第 八 章

醇、酚和醚

alcohol, phenol and ether

醇、酚、醚都是烃的含氧衍生物

醇与酚还有相同的官能团:羟基(－OH)

相同分子式的醇与醚互为同分异构体

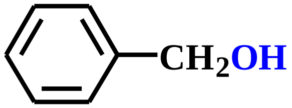
第一节　醇

一、醇的分类和命名

1. 分类

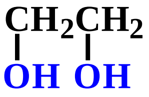
按烃基结构

- 饱和醇　$CH_3CH_2CH_2OH$
- 不饱和醇　$CH_2{=}CHCH_2OH$
- 芳香醇



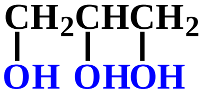
按羟基数目

- 一元醇　CH_3CH_2OH
- 二元醇



$$\underset{OH}{\underset{|}{CH_2}}\underset{OH}{\underset{|}{CH_2}}$$

- 多元醇



$$\underset{OH}{\underset{|}{CH_2}}\underset{OH}{\underset{|}{CH}}\underset{OH}{\underset{|}{CH_2}}$$

按羟基所连碳原子的类型

- 一级醇　RCH_2OH
- 二级醇　R_2CHOH
- 三级醇　R_3COH

2. 命名

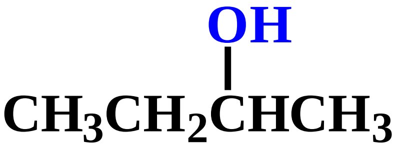
1）普通命名法

$CH_3CH_2CH_2CH_2OH$

正丁醇

$(CH_3)_2CHCH_2OH$

异丁醇



$$\begin{array}{c}OH\\ |\\ CH_3CH_2CHCH_3\end{array}$$

仲丁醇

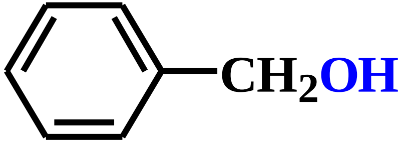
$(CH_3)_3COH$

叔丁醇

一些醇的普通名称被IUPAC接受

$CH_2{=}CHCH_2OH$

烯丙醇



苄醇

$$\begin{array}{ccc}CH_2 & CH & CH_2\\ | & | & |\\ OH & OH & OH\end{array}$$

丙三醇（甘油）

2）系统命名法

A、选取连羟基碳的支链最多的最长碳链作主链；

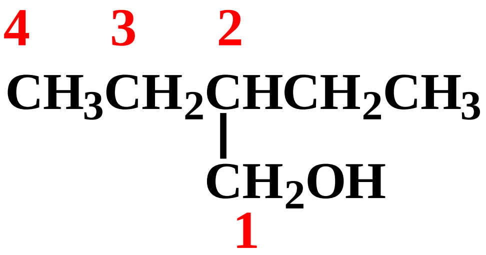
Find the longest carbon chain containing the carbon with the -OH group.

B、从靠近羟基的一端开始编号，并使取代基位次尽可能小；

Number the chain, starting from the end closest to the -OH group.

C、写出取代基的名称、个数、位次，给出主链名称（注意：标出羟基位次）。

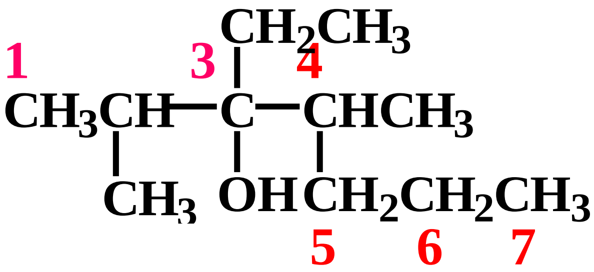
Number and name all substituents.



$CH_3CH_2CH(CH_2OH)CH_2CH_3$

2-乙基丁-1-醇

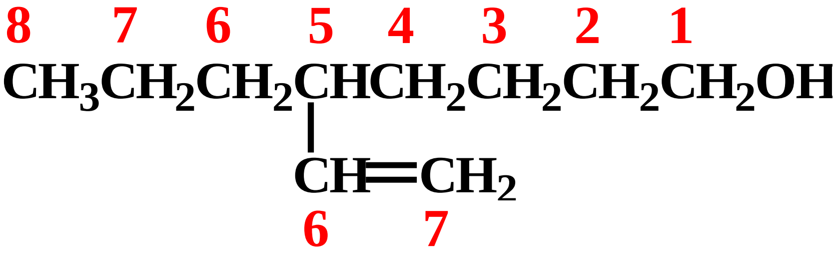
2-ethylbutan-1-ol



$CH_3CH(CH_3)C(OH)(CH_2CH_3)CH(CH_3)CH_2CH_2CH_3$

3-乙基-2,4-二甲基庚-3-醇

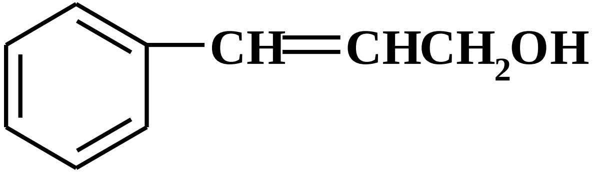
3-ethyl-2,4-dimethylheptan-3-ol



$CH_3CH_2CH_2CH(CH{=}CH_2)CH_2CH_2CH_2CH_2OH$

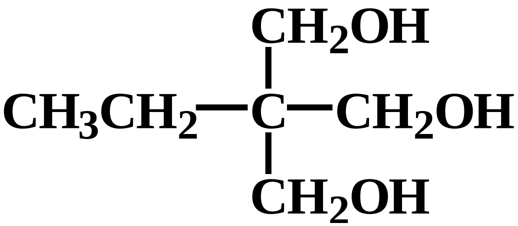
5-乙烯基辛-1-醇

5-vinyloctan-1-ol



3-苯基丙-2-烯-1-醇

3-phenylpropan-2-en-1-ol



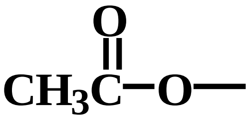
$CH_3CH_2-\overset{CH_2OH}{\underset{CH_2OH}{C}}-CH_2OH$

2-乙基- 2-羟甲基丙-1,3-二醇

2-ethyl-2-hydroxymethylpropane-1,3-diol

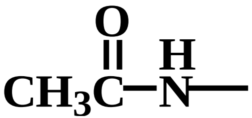
$ClCH_2CH_2-$

2-氯乙基



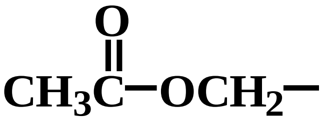
$CH_3\overset{O}{\overset{\|}{C}}-O-$

乙酰氧基



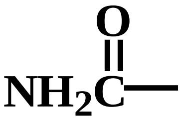
$CH_3\overset{O}{\overset{\|}{C}}-\overset{H}{N}-$

乙酰氨基



$CH_3\overset{O}{\overset{\|}{C}}-OCH_2-$

乙酰氧甲基

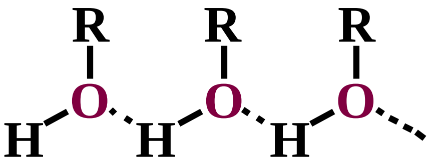


$NH_2\overset{O}{\overset{\|}{C}}-$

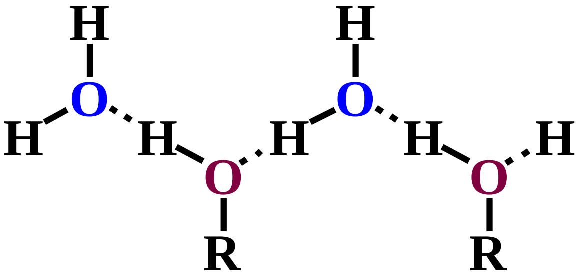
氨甲酰基

二、醇的物理性质

醇是极性分子，分子间能形成氢键，具有较高的熔、沸点。醇和水之间也能形成氢键，水溶性较好。



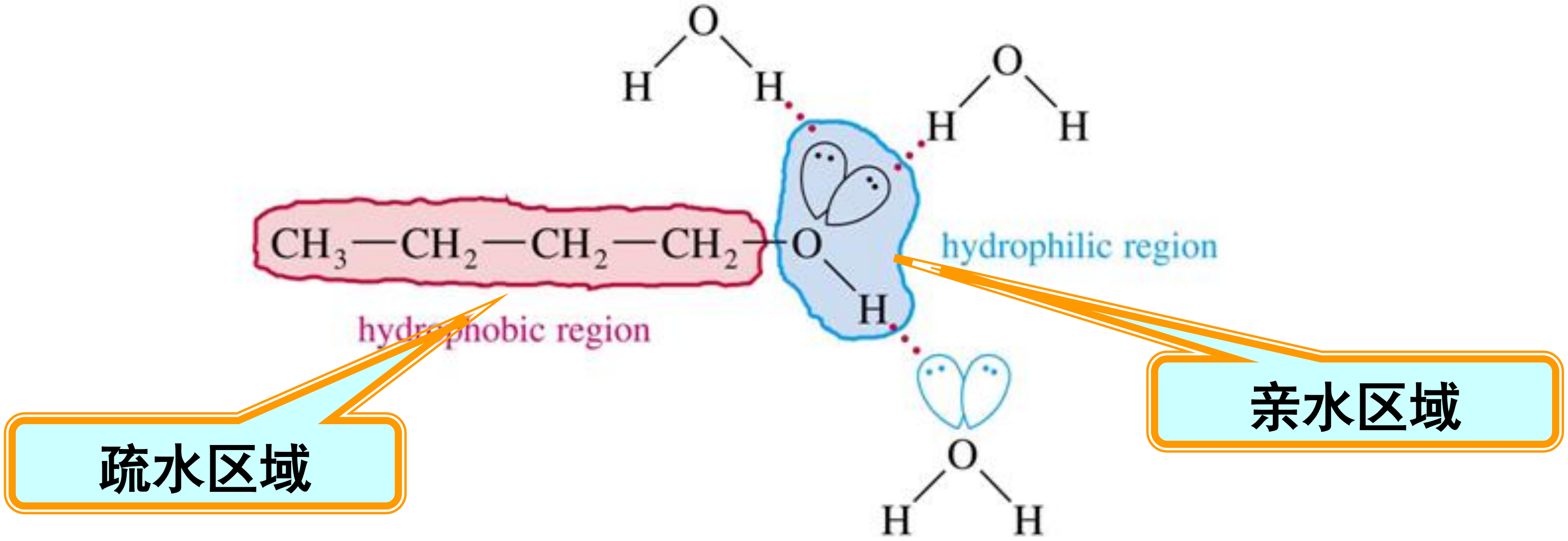
醇分子间氢键



醇与水分子间形成氢键

溶解度

低级醇溶于水，甲醇、乙醇、丙醇与水混溶。随分子量增大，水溶性降低。

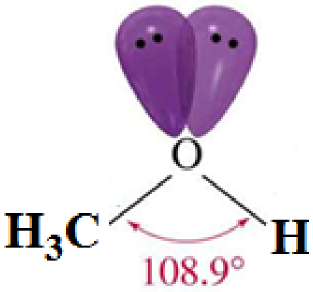


疏水区域

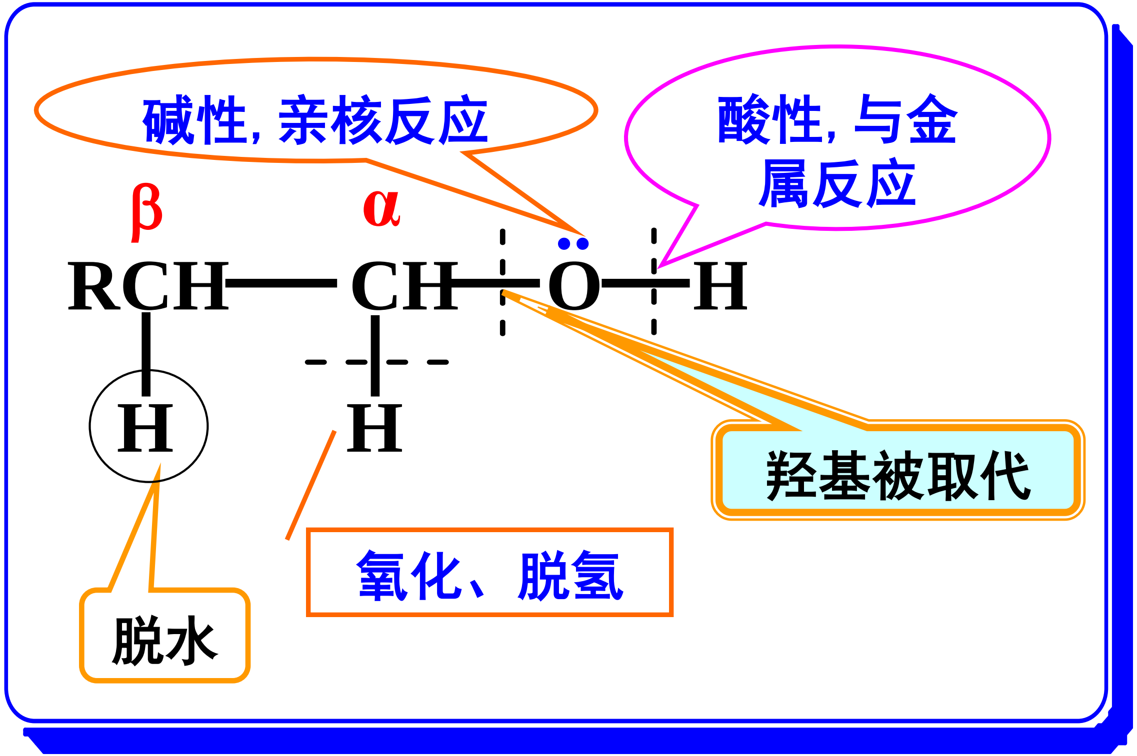
亲水区域

Solubility decreases as the size of the alkyl group increases.

三、醇的化学性质



Oxygen is sp^3 hybridized



（一）醇的酸碱性

1. 酸性

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

$$HOH + Na \longrightarrow NaOH + H_2\uparrow$$

醇的酸性比水弱，反应速度比水慢

反应速度：

$CH_3OH > C_2H_5OH > CH_3CH_2CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$

甲醇　乙醇　正丙醇　异丙醇　叔丁醇

$$\underset{\text{强碱}}{RONa} + \underset{\text{强酸}}{H_2O} \rightleftharpoons \underset{\text{弱酸}}{ROH} + \underset{\text{弱碱}}{NaOH}$$

