

卤代烷的性质及其反应性

脂肪族卤代烷 ($2^\circ > 1^\circ > 3^\circ$) > 氯 > 芳香族

电性效应: $3^\circ > 2^\circ > 1^\circ$

空间位阻: $1^\circ > 2^\circ > 3^\circ$

溶剂化效应: [H₂O, 能更稳定]
 $1^\circ > 2^\circ > 3^\circ$

} $2^\circ > 1^\circ > 3^\circ$

卤代烷的亲核取代

protic: $F^- > Cl^- > Br^- > I^-$

亲核性 $I^- > Br^- > Cl^- > F^-$

aprotic: $F^- > Cl^- > Br^- > I^-$

Basicity $RO^- > RS^-$

Nucleophilicity $RS^- > RO^-$

负电荷集中 $\rightarrow$ 溶剂化强 $\Rightarrow$ 包裹 $\Rightarrow$ Nucleophilicity $\downarrow$

Alkane

isomers constitutional, configurational, conformational

沸点: 分子量/支链 $\downarrow$ 沸点 $\uparrow$

分子量/对称 $\uparrow$ 熔点 $\uparrow$

密度 分子量 $\uparrow$ 密度 $\uparrow$

Reactions

燃烧

卤代

异构化

裂化: 催化重整

Cycloalkane

Ring strain

torsional strain (扭转张力)

bond-angle strain (键角张力)

Configurational

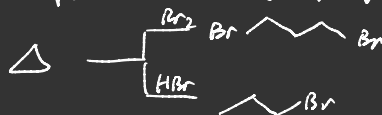


Conformational



开环反应

three- four- membered. Ring opening



Alkene

顺反异构

π键 不稳定, 电子流动性大

cis/trans

E/Z

物理性质: 与烷烃类似

沸点: 末端烷基 $\leftarrow$ 双键在中间

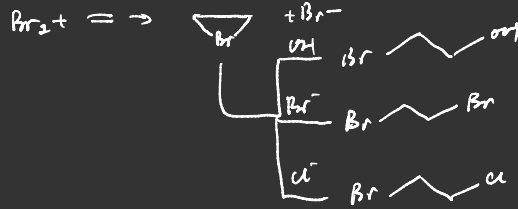
Reactions

X₂ Addition



Rule: 马氏加成 ↑

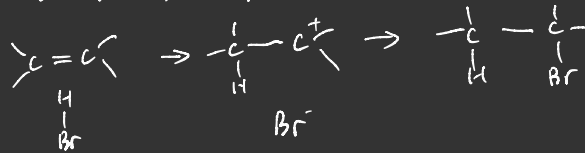
Markovnikov's rule



Anti-stereochemistry → trans only

HX Addition

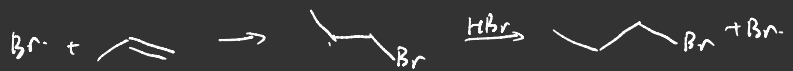
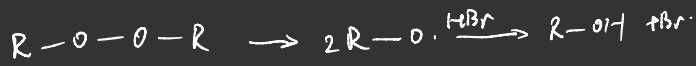
马氏加成 H 加在含氢较多的碳上



Markovnikov's rule

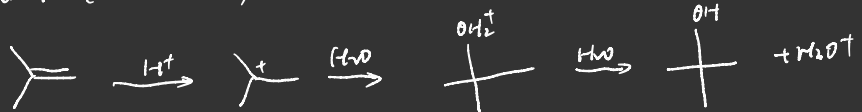


自由基反应

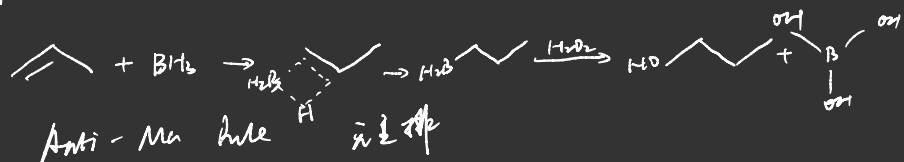


Anti-Markovnikov rule

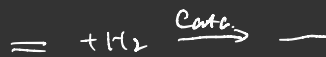
H₂O Addition (Acid Catalyzed)



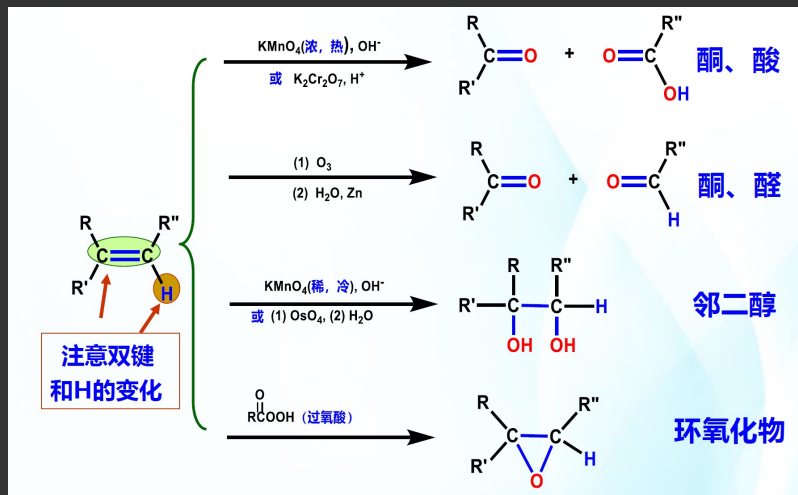
Hydroboration-Oxidation



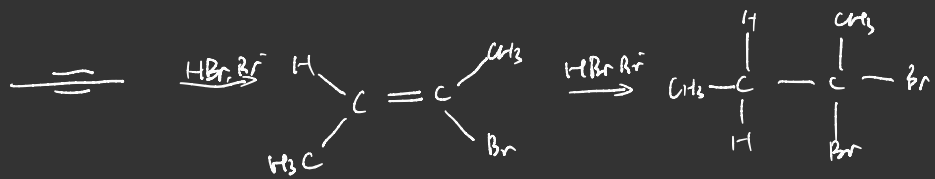
Reduction



加氢反应



Alkyne



Syn Anti

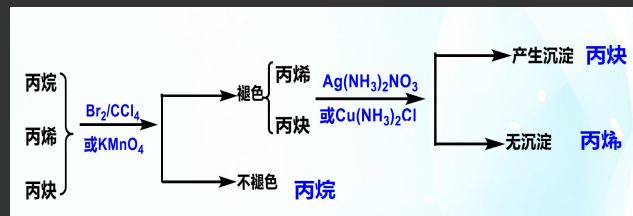
keto-enol tautomerism



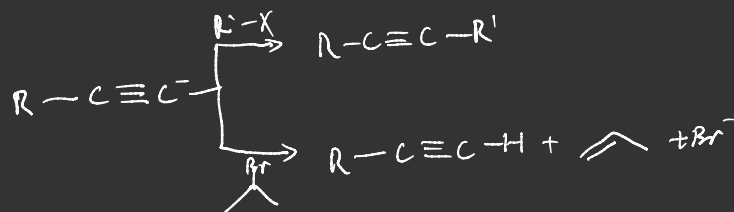
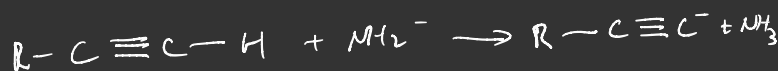
Hydrogenation



