有机化学A2
复习总结

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Content

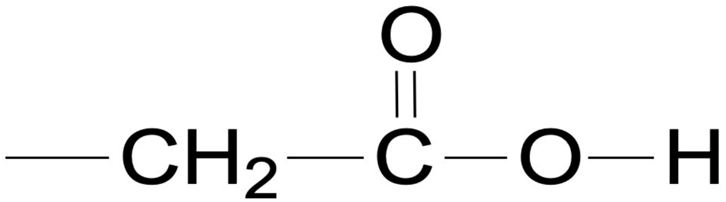
- 羧酸及其衍生物
- 取代羧酸
- 含氮化合物
- 含磷硫硅的化合物
- 杂环化合物
- 周环反应
- 糖、氨基酸

羧酸

- 波谱性质

		缔合(二聚体)	游离(单体)
$\nu_{C=O}$:	RCOOH	1710 cm^{-1}	1750-1770 cm^{-1}
	CH_2=CHCOOH	1690 cm^{-1}	1720 cm^{-1}
	ArCOOH	1680-1700 cm^{-1}	

NMR:



$$-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$$

^{1}HNMR δ 2~2.5 10~12

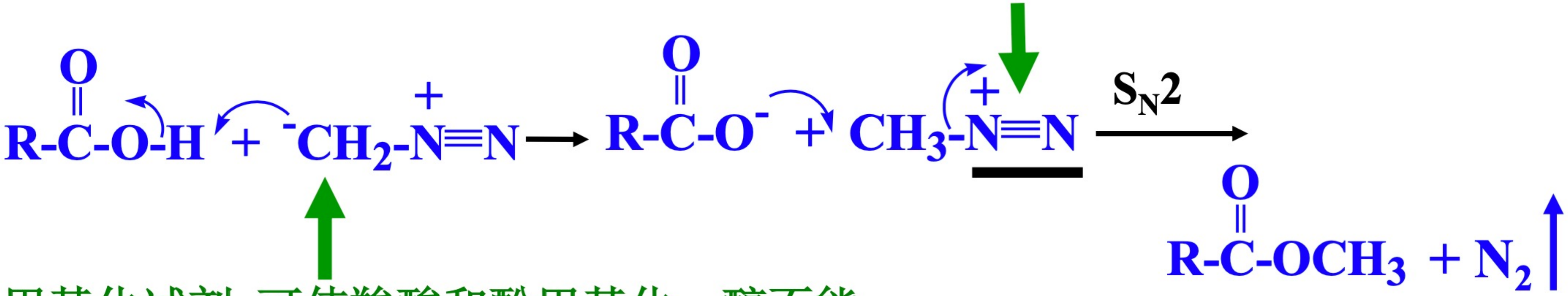
羧酸

羧酸根具有碱性和亲核性, 能与活泼卤代烷发生取代反应

$$RCOO^- + R'X \xrightarrow{S_N2} RCOOR' + X^-$$

羧酸与重氮甲烷的反应 甲基化

正性极强，易发生S_N2反应，是最好的离去基团。

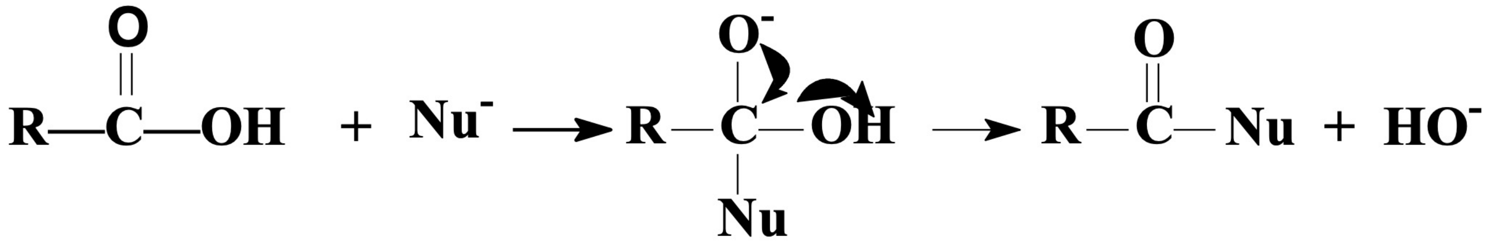


$$R-\overset{O}{\overset{\|}{C}}-O-H + {}^-CH_2-\overset{+}{N}\equiv N \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^- + CH_3-\overset{+}{N}\equiv N \xrightarrow{S_N2} R-\overset{O}{\overset{\|}{C}}-OCH_3 + N_2\uparrow$$

甲基化试剂, 可使羧酸和酚甲基化，醇不能。

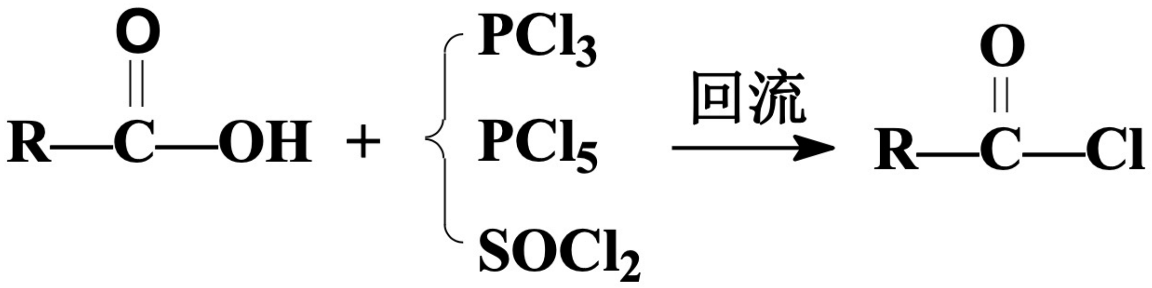
羧酸

- 羟基的取代

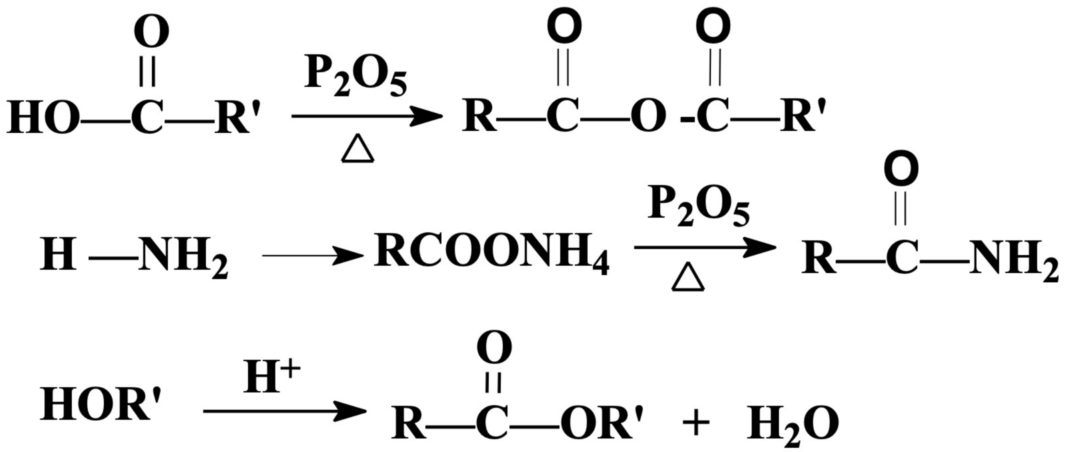


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + Nu^- \longrightarrow R-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle Nu}{|}}{C}}-OH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-Nu + HO^-$$

羧酸衍生物



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + \left\{\begin{array}{l}PCl_3\\PCl_5\\SOCl_2\end{array}\right. \xrightarrow{\text{回流}} R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl$$



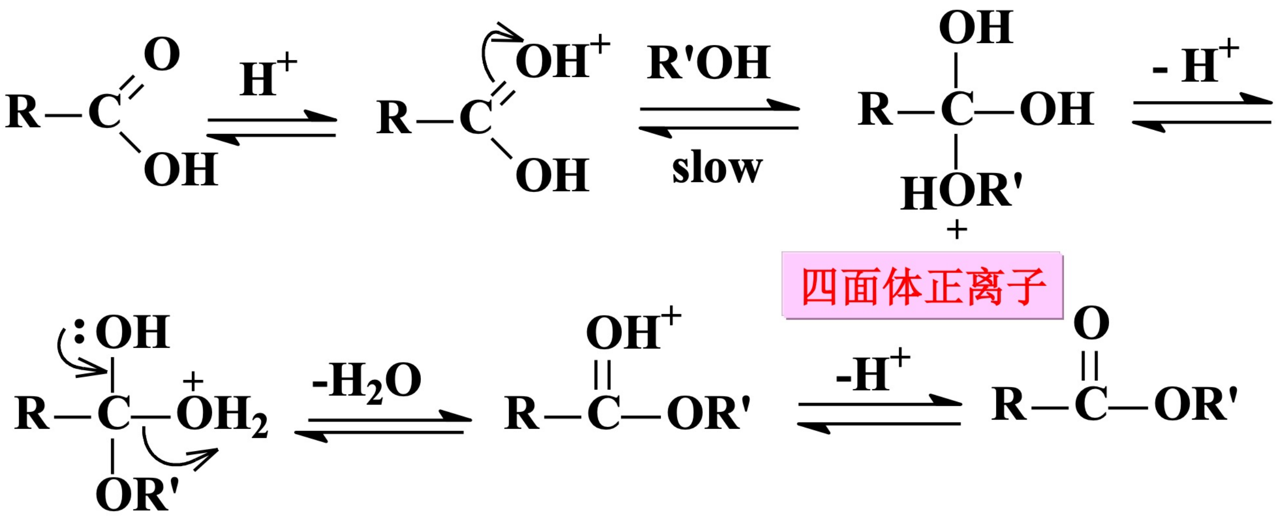
$$HO-\overset{\overset{\displaystyle O}{\|}}{C}-R' \xrightarrow[\triangle]{P_2O_5} R-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R'$$

$$H-NH_2 \longrightarrow RCOONH_4 \xrightarrow[\triangle]{P_2O_5} R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

$$HOR' \xrightarrow{H^+} R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + H_2O$$

羧酸

酯化反应的三种机理：A 加成-消除历程：

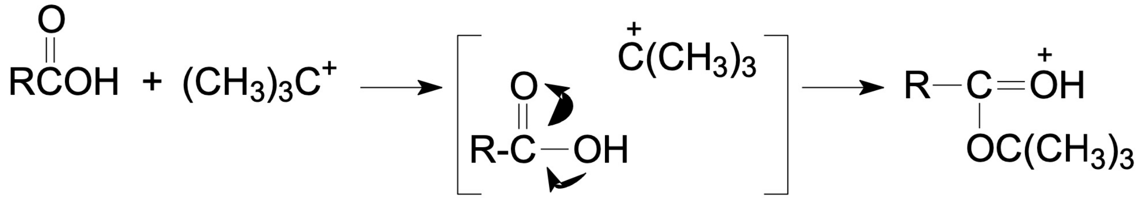


B 碳正离子历程: 3^0醇酯化时，醇提供-OH

$CH_3COOH + (CH_3)_3C\overset{18}{O}H \overset{H^+}{\rightleftharpoons} CH_3COOC(CH_3)_3 + H_2\overset{18}{O}$

历程：

$(CH_3)_3COH \overset{H^+}{\rightleftharpoons} (CH_3)_3C\text{-}\overset{18}{\underset{+}{O}}H_2 \overset{slow}{\rightleftharpoons} (CH_3)_3C^+ + H_2\overset{18}{O}$