醇与Mg、Al反应：

$$CH_3CH_2OH + Mg \xrightarrow{I_2} (CH_3CH_2O)_2Mg$$

$$(CH_3)_2CHOH + Al \xrightarrow{HgCl} [(CH_3)_2CHO]_3Al$$

异丙醇铝

2. 碱性和亲核性

$$R\ddot{O}H + H^+ \longrightarrow ROH_2^+$$

- ROH is weak nucleophile
- RO^- is strong nucleophile

（二）羟基被取代

1. 卤代烃的生成

$$R-OH + HX \rightleftharpoons R-X + H_2O$$

活性：

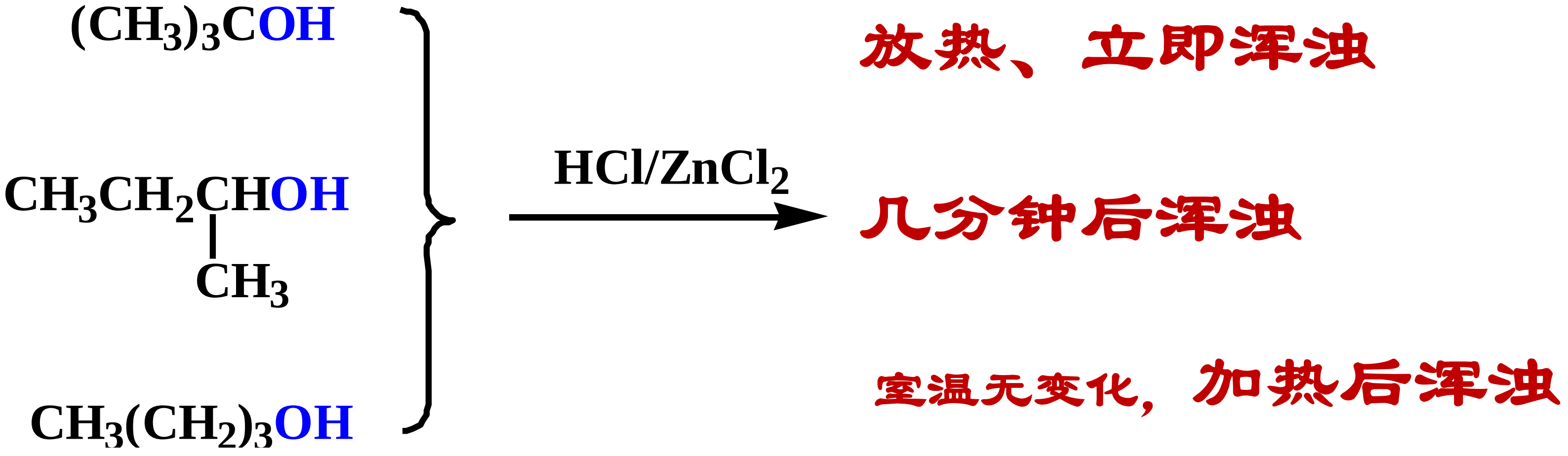
氢卤酸　HI > HBr > HCl > HF

醇　苄基型、烯丙型醇 > 叔醇 > 仲醇 > 伯醇 > 甲醇

卢卡氏试剂 Lucas reagent：

$$\text{Con. } HCl\ /ZnCl_2$$

适用于C6以下叔、仲、伯醇的鉴别



$(CH_3)_3COH$

$CH_3CH_2\underset{\substack{|\\ CH_3}}{C}HOH$

$CH_3(CH_2)_3OH$

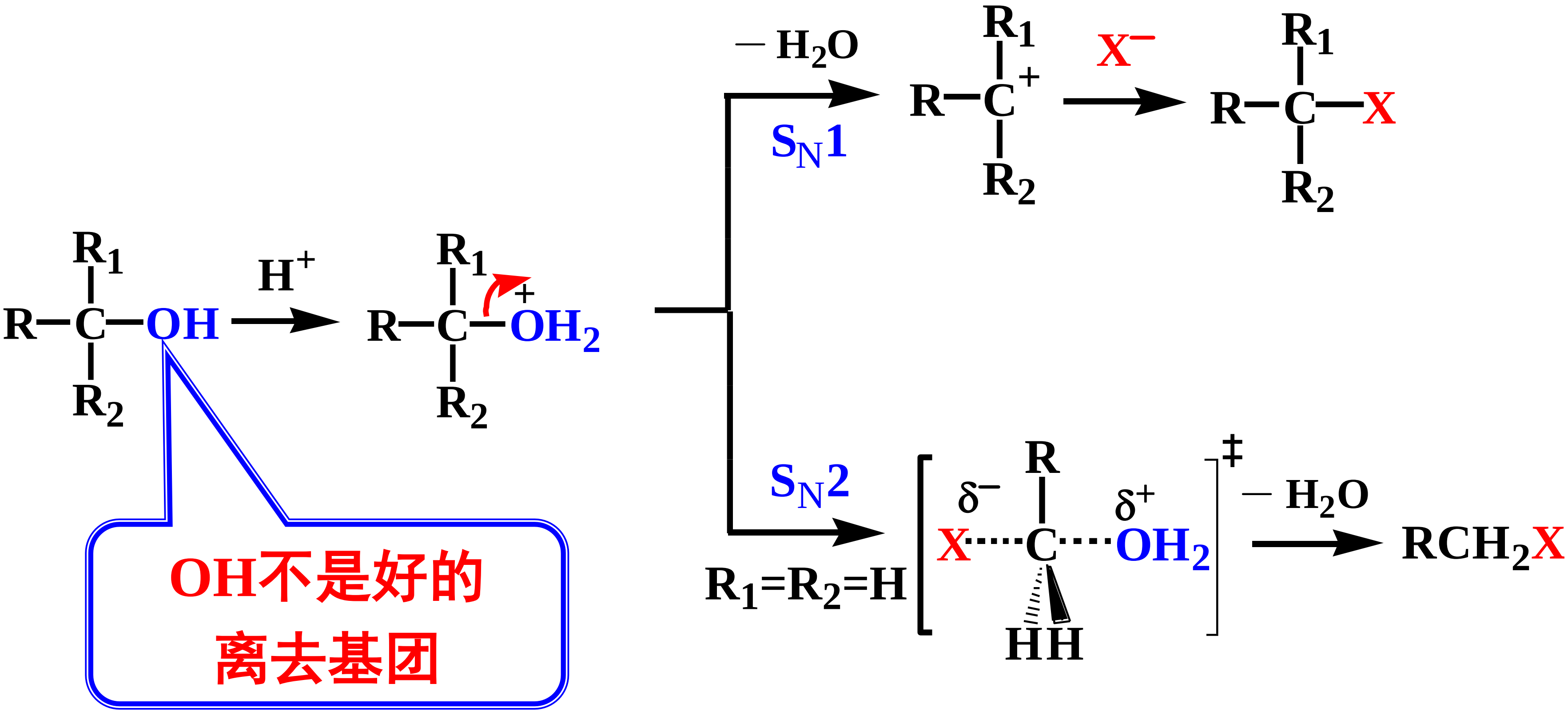
$\xrightarrow{HCl/ZnCl_2}$

放热、立即浑浊

几分钟后浑浊

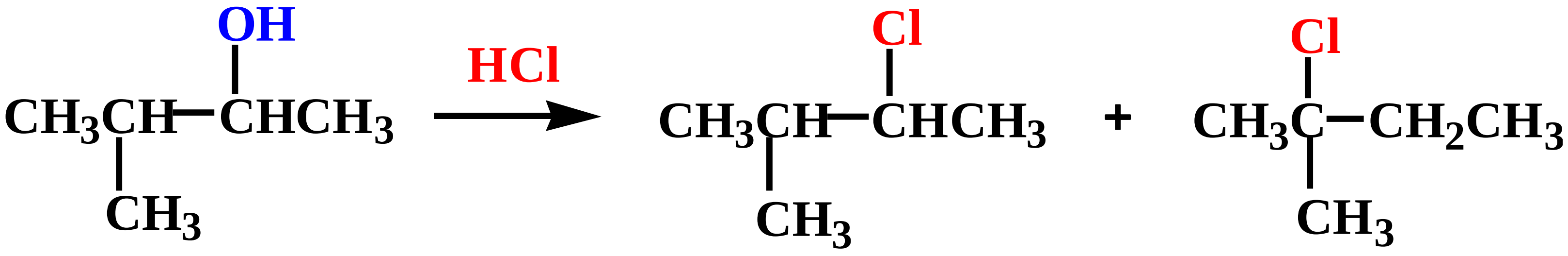
室温无变化，加热后浑浊

机理：



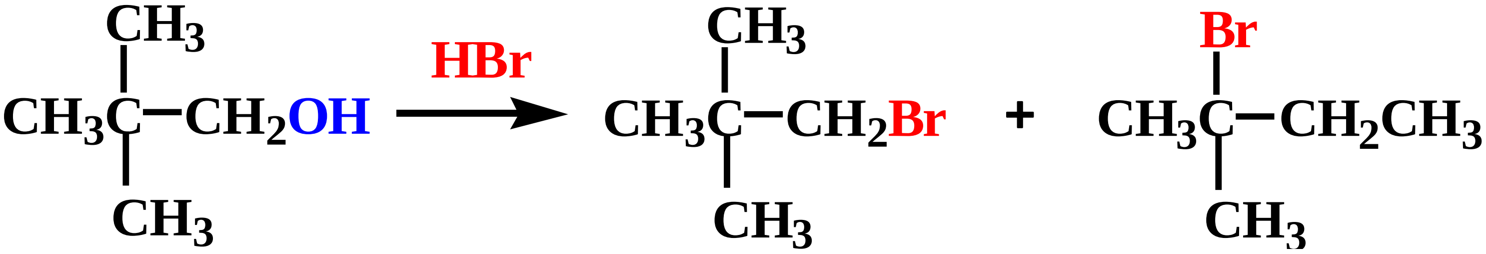
OH不是好的离去基团

反应事实：



$$CH_3\underset{\underset{CH_3}{|}}{C}H-\overset{\overset{OH}{|}}{C}HCH_3 \xrightarrow{HCl} CH_3\underset{\underset{CH_3}{|}}{C}H-\overset{\overset{Cl}{|}}{C}HCH_3 + CH_3\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_3$$

重排产物

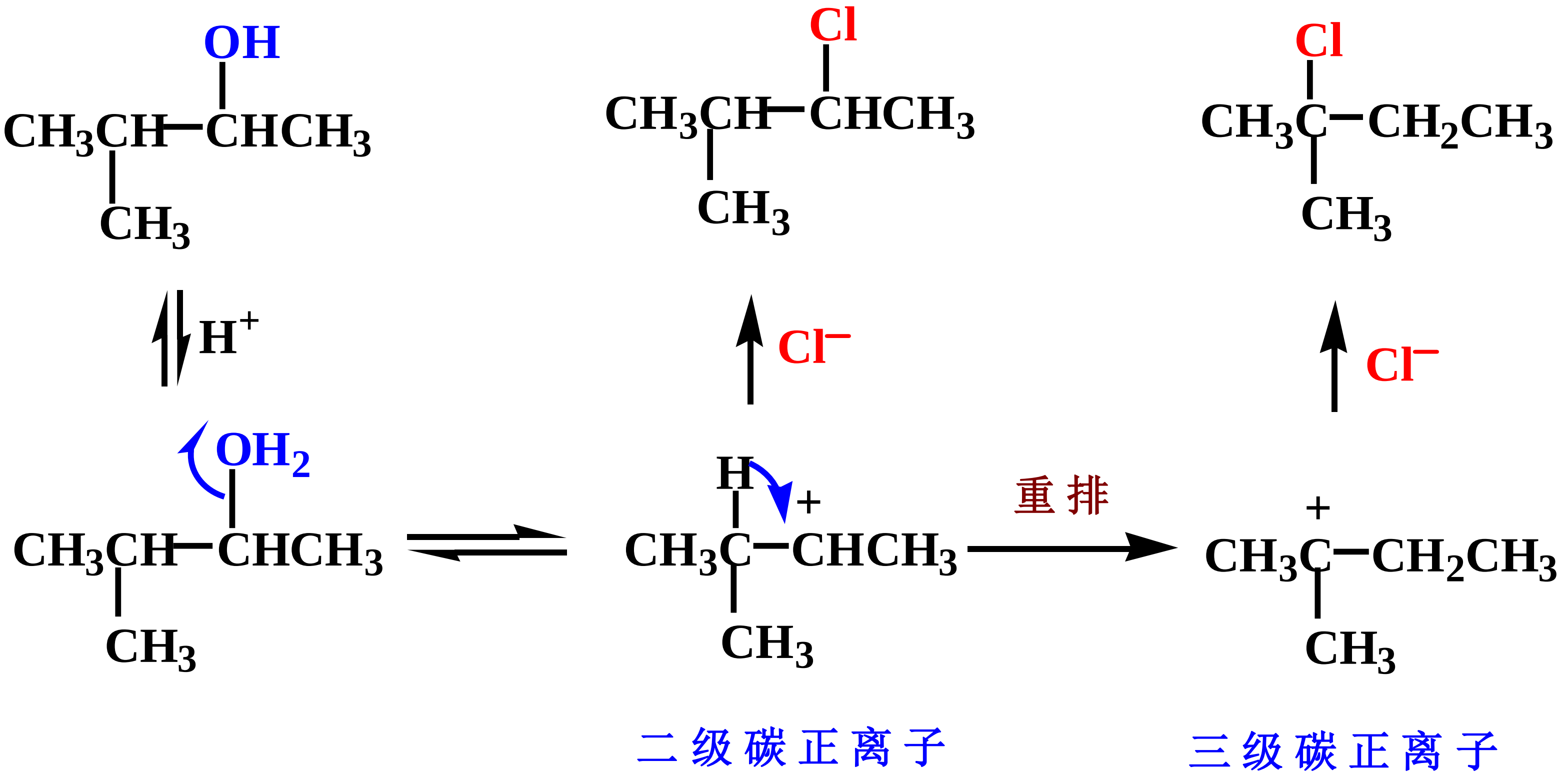


$$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2OH \xrightarrow{HBr} CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2Br + CH_3\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_3$$

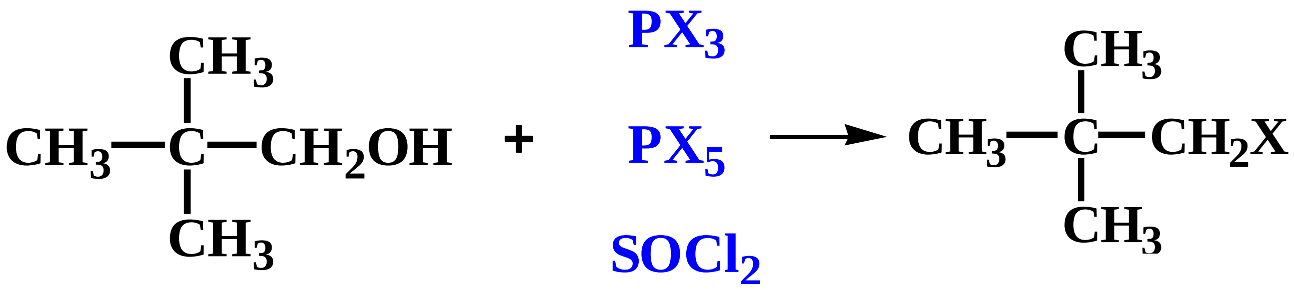
重排产物

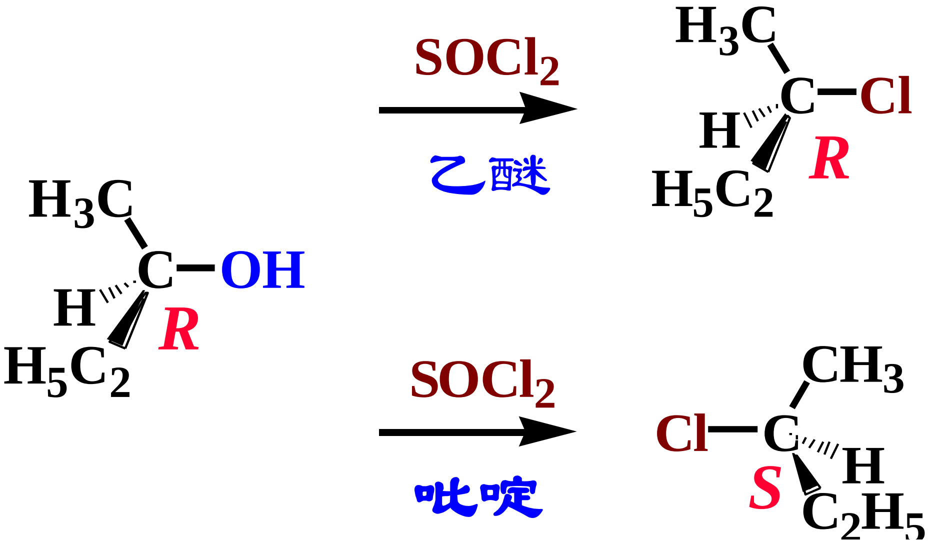
某些情况下，会发生碳正离子重排，得到骨架改变的产物。

反应历程：



OH
CH3CH—CHCH3
CH3
H+
OH2
CH3CH—CHCH3
CH3
Cl
CH3CH—CHCH3
CH3
Cl−
H
+
CH3C—CHCH3
CH3
重 排
Cl
CH3C—CH2CH3
CH3
Cl−
+
CH3C—CH2CH3
CH3
二 级 碳 正 离 子
三 级 碳 正 离 子


$CH_3C(CH_3)_2CH_2OH$
+
PX_3
PX_5
$SOCl_2$
$CH_3C(CH_3)_2CH_2X$


H_3C
H
H_5C_2
OH
R
$SOCl_2$
乙醚
Cl
R
$SOCl_2$
吡啶
CH_3
Cl
H
C_2H_5
S

2. 酸酯的生成

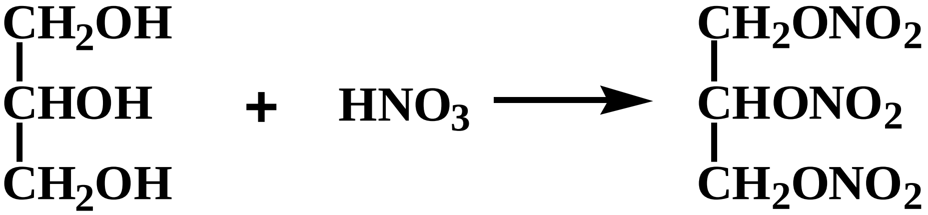
$$CH_3OH + CH_3COOH \xrightleftharpoons{H^+} CH_3COOCH_3$$

$$\begin{tikzcd}
CH_3CH_2OH + H_2SO_4 \arrow[r] & CH_3CH_2OSO_2OH \arrow[d, "\text{减压蒸馏}"] & CH_2{=}CH_2 + H_2SO_4 \arrow[l] \\
 & CH_3CH_2OSO_2OCH_2CH_3 &
\end{tikzcd}$$

硫酸氢乙酯

$(C_2H_5)_2SO_4$

硫酸二乙酯



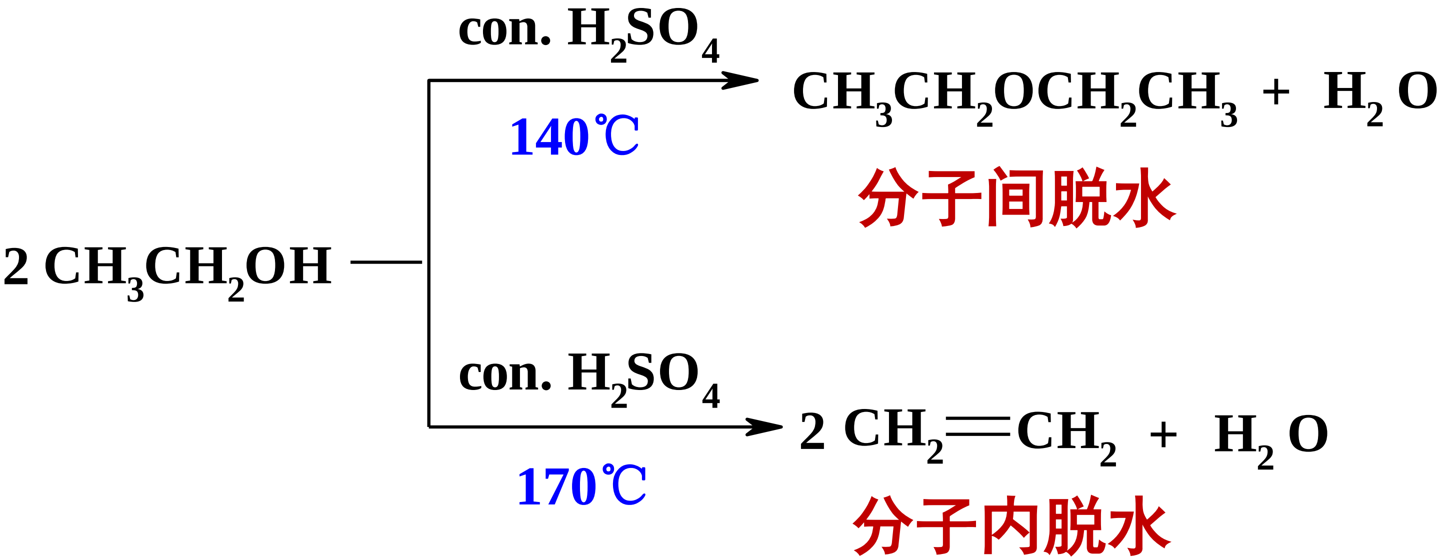
$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + HNO_3 \longrightarrow \begin{array}{l} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2 \end{array}$$

硝酸甘油

抗心绞痛

炸药

（三）脱水反应



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

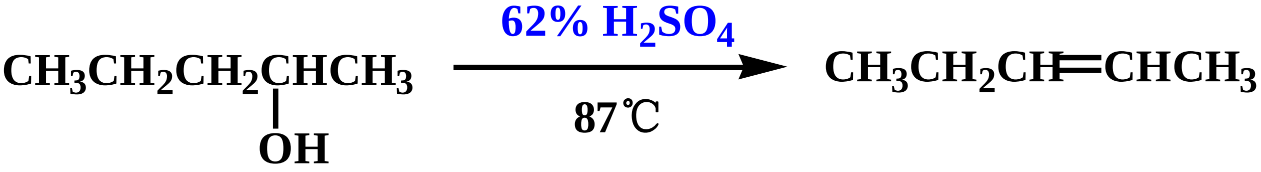
分子间脱水

$$2\,CH_3CH_2OH \xrightarrow[\text{170℃}]{con.\ H_2SO_4} 2\,CH_2{=}CH_2 + H_2O$$

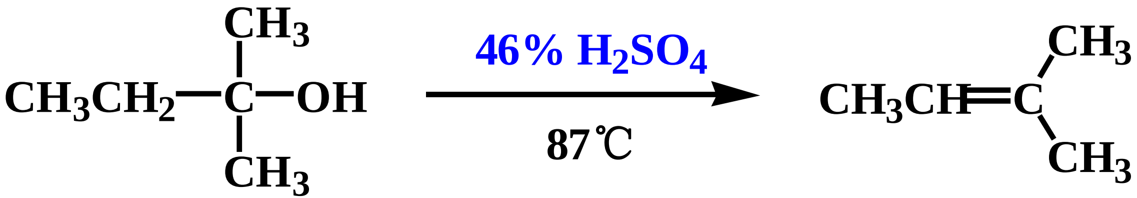
分子内脱水

常用催化剂：H_2SO_4、H_3PO_4、$AlCl_3$

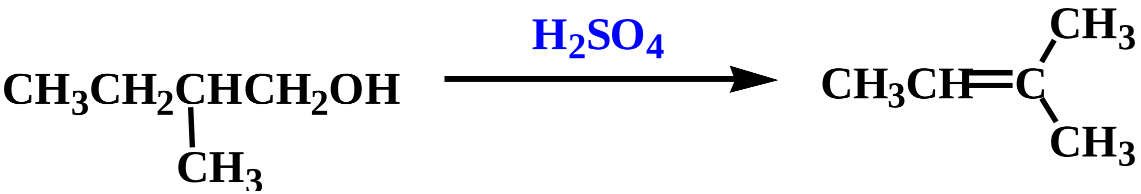
反应事实：



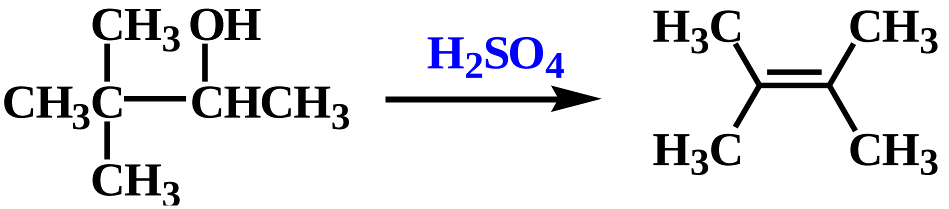
$$CH_3CH_2CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 \xrightarrow[87℃]{62\%\ H_2SO_4} CH_3CH_2CH{=}CHCH_3$$



$$CH_3CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH \xrightarrow[87℃]{46\%\ H_2SO_4} CH_3CH{=}C(CH_3)_2$$