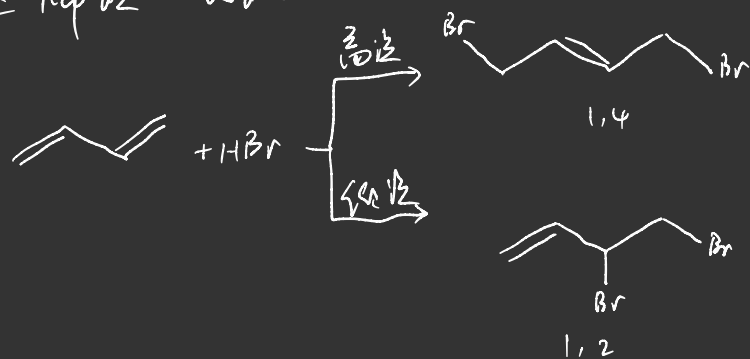
Acidity of alkyne



Alkylation of Terminal Alkyne



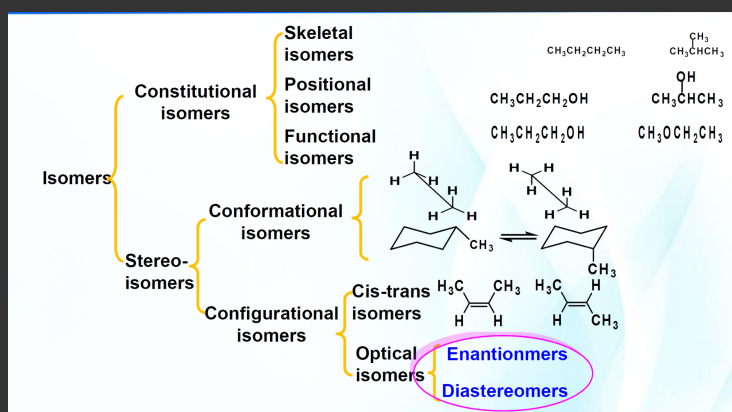
= 烯烃: 更多共轭



Stereoisomerism

旋光不同, 其他一致

成量对映异构体, 外消旋体 (±)



R/S 2^n

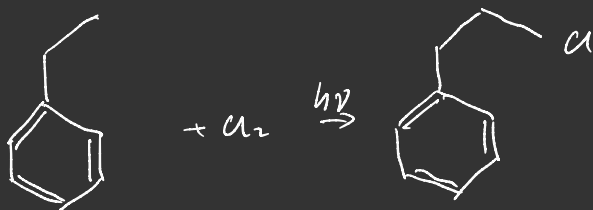
Racemate 外消旋体: 等量一对

Meso Compound 内消旋体: 有手性中心

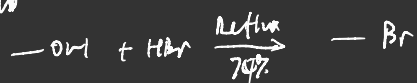
Alkyl Halide

Zn/PAL, Chloro, Fluoro, Bromo, Iodo

Producty
↓
↓
↓

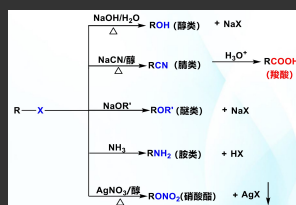
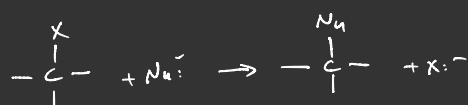


醇制备

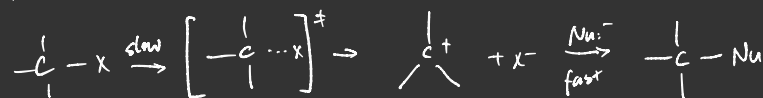


Reactions

Nucleophilic substitution



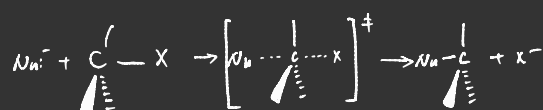
S_N1 Mechanism



$$v = k[RX]$$

Rearrangement

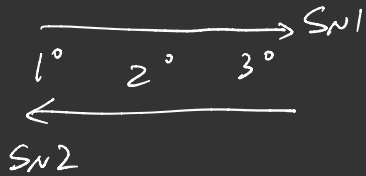
S_N2 Mechanism



$$v = k[RX][Nu^-]$$

Walden 翻转

Factors	S _{N1}	v.s.	S _{N2}
---------	-----------------	------	-----------------



rate $S_N2 \sim$ nucleophilic strength

SW 1 *

$S_N2 \sim$, leaving group stability

S_N1 (F not undergo)

差到比

此剂清毒素

protic : $F^- > Cl^- > Br^- > I^-$

亲核性 $I^- > Br^- > Cl^- > F^-$

aprotic: $F^- > Cl^- > Br^- > I^-$

Basicity $RO^- > RS^-$

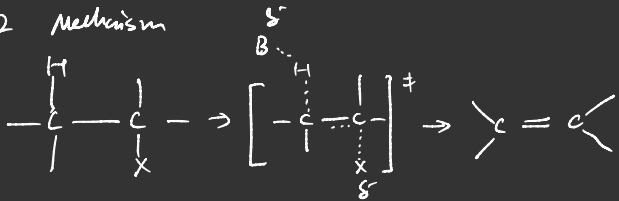
Nucleophilicity $RS^- > RO^-$

负债集中 $\rightarrow$ 流动性强 $\Rightarrow$ 包裹 $\Rightarrow$ Nucleophagy $\downarrow$

Elimination

Zeitser's rule

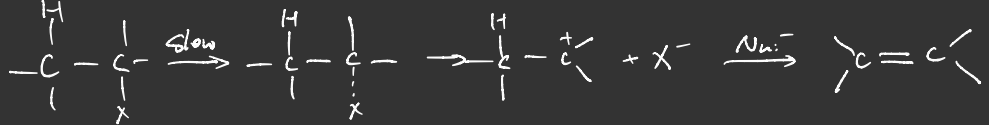
G2 Mechanism



$$v = k [R_x] [B:]$$

H-Br opposite

$\bar{b}_1$ mechanism



$$v = k[Rx]$$

$\overline{G}_2$ vs. $S_N 2$



$\overline{G}_1$ v.s. S_{N1}

急法 $\rightarrow \bar{G}_1$ Base $\rightarrow \bar{G}_1$

α -C 烷基多, β -C 支链多 $\rightarrow$ FI

产生共轭体系的消除反应

Elimination v.s. Substitution

高温 $\rightarrow$ 消除, 断 C-H, C-X

低温 $\rightarrow$ 取代, 断 C-X

S_N1 S_N2 $E1$ $E2$

Methyl

1°

2°

3°

S_N2

S_N2

weak base:

