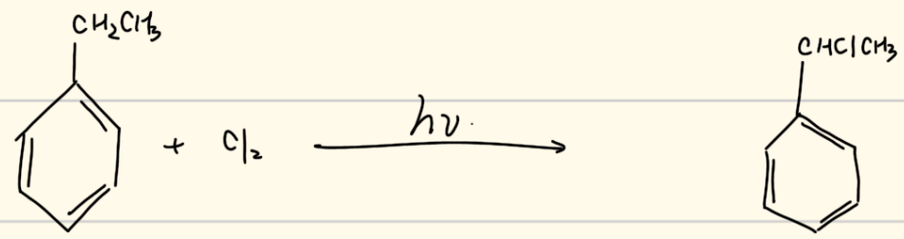
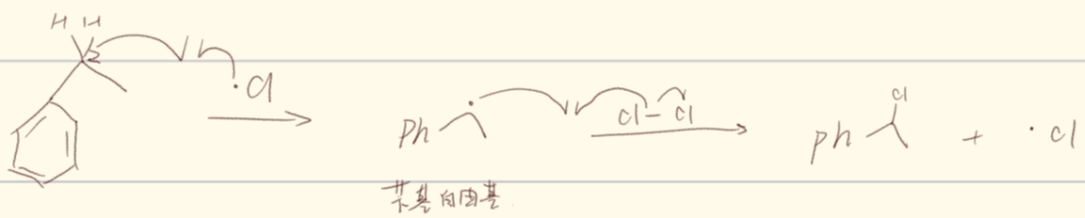
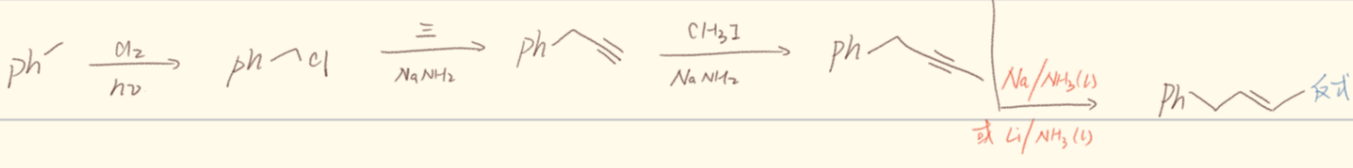
- F　fluoro-
- Cl　chloro-
- Br　bromo-
- I　iodo-

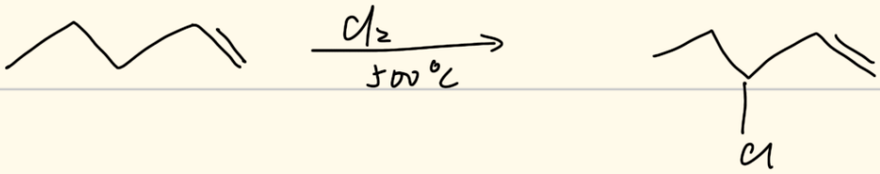
四 卤代烃制法



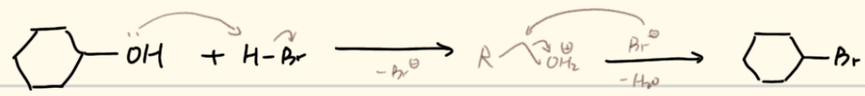
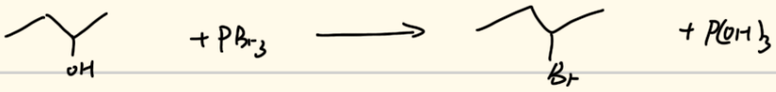


制取.　 