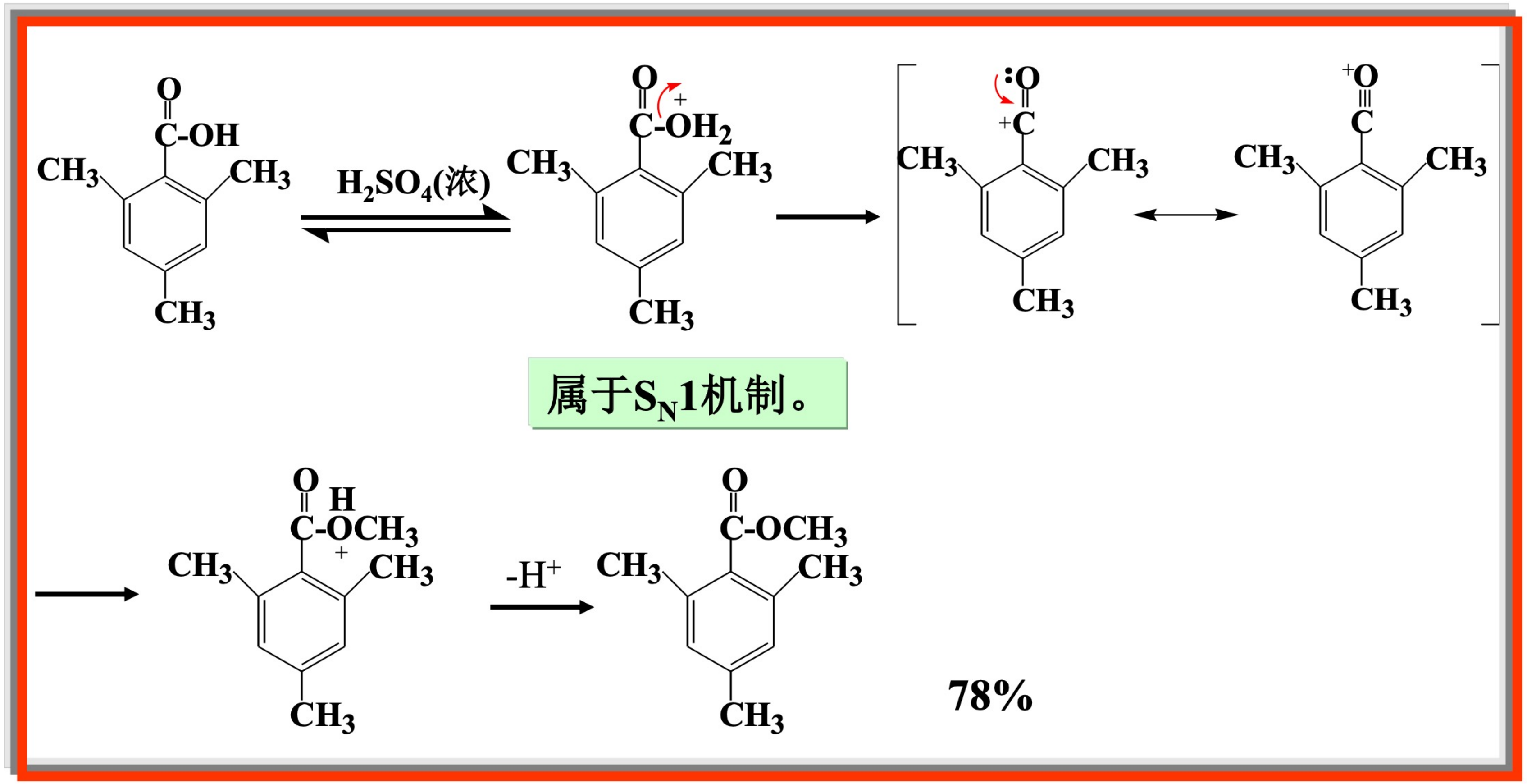


$RCOOH + (CH_3)_3C^+ \longrightarrow \left[R\text{-}C(=O)\text{-}OH \quad \overset{+}{C}(CH_3)_3 \right] \longrightarrow R-C=\overset{+}{O}H \;(OC(CH_3)_3)$

$\overset{-H^+}{\rightleftharpoons} RCOOC(CH_3)_3$

羧酸

C 酰基正离子历程（消除加成历程）



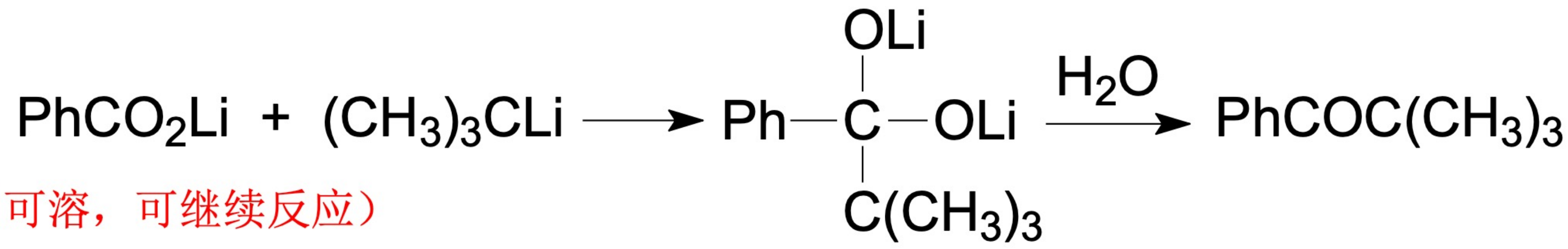
属于S_N1机制。

羧酸

- 与金属化合物反应

$$RCOOH + R'MgX \longrightarrow RCOOMgX \downarrow$$ (不能继续反应)

$$(CH_3)_3CLi + PhCOOH \longrightarrow PhCOOLi + (CH_3)_3CH$$

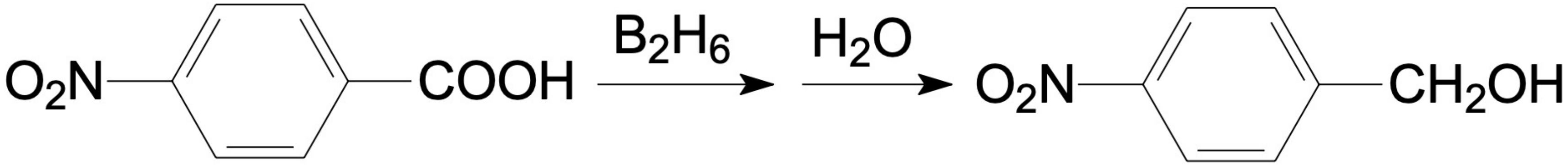


$$PhCO_2Li + (CH_3)_3CLi \longrightarrow Ph-\overset{OLi}{\underset{C(CH_3)_3}{C}}-OLi \xrightarrow{H_2O} PhCOC(CH_3)_3$$

（可溶，可继续反应）

- 还原

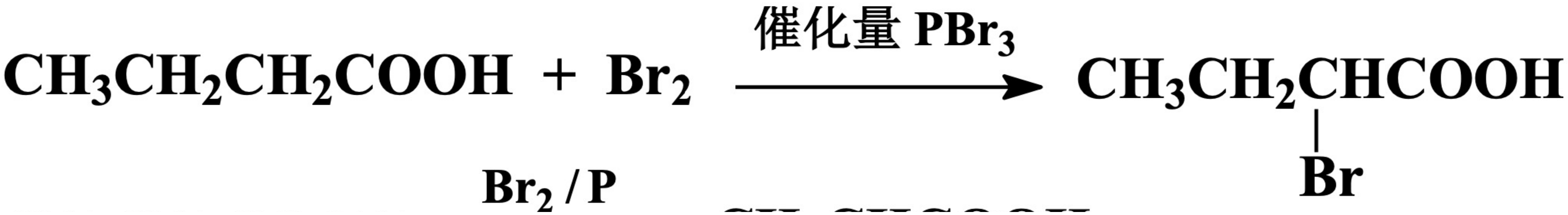
$$RCOOH + LiAlH_4 \longrightarrow RCH_2OH$$ 不能还原孤立的**C=C**



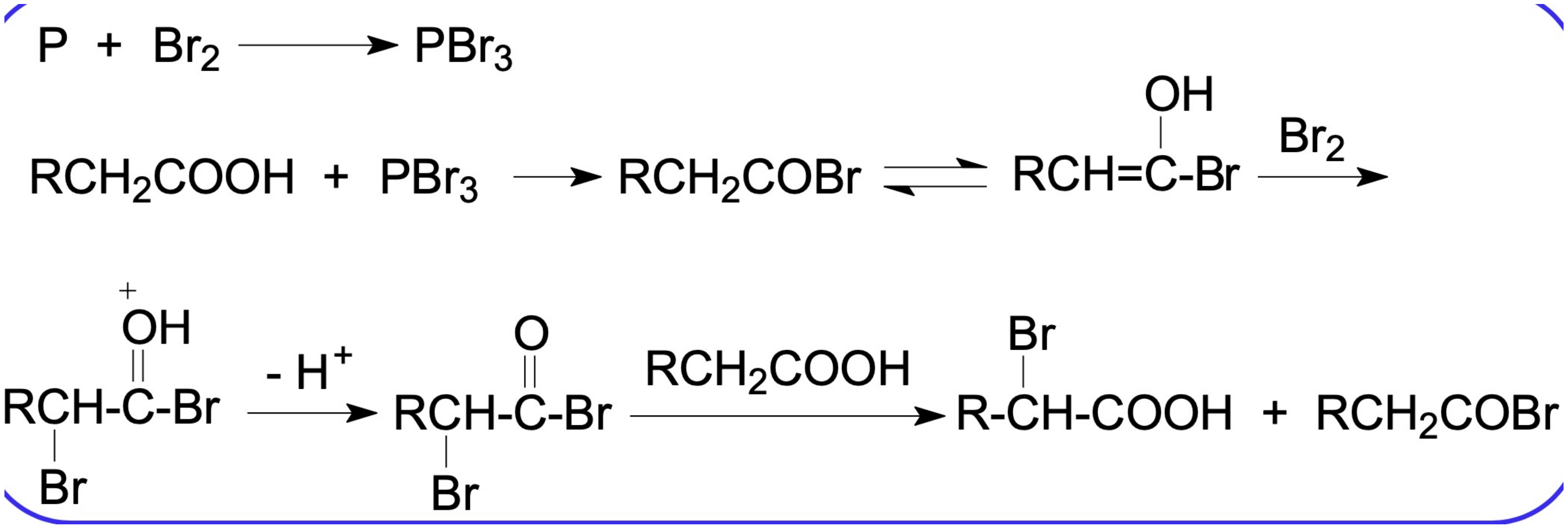
双键可被还原

羧酸

- α-H的反应



$$CH_3CH_2CH_2COOH + Br_2 \xrightarrow{\text{催化量 } PBr_3} CH_3CH_2\underset{\underset{Br}{|}}{CH}COOH$$



$$P + Br_2 \longrightarrow PBr_3$$

$$RCH_2COOH + PBr_3 \longrightarrow RCH_2COBr \rightleftharpoons RCH{=}\overset{\overset{OH}{|}}{C}\text{-}Br \xrightarrow{Br_2}$$

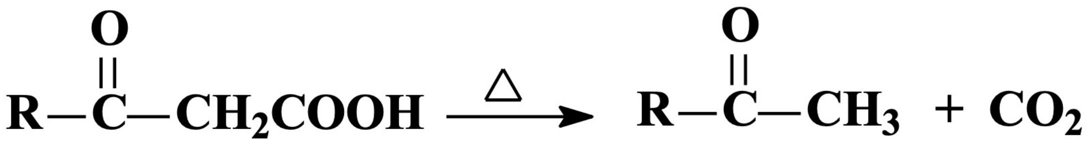
$$\underset{\underset{Br}{|}}{RCH}\text{-}\overset{\overset{\overset{+}{OH}}{\|}}{C}\text{-}Br \xrightarrow{-H^+} \underset{\underset{Br}{|}}{RCH}\text{-}\overset{\overset{O}{\|}}{C}\text{-}Br \xrightarrow{RCH_2COOH} R\text{-}\overset{\overset{Br}{|}}{CH}\text{-}COOH + RCH_2COBr$$