S_N2

No S_N2

solvolysis

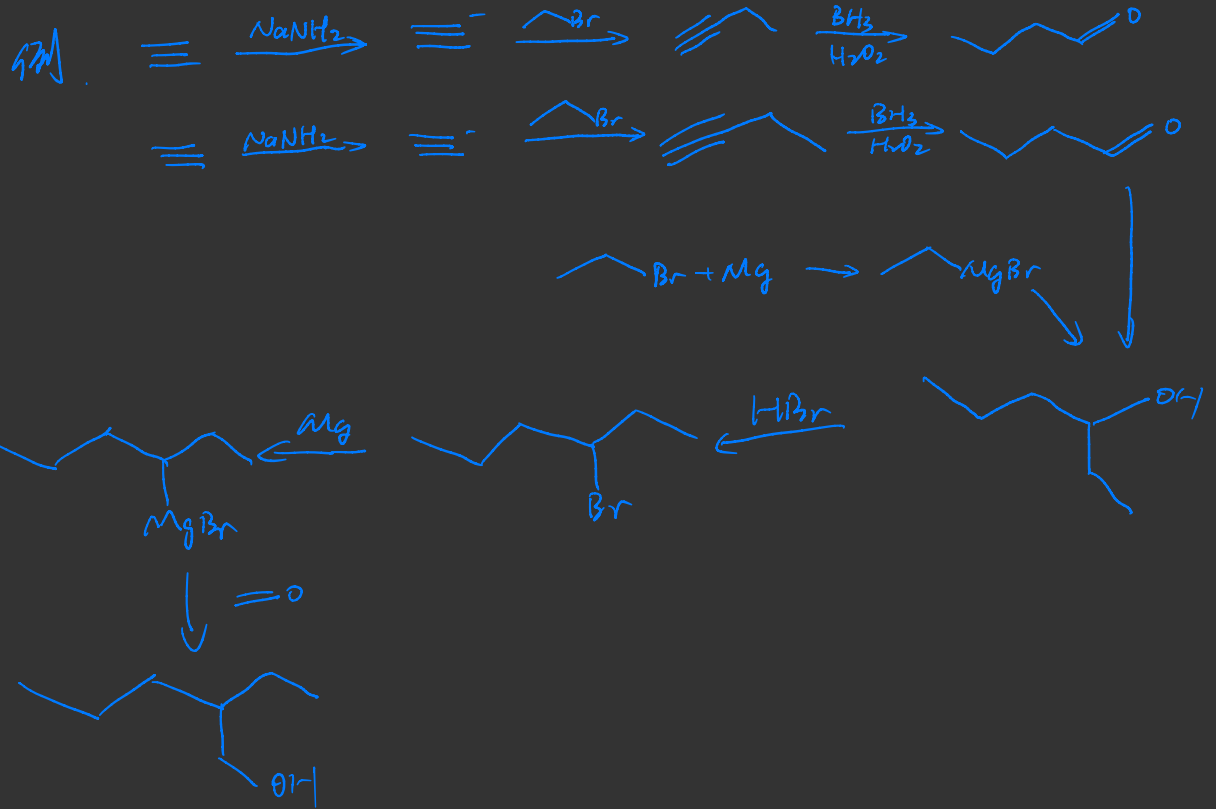
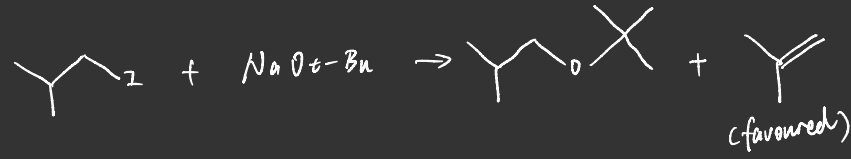
$E1$ high temp.

S_N1 low temp.

hindered strong base: $E2$

strong base $E2$

strong base $E2$



Alcohol

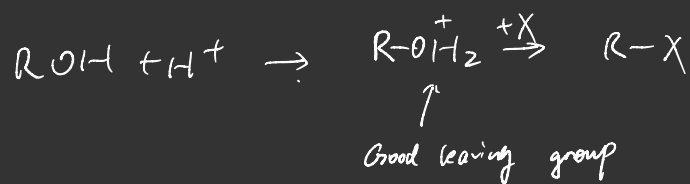
IUPAC -ol

Reactions

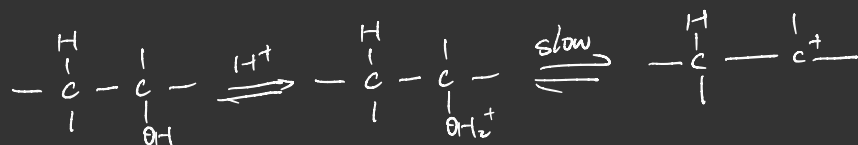
Acidity



Substitution

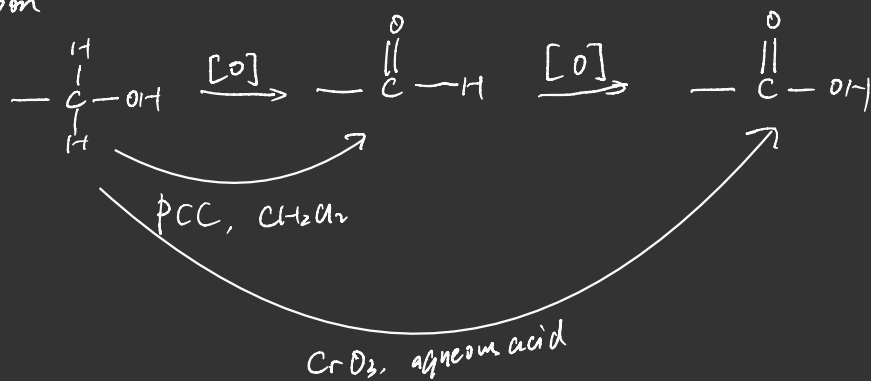


Elimination

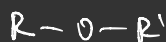


Zaitsev's Rule

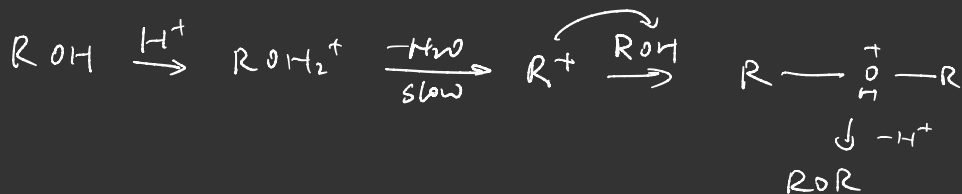
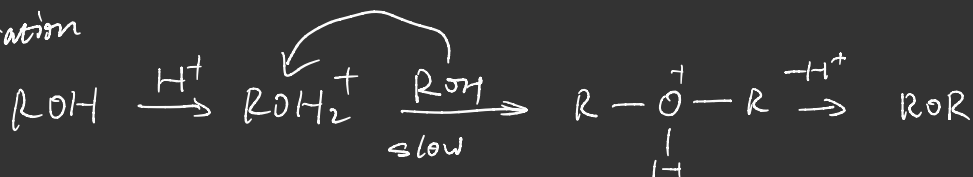
Oxidation