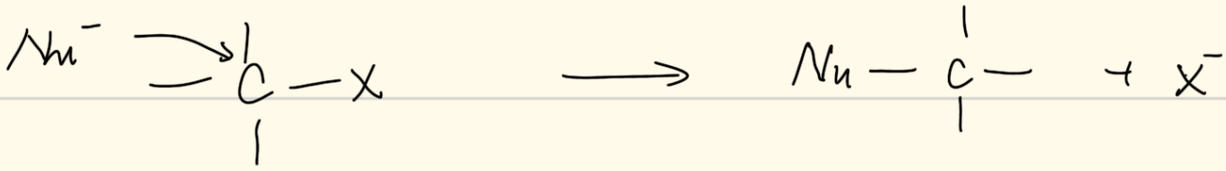


③由醇制备

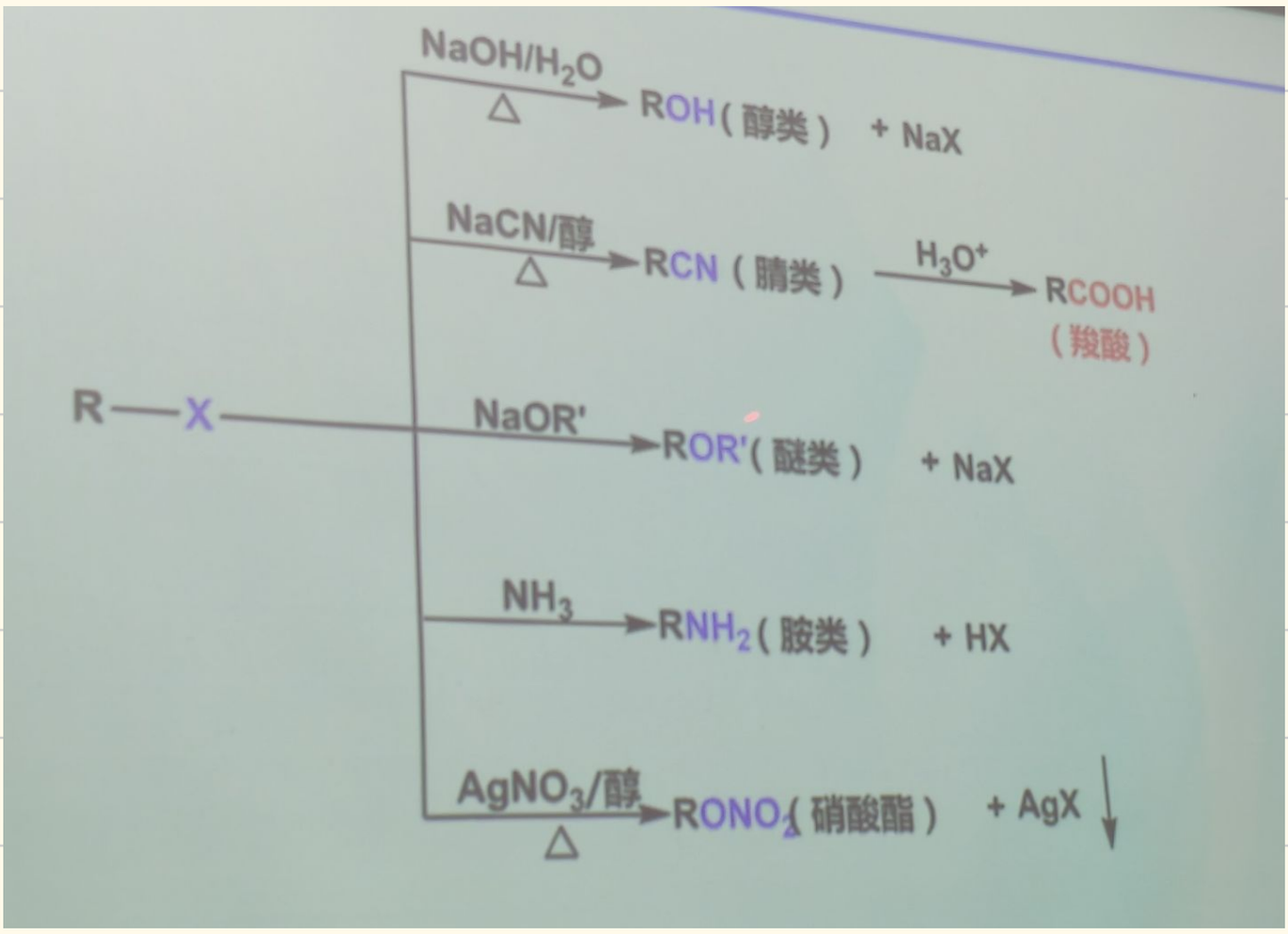
- 氢卤酸： 
- 卤化磷： 
- 亚硫酰氯：$ROH + SOCl_2 \longrightarrow RCl + SO_2 + HCl$

