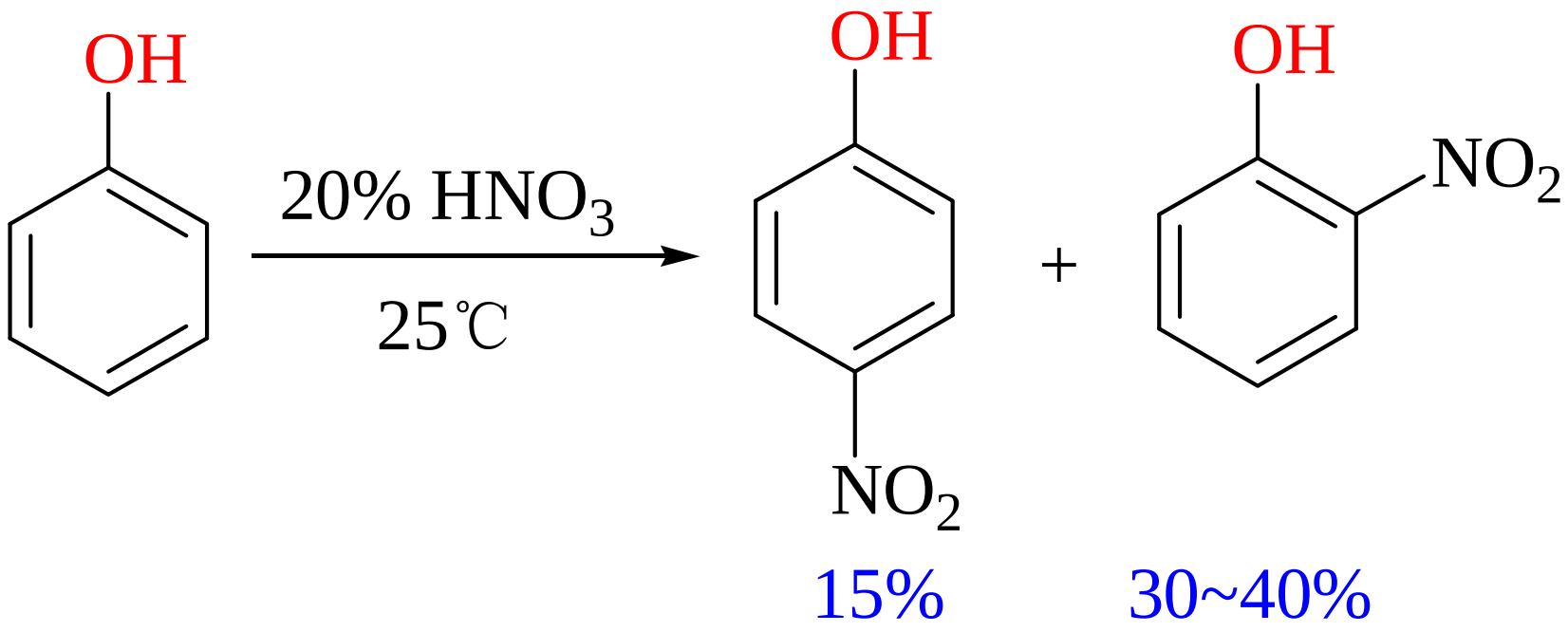


67%　　33%

(2)磺化反应

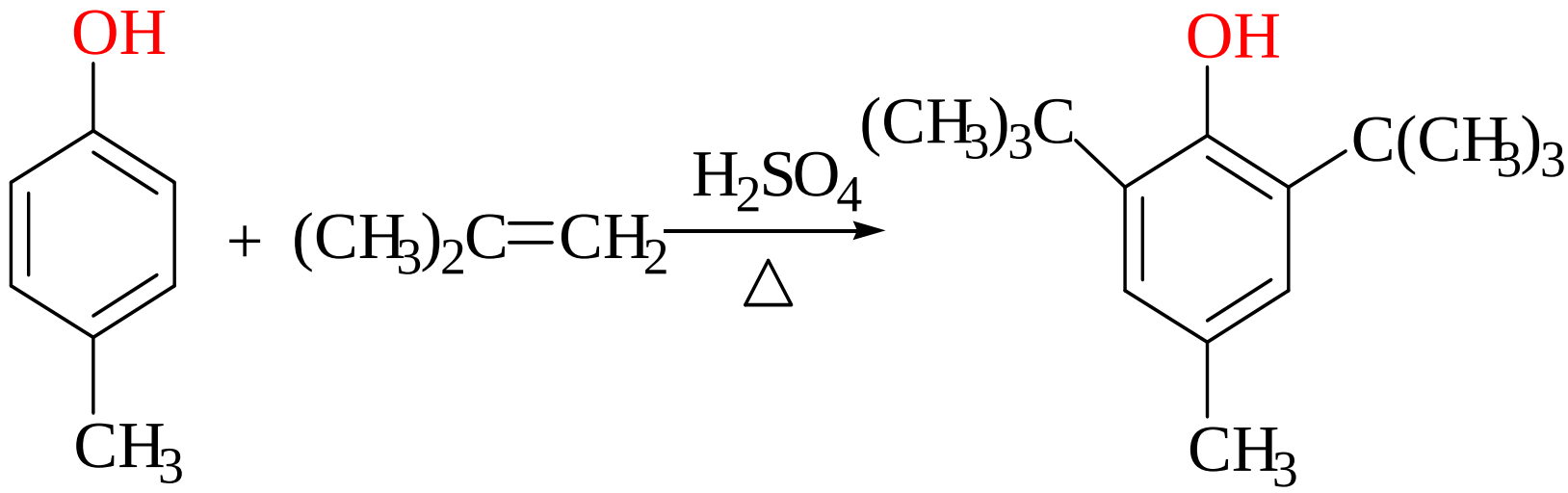


(3) 硝化反应

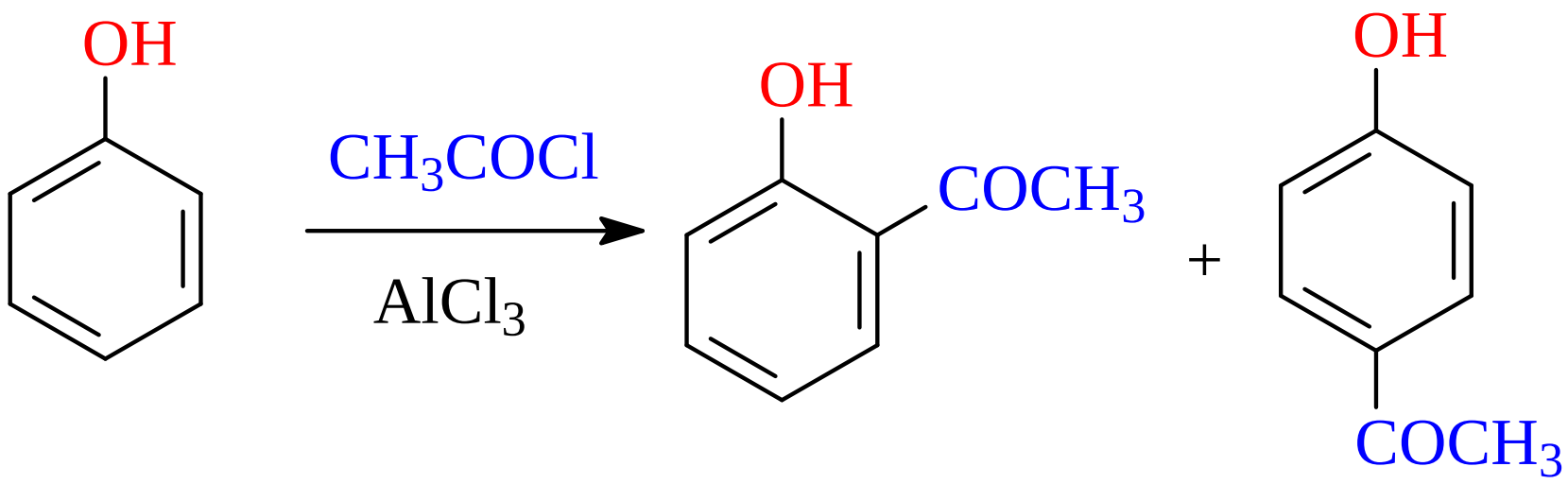


15%　　30~40%

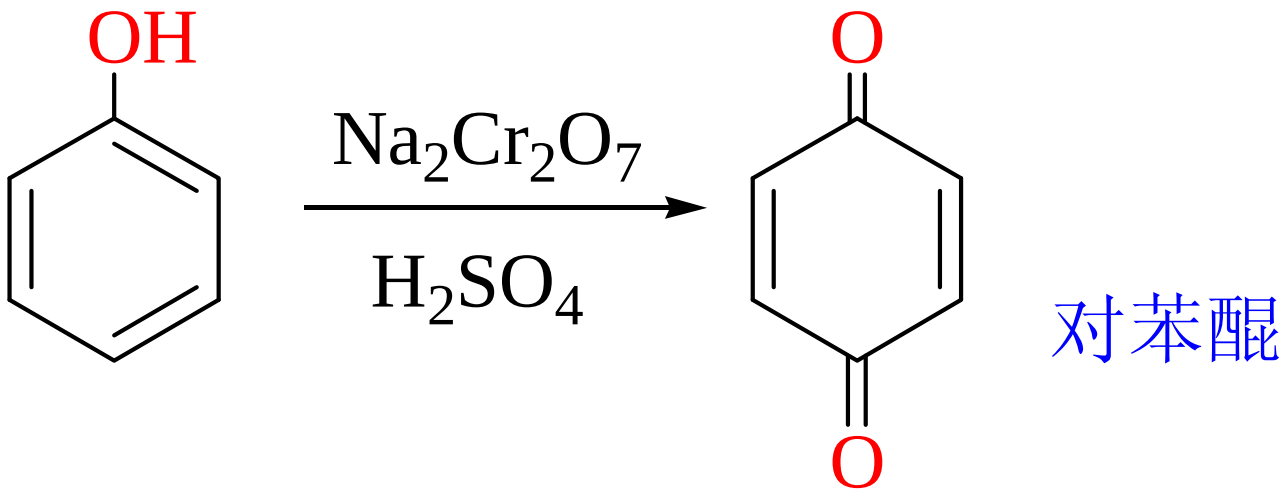
(4) 烷基化反应