Ether



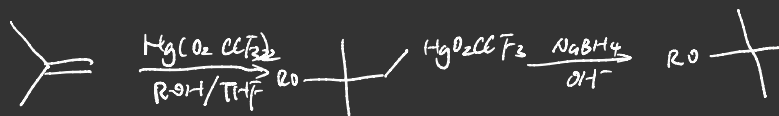
Preparation



Williamson Ether Synthesis



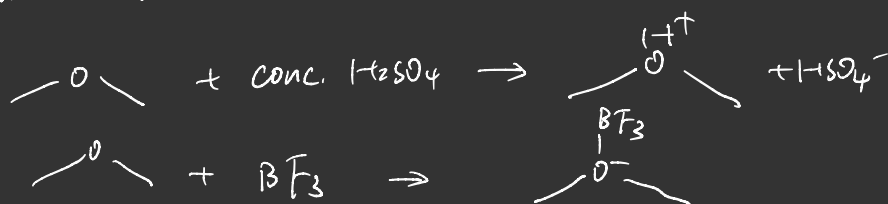
better 1° alkyl halide



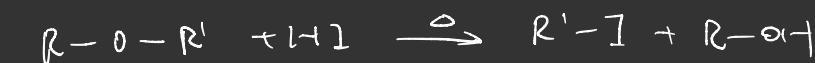
Reactions

unreactive

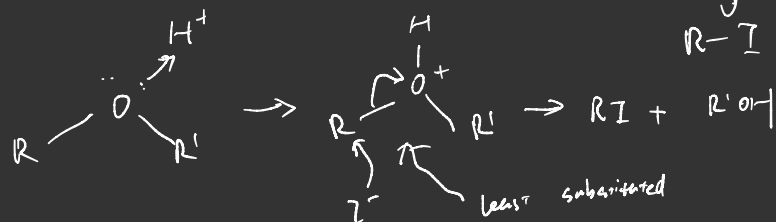
Oxonium salt



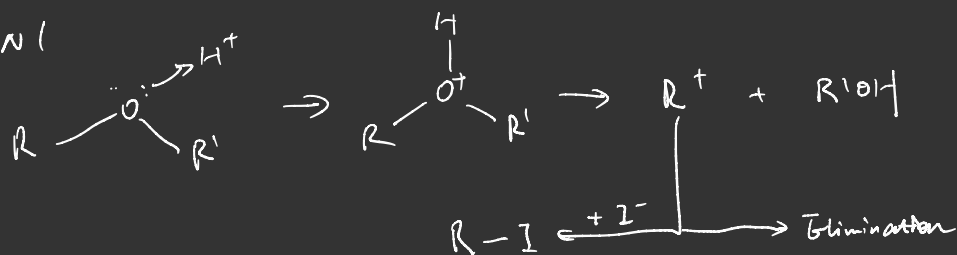
Cleavage



S_N2



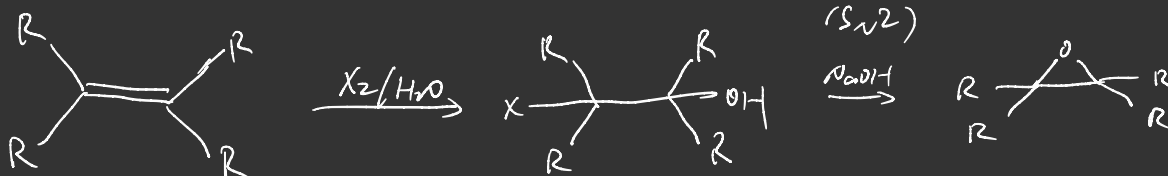
S_N1

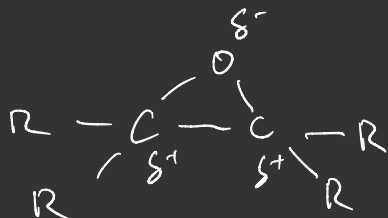


Oxidation



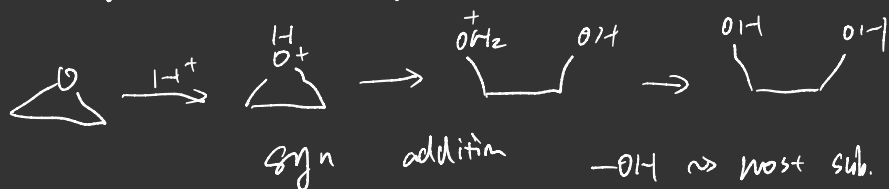
Epoxydes



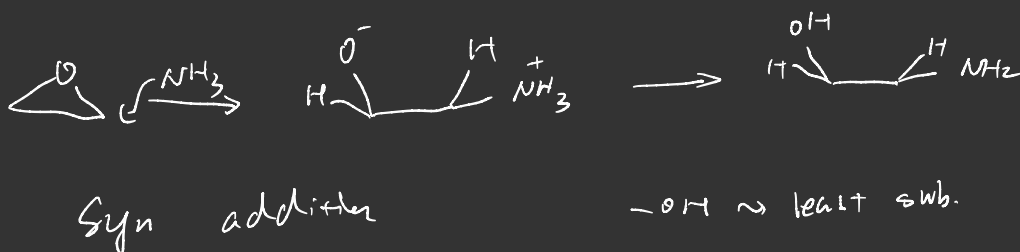


Reactions

Acid-Catalyzed Ring Opening



Base-Catalyzed Ring Opening



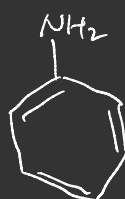
Aromatic



Toluene



Phenol



Aniline



Benzoic acid



phenyl



benzyl



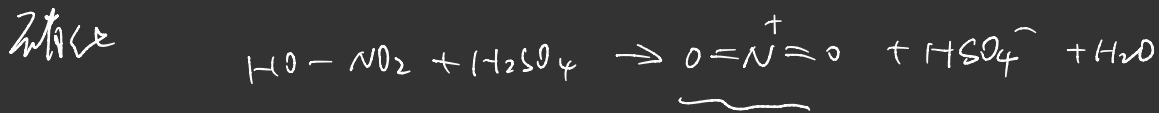
ortho-

meta-

para-

Reaction

Electrophilic Substitution Cl, AlCl_3
 Br, FeBr_3



Friedel-Crafts

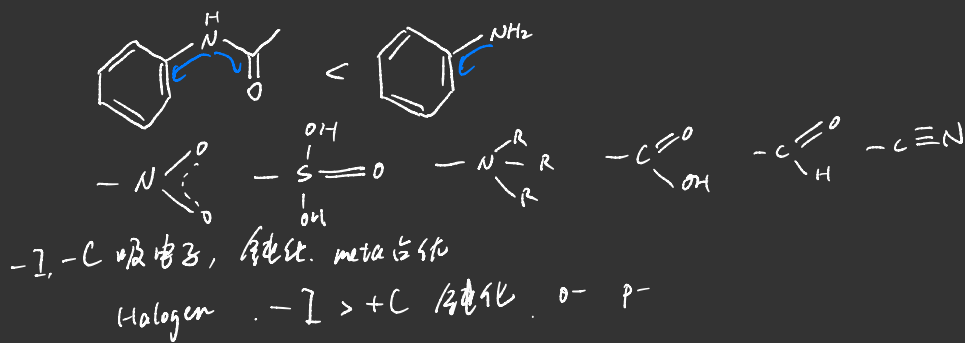