$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH \xrightarrow{H_2SO_4} CH_3CH{=}C(CH_3)_2$$



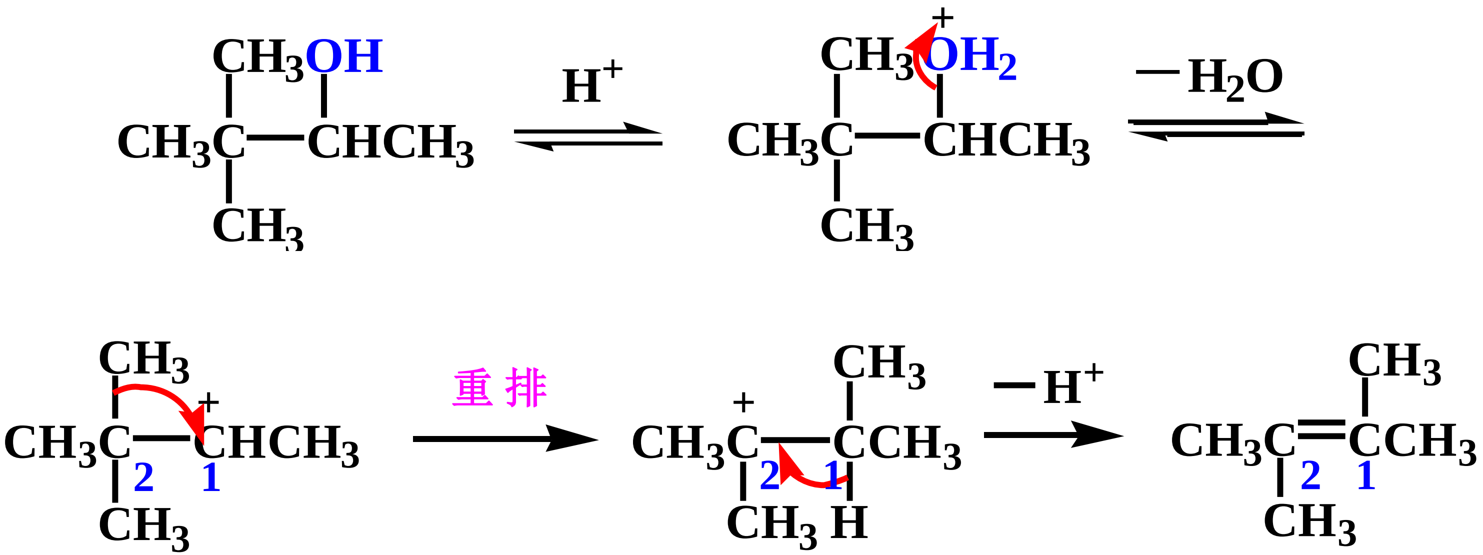
$$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\overset{\displaystyle OH}{C}HCH_3 \xrightarrow{H_2SO_4} (H_3C)_2C{=}C(CH_3)_2$$

1）难易程度：$R_3COH > R_2CHOH > RCH_2OH$

2）消除方向：符合Saytzeff’s rule

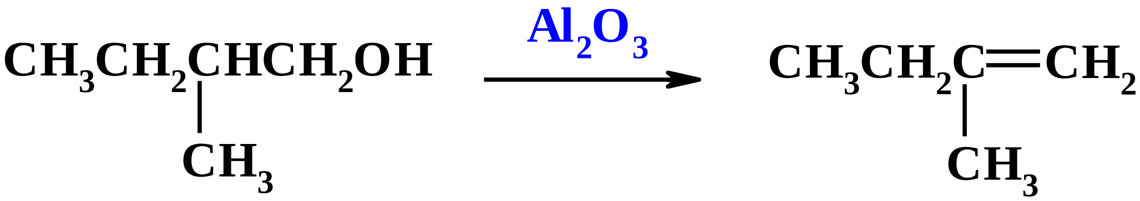
3）可能会发生碳正离子重排

反应机理：



$$CH_3\overset{CH_3}{\underset{CH_3}{C}}-\overset{OH}{C}HCH_3 \xrightleftharpoons{H^+} CH_3\overset{CH_3}{\underset{CH_3}{C}}-\overset{\overset{+}{O}H_2}{C}HCH_3 \xrightleftharpoons{-H_2O}$$

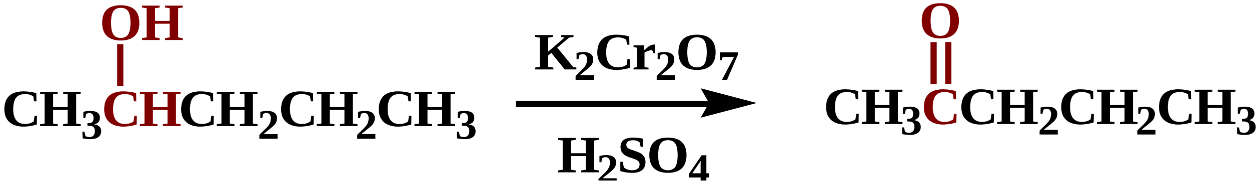
$$CH_3\overset{CH_3}{\underset{CH_3}{C}}-\overset{+}{C}HCH_3 \xrightarrow{重排} CH_3\overset{+}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{H}{C}}CH_3 \xrightarrow{-H^+} CH_3\underset{CH_3}{C}=\overset{CH_3}{C}CH_3$$



$$CH_3CH_2\underset{CH_3}{C}HCH_2OH \xrightarrow{Al_2O_3} CH_3CH_2\underset{CH_3}{C}=CH_2$$

（四）氧化和脱氢

$$RCH_2OH \xrightarrow[H_2SO_4]{KMnO_4} RCHO \xrightarrow[H_2SO_4]{KMnO_4} RCOOH$$



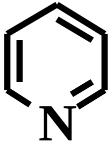
$$CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_2CH_2CH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CH_3$$

$$(CH_3)_3COH \longrightarrow \times$$

选择性氧化剂:

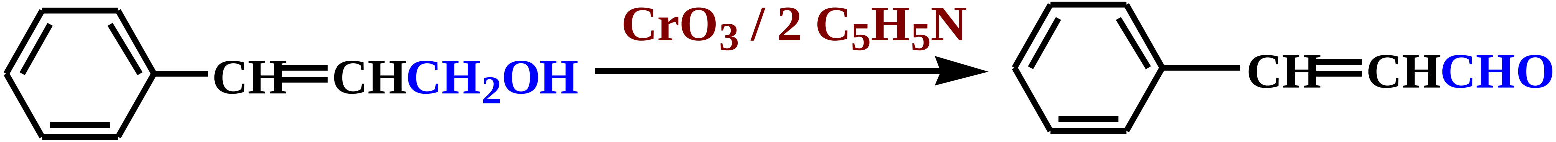
1）琼斯试剂(Jones’ Reagent)：CrO_3/H_2SO_4

2）沙瑞特试剂(Sarrett Reagent): CrO_3 /



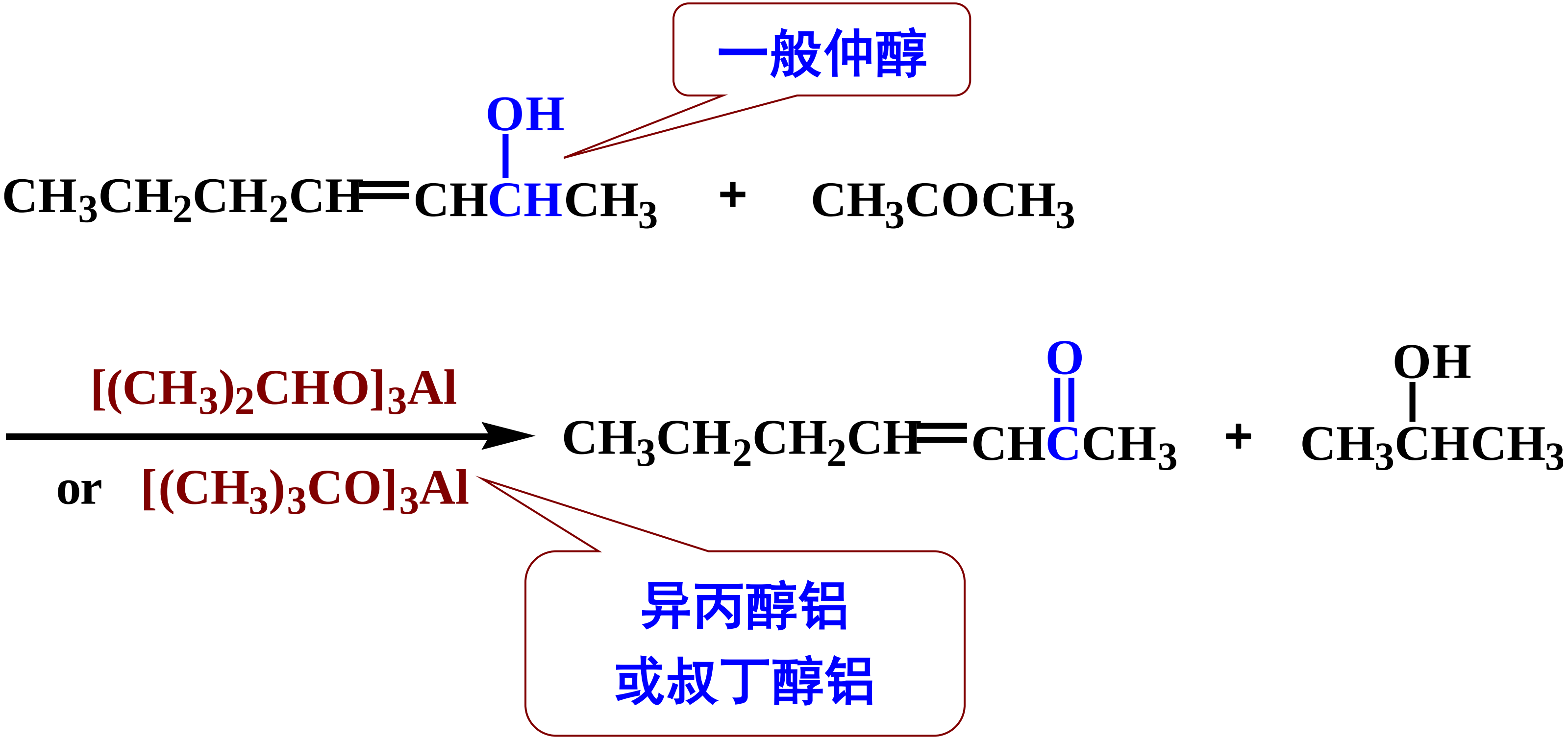
3）活性二氧化锰 MnO_2

$$CH_2{=}CHCH_2OH \xrightarrow{MnO_2} CH_2{=}CHCHO$$



欧芬脑尔氧化：

Oppenauer Oxidation



$$CH_3CH_2CH_2CH{=}CH\overset{OH}{\overset{|}{C}H}CH_3 + CH_3COCH_3 \xrightarrow[\text{or } [(CH_3)_3CO]_3Al]{[(CH_3)_2CHO]_3Al} CH_3CH_2CH_2CH{=}CH\overset{O}{\overset{\|}{C}}CH_3 + CH_3\overset{OH}{\overset{|}{C}H}CH_3$$

一般仲醇

异丙醇铝
或叔丁醇铝

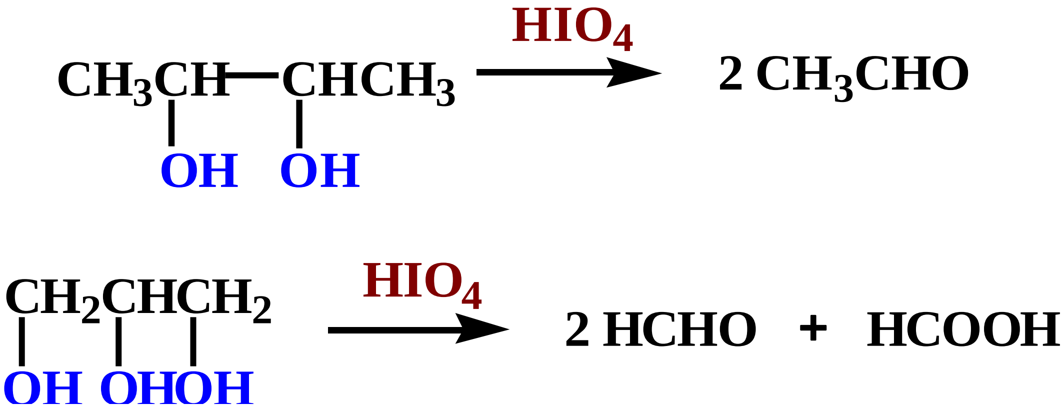
四、邻二醇

两个羟基连在两个叔碳原子上的邻二醇 ——频哪醇类化合物

化学性质

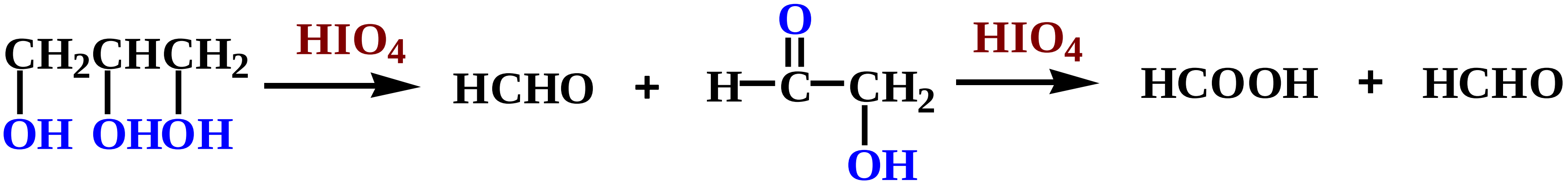
1. 氧化

高碘酸 HIO_4和四醋酸铅 $Pb(OAc)_4$



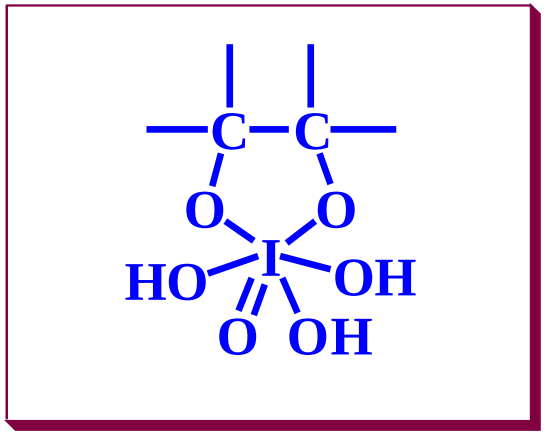
$$CH_3\underset{OH}{CH}-\underset{OH}{CH}CH_3 \xrightarrow{HIO_4} 2\,CH_3CHO$$

$$\underset{OH}{CH_2}\underset{OH}{CH}\underset{OH}{CH_2} \xrightarrow{HIO_4} 2\,HCHO + HCOOH$$



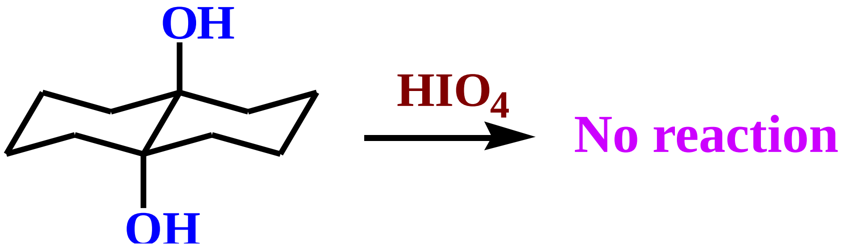
$$\underset{\mathrm{OH}}{\mathrm{CH_2}}\underset{\mathrm{OH}}{\mathrm{CH}}\underset{\mathrm{OH}}{\mathrm{CH_2}} \xrightarrow{\mathrm{HIO_4}} \mathrm{HCHO} + \mathrm{H}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{OH}}{\mathrm{CH_2}} \xrightarrow{\mathrm{HIO_4}} \mathrm{HCOOH} + \mathrm{HCHO}$$