羧酸

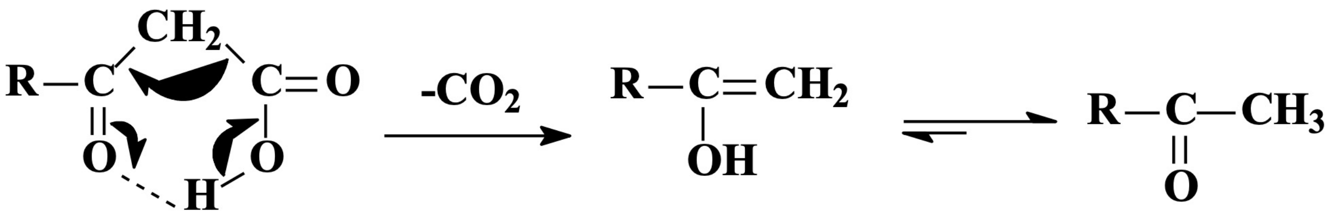
- 脱羧反应

a. 环状过渡态机理: 羧酸α-C与不饱和碳相连。

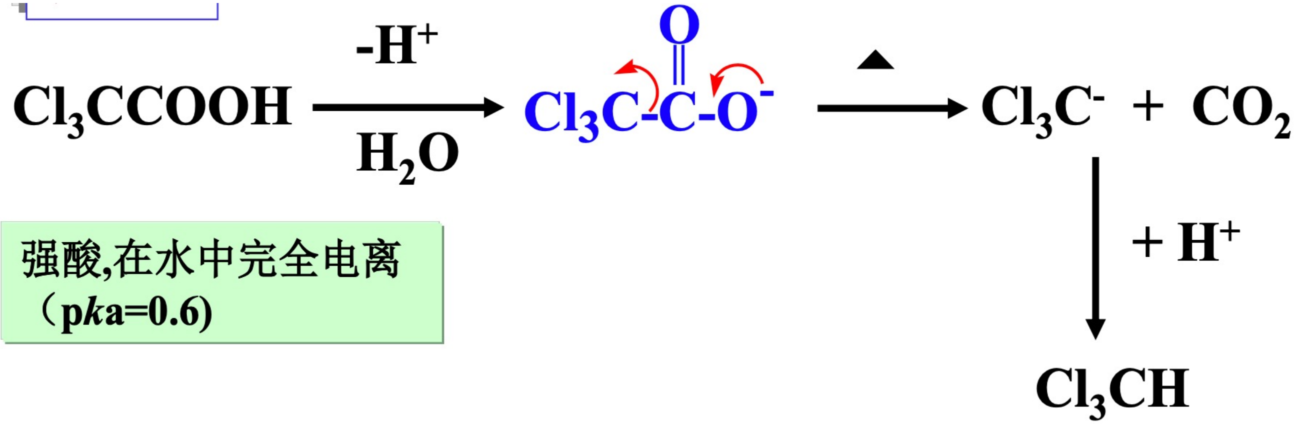
例如：



$$R-\overset{O}{\overset{\|}{C}}-CH_2COOH \xrightarrow{\triangle} R-\overset{O}{\overset{\|}{C}}-CH_3 + CO_2$$



b. 负离子机理: 羧基直接连有强吸电子基团



强酸,在水中完全电离（$pka=0.6$)

羧酸

反应名称	反 应 式
柯尔伯法	$2CH_3COONa \xrightarrow[2H_2O]{\text{电解}} C_2H_6 + CO_2 + NaOH + H_2$
汉斯狄克法	$RCH_2COOH \xrightarrow{AgNO_3\ \ KOH} RCH_2COOAg$ $\xrightarrow{Br_2\ \ CCl_4\ \ \Delta} RCH_2Br$
克利斯脱法	$RCH_2COOH \xrightarrow{HgO} (RCH_2COO)_2Hg$ $\xrightarrow{Br_2\ \ CCl_4\ \ \Delta} RCH_2Br$
柯齐法	$RCOOH \xrightarrow{Pb(OAc)_4\ \ I_2} RCOOPb(OAc)_3$ $\xrightarrow{LiCl\ \ C_6H_6\ \ \Delta} RCl$

机理：游离基历程

$$RCOOAg \xrightarrow{Br_2} RCOOBr$$

$$RCOOBr \xrightarrow{\text{加热}} RCOO\cdot + Br\cdot$$

$$RCOO\bullet \longrightarrow R\cdot + CO_2$$

$$R\cdot + Br\cdot \longrightarrow RBr$$

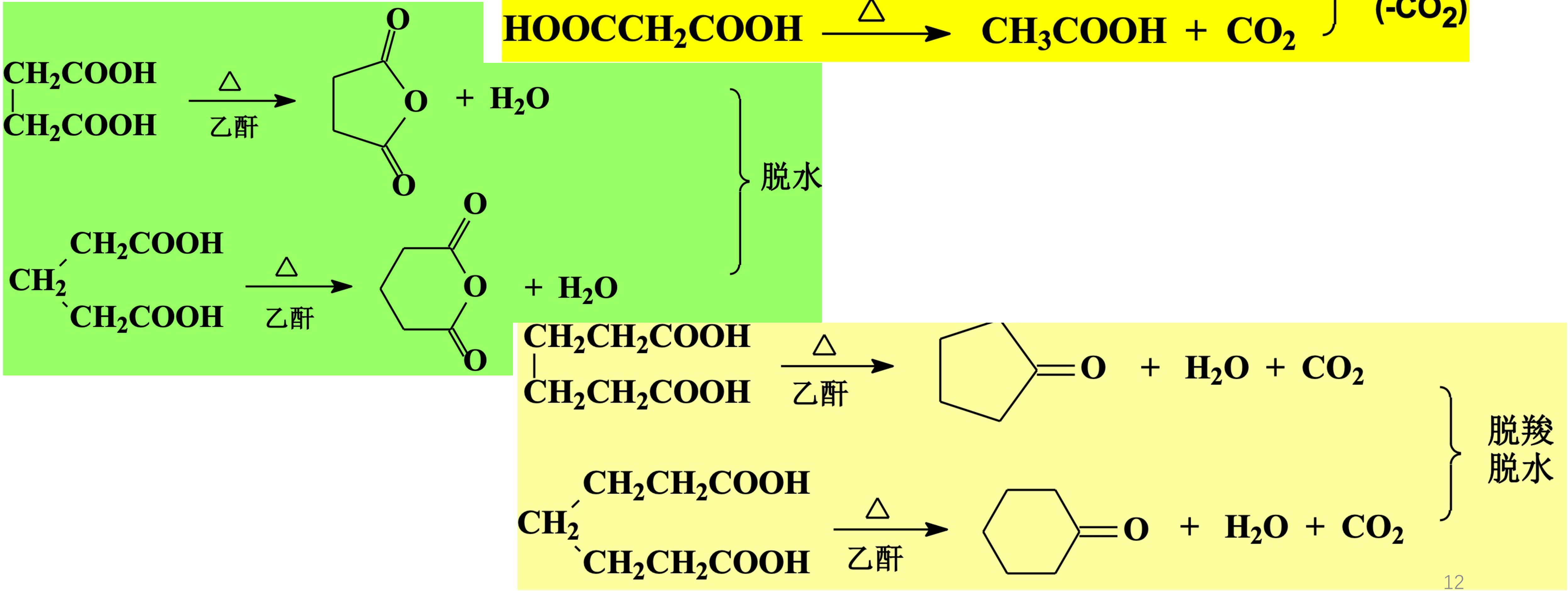
羧酸

- 二元酸的热分解

$$\mathrm{HOOCCOOH} \xrightarrow{\triangle} \mathrm{HCOOH} + \mathrm{CO_2}$$

$$\mathrm{HOOCCH_2COOH} \xrightarrow{\triangle} \mathrm{CH_3COOH} + \mathrm{CO_2}$$

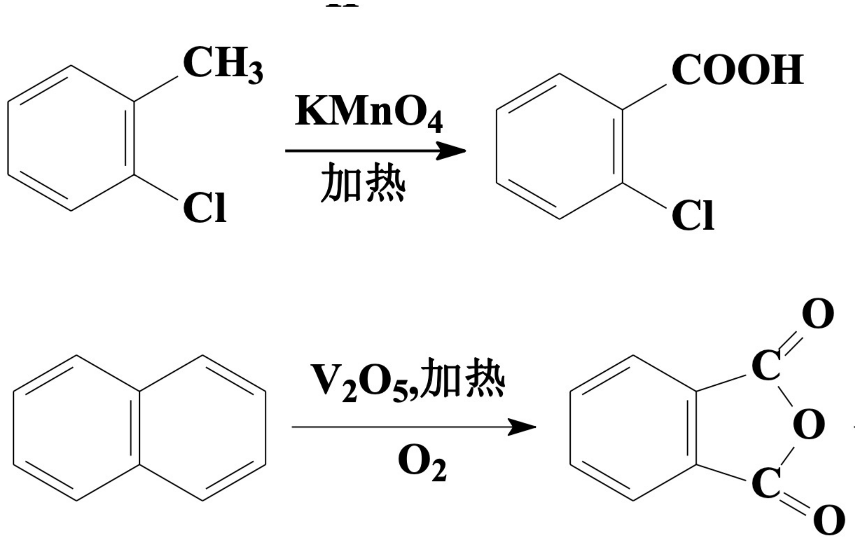
脱羧 (-CO_2)



羧酸

- 制备

氧化



腈的水解

$$RX + NaCN \longrightarrow RCN \xrightarrow[\text{or } HO^-]{H^+} RCOOH\ (\text{or } RCOO^-)$$

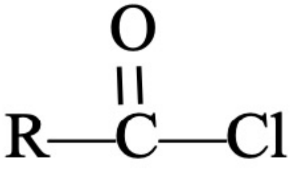
格氏试剂

$$RX \xrightarrow{Mg} RMgX \xrightarrow{CO_2} RCOOH$$

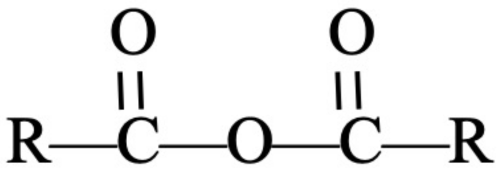
羧酸衍生物

波谱性质

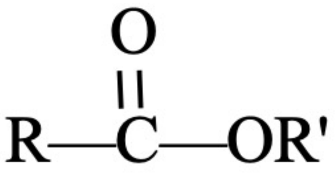
IR:(cm^{-1})



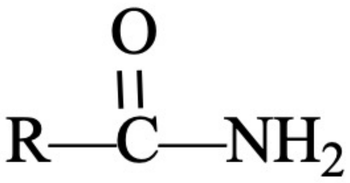
$R-\overset{\overset{O}{\|}}{C}-Cl$



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



$R-\overset{\overset{O}{\|}}{C}-OR'$



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

$\nu_{C=O}$ 1800 1800~1750 1735 1690游离

1860~1800 1650缔合

线型酸酐，高频强于低频

环型酸酐，低频强于高频

ν_{N-H} 3500

游离 3400

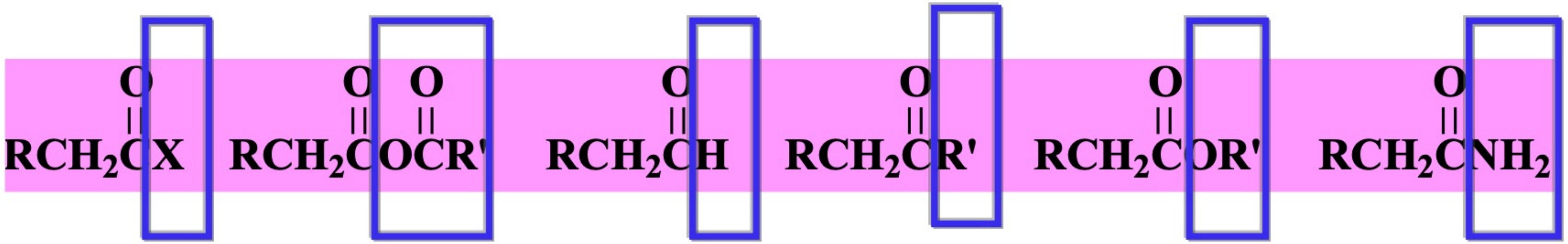
缔合 3350

3180

ArCOCl C=CCOOR

$\nu_{C=O}$ 1770 1720

羧酸衍生物



$RCH_2\overset{\overset{O}{\|}}{C}X$　$RCH_2\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}R'$　$RCH_2\overset{\overset{O}{\|}}{C}H$　$RCH_2\overset{\overset{O}{\|}}{C}R'$　$RCH_2\overset{\overset{O}{\|}}{C}OR'$　$RCH_2\overset{\overset{O}{\|}}{C}NH_2$