transition state $\sim$ carbocation

phenols, ethers, amines, amides $\rightarrow$ activate

$\rightarrow$ o-p

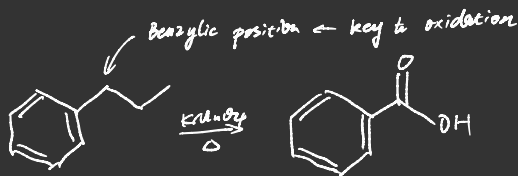
孤对电子 $+C > -1$, 活化基团



-I, -C 吸电子, 钝化, meta 活化

Halogen: $-\text{I} > +C$ 钝化, o-p

Oxidation

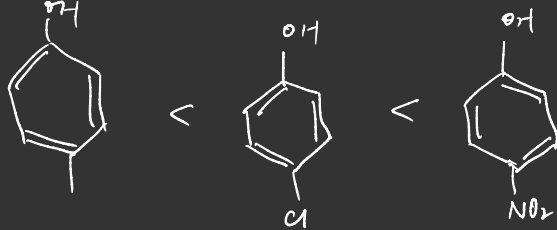


Reduction

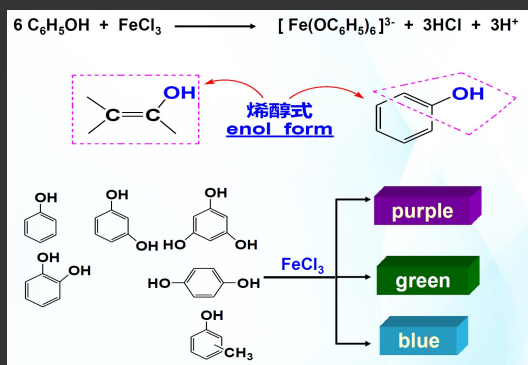


Phenol

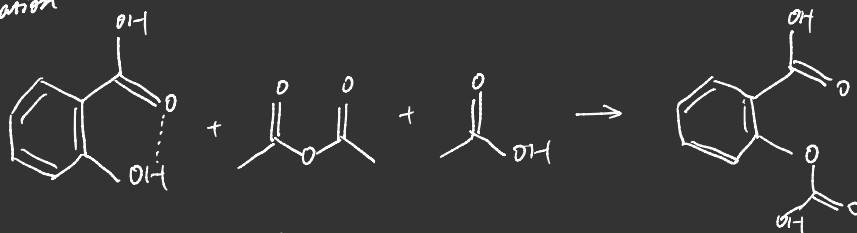
活性在苯环，—OH 不易被取代，酸性加强



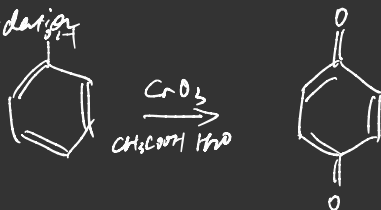
Color reaction



Esterification

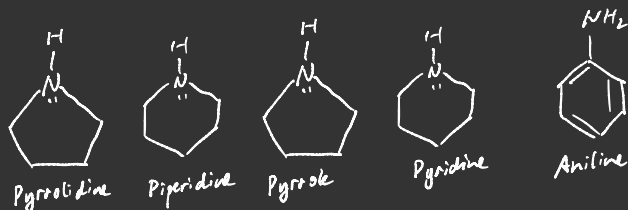


Oxidation



Amines

-Amine



Ammonia 氨
Amine 胺
Ammonium 铵

Hydrogen bond

氢键

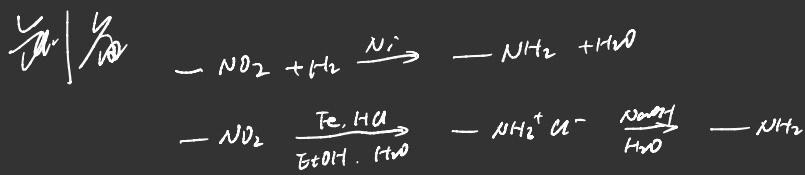
脂肪胺 (2° > 1° > 3°) > 氨 > 芳香胺

电性效应: 3° > 2° > 1°

空间位阻: 1° > 2° > 3°

溶剂化效应: [H₂O, 能正氢键] 1° > 2° > 3°

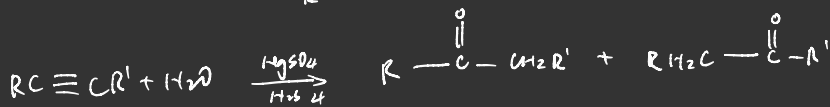
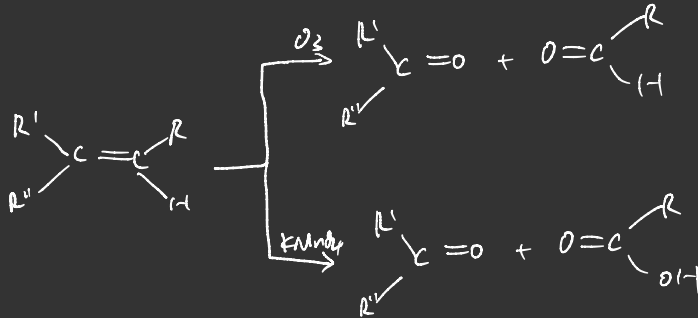
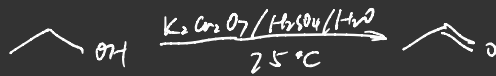
2° > 1° > 3°