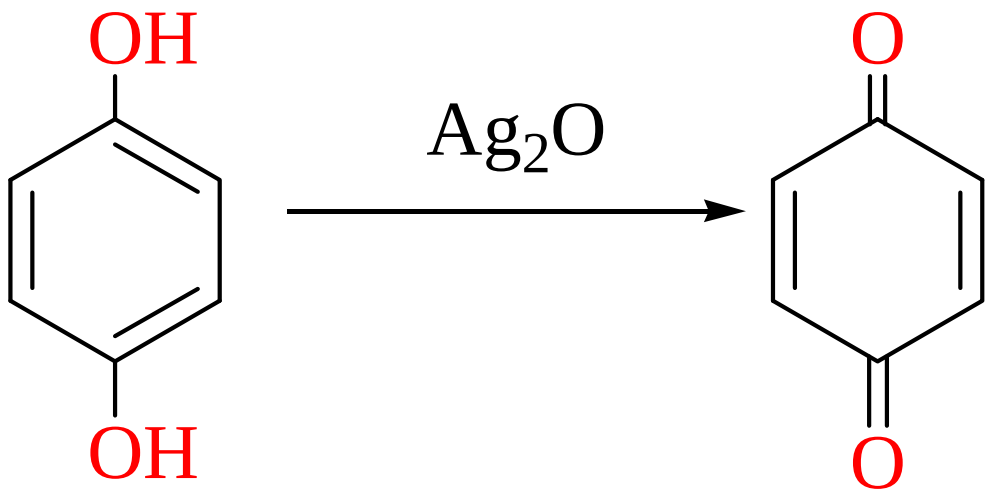
(5) 酰基化反应



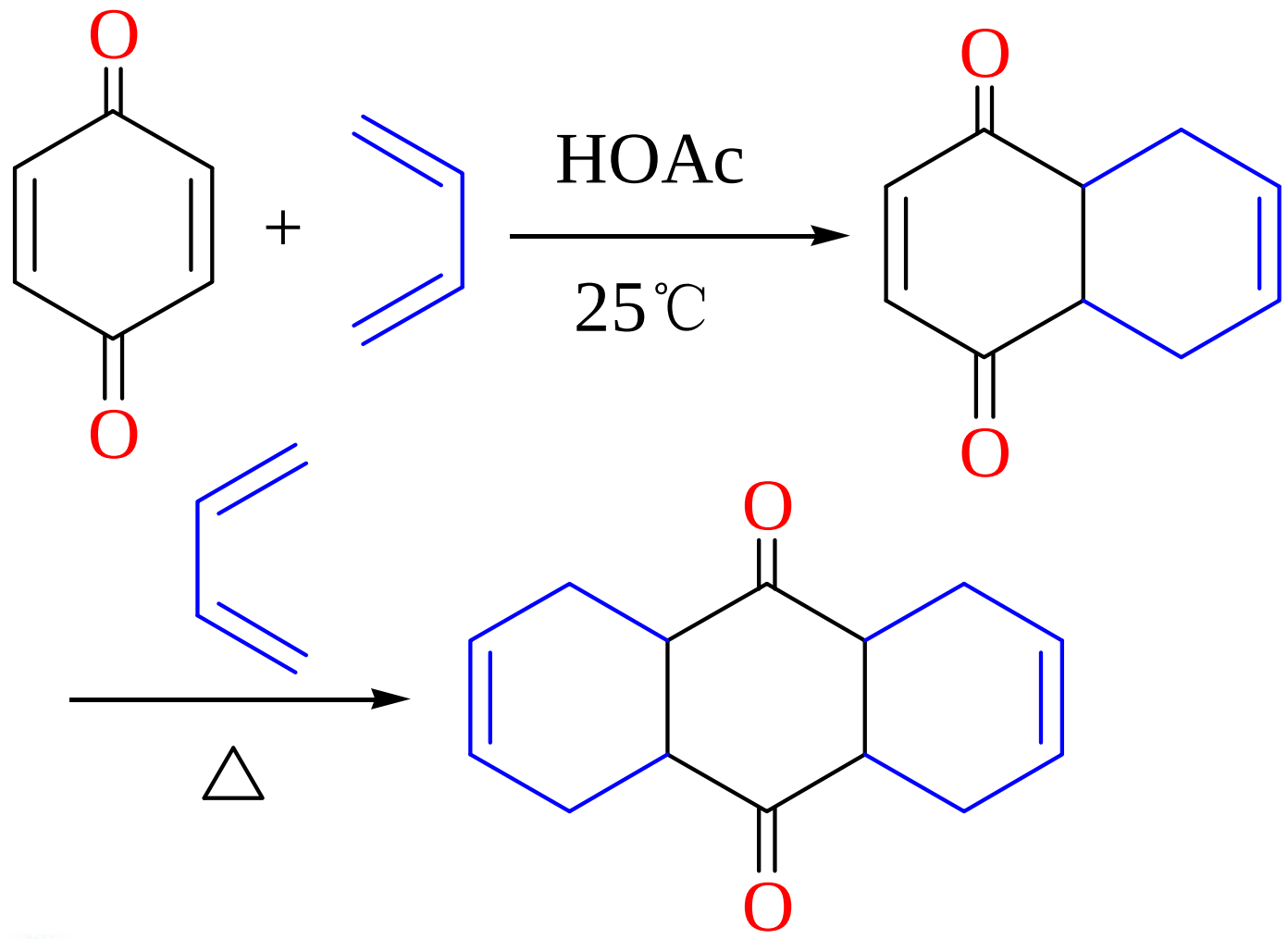
3. 氧化反应



对苯醌

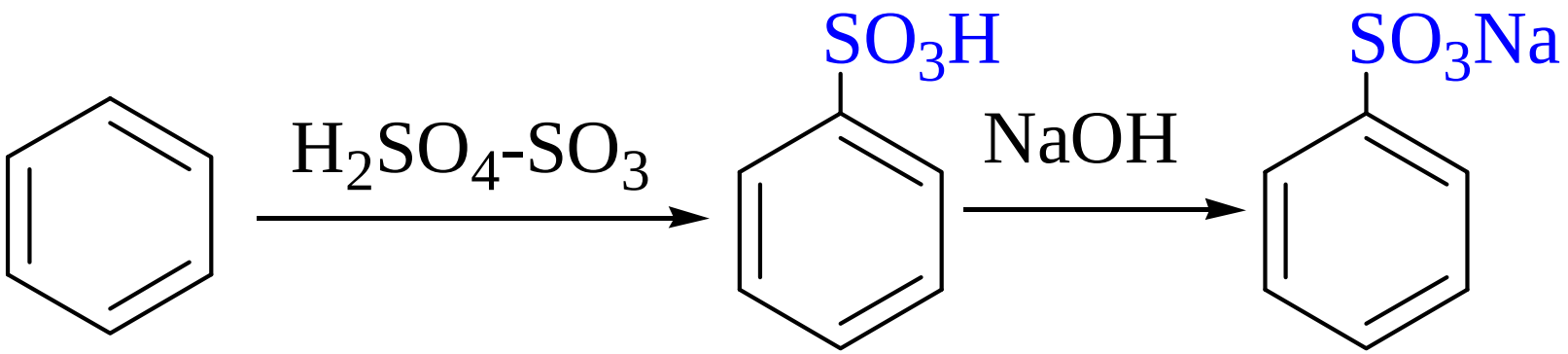


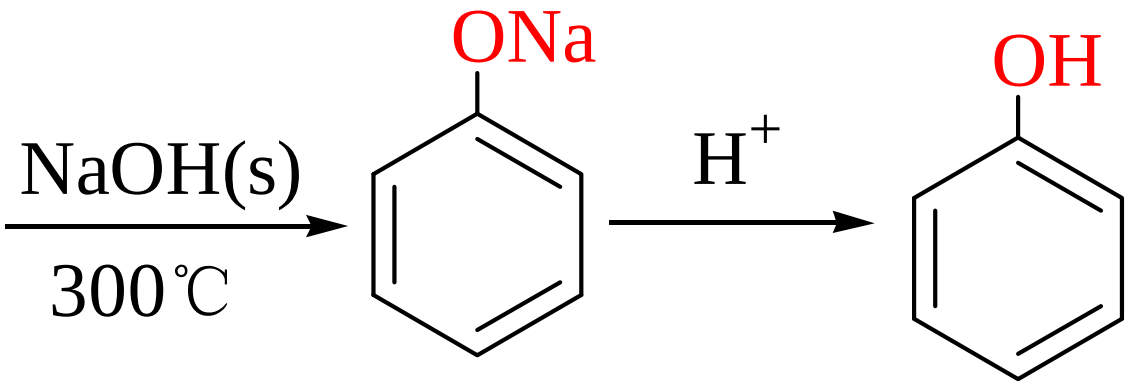
对苯醌可做为亲双烯体发生Diels—Alder反应