从左往右

α-H的活性减小（ α-H的 p*k*a 值增大）

离去基团的离去能力减小（离去基团的稳定性减小）

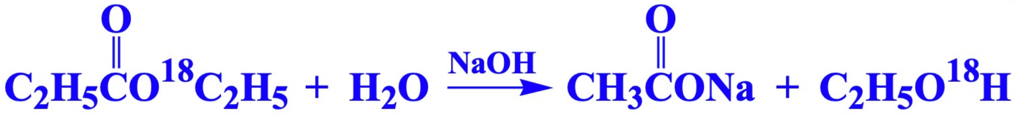
羰基的活性减小（取决于综合电子效应）

羧酸衍生物

- 酰卤的取代 （水解、醇解、胺解、酸解）
- 酸酐的取代 （水解、醇解、胺解）
- 酯的取代 （水解、醇解、胺解）

酯的水解反应

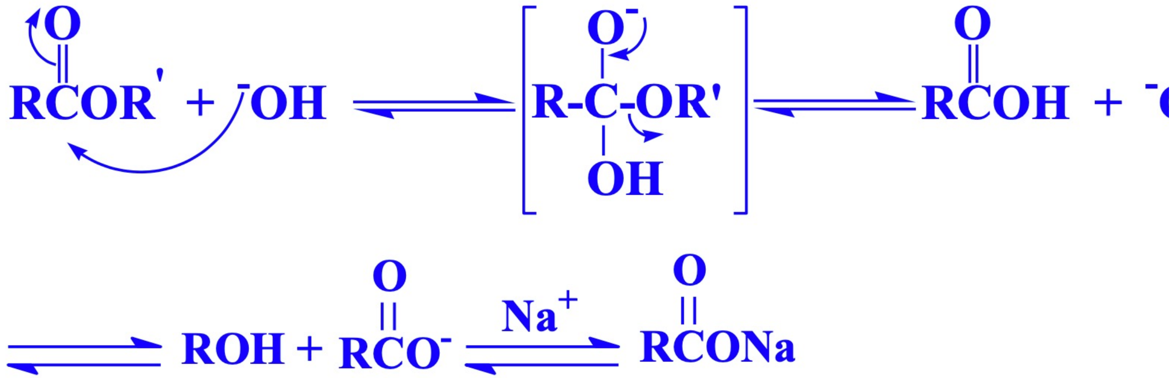
碱性水解:



$$C_2H_5\overset{O}{\overset{\|}{C}}O^{18}C_2H_5 + H_2O \xrightarrow{NaOH} CH_3\overset{O}{\overset{\|}{C}}ONa + C_2H_5O^{18}H$$

机理:

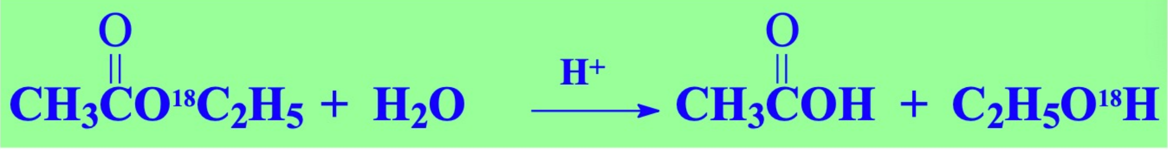
四面体中间体是负离子



$$R\overset{O}{\overset{\|}{C}}OR' + {}^-OH \rightleftharpoons \left[R-\underset{OH}{\overset{O^-}{C}}-OR'\right] \rightleftharpoons R\overset{O}{\overset{\|}{C}}OH + {}^-($$

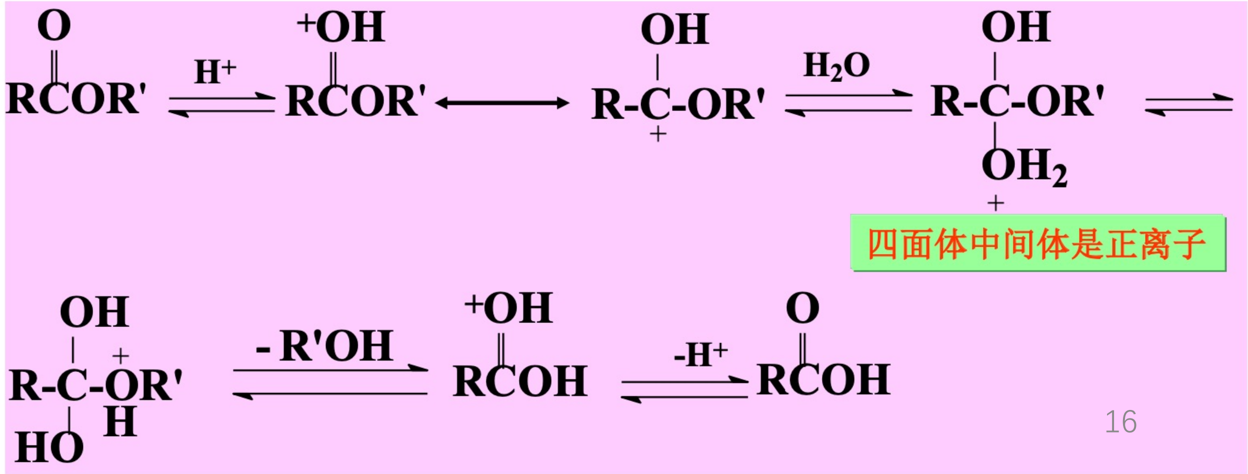
$$\rightleftharpoons ROH + R\overset{O}{\overset{\|}{C}}O^- \xrightleftharpoons{Na^+} R\overset{O}{\overset{\|}{C}}ONa$$

酸性水解:



$$CH_3\overset{O}{\overset{\|}{C}}O^{18}C_2H_5 + H_2O \xrightarrow{H^+} CH_3\overset{O}{\overset{\|}{C}}OH + C_2H_5O^{18}H$$

机理:



$$R\overset{O}{\overset{\|}{C}}OR' \xrightleftharpoons{H^+} R\overset{^+OH}{\overset{\|}{C}}OR' \longleftrightarrow R-\underset{+}{\overset{OH}{C}}-OR' \xrightleftharpoons{H_2O} R-\underset{\underset{+}{OH_2}}{\overset{OH}{C}}-OR' \rightleftharpoons$$

$$R-\underset{HO}{\overset{OH}{C}}-\underset{H}{\overset{+}{O}}R' \xrightleftharpoons{-R'OH} R\overset{^+OH}{\overset{\|}{C}}OH \xrightleftharpoons{-H^+} R\overset{O}{\overset{\|}{C}}OH$$

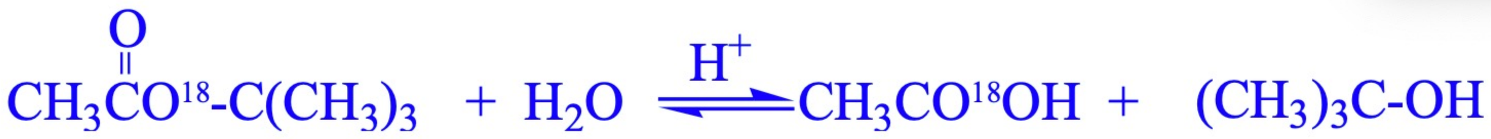
四面体中间体是正离子

羧酸衍生物

碱性催化：1ºROH > 2ºROH > 3ºROH

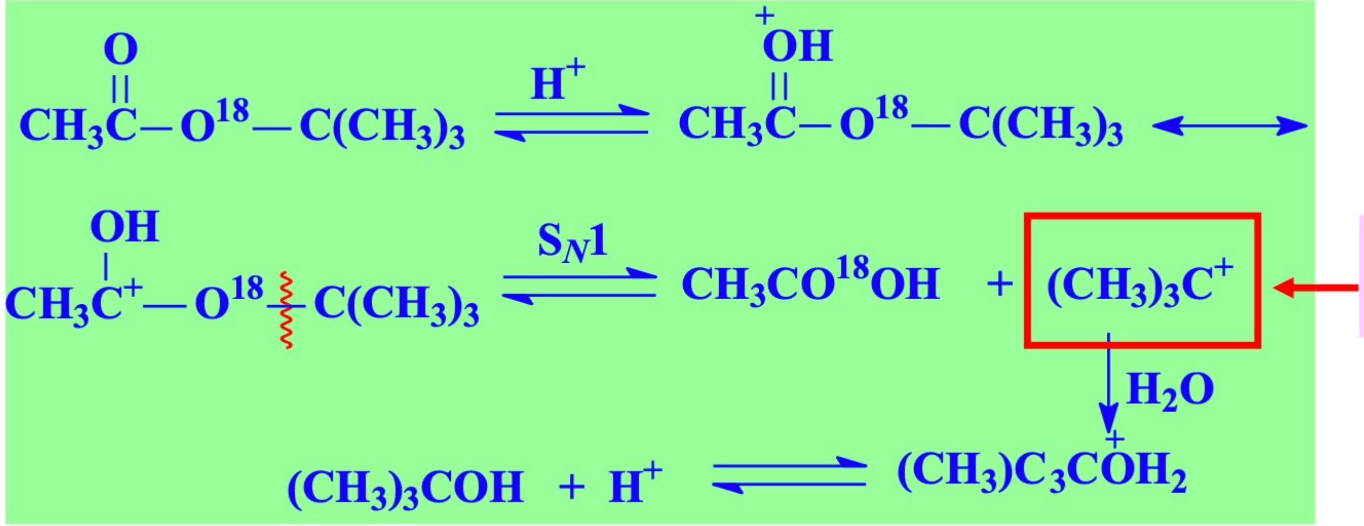
酸性催化：3ºROH > 1ºROH > 2ºROH

3º醇酯



$$CH_3\overset{O}{\overset{\|}{C}}O^{18}\text{-}C(CH_3)_3 + H_2O \overset{H^+}{\rightleftharpoons} CH_3CO^{18}OH + (CH_3)_3C\text{-}OH$$

反应机理



$$CH_3\overset{O}{\overset{\|}{C}}-O^{18}-C(CH_3)_3 \overset{H^+}{\rightleftharpoons} CH_3\overset{\overset{+}{O}H}{\overset{\|}{C}}-O^{18}-C(CH_3)_3 \longleftrightarrow$$

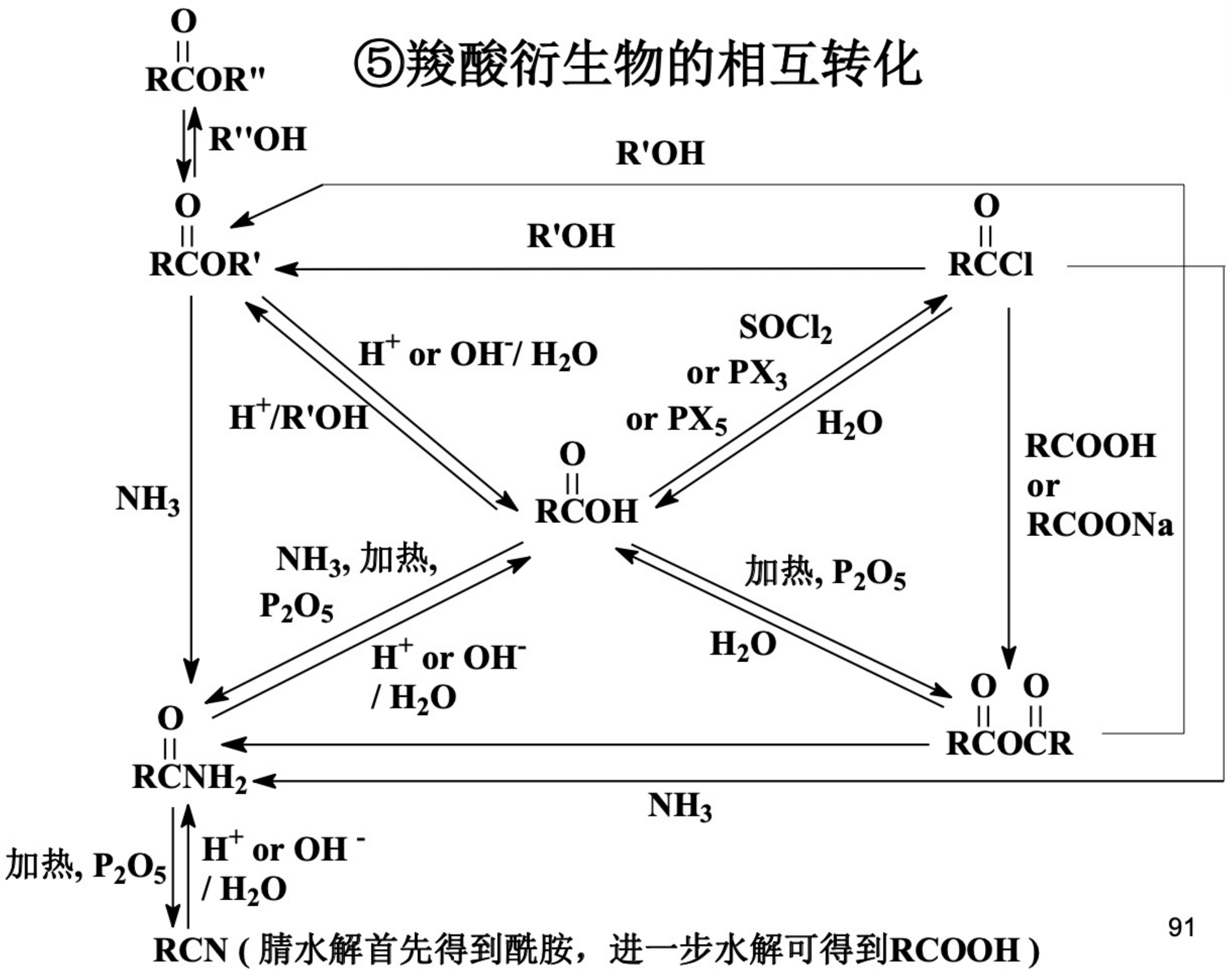
$$CH_3\overset{OH}{\overset{|}{C^+}}-O^{18}\text{≀}C(CH_3)_3 \overset{S_N1}{\rightleftharpoons} CH_3CO^{18}OH + \boxed{(CH_3)_3C^+}$$