性质

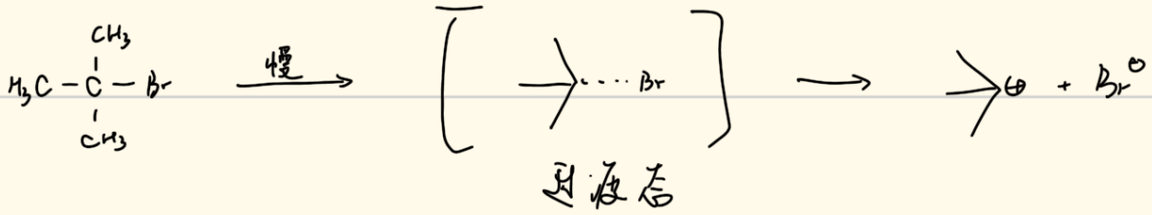
①亲核取代

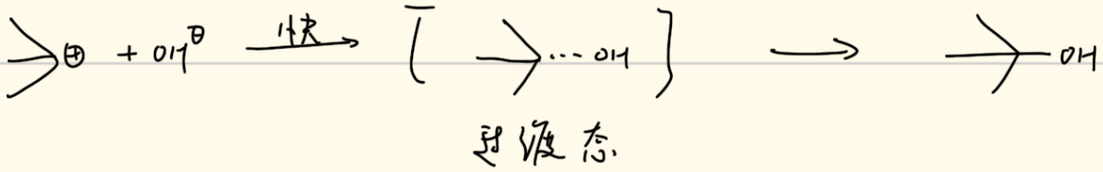


Nu^- 亲核性：$RO^- > HO^- > RCO_2^- > ROH > H_2O$ （亲核活性）



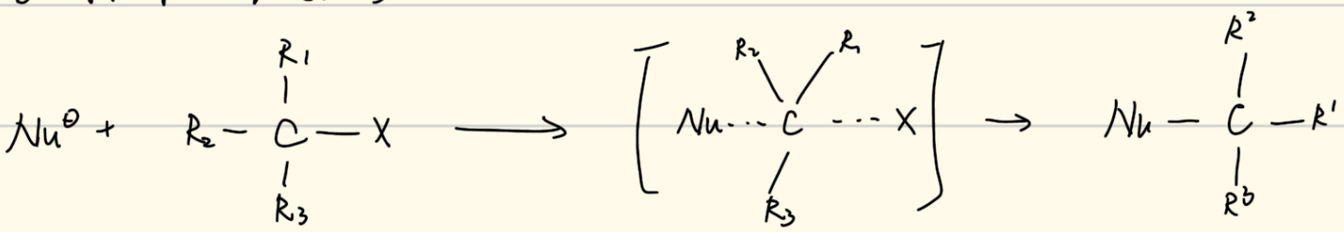
单分子亲核取代（S_N1）



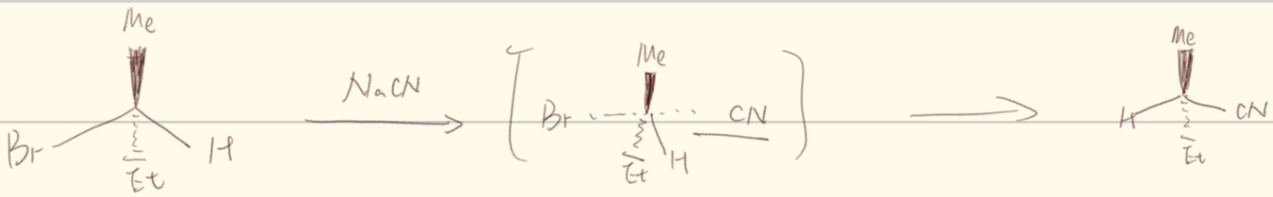


中间体为平面构型，产物为外消旋

双分子亲核取代反应（S_N2）



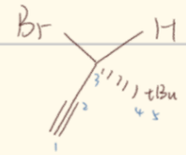
构型翻转



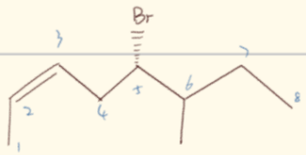
S_N2 速率与位阻有很大关系

一级卤代烃 ⇒ S_N2 ⟵ 二级

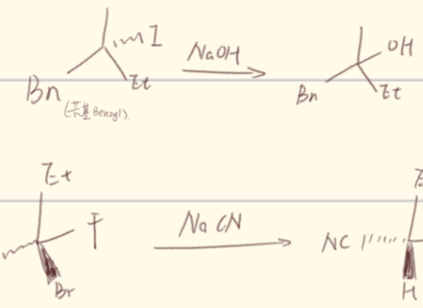
三级 ⇒ S_N1

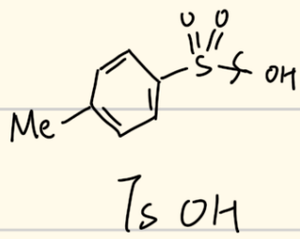
1) 

(R) - 3-bromo - 4, 4-dimethylpent - 1-yne

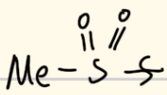
2) 

(2, 5S,) - 5-bromo - 6- methyloct - 2-ene

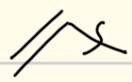
(3) 