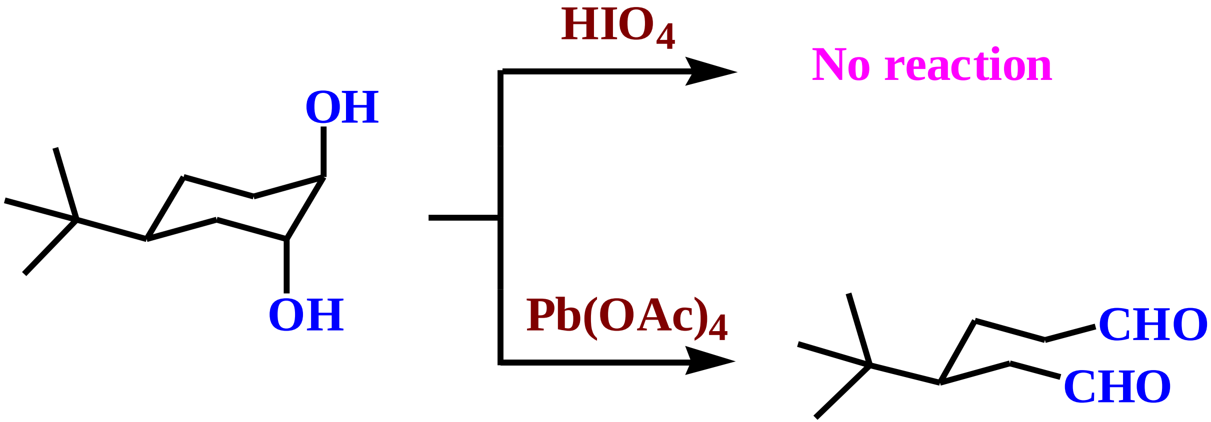
α-羟基乙醛



环状高碘酸酯

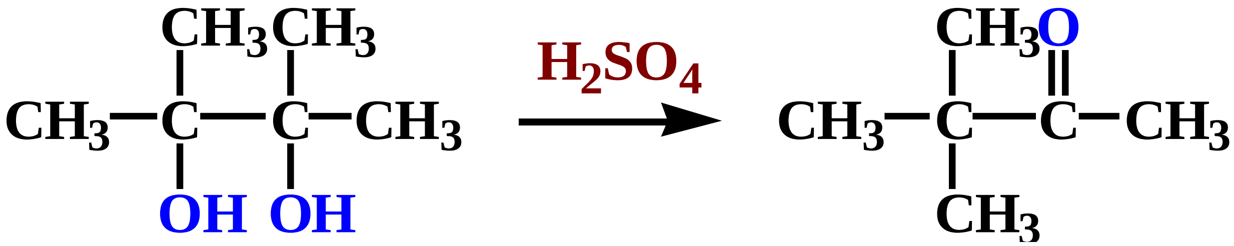

OH
OH
HIO$_4$
CHO
CHO


OH
OH
HIO$_4$
No reaction


OH
OH
HIO$_4$
No reaction
Pb(OAc)$_4$
CHO
CHO

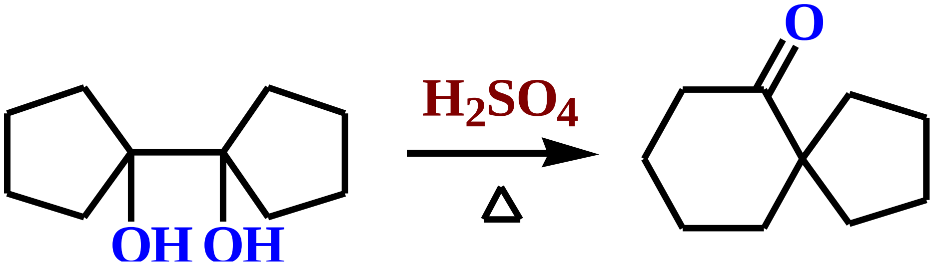
2. 频那醇重排

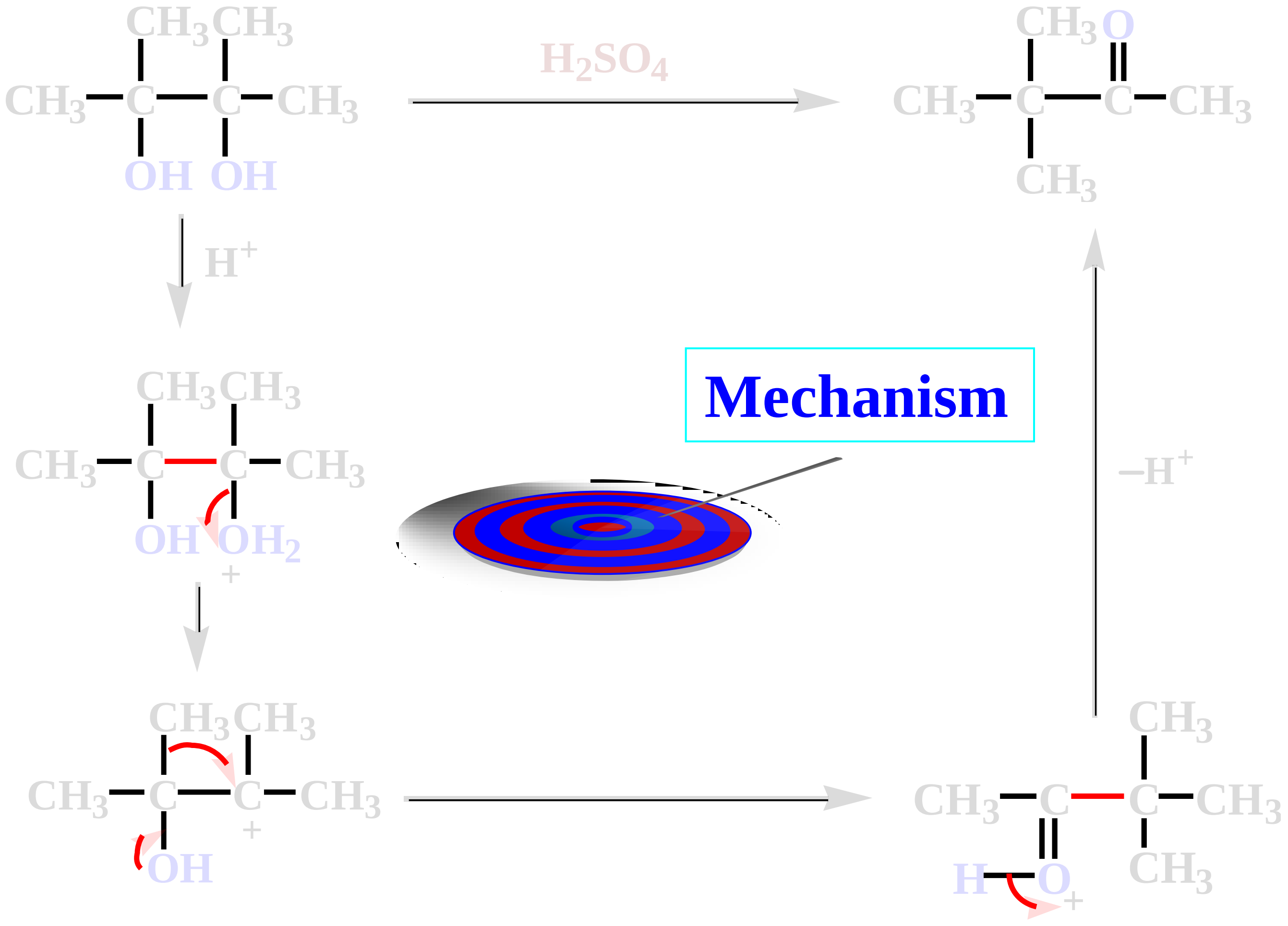
Pinacol Rearrangement



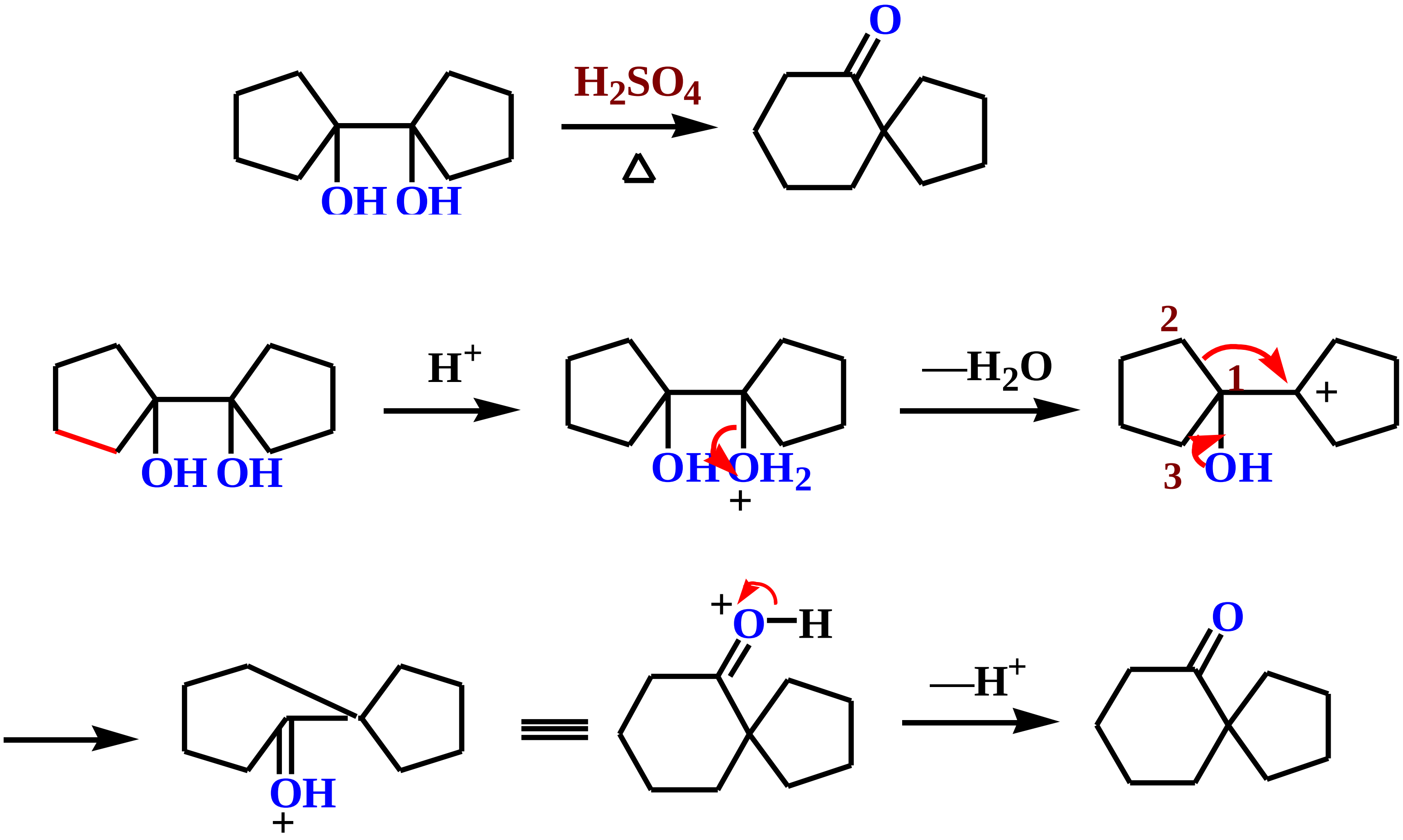
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}-CH_3 \xrightarrow{H_2SO_4} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$

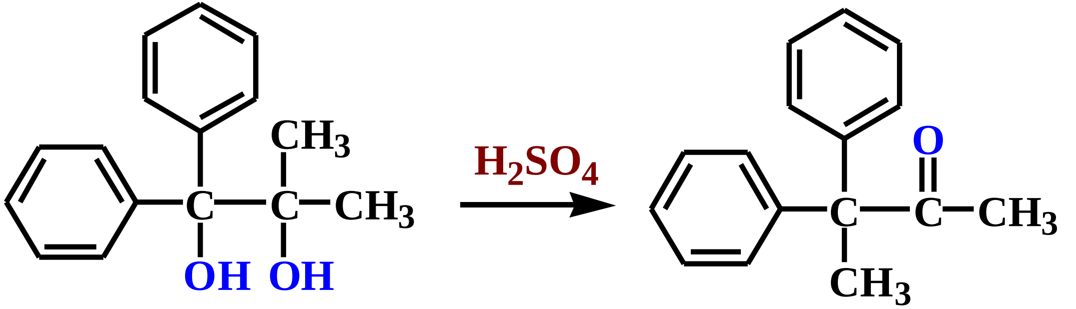
频哪醇　　　　频哪酮

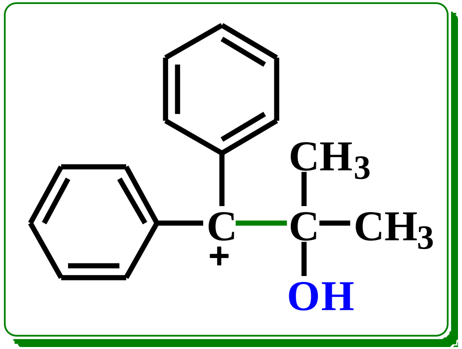



CH3 CH3
CH3 C C CH3
OH OH
H2SO4
CH3 O
CH3 C C CH3
CH3
H+
CH3 CH3
CH3 C C CH3
OH OH2
+
−H+
CH3 CH3
CH3 C C CH3
+
OH
CH3
CH3 C C CH3
H O
+
CH3

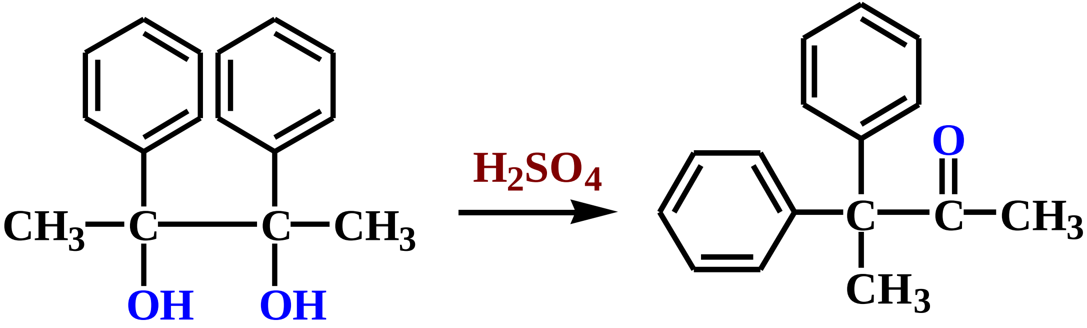
Mechanism

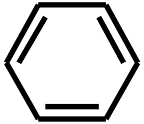

OH
OH
H_2SO_4
Δ
O
OH
OH
H^+
OH
OH_2
+
$-H_2O$
2
1
+
3
OH
OH
+
+
O
H
$-H^+$
O



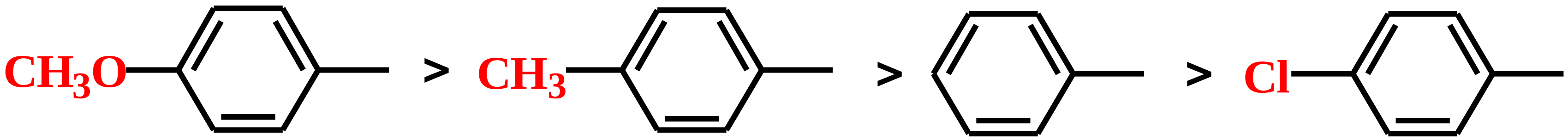


重排产物取决于碳正离子的稳定性



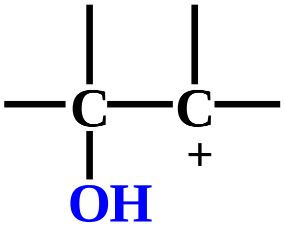


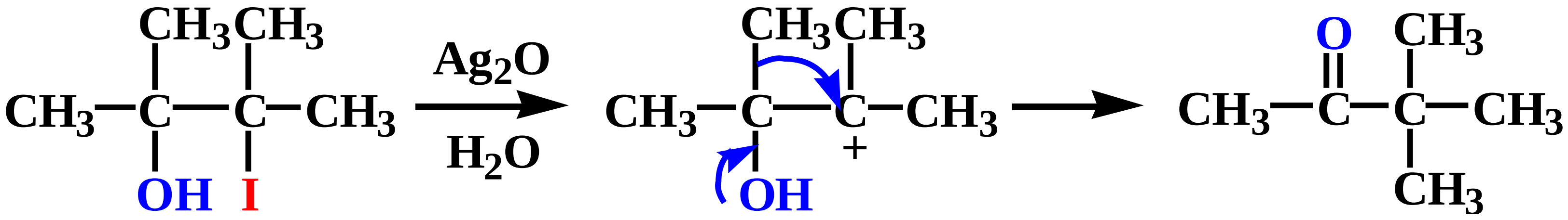
> R



迁移顺序取决于原子及基团电荷的密集程度

近似的频哪醇重排





$$CH_3-\overset{CH_3}{\underset{OH}{C}}-\overset{CH_3}{\underset{I}{C}}-CH_3 \xrightarrow[H_2O]{Ag_2O} CH_3-\overset{CH_3}{\underset{OH}{C}}-\overset{CH_3}{\underset{+}{C}}-CH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

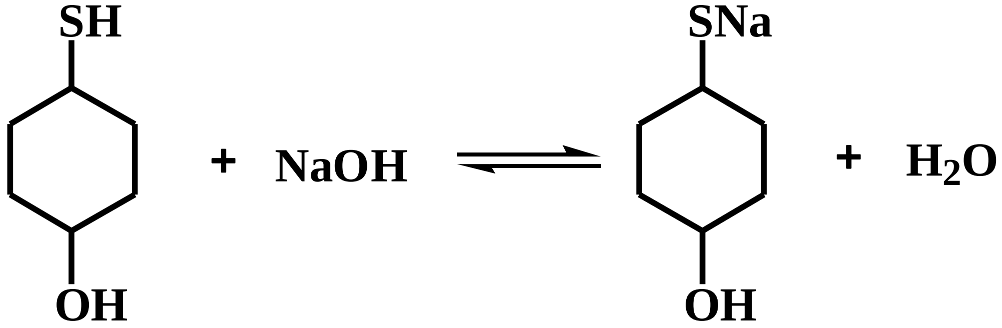
五、硫醇

R—SH　　　　—SH **硫基**

CH_3SH 甲硫醇　　C_2H_5SH 乙硫醇

1. 酸性比醇强

$$RSH + NaOH \rightleftharpoons RSNa + H_2O$$

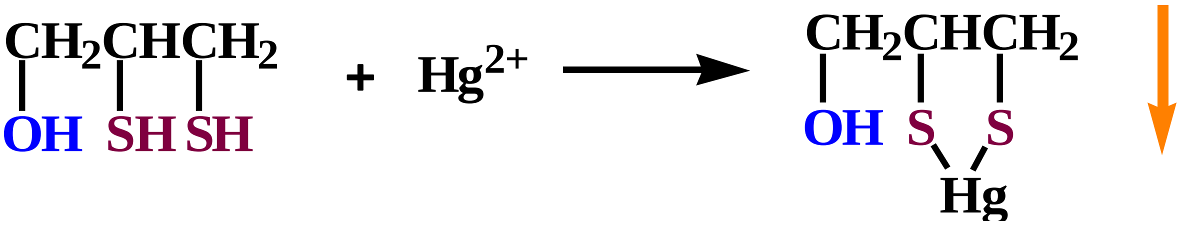


2. 易氧化

$$2RSH + I_2 \longrightarrow RS{-}SR + 2HI$$

$$2CH_3SH + H_2O_2 \longrightarrow CH_3S{-}SCH_3$$

3. 与重金属反应



$$\underset{\text{OH}}{\underset{|}{CH_2}}\underset{\text{SH}}{\underset{|}{CH}}\underset{\text{SH}}{\underset{|}{CH_2}} + Hg^{2+} \longrightarrow \underset{\text{OH}}{\underset{|}{CH_2}}\underbrace{\underset{\text{S}}{\underset{|}{CH}}\underset{\text{S}}{\underset{|}{CH_2}}}_{Hg}\downarrow$$