$$\boxed{(CH_3)_3C^+} \xrightarrow{H_2O} (CH_3)C_3\overset{+}{C}OH_2$$

$$(CH_3)_3COH + H^+ \rightleftharpoons (CH_3)C_3\overset{+}{C}OH_2$$

关键中间体

羧酸衍生物



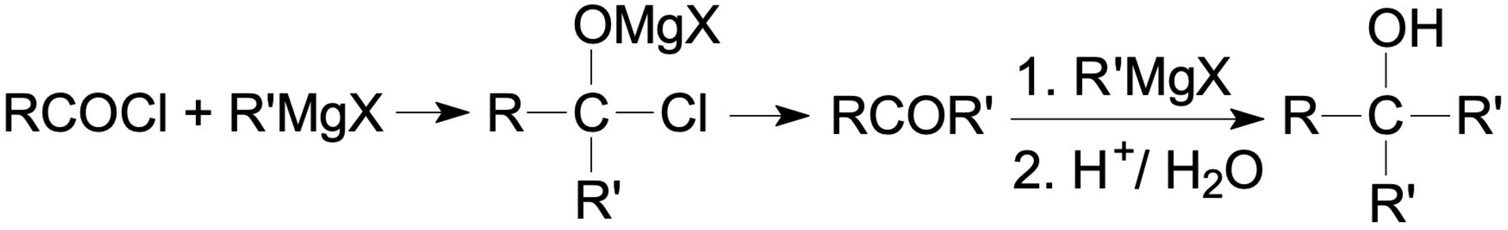
⑤羧酸衍生物的相互转化

RCN (腈水解首先得到酰胺，进一步水解可得到RCOOH)

羧酸衍生物

- 与金属试剂的反应

酰卤



$$RCOCl + R'MgX \longrightarrow R-\overset{\overset{\displaystyle OMgX}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}-Cl \longrightarrow RCOR' \xrightarrow[2.\ H^+/\ H_2O]{1.\ R'MgX} R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}-R'$$

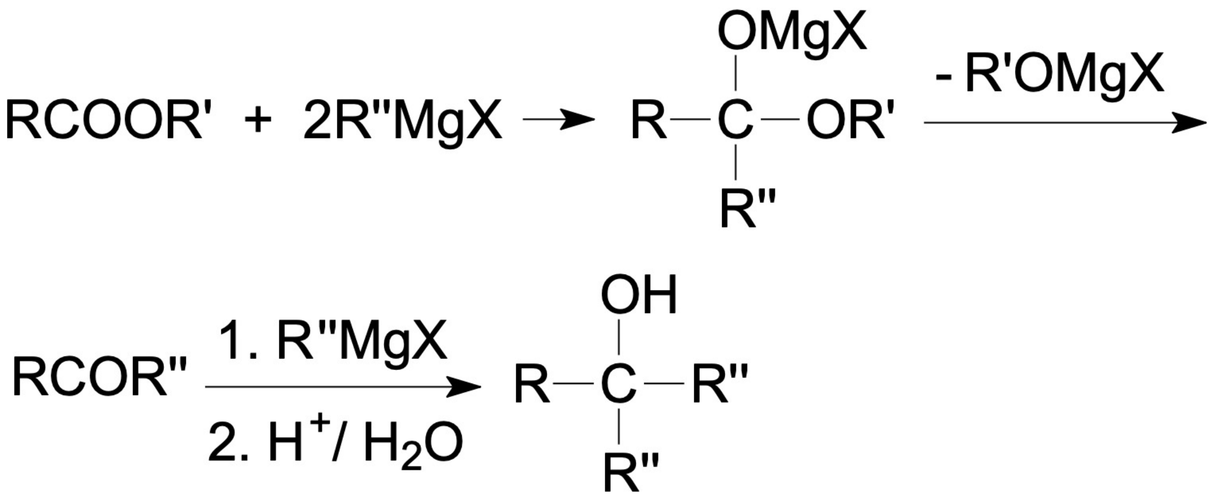
$$(CH_3)_3CCOCl \ + \ (CH_3)_2CuLi \xrightarrow[-78^0C]{Et_2O} (CH_3)_3CCOCH_3$$

$$CH_3OOCCH_2CH_2COCl \ + \ (CH_3CH_2CH_2)_2Cd \longrightarrow$$

$$CH_3OOCCH_2CH_2COCH_2CH_2CH_3 \quad 75\%$$

羧酸衍生物

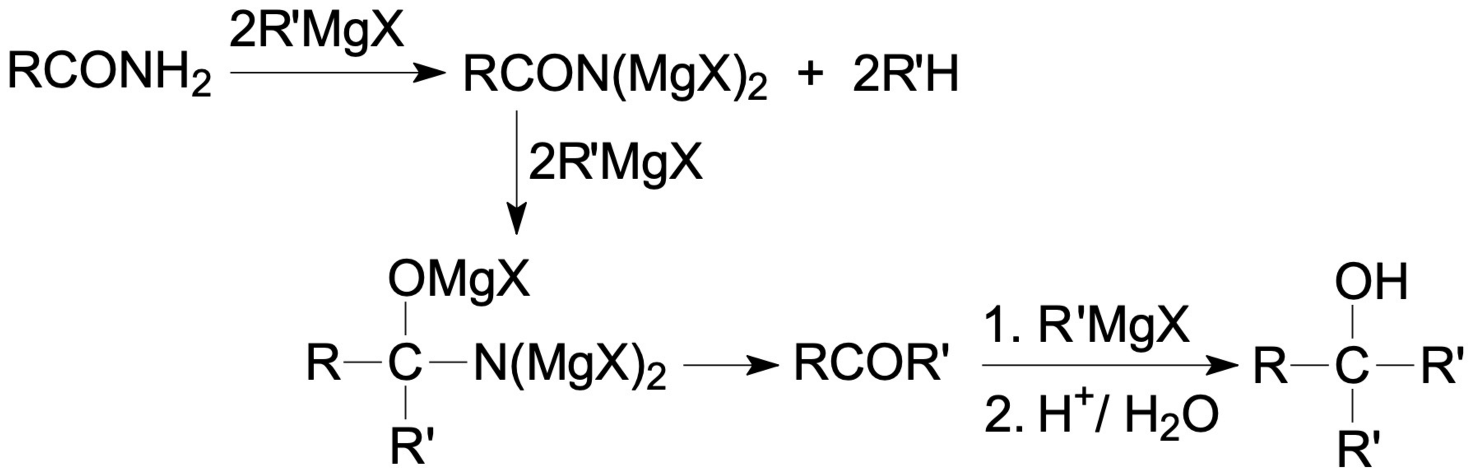
酯



$$\mathrm{RCOOR'} + \mathrm{2R''MgX} \longrightarrow \mathrm{R{-}\overset{OMgX}{\underset{R''}{C}}{-}OR'} \xrightarrow{-\,\mathrm{R'OMgX}}$$

$$\mathrm{RCOR''} \xrightarrow[2.\ \mathrm{H^+/\ H_2O}]{1.\ \mathrm{R''MgX}} \mathrm{R{-}\overset{OH}{\underset{R''}{C}}{-}R''}$$

酰胺



$$\mathrm{RCONH_2} \xrightarrow{\mathrm{2R'MgX}} \mathrm{RCON(MgX)_2} + \mathrm{2R'H}$$

$$\Big\downarrow \mathrm{2R'MgX}$$

$$\mathrm{R{-}\overset{OMgX}{\underset{R'}{C}}{-}N(MgX)_2} \longrightarrow \mathrm{RCOR'} \xrightarrow[2.\ \mathrm{H^+/\ H_2O}]{1.\ \mathrm{R'MgX}} \mathrm{R{-}\overset{OH}{\underset{R'}{C}}{-}R'}$$

羧酸衍生物

- 还原反应

酰卤

$$CH_3OOCCH_2CH_2COCl + H_2 \xrightarrow[S - 喹啉]{Pd / BaSO_4} CH_3OOCCH_2CH_2CHO$$

或者：

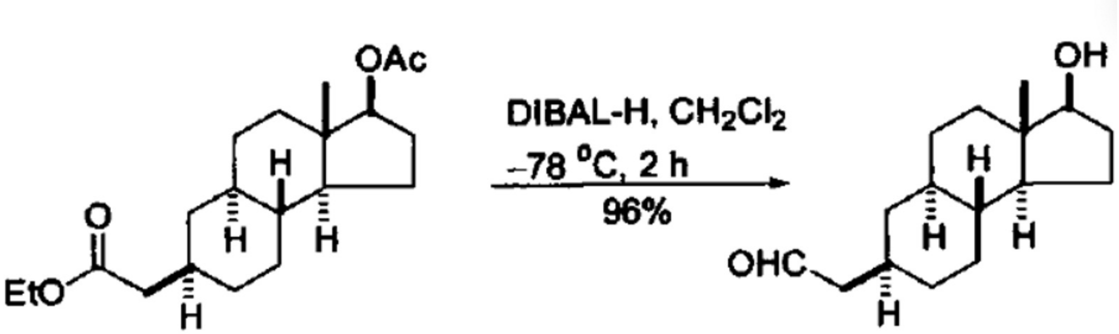
$$C_6H_5COCl \xrightarrow{Li[OC(CH_3)_3]_3AlH} \xrightarrow{H_2O} C_6H_5CHO$$

104

$$CH_3CH{=}CHCH_2COOCH_3 \xrightarrow[2)\ H_2O]{1)\ LiAlH_4} CH_3CH{=}CHCH_2CH_2OH + CH_3OH$$

$$RCOOR' + H_2 \xrightarrow[200\sim300^0C,\ 加压]{CuO.CuCrO_4} RCH_2OH + R'OH$$

酯



羧酸衍生物

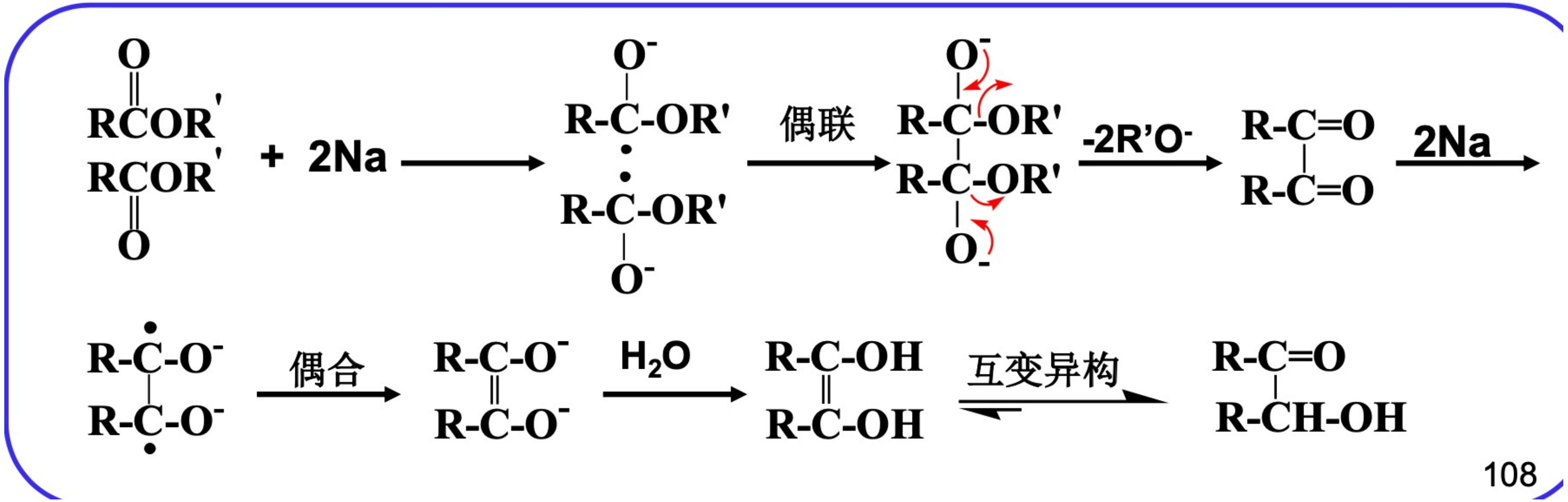
单分子还原

$$CH_3(CH_2)_8COOH \xrightarrow[H^+]{C_2H_5OH} CH_3(CH_2)_8COOC_2H_5$$

$$\xrightarrow[EtOH]{Na} CH_3(CH_2)_8CH_2OH + C_2H_5OH$$

双分子还原

$$\begin{array}{c} RCOOR' \\ RCOOR' \end{array} \xrightarrow[\text{惰性溶剂}]{Na} \begin{array}{c} R\text{-}C\text{-}ONa \\ \| \\ R\text{-}C\text{-}ONa \end{array} \xrightarrow{H_2O} \begin{array}{c} R\text{-}C{=}O \\ | \\ R\text{-}CH\text{-}OH \end{array}$$