TsOH

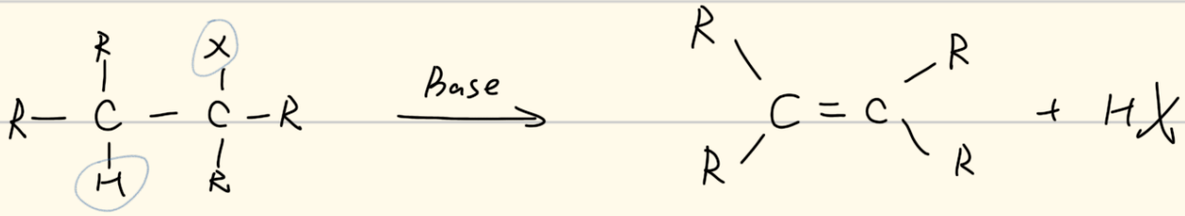


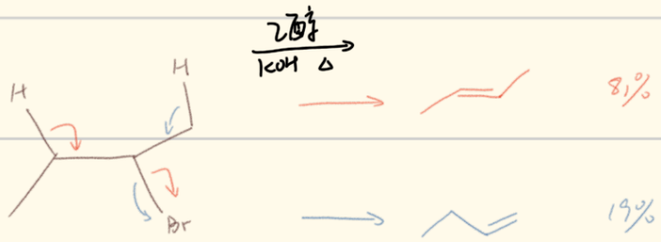
Ms



烯基 Vinyl

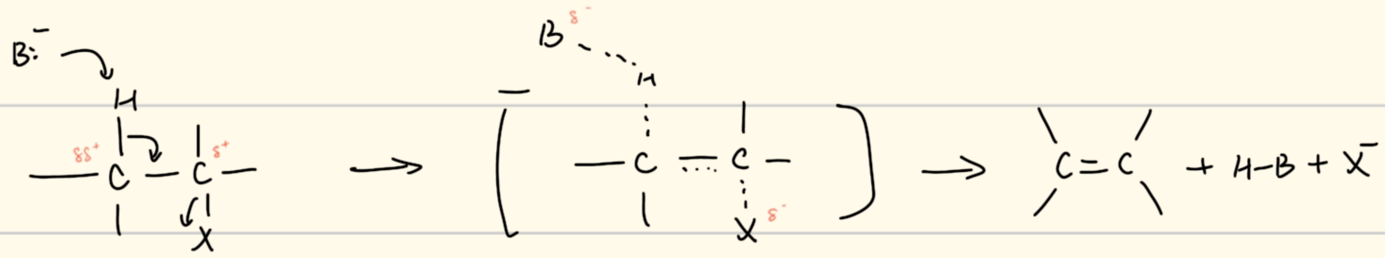
2) 消去



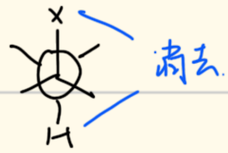


Zaitsev's rules: 得到取代基多的烯烃

双分子消除 E2



反式共平面消除



→更易形成稳定烯

反应活性
- $RF < RCl < RBr < RI$
- $RCH_2\text{-}X < R_2CH\text{-}X < R_3C\text{-}X$

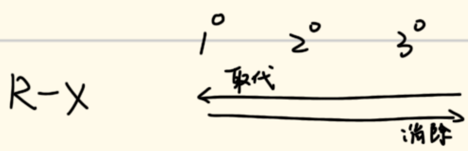
单分子消除 E1

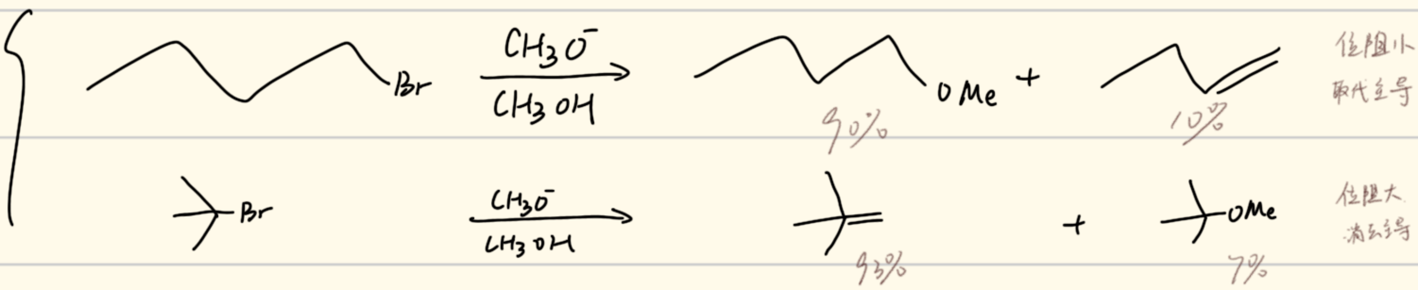
$(CH_3)_3C—Br \xrightarrow{slow} (CH_3)_3\overset{\delta^+}{C}\cdots\overset{\delta^-}{Br} \longrightarrow (CH_3)_3C^+ + Br^-$

$HO^- + H—CH_2—\overset{+}{C}(CH_3)_2 \xrightarrow{fast} [HO\cdots H\cdots CH_2\cdots C(CH_3)_2] \xrightarrow[-H_2O]{fast} CH_2=C(CH_3)_2$