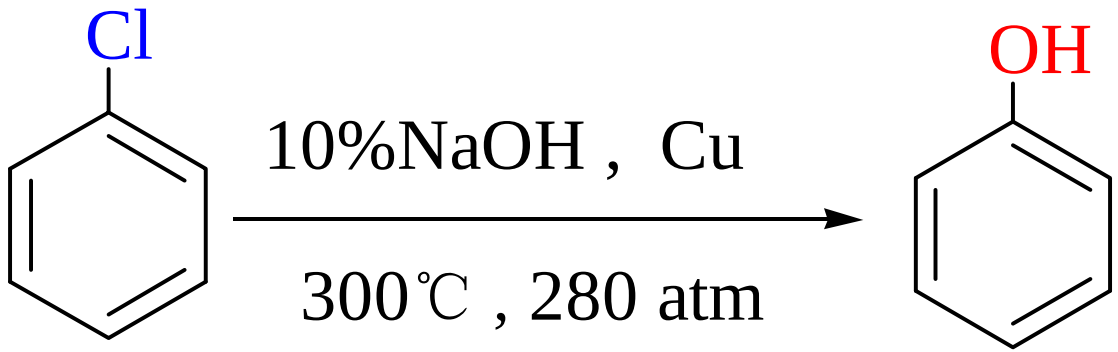
8.2.3 酚的制法

1. 磺酸盐碱熔法

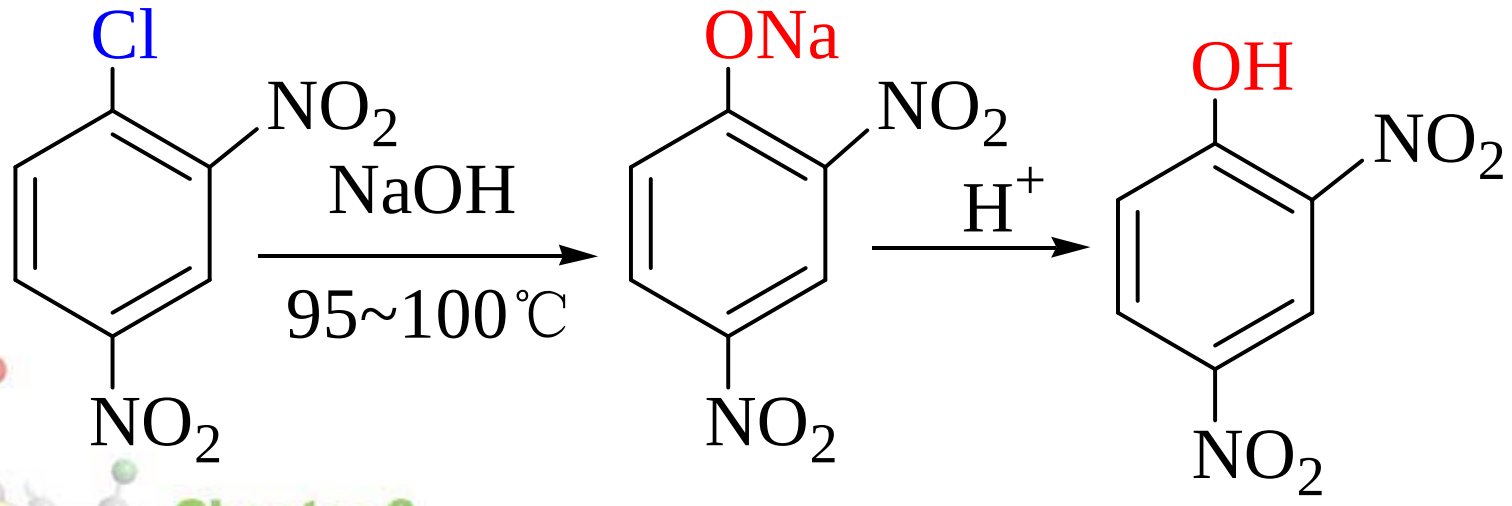




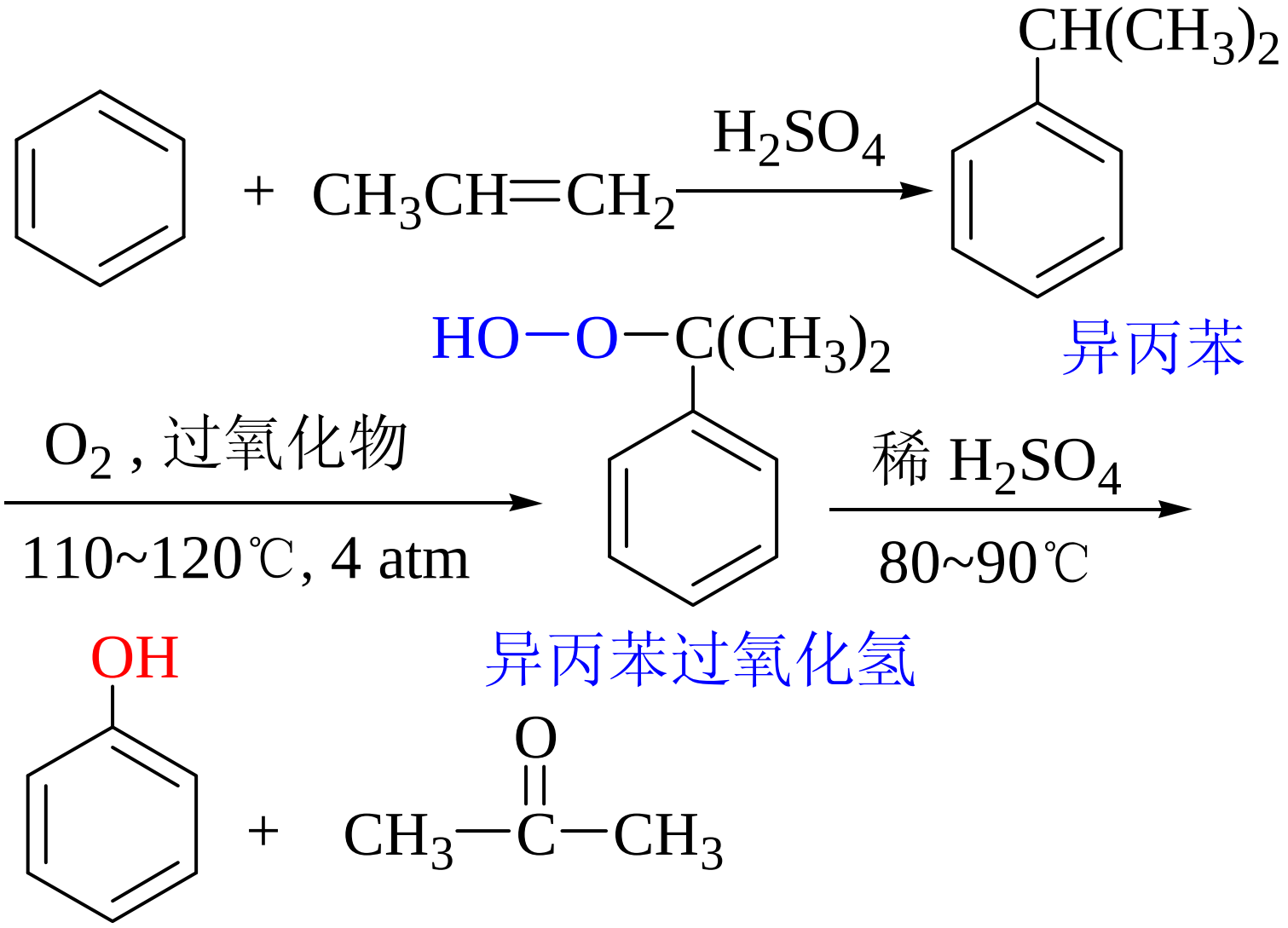
2. 氯苯水解法



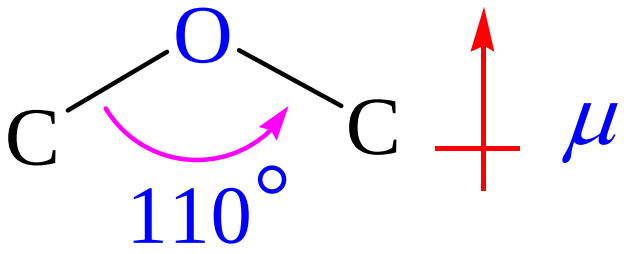
卤素的邻、对位有强吸电子基团时，水解变得容易进行：