$$\begin{array}{c} O \\ \| \\ RCOR' \\ RCOR' \\ \| \\ O \end{array} + 2Na \longrightarrow \begin{array}{c} O^- \\ | \\ R\text{-}\dot{C}\text{-}OR' \\ \\ R\text{-}\dot{C}\text{-}OR' \\ | \\ O^- \end{array} \xrightarrow{\text{偶联}} \begin{array}{c} O^- \\ | \\ R\text{-}C\text{-}OR' \\ | \\ R\text{-}C\text{-}OR' \\ | \\ O^- \end{array} \xrightarrow{-2R'O^-} \begin{array}{c} R\text{-}C{=}O \\ | \\ R\text{-}C{=}O \end{array} \xrightarrow{2Na}$$

$$\begin{array}{c} R\text{-}\dot{C}\text{-}O^- \\ | \\ R\text{-}\dot{C}\text{-}O^- \end{array} \xrightarrow{\text{偶合}} \begin{array}{c} R\text{-}C\text{-}O^- \\ \| \\ R\text{-}C\text{-}O^- \end{array} \xrightarrow{H_2O} \begin{array}{c} R\text{-}C\text{-}OH \\ \| \\ R\text{-}C\text{-}OH \end{array} \xrightleftharpoons{\text{互变异构}} \begin{array}{c} R\text{-}C{=}O \\ | \\ R\text{-}CH\text{-}OH \end{array}$$

108

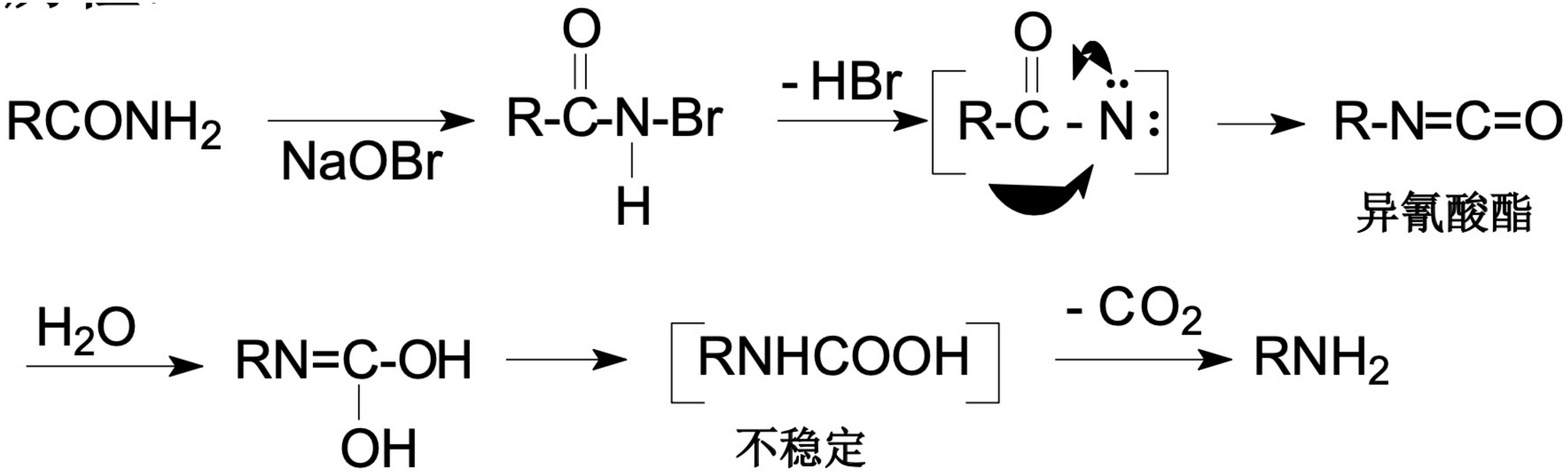
羧酸衍生物

酰胺

$$RCONHR \xrightarrow{LiAlH_4} RCH_2NHR$$

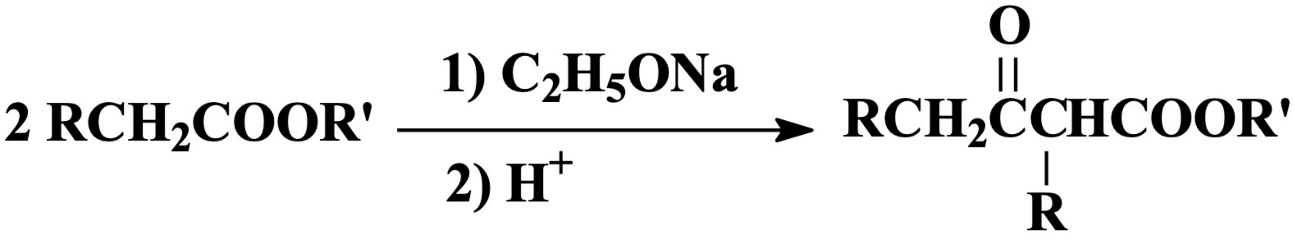
$$NO_2CH_2CONH_2 \xrightarrow[THF]{BH_3} NO_2CH_2CH_2NH_2$$

$$RCONH_2 \xrightarrow[NaOH]{Br_2} RNH_2$$ **Hofmann**降解反应

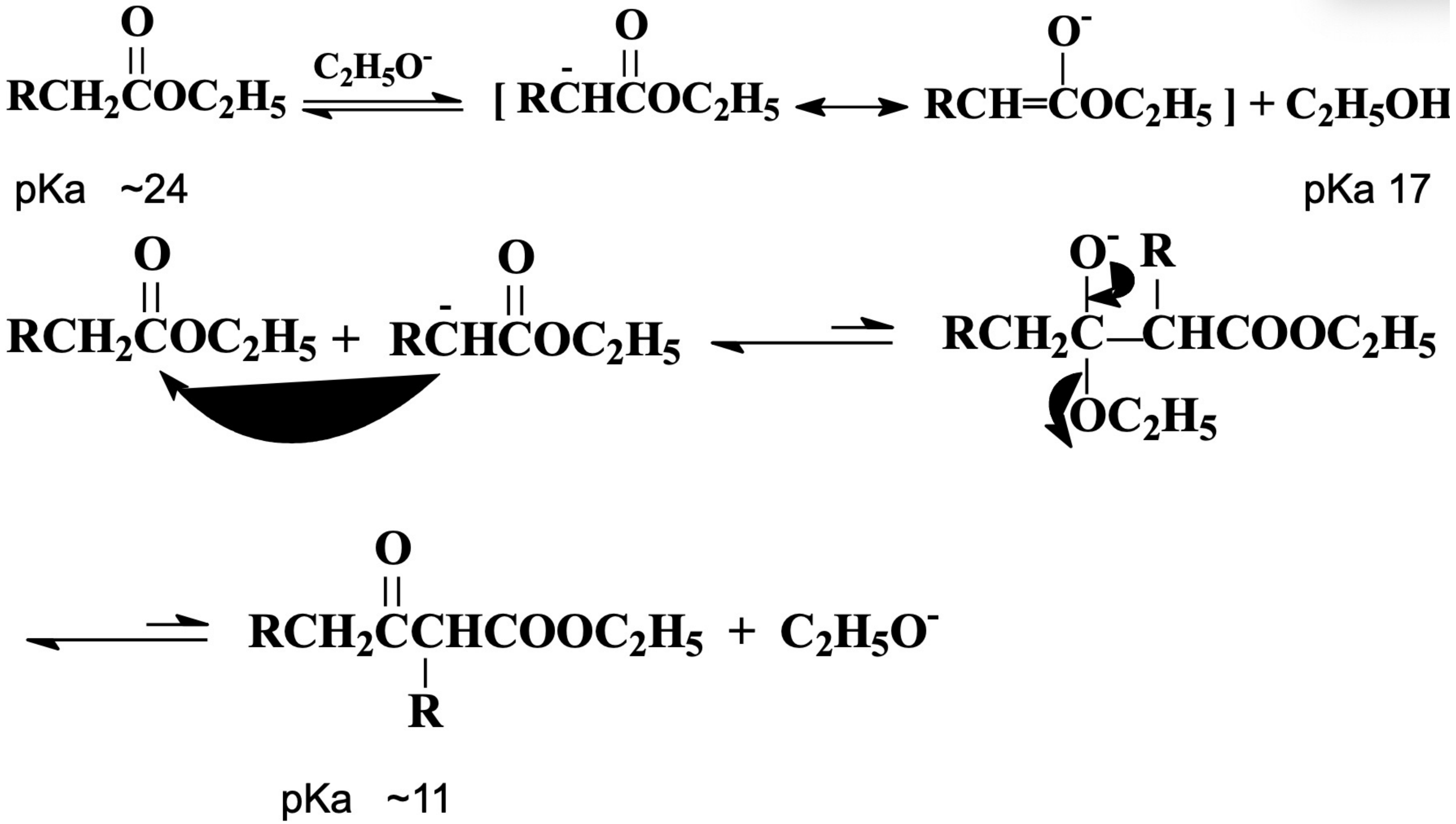


羧酸衍生物

- 酯缩合反应



$$2\ RCH_2COOR' \xrightarrow[2)\ H^+]{1)\ C_2H_5ONa} RCH_2\overset{\overset{O}{\|}}{C}\underset{\underset{R}{|}}{C}HCOOR'$$



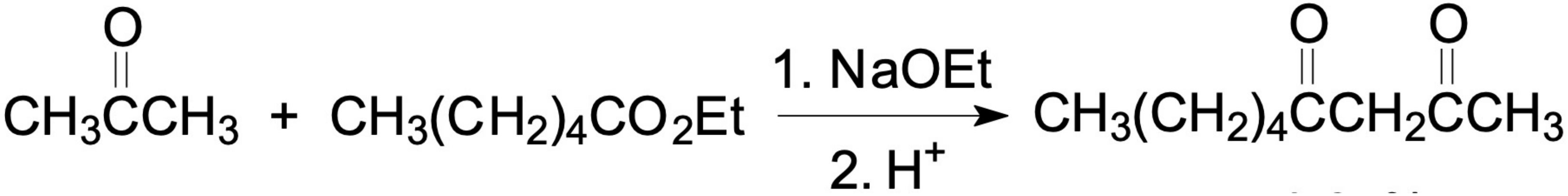
$$RCH_2\overset{\overset{O}{\|}}{C}OC_2H_5 \overset{C_2H_5O^-}{\rightleftharpoons} [\,R\overset{-}{C}H\overset{\overset{O}{\|}}{C}OC_2H_5 \longleftrightarrow RCH{=}\overset{\overset{O^-}{|}}{C}OC_2H_5\,] + C_2H_5OH$$

$$RCH_2\overset{\overset{O}{\|}}{C}OC_2H_5 + R\overset{-}{C}H\overset{\overset{O}{\|}}{C}OC_2H_5 \rightleftharpoons RCH_2\underset{\underset{OC_2H_5}{|}}{\overset{\overset{O^-}{|}}{C}}-\overset{\overset{R}{|}}{C}HCOOC_2H_5$$

$$\rightleftharpoons RCH_2\overset{\overset{O}{\|}}{C}\underset{\underset{R}{|}}{C}HCOOC_2H_5 + C_2H_5O^-$$