E与SN反应的竞争

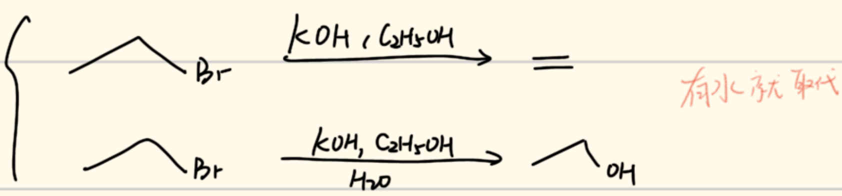
SN2 与 E2



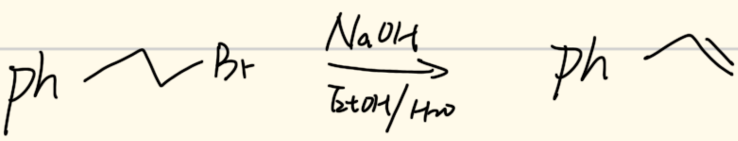


⇒低极性溶剂有利于消除

低温有利于取代



☆☆☆

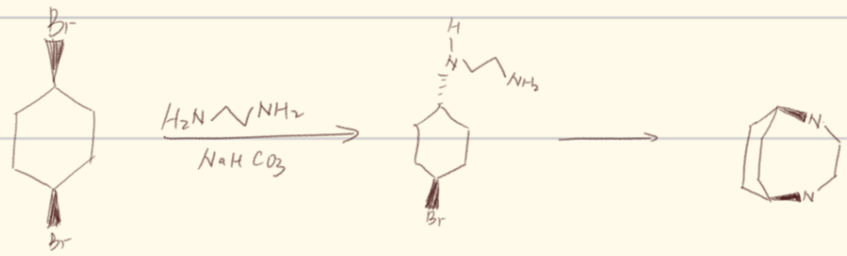


共轭不考虑水，生成更稳定共轭

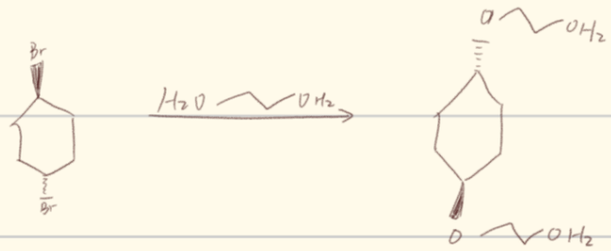
S_N1 与 E_1 竞争

无碱取代为主　　修旧 艾邪书考点

- 1^0　S_N2 / E_2