二巯基丙醇

六、醇的制备

(一) 一元醇的制备

1. 由烯烃制备

（1）直接、间接水合

（2）硼氢化-氧化

2. 由卤烃制备

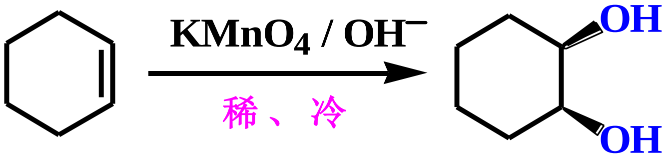
3. 由醛、酮制备

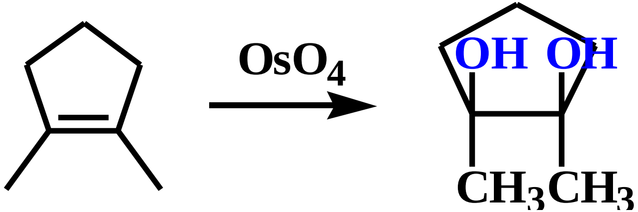
（1）醛、酮还原

（2）醛、酮与格氏试剂反应

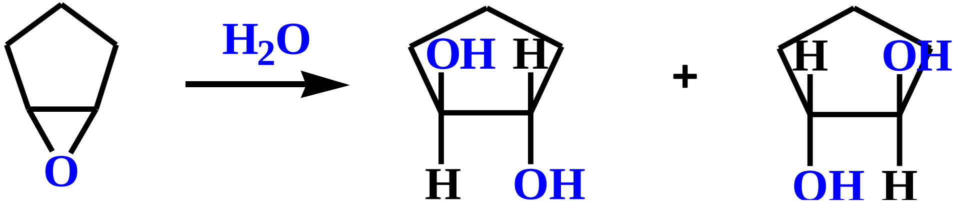
(二) 邻二醇的制备

1. 烯烃氧化





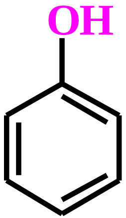
2. 环氧化物水解



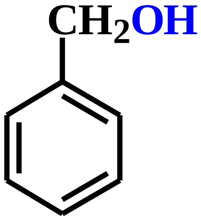
第二节 酚

酚：OH直接与芳环相连，简写为Ar－OH

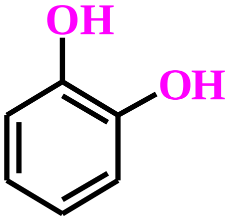
一、酚的命名



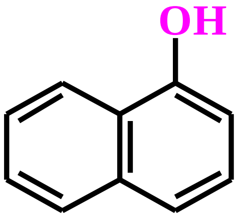
苯酚
phenol



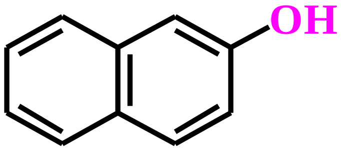
苯甲醇（苄醇）
Benzyl alcohol



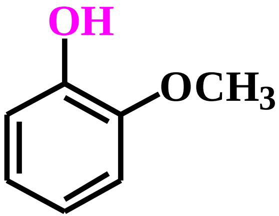
邻苯二酚
O-benzenediol



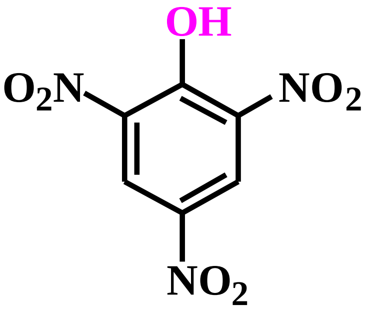
α-萘酚 α-naphthol



β-萘酚 β-naphthol

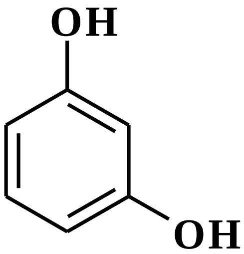


2-甲氧基苯酚
2-methoxyphenol



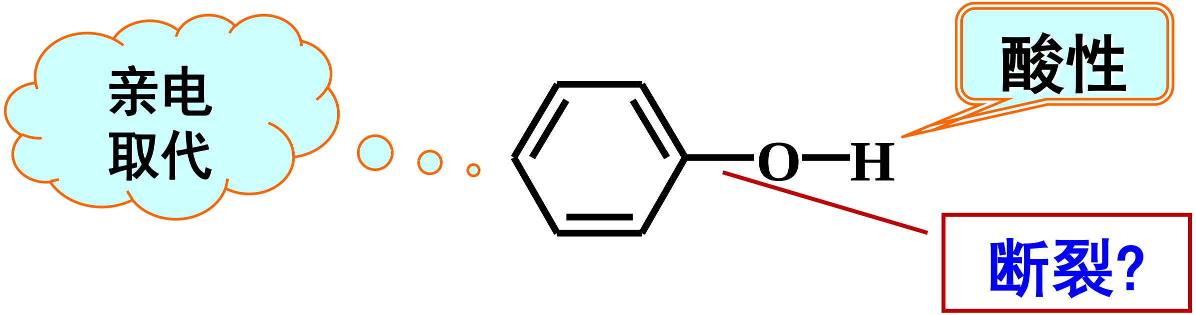
2,4,6-三硝基苯酚（苦味酸）
2,4,6-trinitrophenol

二、酚的物理性质



123g/100mL水

三、酚的化学性质



O—H键

极性更大，易于解离

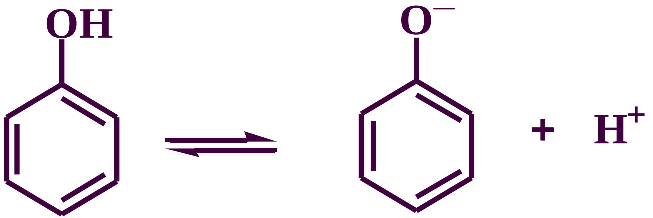
电子效应

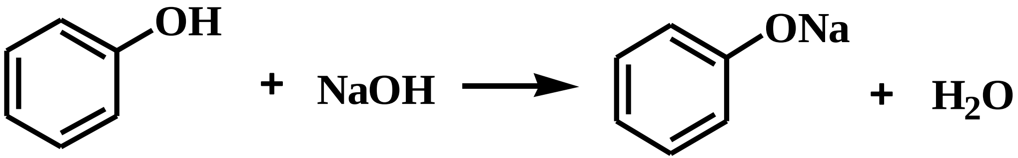
pπ共轭，使C—O键结合更牢固，不易断裂

苯环上的亲电取代比苯更容易

（一）羟基上的反应

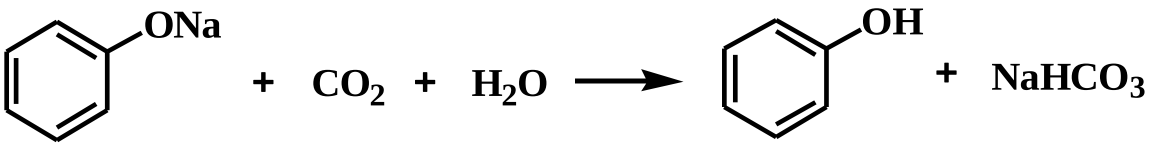
1. 酸性

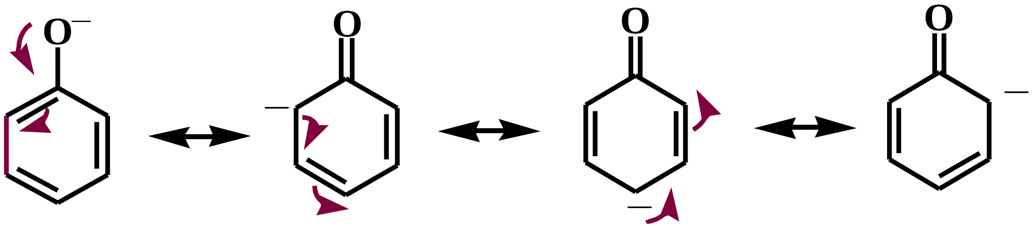




$$C_2H_5OH + Na \longrightarrow C_2H_5ONa + H_2$$

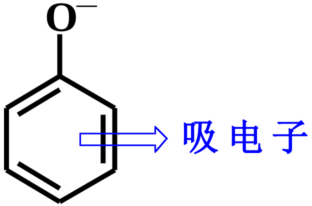
	苯酚	水	乙醇	碳酸
p*K*a	10	15.7	16	6.38



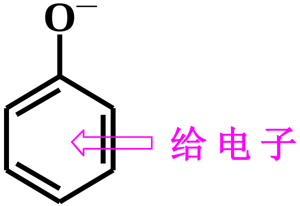


共轭使苯氧负离子稳定，烷氧负离子无这种稳定作用。

苯环上连有吸电子基时酸性增强，特别是连在邻对位时。



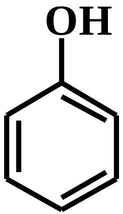
稳定性提高



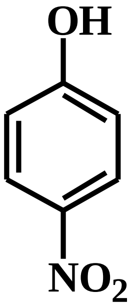
稳定性降低

比较酸性：

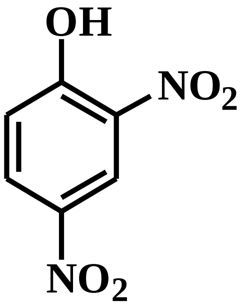
(1)



(2)

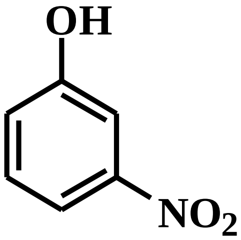


(3)

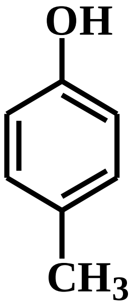


p*K*a 10 7.15 4.09

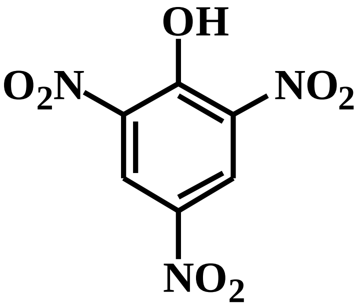
(4)



(5)



(6)



8.39 10.26 0.25

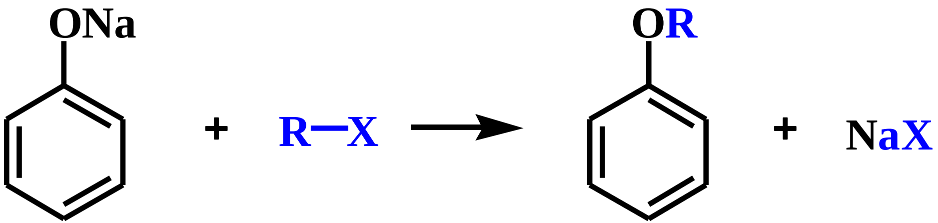
2. 与三氯化铁的显色反应

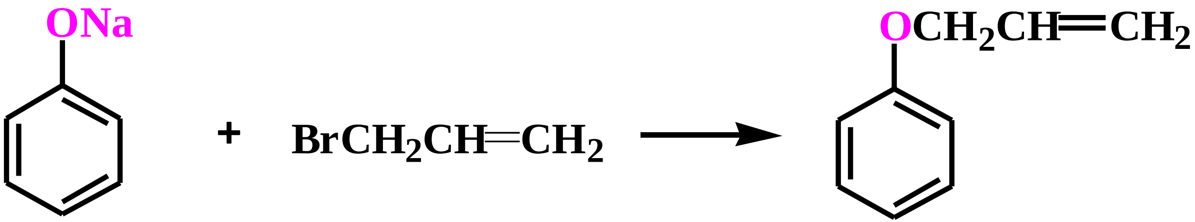
$$6\,C_6H_5OH + FeCl_3 \longrightarrow H_3[Fe(C_6H_5O)_6] + 3\,HCl$$

蓝紫色

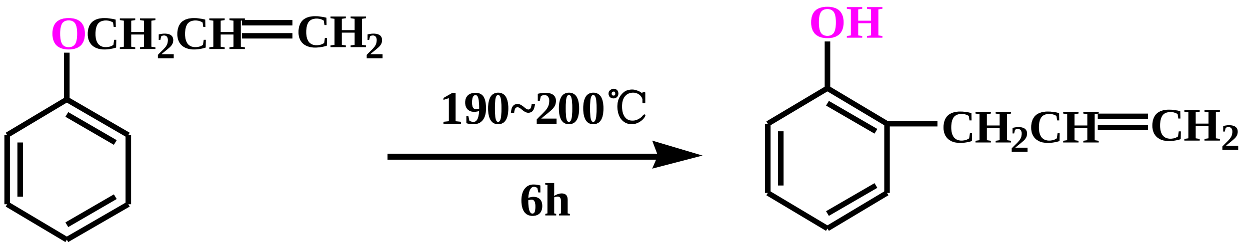
凡具有烯醇式结构的化合物
都有这一显色反应

3. 酚醚的形成与克莱生（Claisen）重排

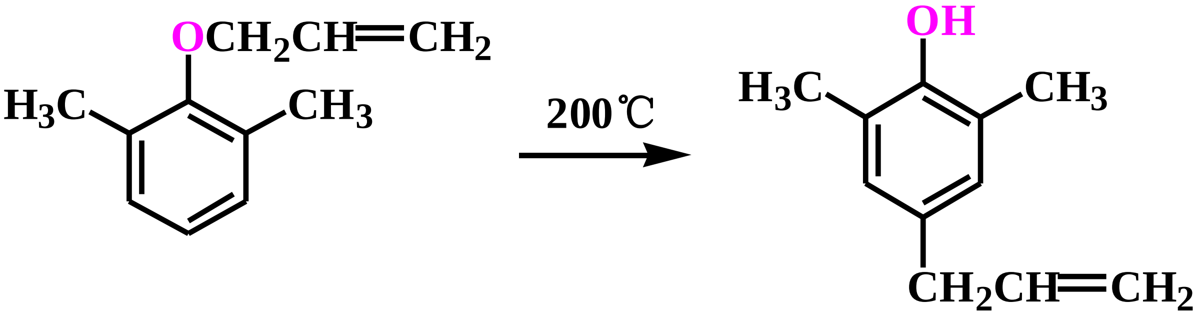




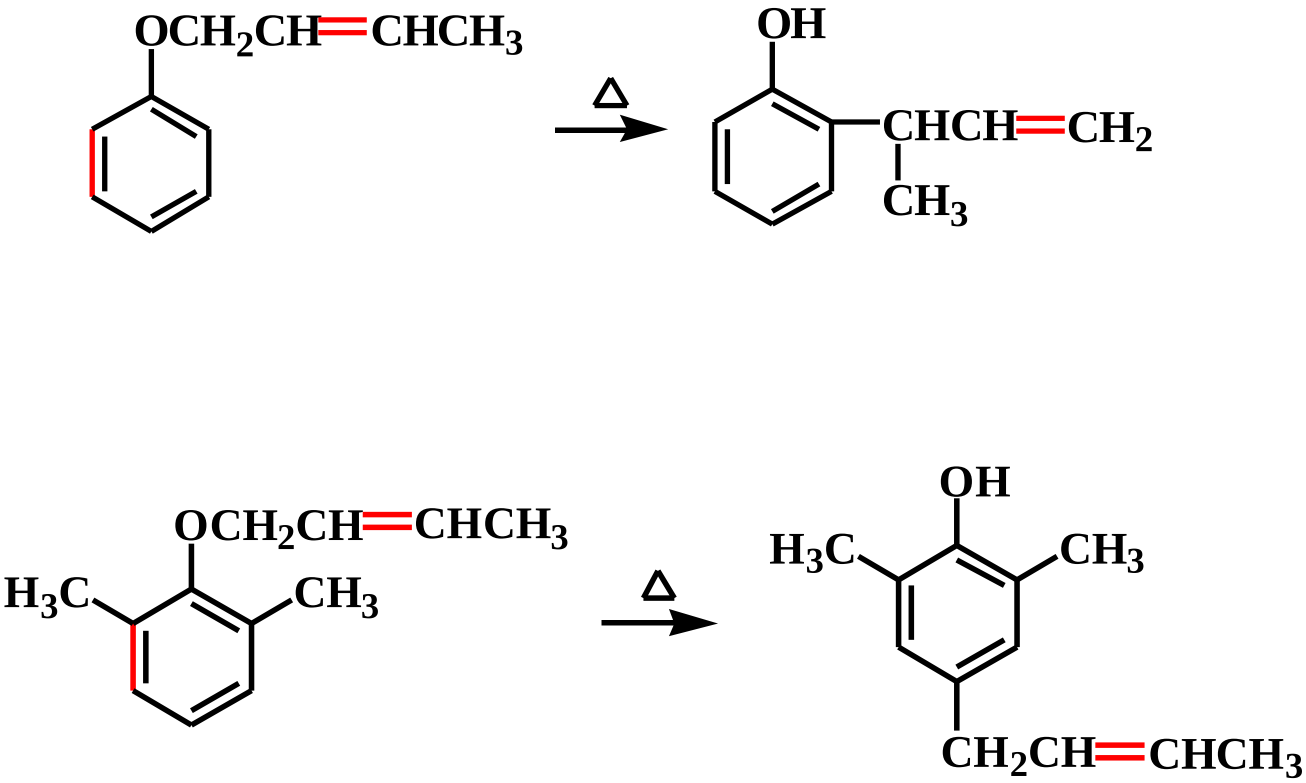
烯丙基苯基醚



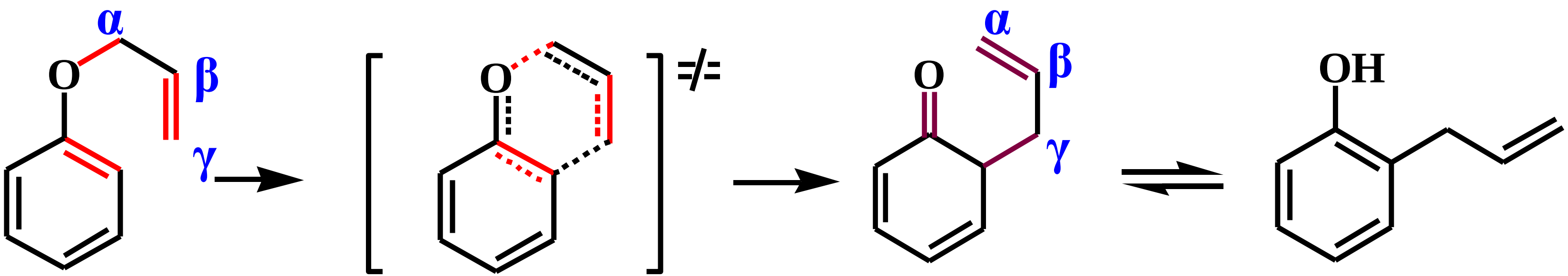
Claisen rearrangement

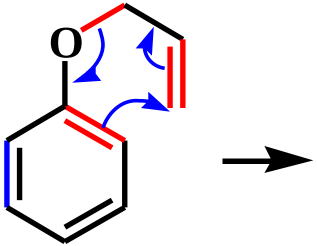


一般重排到邻位，两个邻位被占据，重排到对位。

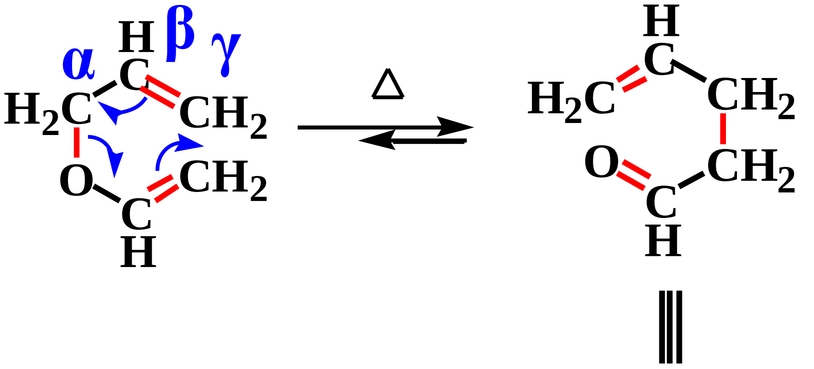

OCH₂CH=CHCHCH₃
Δ
OH
CHCH=CH₂
CH₃
H₃C
CH₃
OCH₂CH=CHCHCH₃
Δ
OH
H₃C
CH₃
CH₂CH=CHCH₃

Mechanism of the Claisen Rearrangement





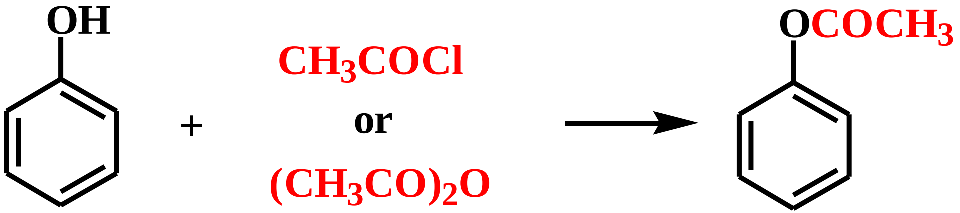
$H_2C{=}CHOCH_2CH{=}CH_2 \xrightarrow{\Delta}$?