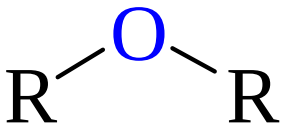


3. 异丙苯氧化法

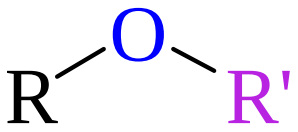

CH(CH3)2
H2SO4
+ CH3CH=CH2
异丙苯
HO−O−C(CH3)2
O2 , 过氧化物
110~120℃, 4 atm
稀 H2SO4
80~90℃
异丙苯过氧化氢
OH
O
CH3—C—CH3
+

8.3 醚

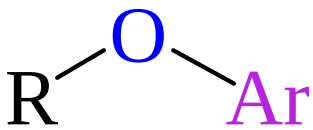
醚键 



简单醚
(对称醚)



混合醚
(不对称醚)



芳醚

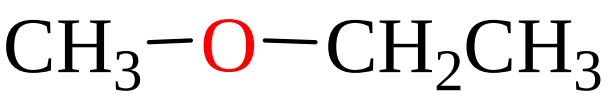
8.3.1 分类、命名和物理性质

1. 分类与命名

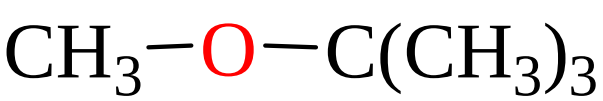
(1) 无环醚

根据烃基结构可分为饱和醚、不饱和醚和芳醚