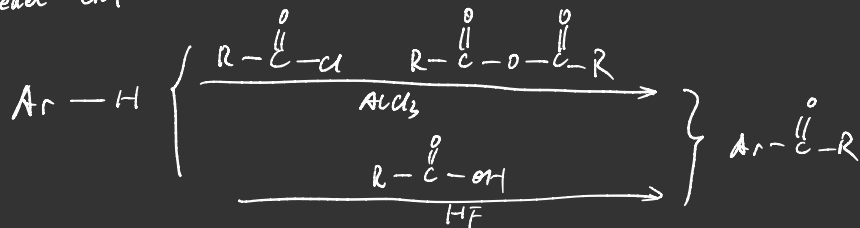
Alddehyde & ketone



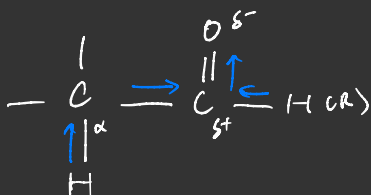
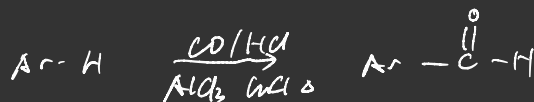
Preparation



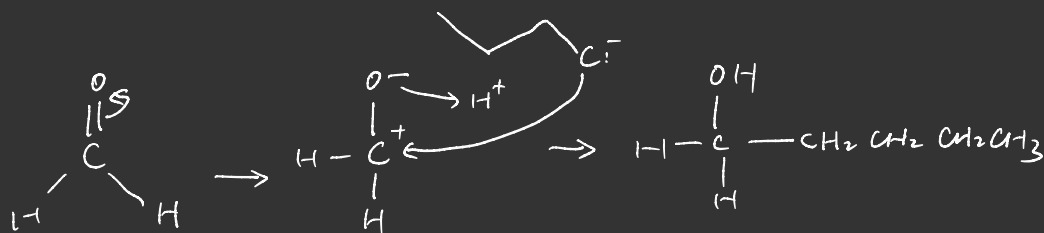
Friedel-Crafts



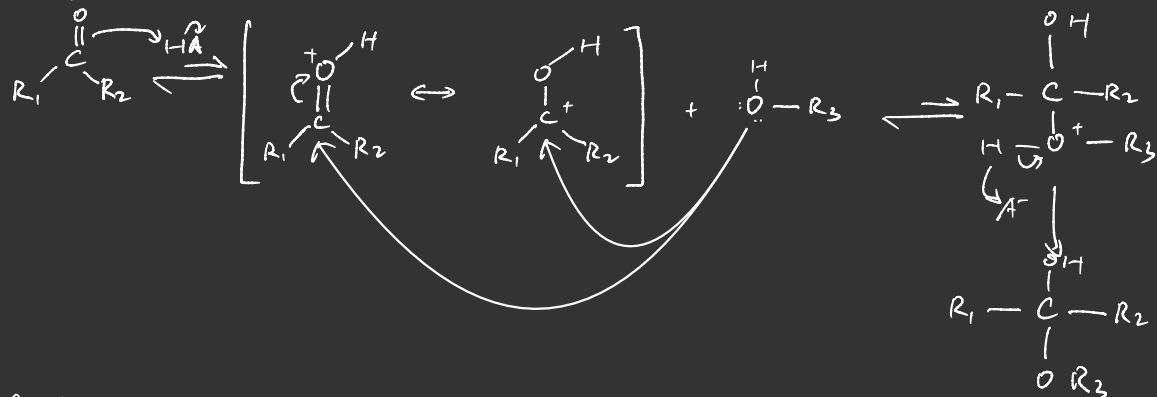
Barter - code



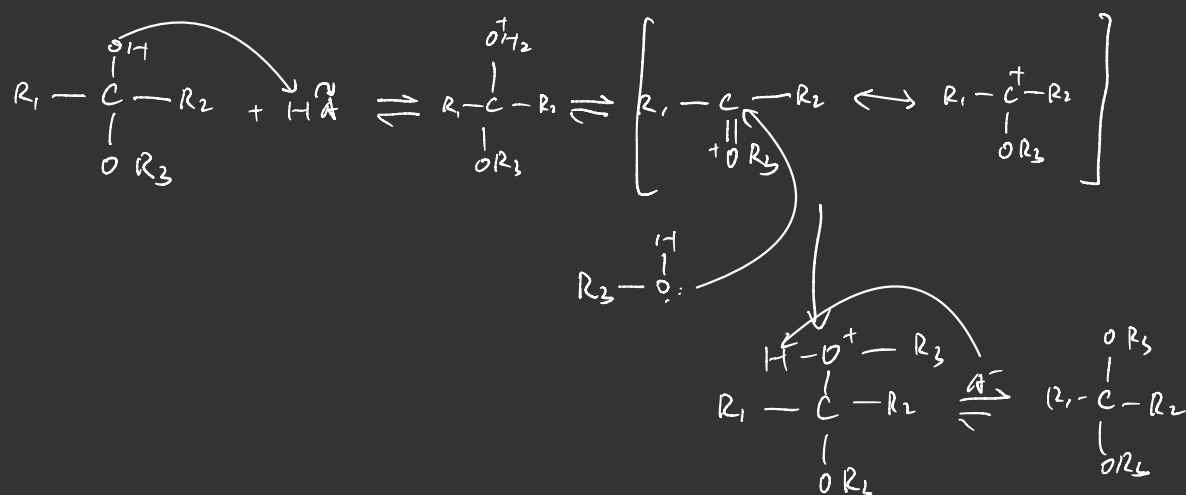
Grignard 试剂



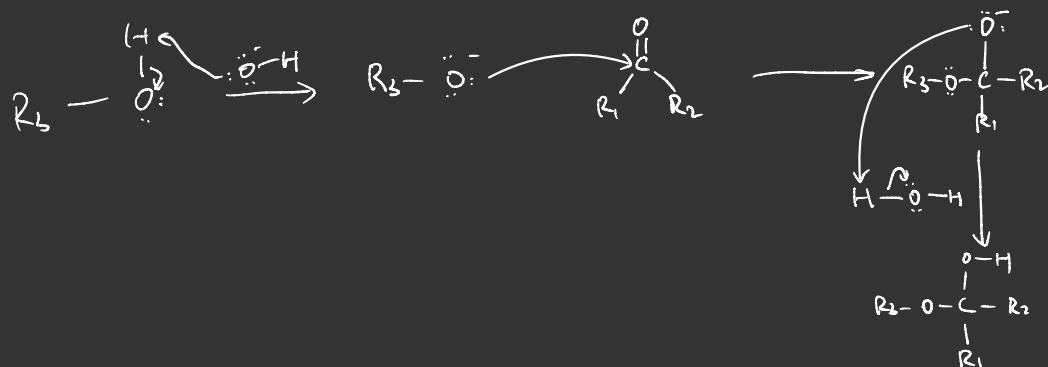
Acid-Cat. Hemiacetal



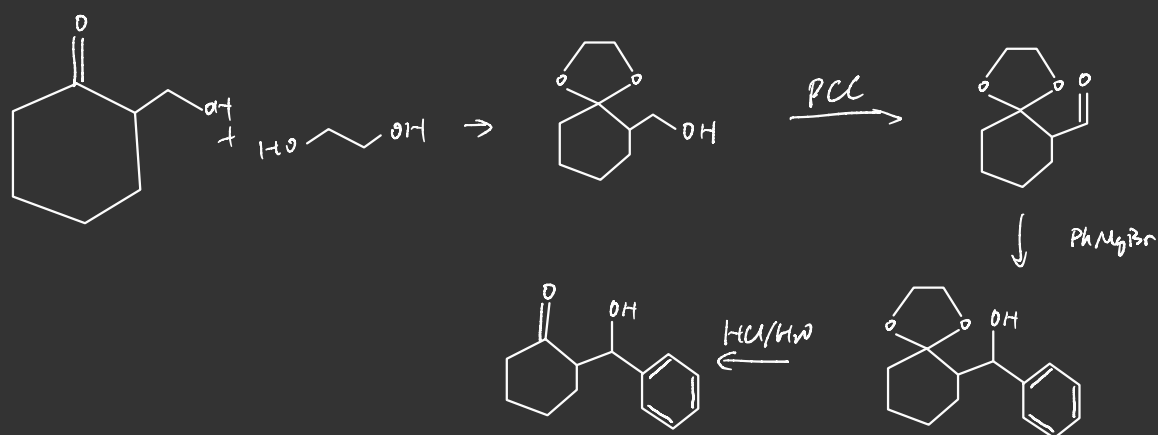