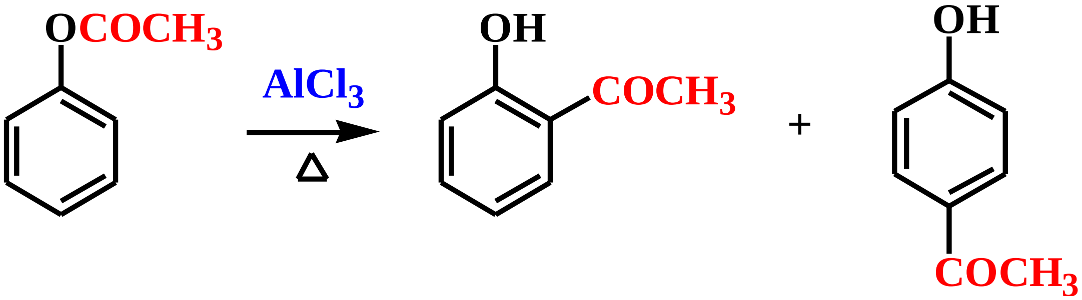


$H_2C{=}CHCH_2CH_2CHO$

Aliphatic Claisen Rearrangement

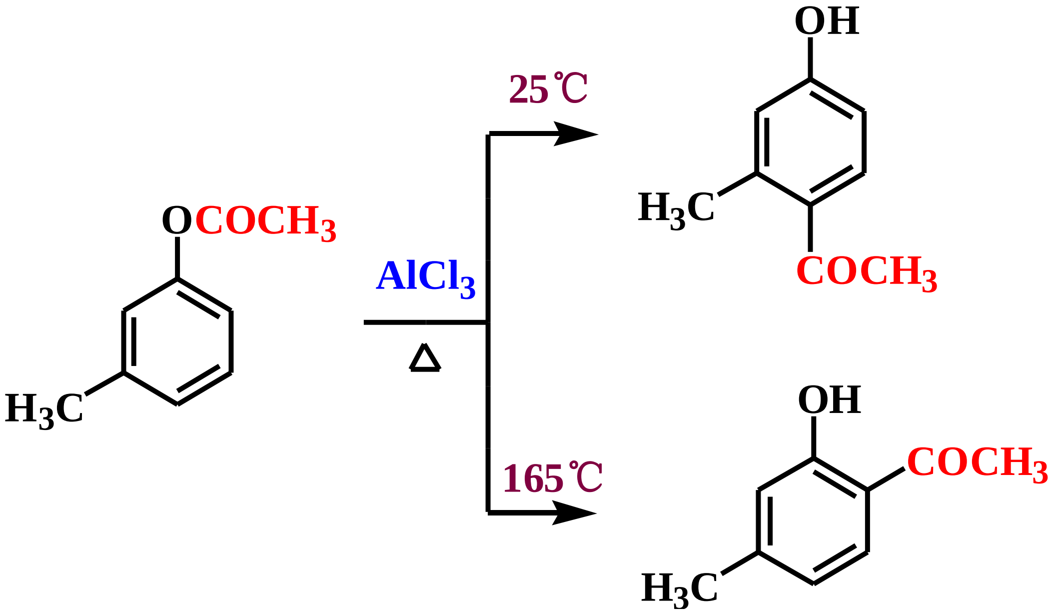
4. 酚酯的形成与傅瑞斯（Fries）重排





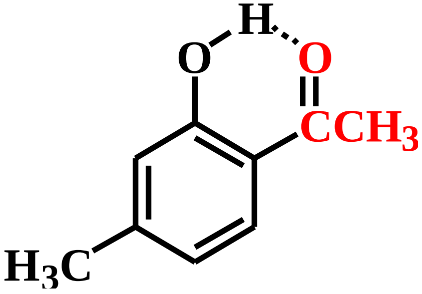
可通过水蒸气蒸馏分离

Fries rearrangement


OCOCH3
H3C
AlCl3
Δ
25℃
165℃
OH
H3C
COCH3
OH
COCH3
H3C

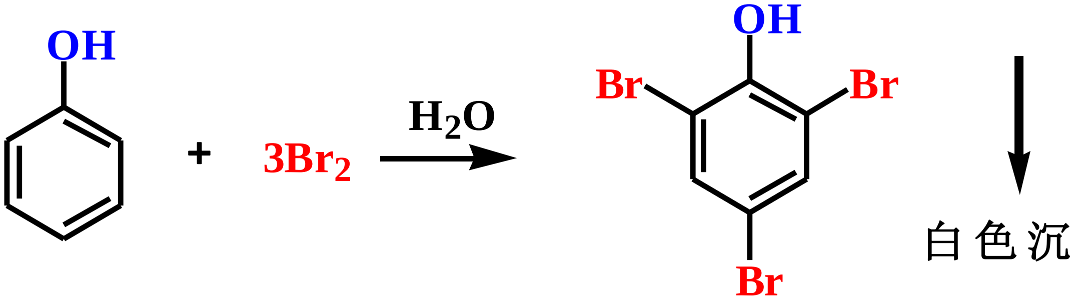
低温对位

高温邻位

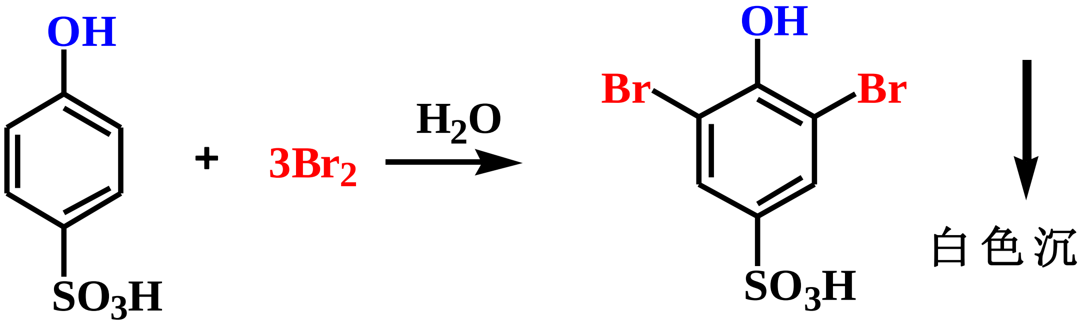

H
O
O
CCH3
H3C

（二）芳环上的取代反应

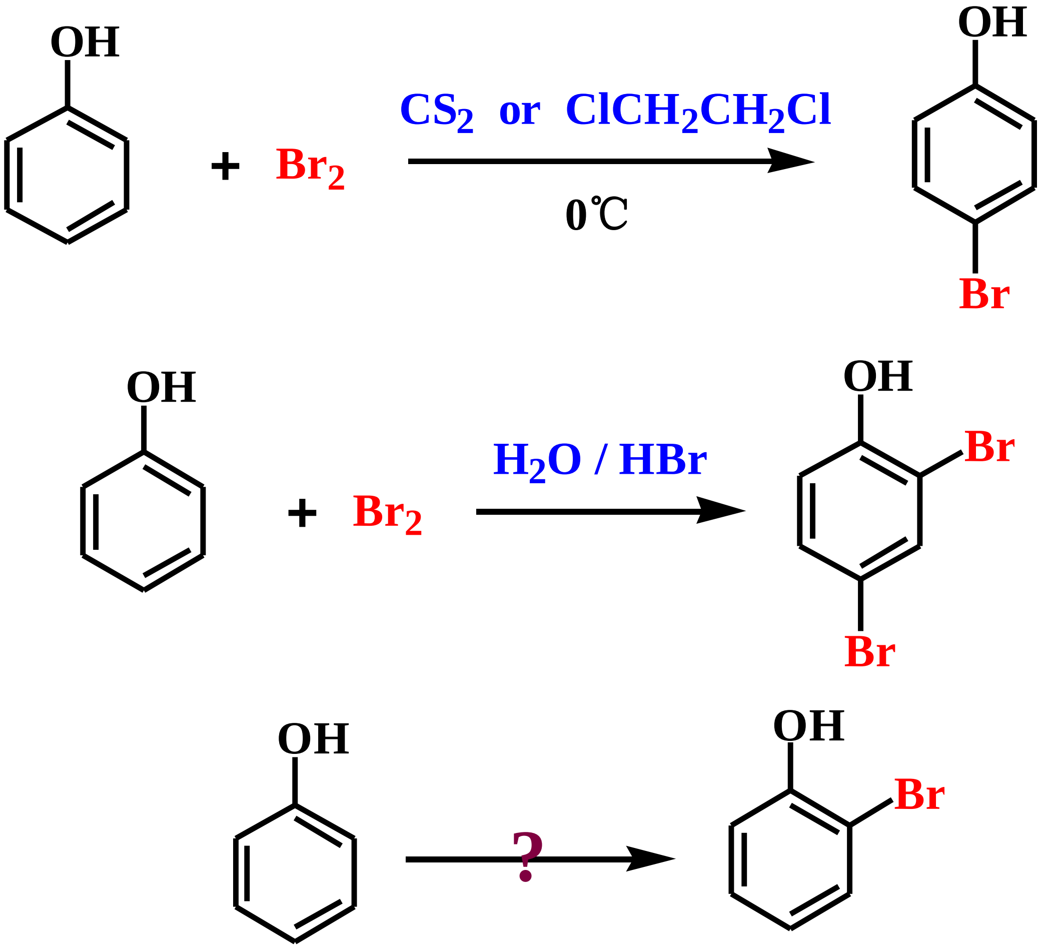
1. 卤代反应



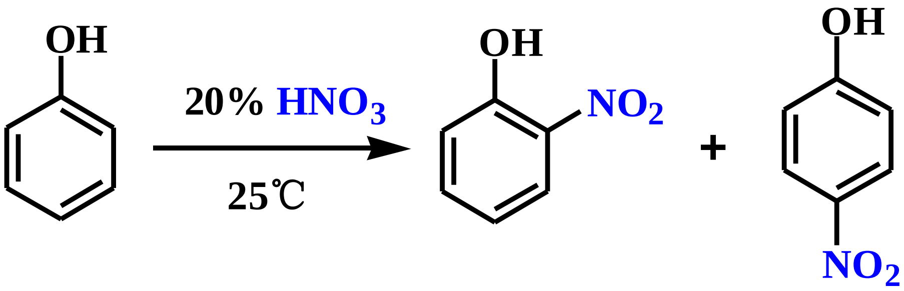
白色沉淀



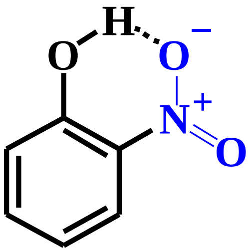
白色沉淀


OH
+ Br2
CS2 or ClCH2CH2Cl
0℃
OH
Br
OH
+ Br2
H2O / HBr
OH
Br
Br
OH
?
OH
Br

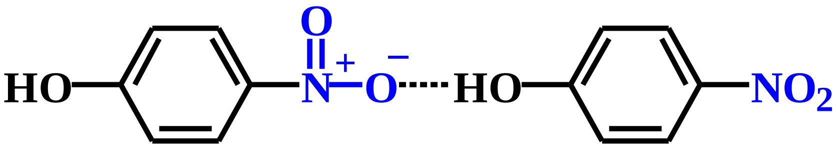
2. 硝化反应



两种异构体可通过水蒸汽蒸馏的方法分离

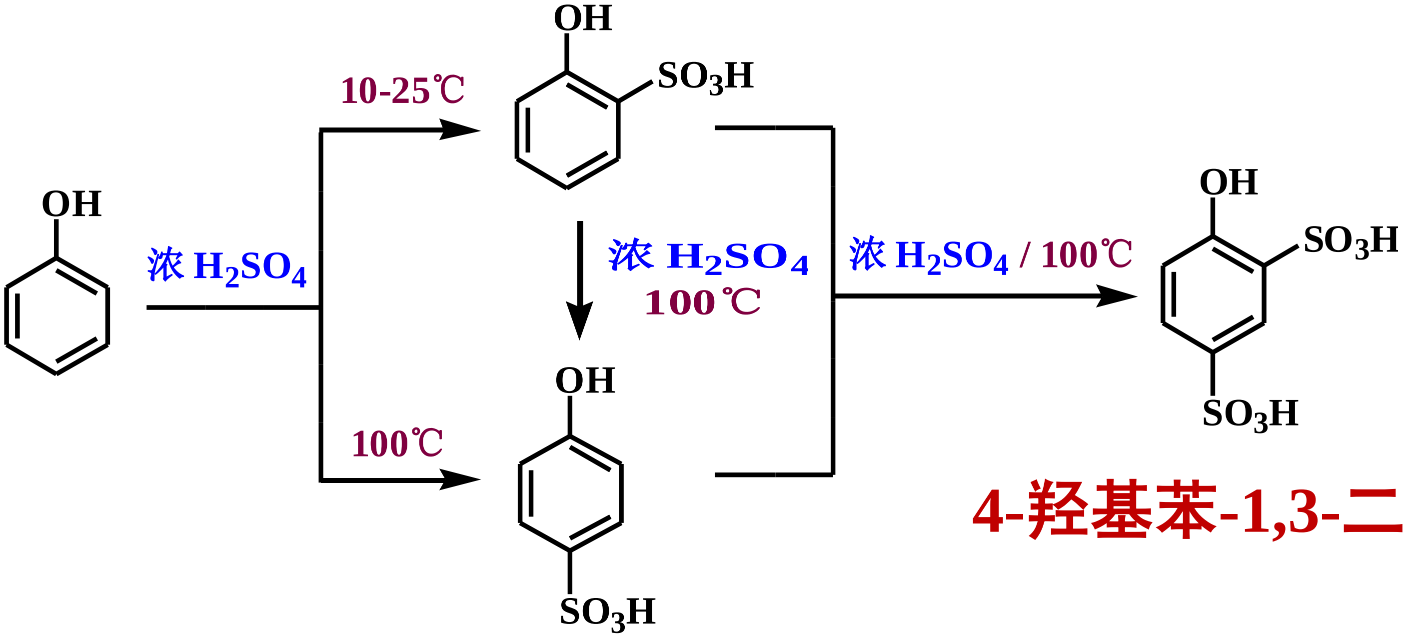


分子内氢键，挥发性大

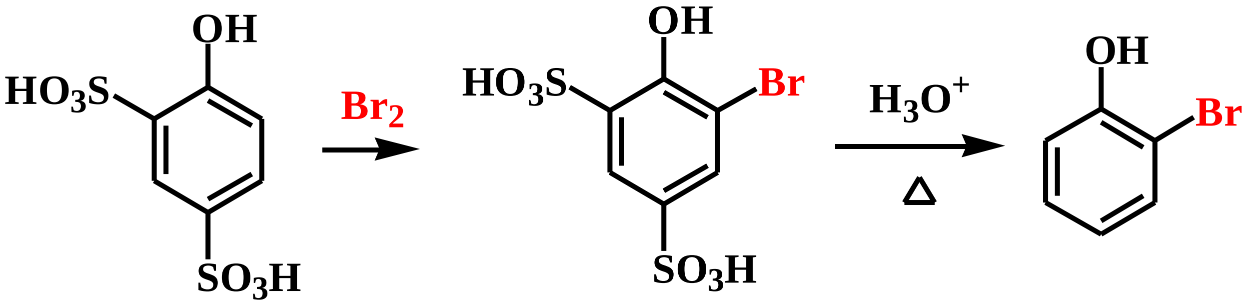


分子间氢键，挥发性小

3. 磺化反应

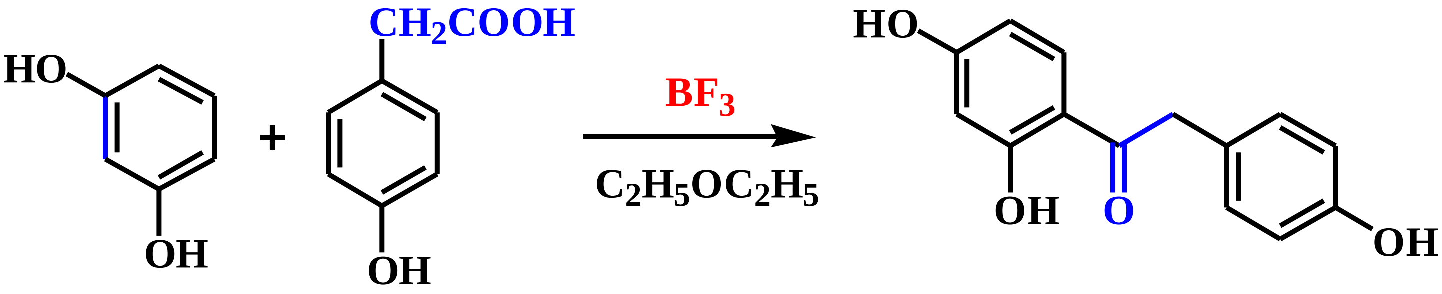


4-羟基苯-1,3-二磺酸



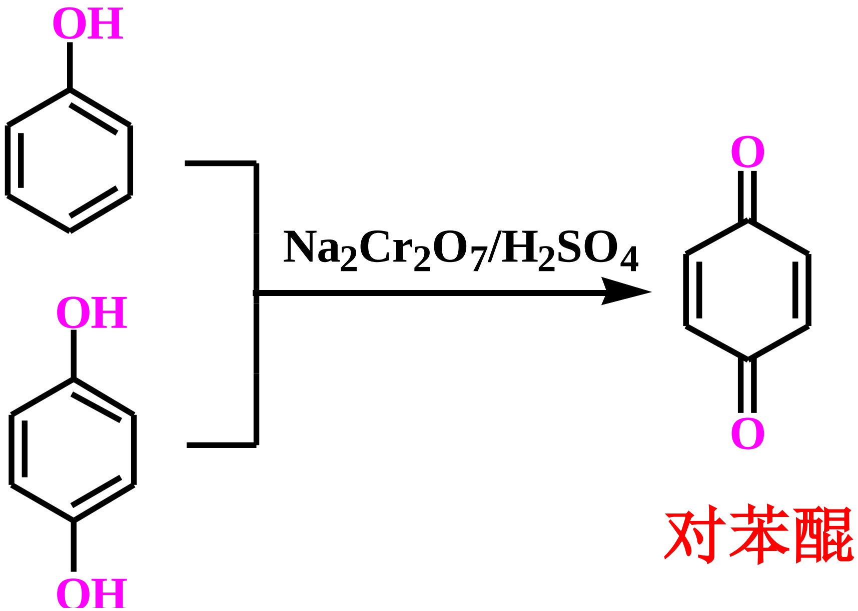
4. 傅克反应

用$AlCl_3$作催化剂反应难以进行，常用硫酸、磷酸、三氟化硼等作催化剂。



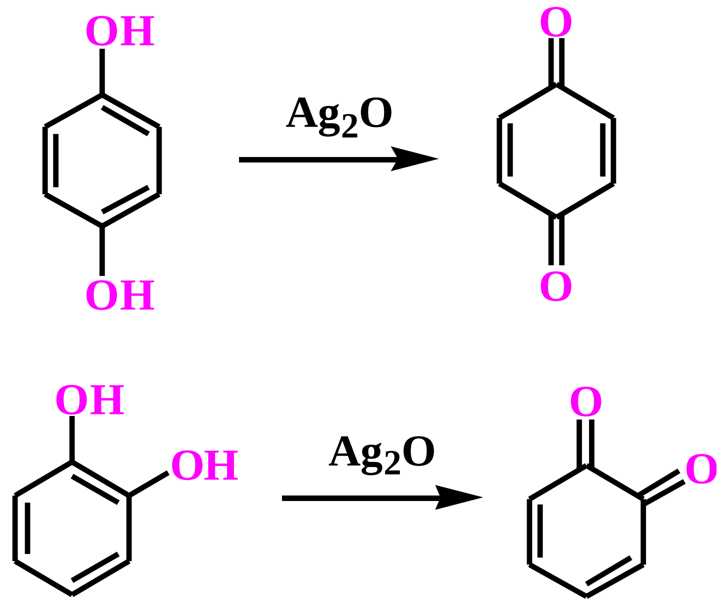
（三）氧化和还原反应

- 很易于氧化。在空气中放置过久，也会被氧化而呈深红色。



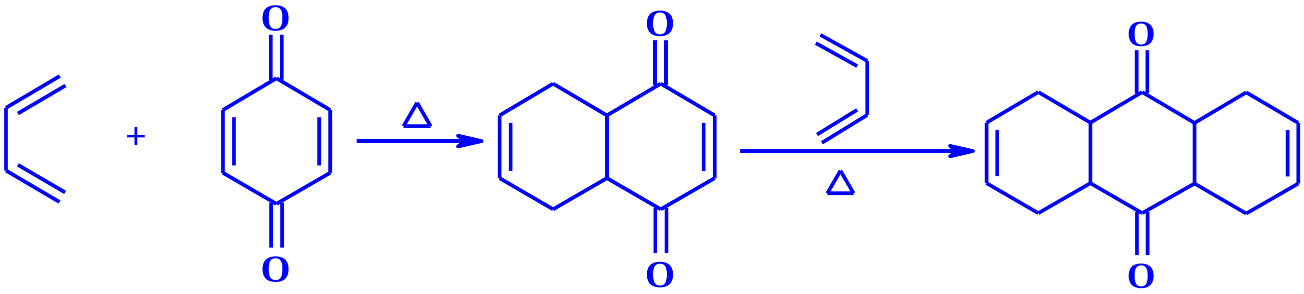
$$\xrightarrow{Na_2Cr_2O_7/H_2SO_4}$$

对苯醌

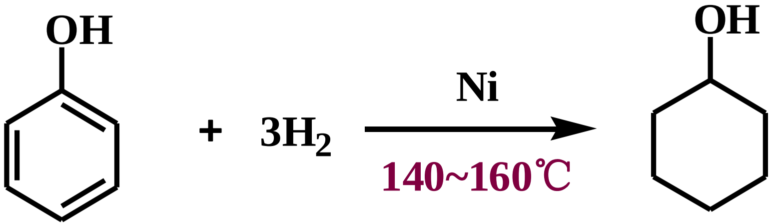


邻苯醌

利用这一特性，可将酚类化合物用于食品、橡胶、塑料等的抗氧剂。



+
O
O
Δ
O
O
Δ
O
O



OH
+
3H2
Ni
140~160℃
OH

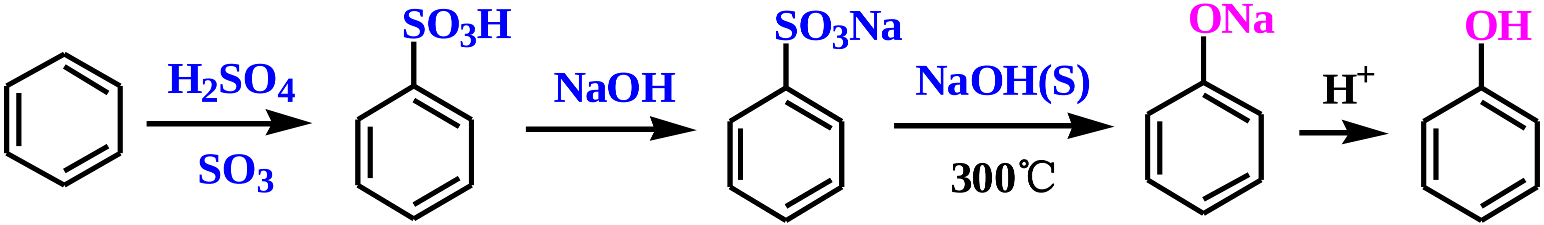
四、酚的制备

苯酚下游产品酚醛树脂和双酚A↑

带动了苯酚需求的强劲增长

目前工业生产苯酚的工艺主要有异丙苯法和磺化法（磺酸盐碱熔融法）等。还可通过芳卤烃水解制备。

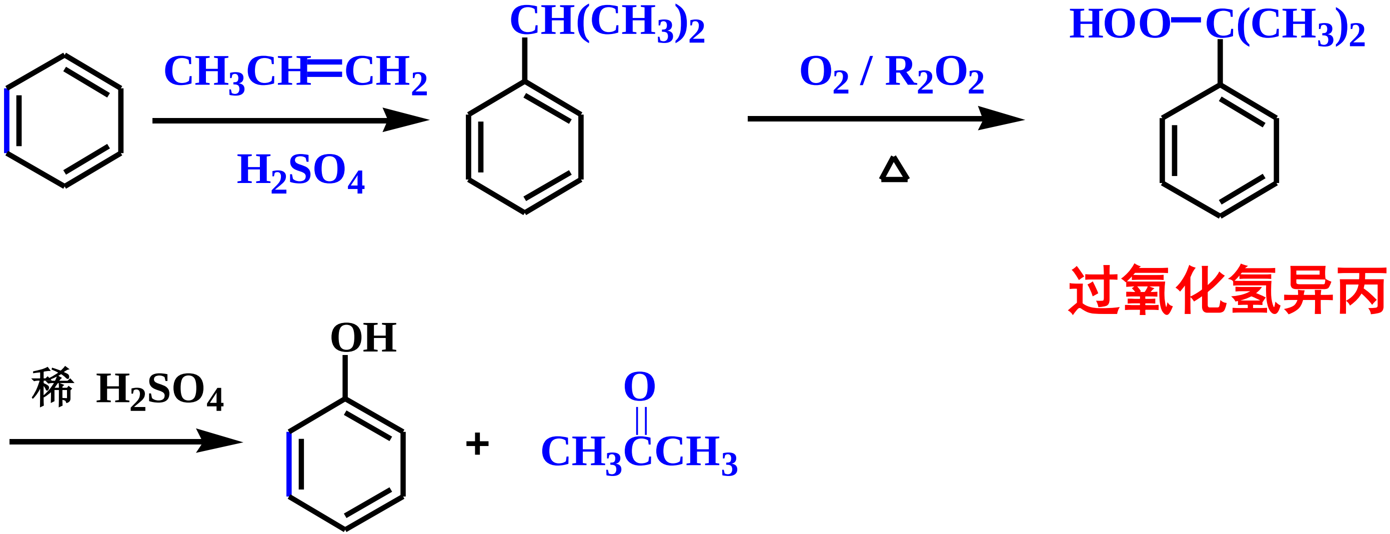
1. 磺酸盐碱熔融法



条件剧烈, 有X、NO_2、COOH等基团时，不能用此法。

工艺落后、反应复杂、消耗大量硫酸和烧碱、严重腐蚀设备、维修费用高等，基本上已被淘汰。

2. 异丙苯法



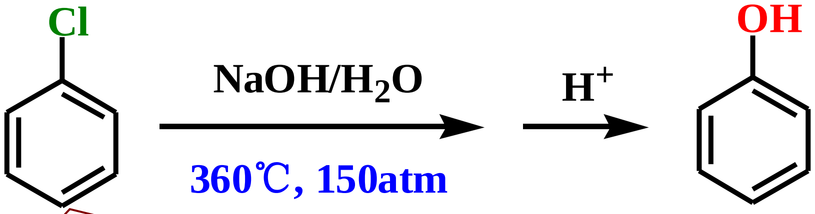
过氧化氢异丙苯

每吨苯酚约联产丙酮0.6t。

目前采用该工艺生产的苯酚已占世界苯酚产量的90%以上（只用于生产苯酚，不能套用）。

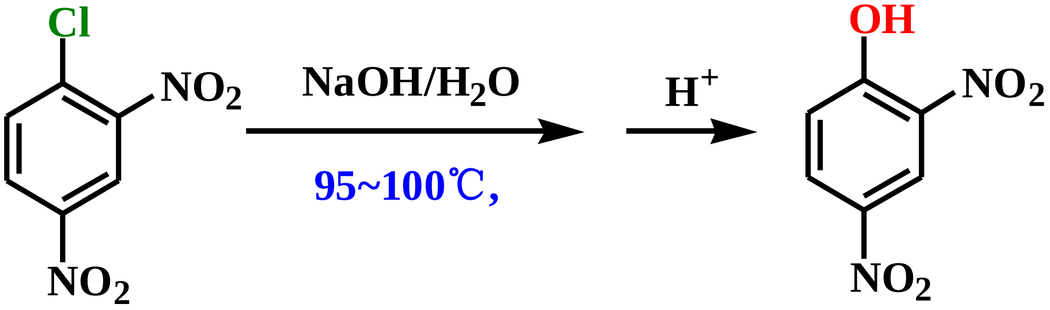
异丙苯法工艺联产大量的丙酮，丙酮的价格波动严重制约了生产的整体经济性。如何合理利用丙酮或妥善解决丙酮的出路问题，是目前异丙苯法生产苯酚工艺亟待解决的问题。

3. 芳卤烃水解



乙烯型（卤代苯型）卤代烃，难以亲核取代

卤原子邻、对位有吸电子基团时，水解容易进行



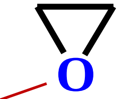
第三节 醚

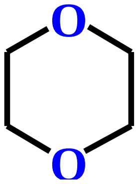
一、醚的分类和命名

1. 醚的分类

简单醚 R—O—R； 混合醚 R—O—R’

环 醚





三元环醚：
环氧化物（epoxide）

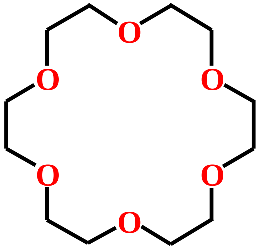
二氧六环
dioxan

硫醚　　$CH_3SC_2H_5$

乙基甲基硫醚

ethyl methyl sulfide

冠醚



18-冠-6

18-Crown-6

2. 醚的命名

两个烃基名＋醚

中文一般按次序规则，英文按字母顺序。

$CH_3OC_2H_5$

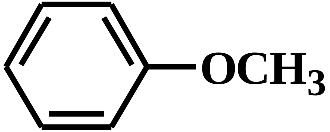
乙基甲基醚

ethyl methyl ether