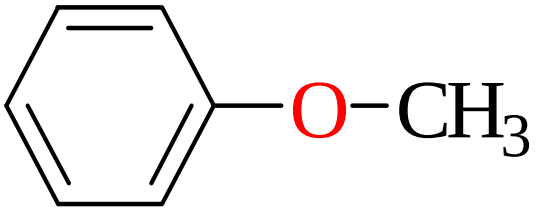
普通命名法：二个烃基名＋醚
二个烃基名中文按“次序规则”，



甲基乙基醚



甲基叔丁基醚



苯甲醚(茴香醚)

$CH_3CH_2-O-CH=CH_2$

乙基乙烯基醚

CH_3-O-CH_3

二甲醚(甲醚)

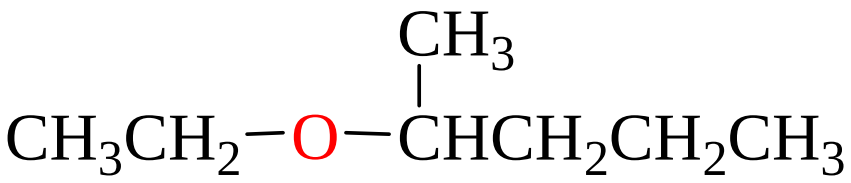
$CH_3CH_2-O-CH_2CH_3$

二乙醚(乙醚)