- 2^0　具体分析，弱Base S_N2 / 强Base E_2
- 3^0　S_N1 / E_2



$\Rightarrow$ 2° R-X $\rightarrow$ S_N2

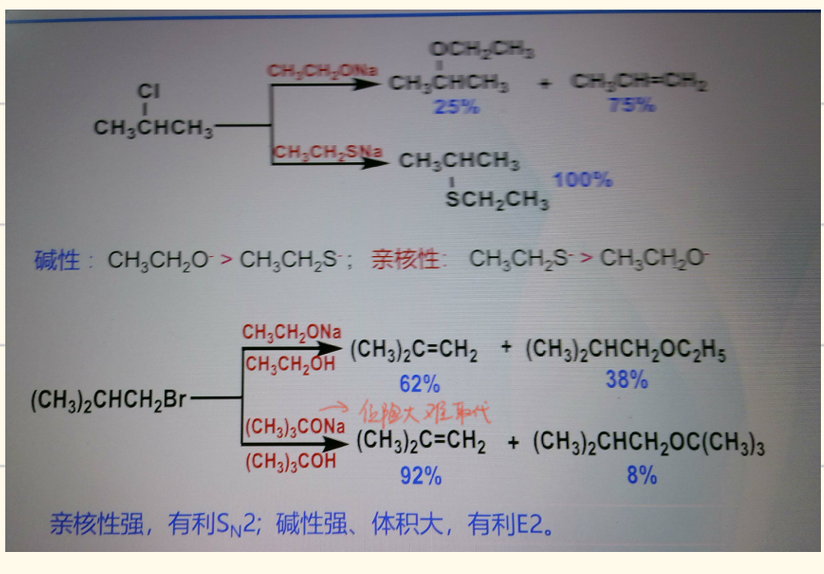


碱性

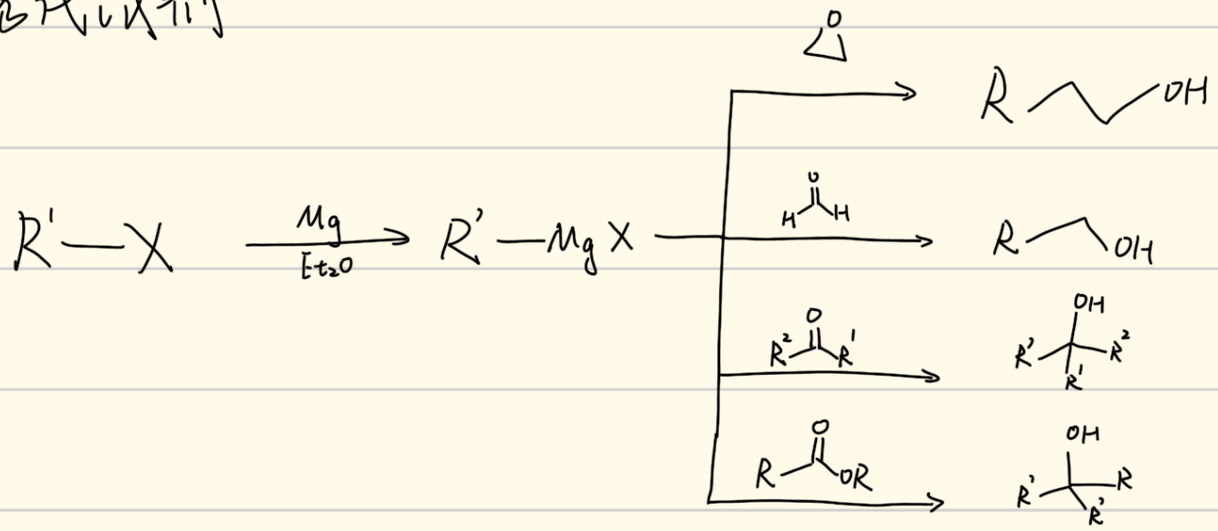
O^- > S^-

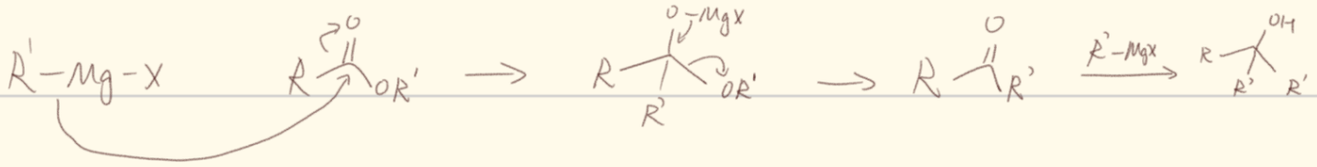
亲核性

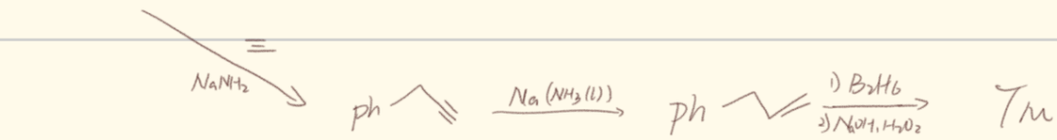
S^- > O^-　$\Rightarrow$ 硫可极化性 > 氧