$CH_3OC(CH_3)_3$

叔丁基甲基醚

tert-butyl methyl ether



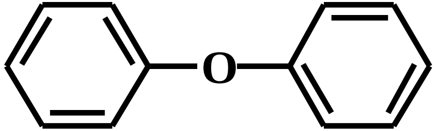
甲基苯基 醚

methyl phenyl ether

$C_2H_5OC_2H_5$

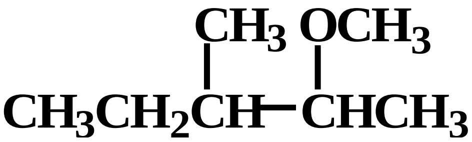
（二）乙醚

ethyl ether



（二）苯醚

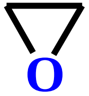
diphenyl ether



$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}H-\overset{\overset{\displaystyle OCH_3}{|}}{C}HCH_3$$

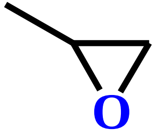
2-甲氧基-3-甲基戊烷

2-methoxy-3-methyl pentane



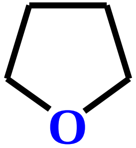
环氧乙烷

ethylene oxide



1,2-环氧丙烷

1,2-epoxypropane

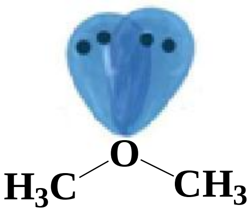


四氢呋喃

THF

二、醚的物理性质

三、醚的化学性质

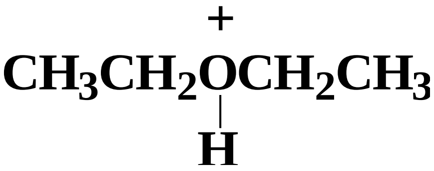


性质稳定

常作溶剂

1. 形成𬭩盐

与浓强酸在室温或低温时能形成𬭩盐。所以醚能溶于浓强酸中。

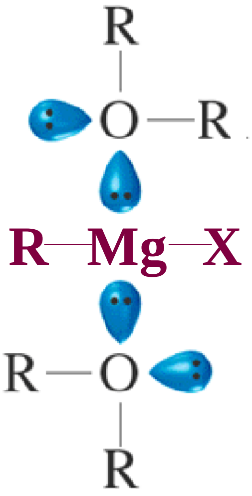


$$CH_3CH_2OCH_2CH_3 \xrightarrow[\text{or 浓 HCl}]{\text{浓 } H_2SO_4} CH_3CH_2\overset{+}{\underset{\overset{|}{H}}{O}}CH_2CH_3$$

$$\xrightarrow{\text{ice } H_2O} CH_3CH_2OCH_2CH_3 + H_3O^+$$

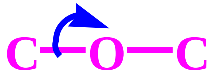
$$R_2O: \; + \; \begin{matrix} BF_3 \\ AlCl_3 \\ R'MgX \end{matrix} \; \longrightarrow \; \begin{matrix} R_2O : BF_3 \\ R_2O : AlCl_3 \\ R_2O : R'MgX \end{matrix}$$

形成配合物

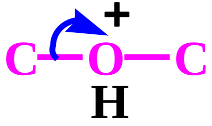


格氏试剂在乙醚中以配合物形式存在

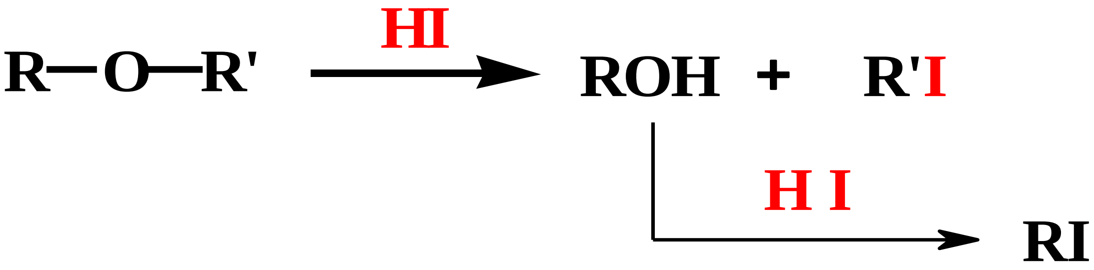
2. 醚键的断裂



不易断裂



形成氧正离子后
吸电子能力增强
碳氧键易断裂



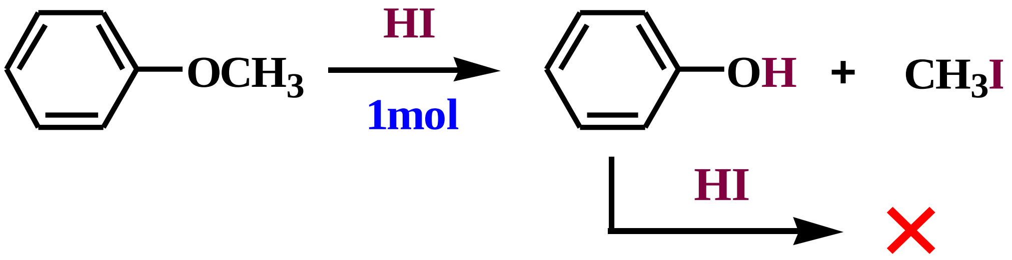
$$R-O-R' \xrightarrow{HI} ROH + R'I$$

$$ROH \xrightarrow{HI} RI$$

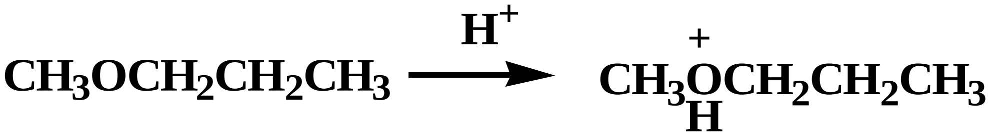
反应活性：HI > HBr > HCl

一般小基团先形成卤烃：

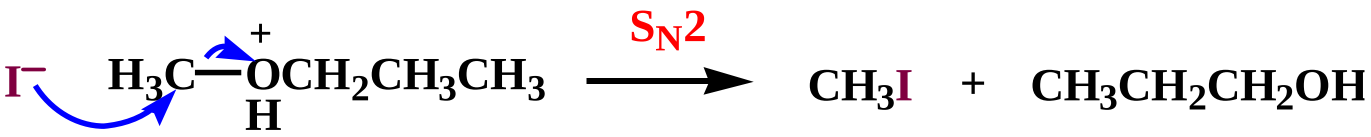
$$CH_3OCH_2CH_3 \xrightarrow[1mol]{HI} CH_3I + CH_3CH_2OH$$



原因?

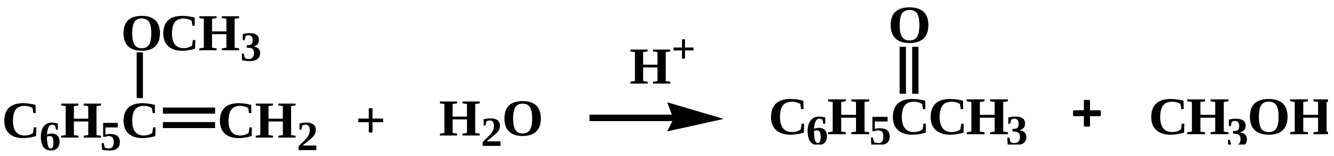


$$CH_3OCH_2CH_2CH_3 \xrightarrow{H^+} CH_3\underset{H}{\overset{+}{O}}CH_2CH_2CH_3$$



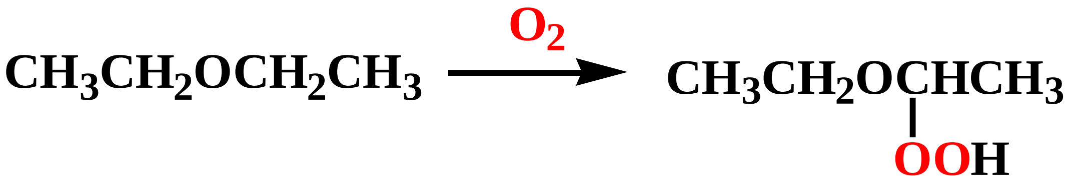
$$I^- \quad H_3C-\underset{H}{\overset{+}{O}}CH_2CH_3CH_3 \xrightarrow{S_N2} CH_3I + CH_3CH_2CH_2OH$$

$$CH_3OC(CH_3)_3 \xrightarrow{H^+} ?$$



$$C_6H_5\overset{\overset{OCH_3}{|}}{C}{=}CH_2 + H_2O \xrightarrow{H^+} C_6H_5\overset{\overset{O}{\|}}{C}CH_3 + CH_3OH$$

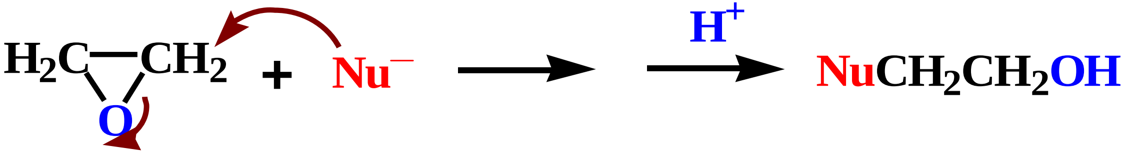
3. 过氧化物的生成



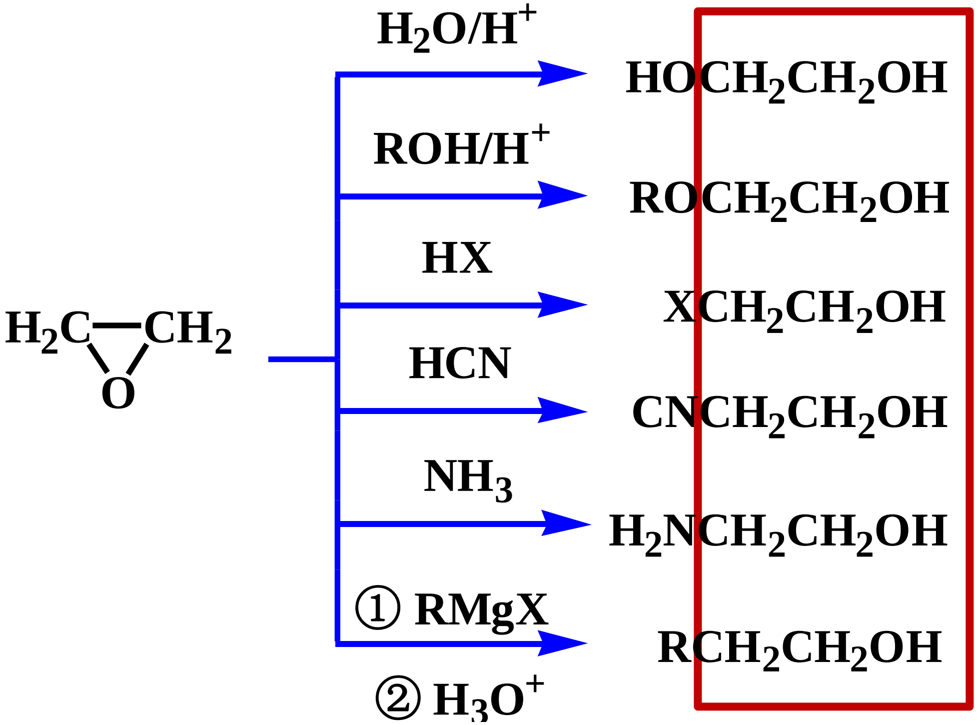
$$CH_3CH_2OCH_2CH_3 \xrightarrow{O_2} CH_3CH_2O\underset{\underset{OOH}{|}}{C}HCH_3$$