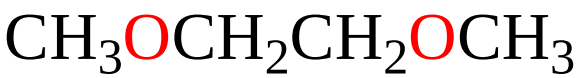
系统命名法

把醚看成是烃的烷氧衍生物，取较长的烃基做母体

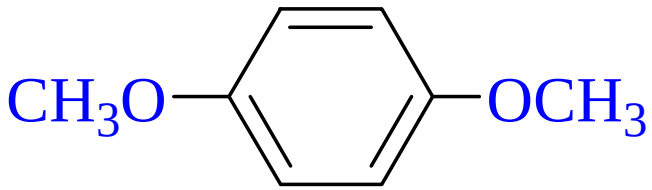
—OR　烷氧基



2－乙氧基戊烷

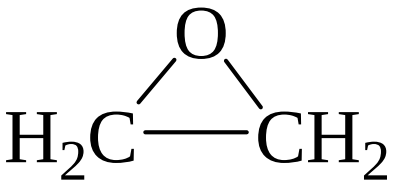


1,2－二甲氧基乙烷

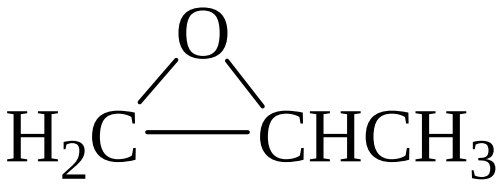


1,4－二甲氧基苯

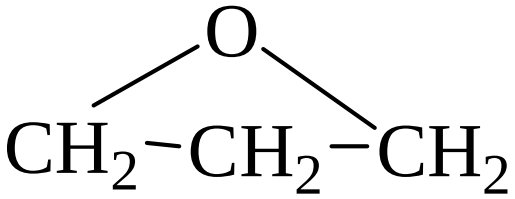
(2) 环醚



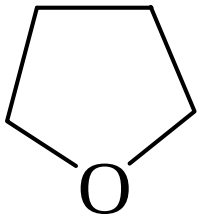
环氧乙烷



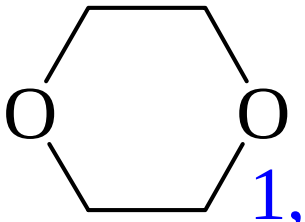
1,2-环氧丙烷



1,3－环氧丙烷



四氢呋喃
(THF)



1,4－二氧六环

2. 物理性质

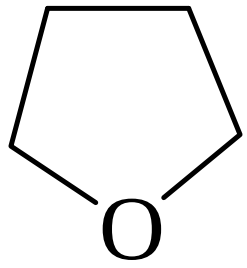
- 沸点 比同碳原子数的醇低得多
- 水中溶解度小(环醚除外)