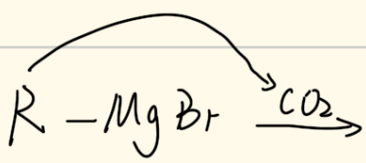


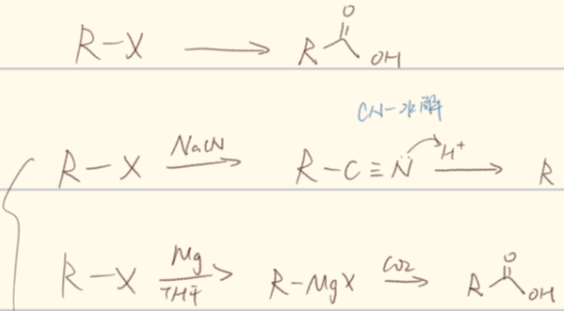
格氏试剂

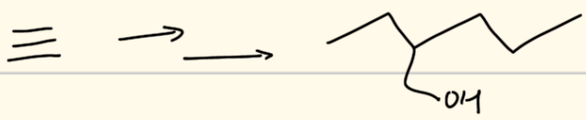




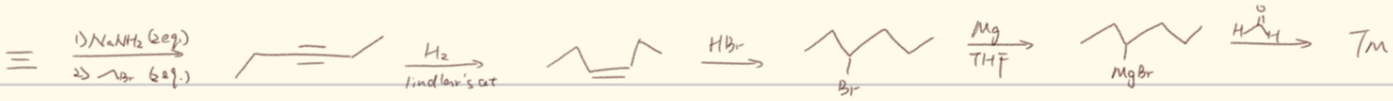







OH


H2
lindlar's cat
HBr
Br


1) NaNH2 (2eq.)
2)
Br (1eq.)
H2
lindlar's cat
HBr
Br
Mg
THF
MgBr
TM