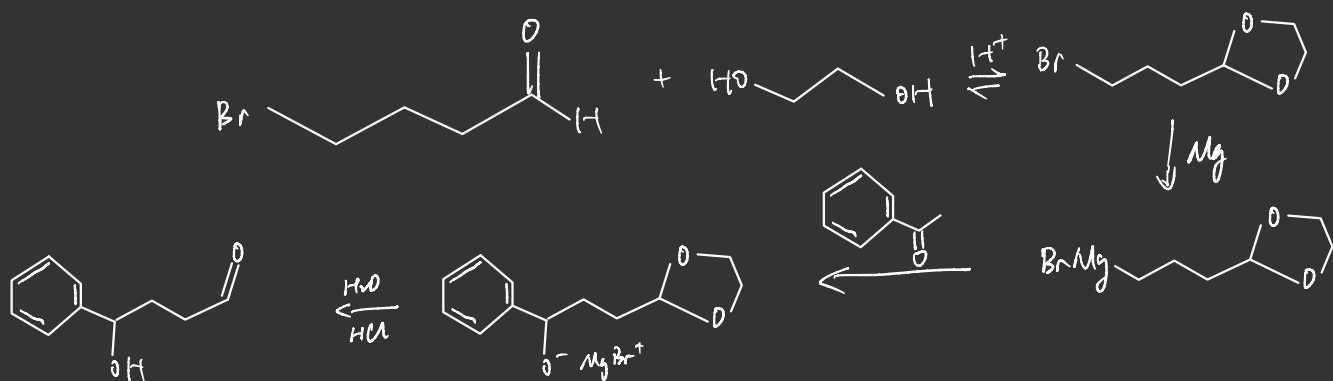
Acid-Cat. acetal



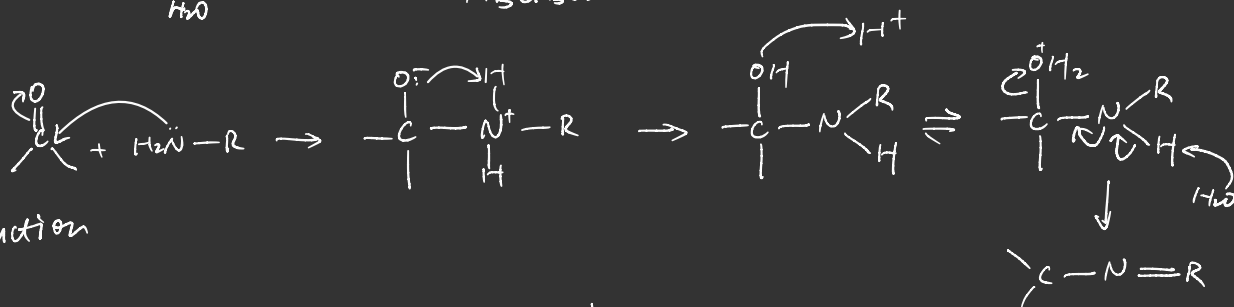
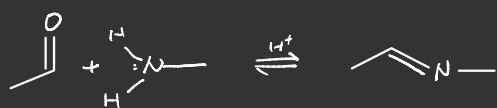
Base-Cat. hemiacetal



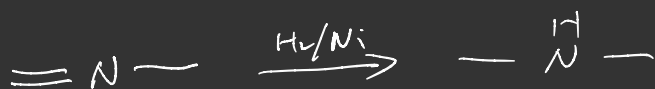
Acetal protecting carbonyl



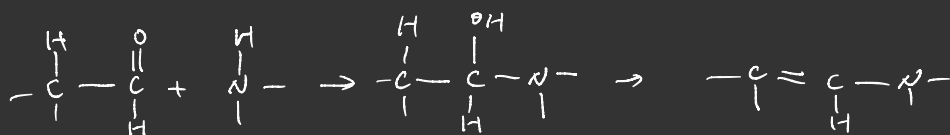
Imines (Schiff base)

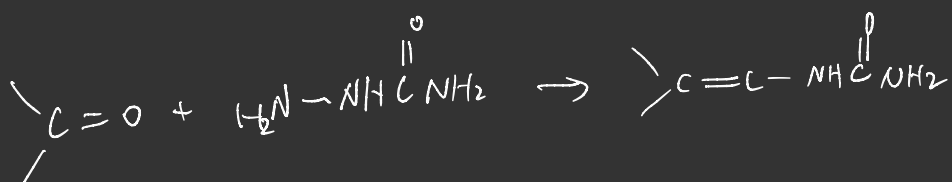
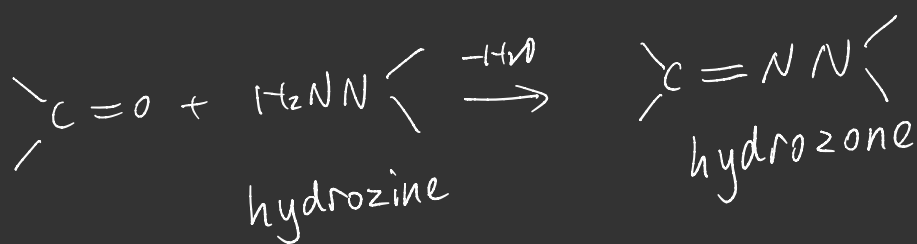
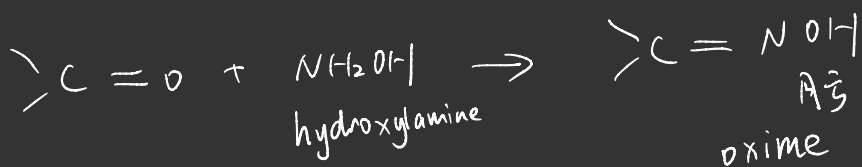