	CH_3OCH_3	$CH_3CH_2OCH_2CH_3$
b.p.(℃)	-24.9	34.6
	CH_3CH_2OH	$CH_3CH_2CH_2CH_2OH$
b.p.(℃)	78.4	117.8

8.3.2 醚的制法

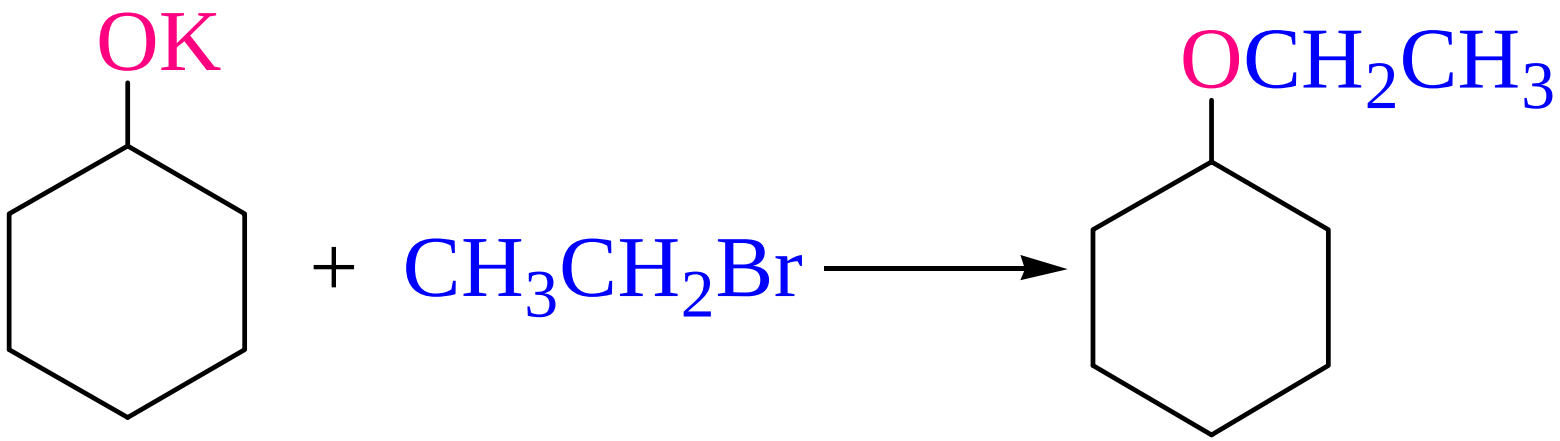
1. 醇的分子间脱水

$$2ROH \xrightarrow[\triangle]{H_2SO_4} ROR$$

$$HOCH_2CH_2CH_2CH_2OH \xrightarrow[\triangle]{H_2SO_4} \text{  }$$

2. Williamson 合成法

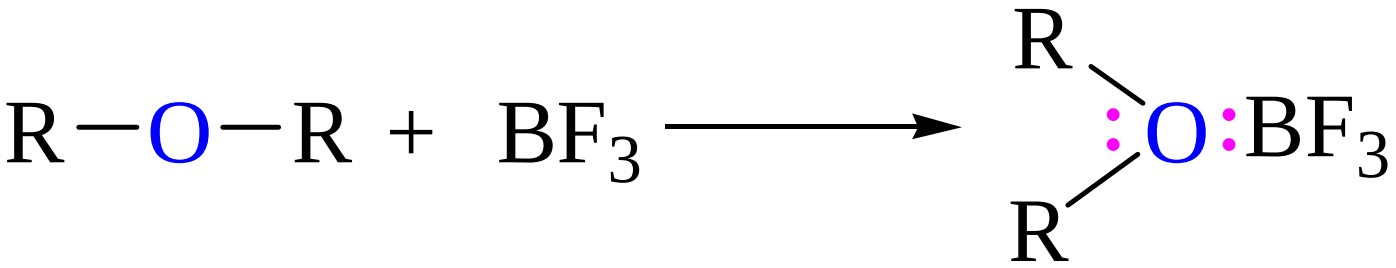
$$\begin{matrix} RONa \\ ArONa \end{matrix} + R'X \longrightarrow \begin{matrix} ROR' \\ ArOR' \end{matrix}$$

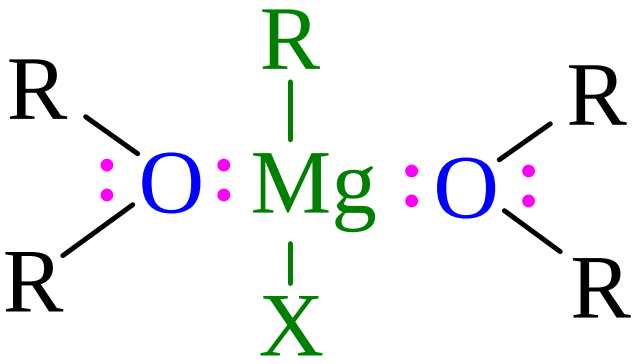


$$(CH_3)_3CONa + CH_3I \longrightarrow (CH_3)_3COCH_3$$

8.3.3 醚的反应

1. 形成鎓盐





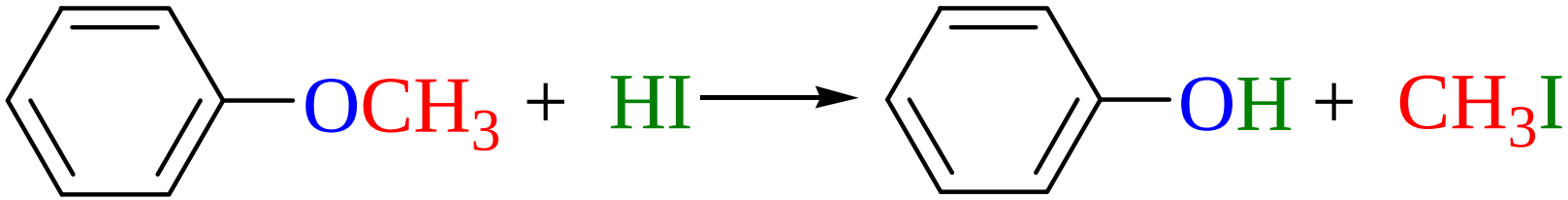
2. 醚键的断裂

$$CH_3-O-CH_3 + HI \longrightarrow CH_3OH + CH_3I$$

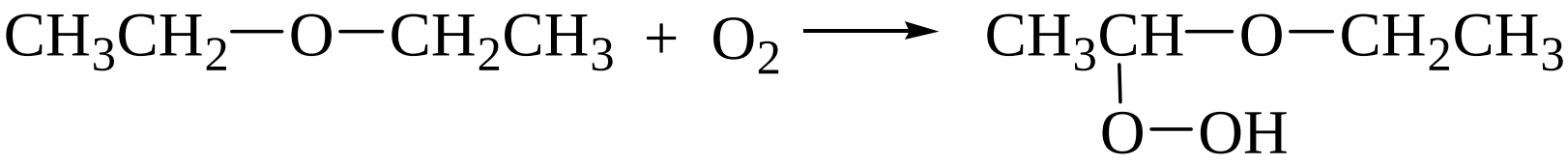
$$CH_3OH \xrightarrow{HI} CH_3I$$

$$(CH_3)_3C-O-CH_3 + HI \longrightarrow (CH_3)_3CI + CH_3OH$$

更正：**P183**



3. 过氧化物的生成



检验：淀粉－碘化钾试纸

除去过氧化物的方法：$FeSO_4$洗涤

储存时加Fe可防止形成过氧化物

8.3.4 环氧化合物的反应