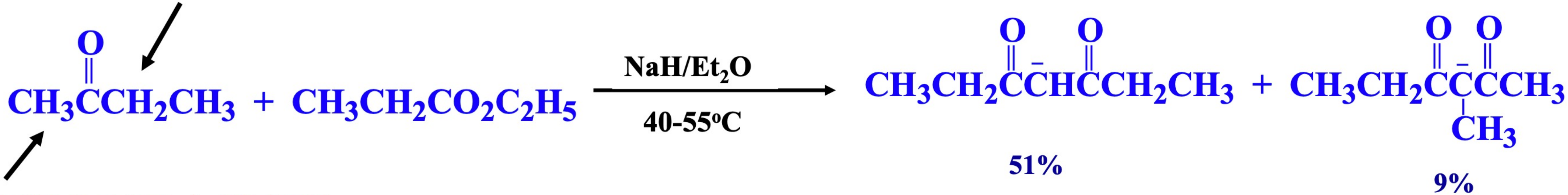
羧酸衍生物

- 酮酯缩合



$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + CH_3(CH_2)_4CO_2Et \xrightarrow[2.\ H^+]{1.\ NaOEt} CH_3(CH_2)_4\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$$

稳定性好，对热力学有利。

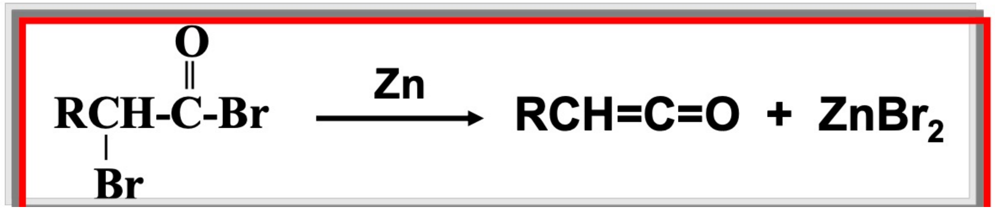


$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3 + CH_3CH_2CO_2C_2H_5 \xrightarrow[40\text{-}55^oC]{NaH/Et_2O} \underset{51\%}{CH_3CH_2\overset{O}{\overset{\|}{C}}CH\overset{O}{\overset{\|}{C}}CH_2CH_3} + \underset{9\%}{CH_3CH_2\overset{O}{\overset{\|}{C}}\underset{CH_3}{C}\overset{O}{\overset{\|}{C}}CH_3}$$

空阻小对动力学有利。

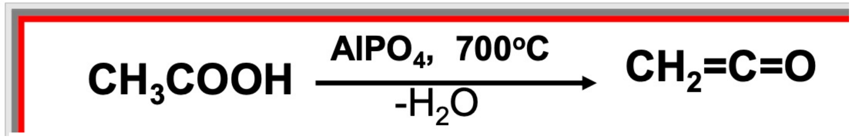
羧酸衍生物

- 烯酮 $CH_2{=}C{=}O$ (乙)烯酮
- 制备 α-溴代酰溴脱溴



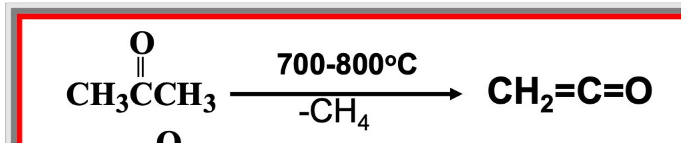
$$\underset{\underset{\mathrm{Br}}{|}}{\mathrm{RCH}}\text{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{-}\mathrm{Br} \xrightarrow{Zn} RCH{=}C{=}O + ZnBr_2$$

羧酸的脱水



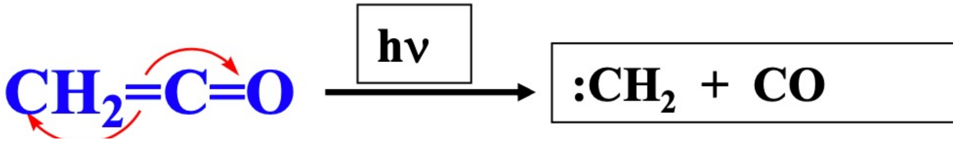
$$CH_3COOH \xrightarrow[-H_2O]{AlPO_4,\ 700^\circ C} CH_2{=}C{=}O$$

甲基酮脱甲烷

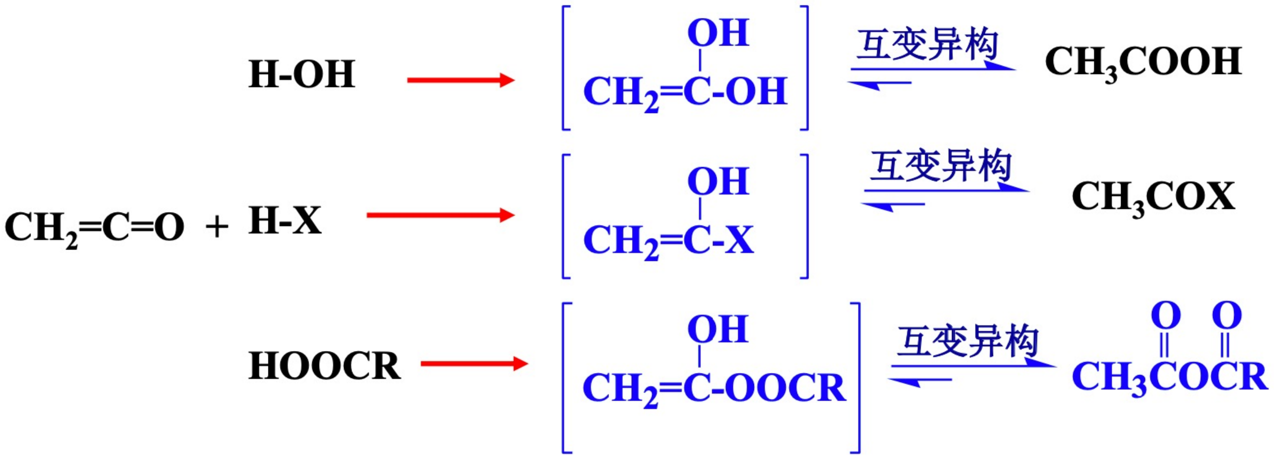


$$CH_3\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow[-CH_4]{700\text{-}800^\circ C} CH_2{=}C{=}O$$

- 反应



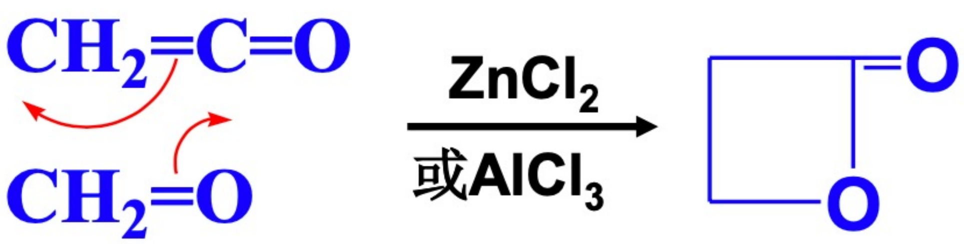
$$CH_2{=}C{=}O \xrightarrow{\boxed{h\nu}} \boxed{:CH_2 + CO}$$

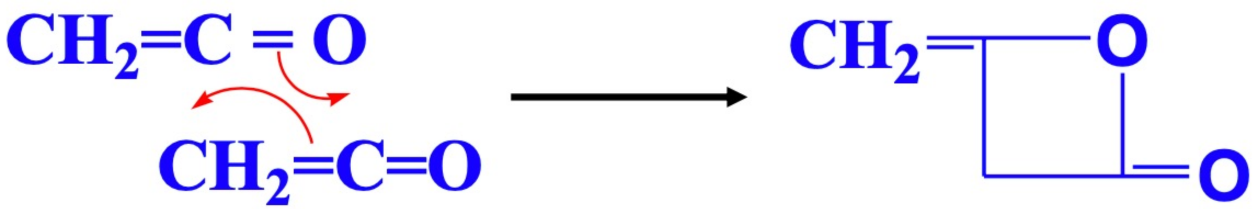


$$CH_2{=}C{=}O + \begin{cases} H\text{-}OH \longrightarrow \left[CH_2{=}\overset{\overset{OH}{|}}{C}\text{-}OH\right] \xrightleftharpoons{\text{互变异构}} CH_3COOH \\ H\text{-}X \longrightarrow \left[CH_2{=}\overset{\overset{OH}{|}}{C}\text{-}X\right] \xrightleftharpoons{\text{互变异构}} CH_3COX \\ HOOCR \longrightarrow \left[CH_2{=}\overset{\overset{OH}{|}}{C}\text{-}OOCR\right] \xrightleftharpoons{\text{互变异构}} CH_3\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}R \end{cases}$$

乙酰化试剂

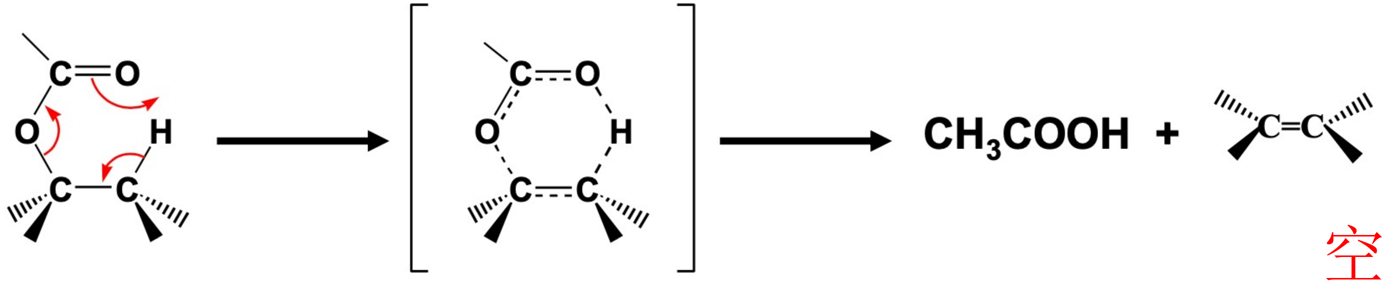
羧酸衍生物





酯的热解

$$CH_3COO\boxed{\text{-}CH_2CH_2\text{-}}H \xrightarrow{400\text{-}500^oC} CH_3COOH + CH_2=CH_2$$