Reduction

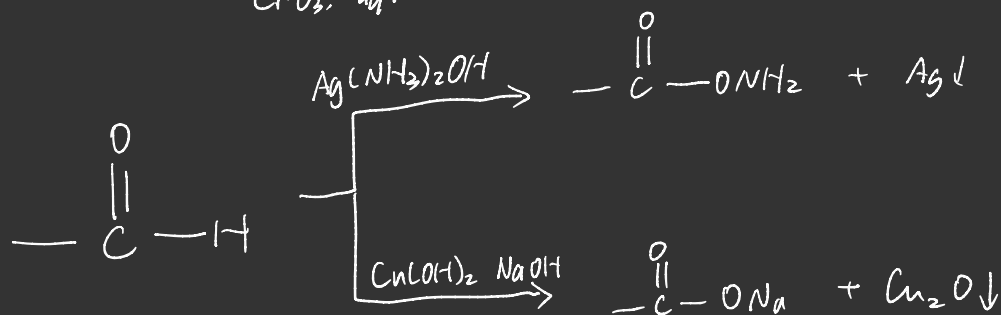
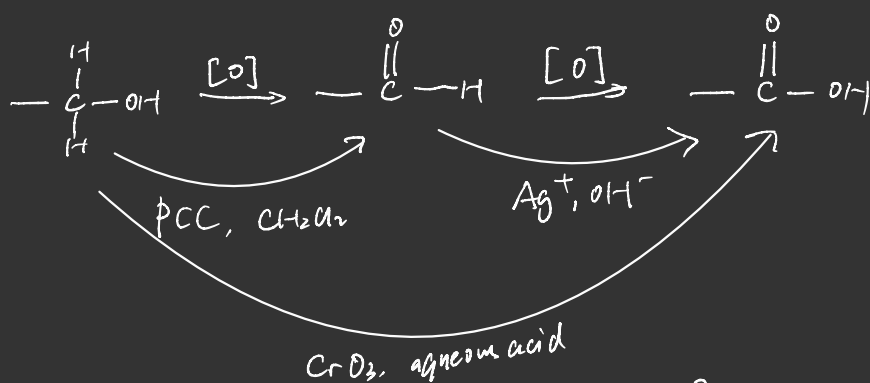
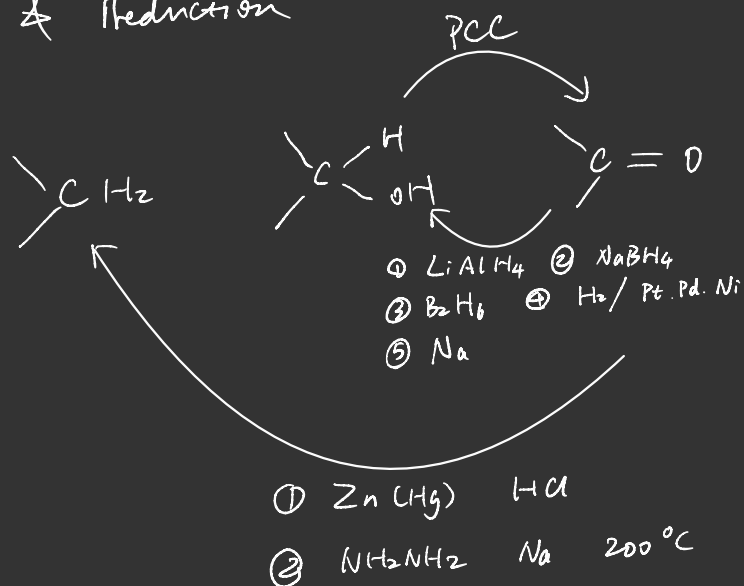


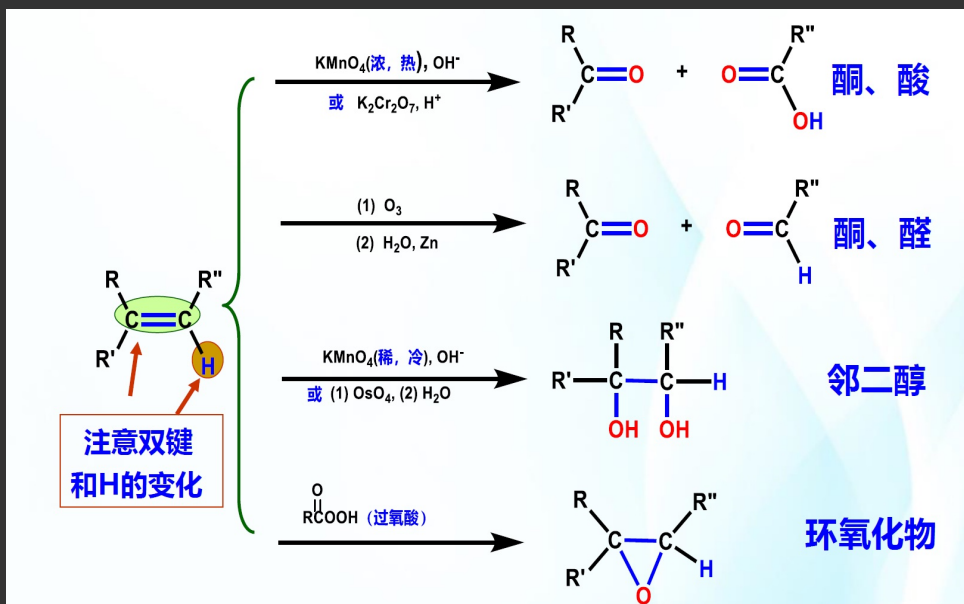
Enamine

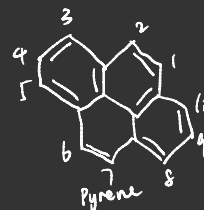
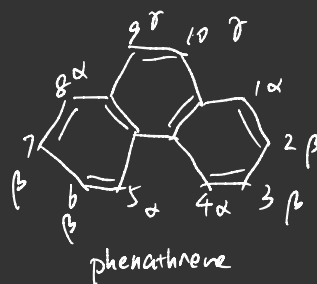
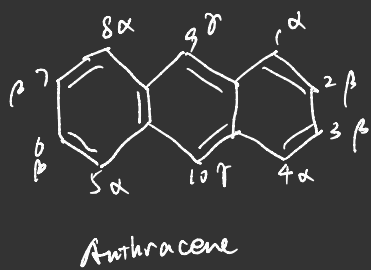
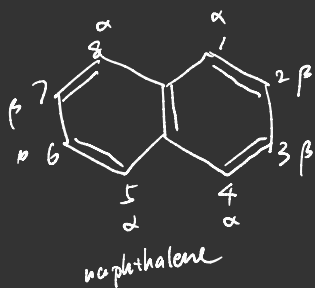




Oxidation & Reduction







Pyrrolidine



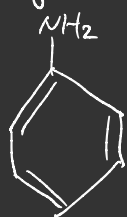
Piperidine



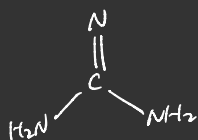
Pyrrole



Pyridine



Aniline



Guanidine