遇热爆炸

四、环氧化合物



$+ \ Nu^- \longrightarrow \xrightarrow{H^+} NuCH_2CH_2OH$



$\xrightarrow{H_2O/H^+} HOCH_2CH_2OH$

$\xrightarrow{ROH/H^+} ROCH_2CH_2OH$

$\xrightarrow{HX} XCH_2CH_2OH$

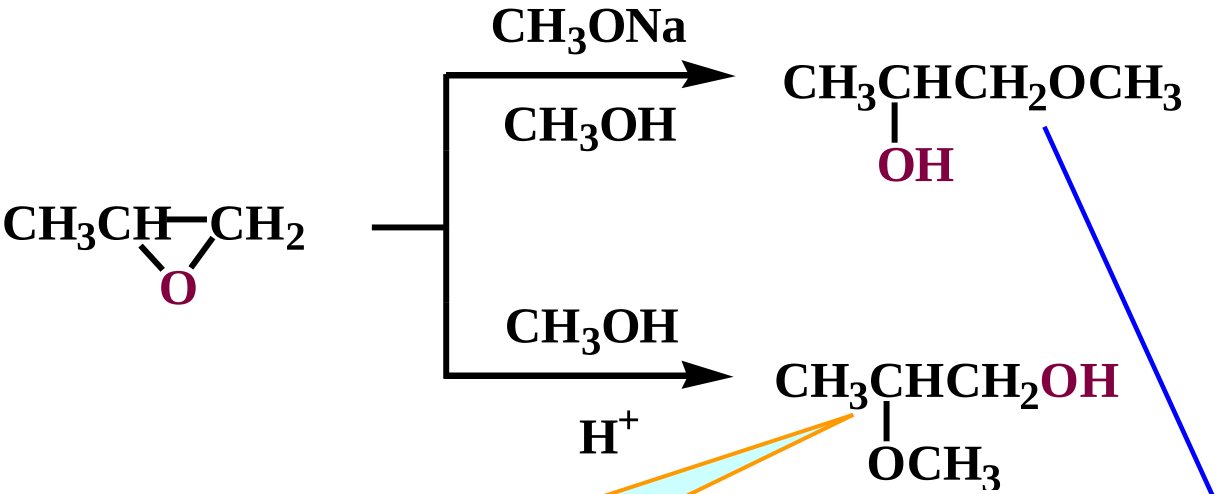
$\xrightarrow{HCN} CNCH_2CH_2OH$

$\xrightarrow{NH_3} H_2NCH_2CH_2OH$

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

不对称的环氧化合物：

区域选择性



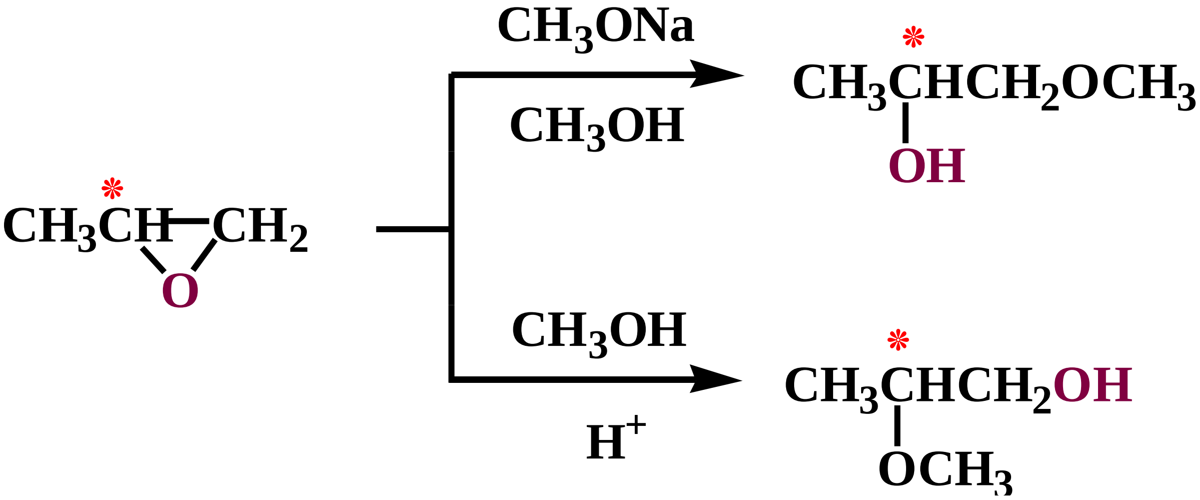
$$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2OCH_3$$

$$CH_3\underset{\displaystyle OCH_3}{\underset{|}{C}}HCH_2OH$$

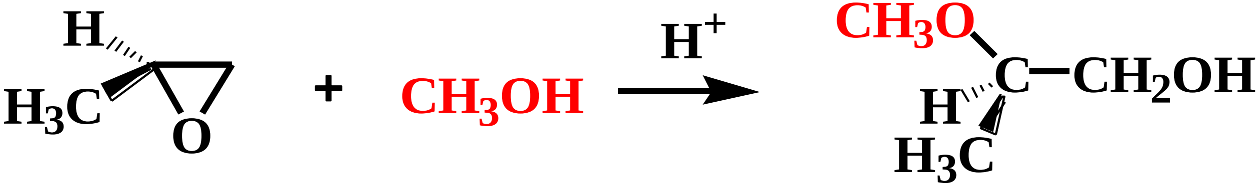
进攻取代较多的
与氧相连的碳原子

进攻取代较少的
与氧相连的碳原子

立体选择性?

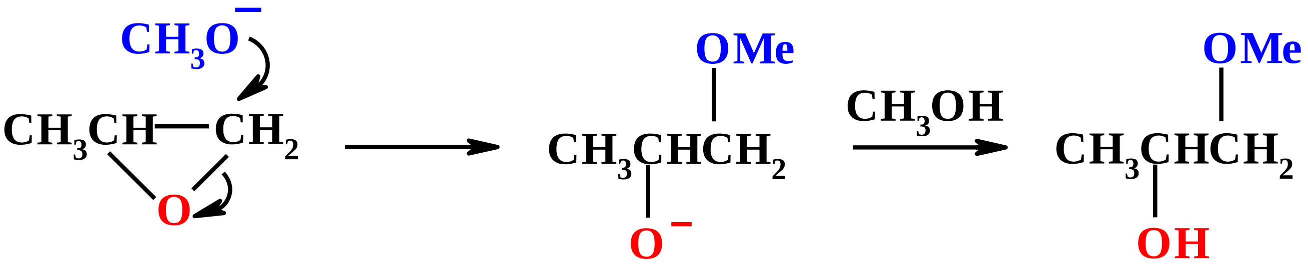


$CH_3\overset{*}{C}H-CH_2$
O
CH_3ONa
CH_3OH
$CH_3\overset{*}{C}HCH_2OCH_3$
OH
CH_3OH
H^+
$CH_3\overset{*}{C}HCH_2OH$
OCH_3

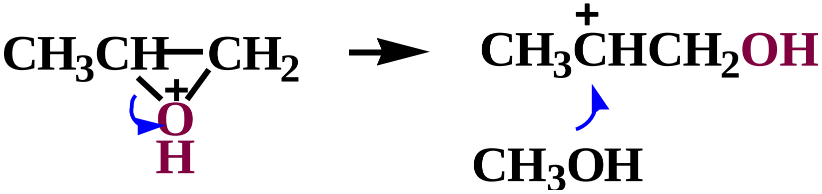


H
H_3C
O
+
CH_3OH
H^+
CH_3O
C
CH_2OH
H
H_3C

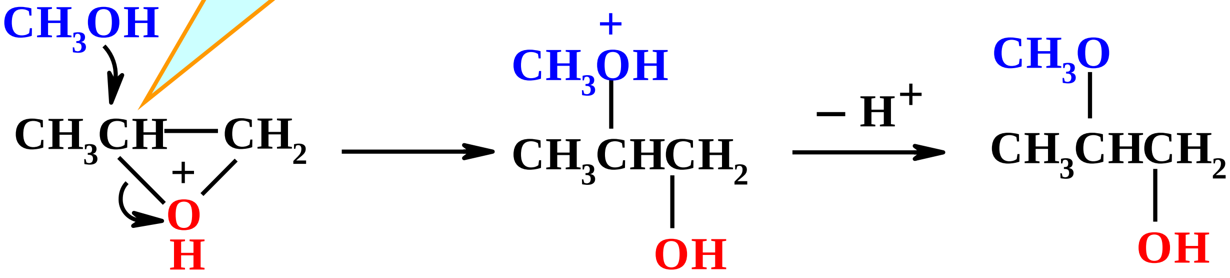
构型转化



碱性条件下按S_N2历程进行

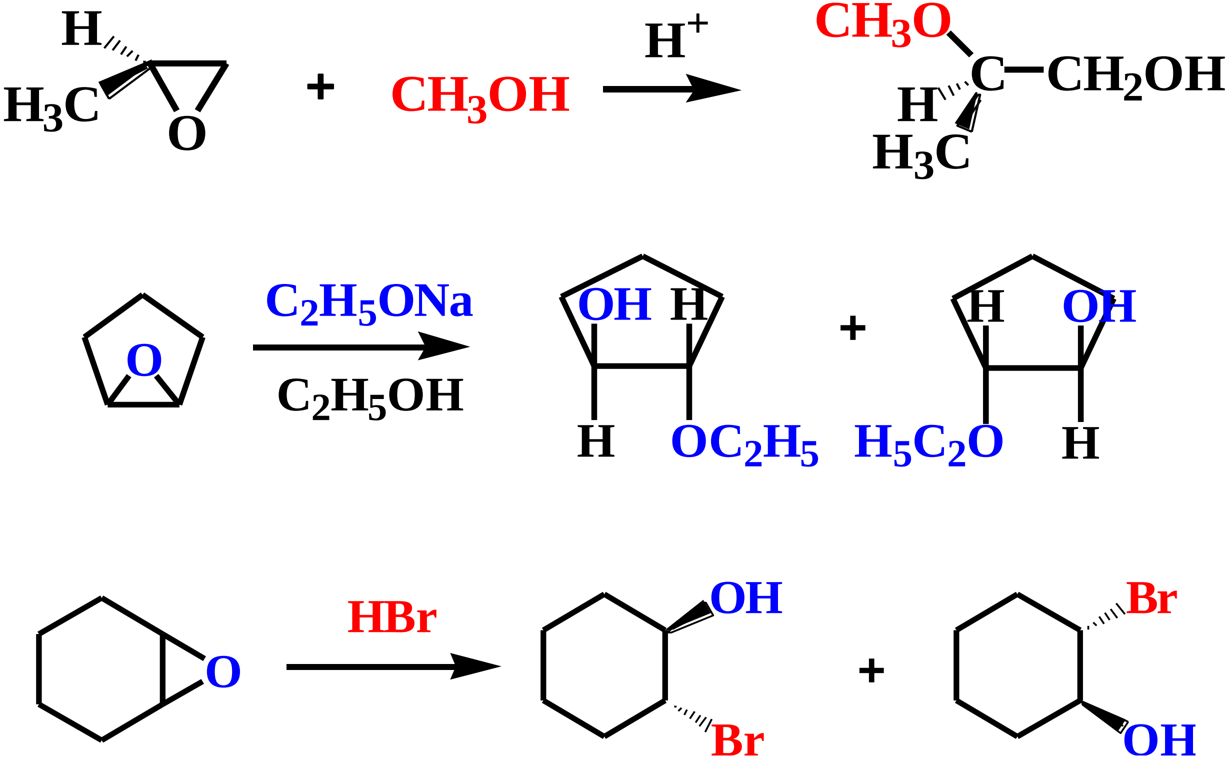


能容纳较多正电荷



酸性条件下带有S_N1特性的S_N2反应

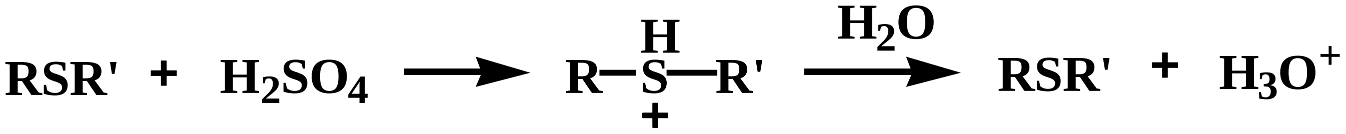
无论酸性或碱性条件，均从氧桥背面进攻，**形成反式产物。**



五、硫醚

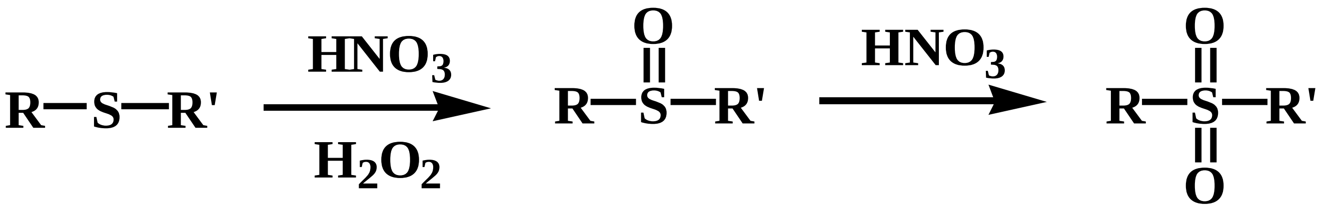
R—S—R’ 含硫，有臭味，较稳定

1. 形成锍盐



$$RSR' + H_2SO_4 \longrightarrow R-\overset{H}{\underset{+}{S}}-R' \xrightarrow{H_2O} RSR' + H_3O^+$$

2. 氧化

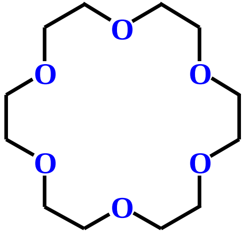


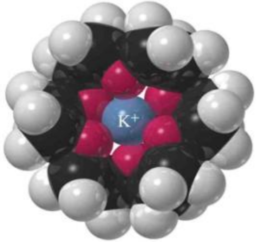
$$R-S-R' \xrightarrow[H_2O_2]{HNO_3} R-\overset{O}{\overset{\|}{S}}-R' \xrightarrow{HNO_3} R-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-R'$$

亚砜　　　　砜

CH_3SOCH_3 二甲亚砜DMSO

六、冠醚

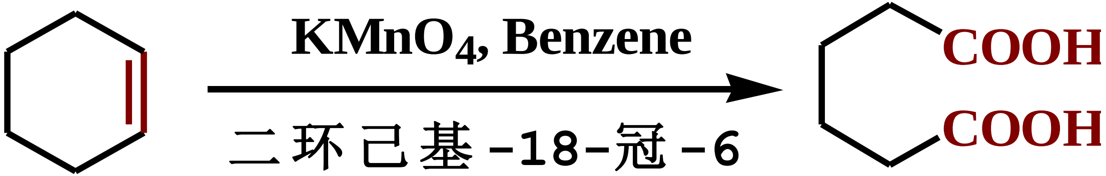




18-冠-6（18-crown-6）

相转移催化剂（PTC）

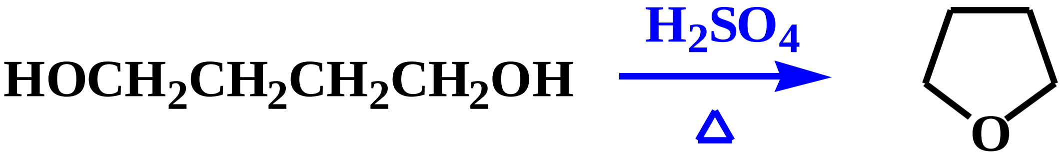
使互不相溶的两相中的物质发生反应或加速反应进行



七、醚的制备

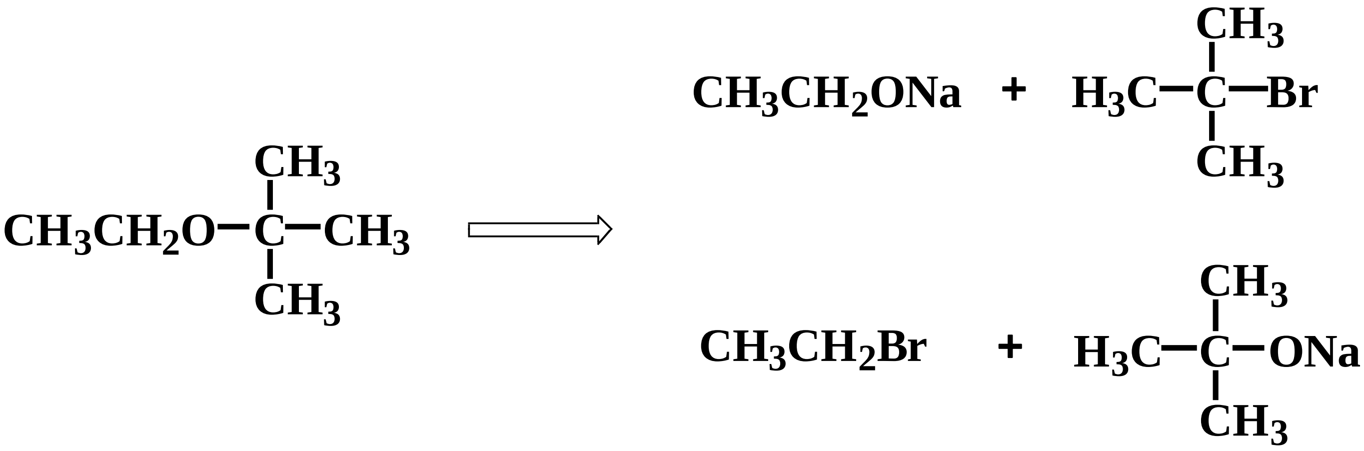
1. 醇的分子间脱水—简单醚的制备

$$2\ ROH \xrightarrow[\Delta]{H_2SO_4} ROR + H_2O$$

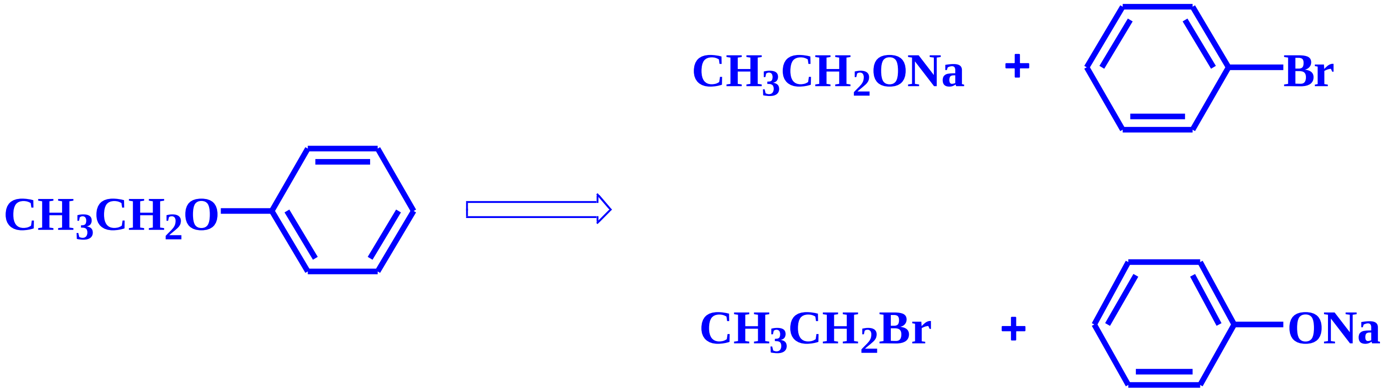


2. Willianmson合成法—混合醚的制备

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



$$CH_3CH_2O-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 \Longrightarrow \begin{array}{l} CH_3CH_2ONa + H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Br \\ CH_3CH_2Br + H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-ONa \end{array}$$



3. 环醚的制备

1）直接氧化

2）通过卤代醇制备