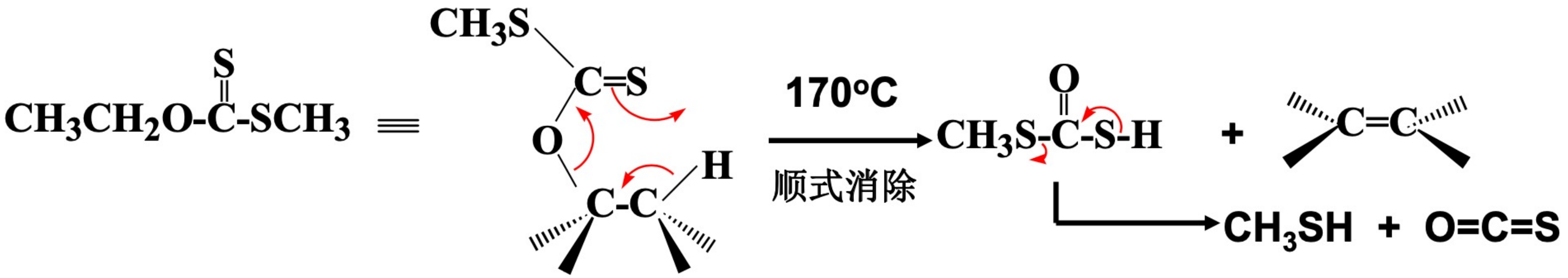


六中心过渡态

顺式消除

空阻小，酸性大的**β-H**

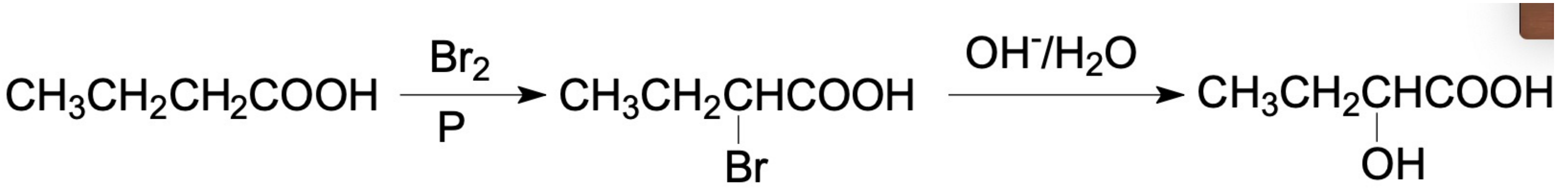
黄原酸酯的热裂



羟基酸

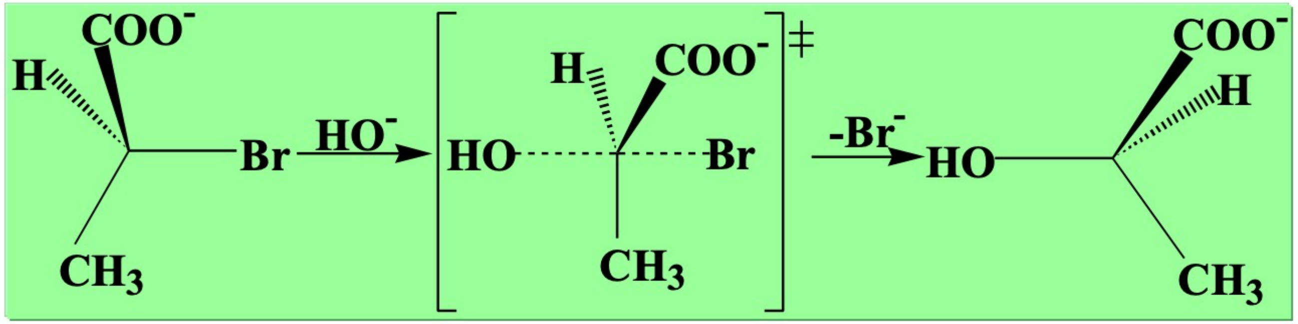
- 制备

卤代酸水解



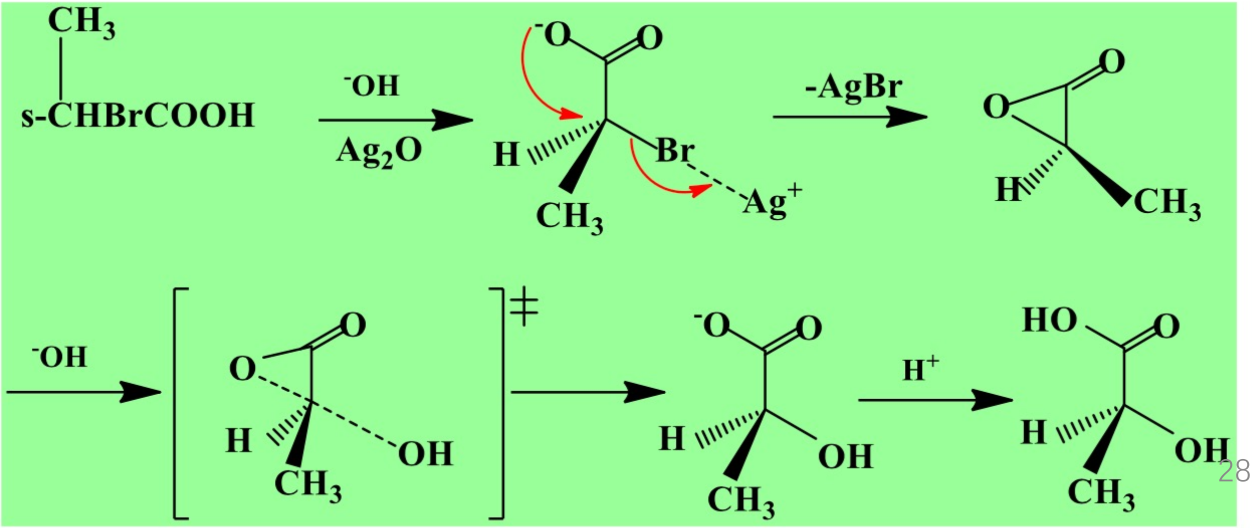
$$CH_3CH_2CH_2COOH \xrightarrow[P]{Br_2} CH_3CH_2\underset{Br}{\underset{|}{C}}HCOOH \xrightarrow{OH^-/H_2O} CH_3CH_2\underset{OH}{\underset{|}{C}}HCOOH$$

浓碱，
构型翻转
S_N2。



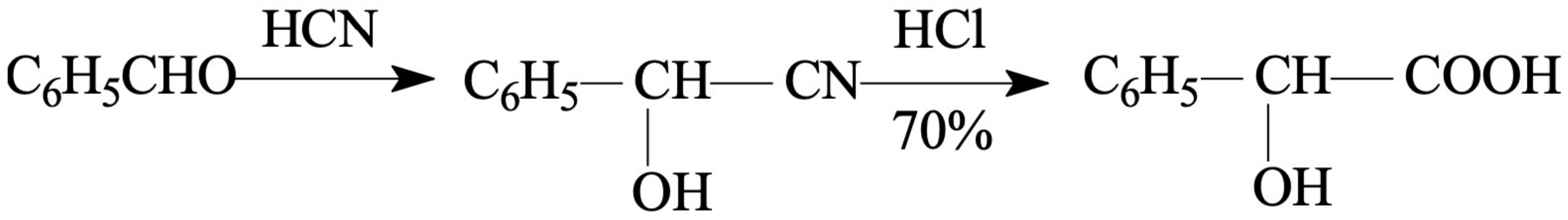
Ag_2O，稀碱，
构型保持，

邻基参与。



羟基酸

- 腈醇水解



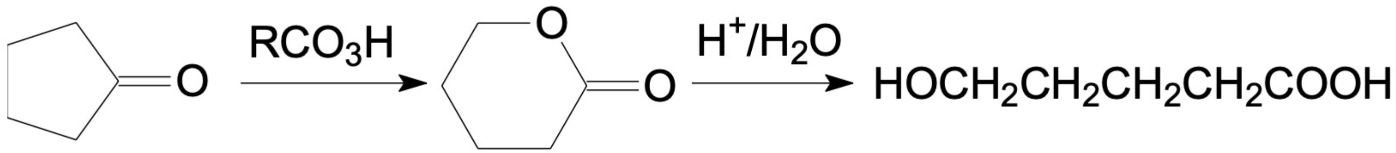
$$C_6H_5CHO \xrightarrow{HCN} C_6H_5-\underset{\displaystyle OH}{\underset{|}{CH}}-CN \xrightarrow[70\%]{HCl} C_6H_5-\underset{\displaystyle OH}{\underset{|}{CH}}-COOH$$

α-羟基酸

- 二元酸单酯还原

$$HOOC(CH_2)_nCOOC_2H_5 \xrightarrow[\text{or } LiBH_4]{Na + C_2H_5OH} \xrightarrow{H_2O} HOOC(CH_2)_nCH_2OH$$

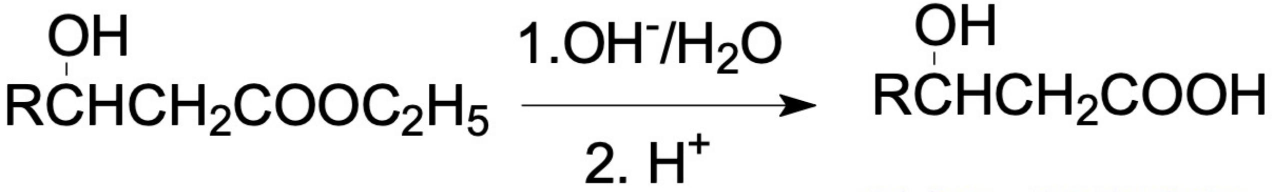
- 内酯的水解



$$\xrightarrow{RCO_3H} \xrightarrow{H^+/H_2O} HOCH_2CH_2CH_2CH_2COOH$$

- reformatsky反应

$$BrCH_2COOC_2H_5 \xrightarrow{Zn} BrZnCH_2COOC_2H_5 \xrightarrow{RCHO} R\overset{\displaystyle OH}{\overset{|}{C}}HCH_2COOC_2H_5$$



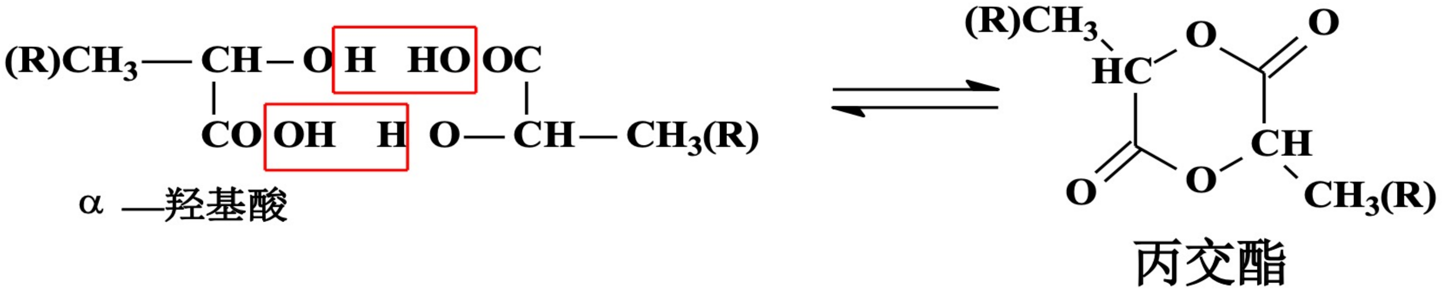
$$R\overset{\displaystyle OH}{\overset{|}{C}}HCH_2COOC_2H_5 \xrightarrow[2.\ H^+]{1.OH^-/H_2O} R\overset{\displaystyle OH}{\overset{|}{C}}HCH_2COOH$$

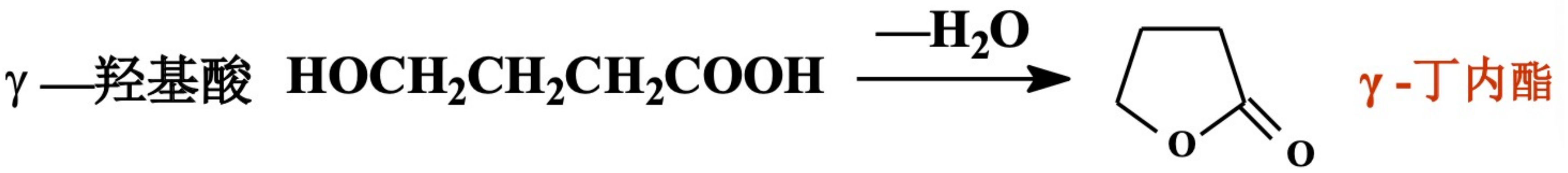
制备β-羟基酸和α, β-不饱和酸

羟基酸

- 性质

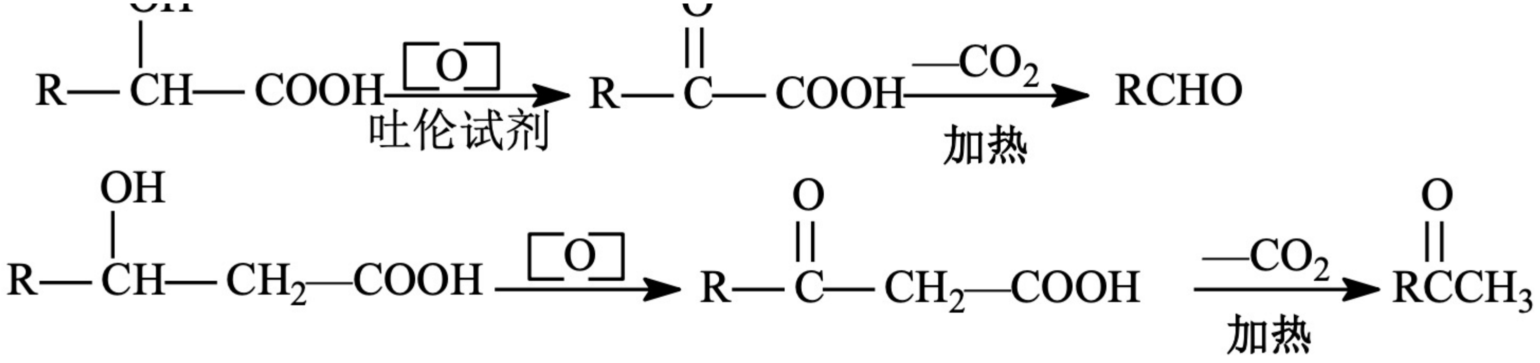
脱水





$$HOCH_2CH_2CH_2COOH \xrightarrow{-H_2O}$$

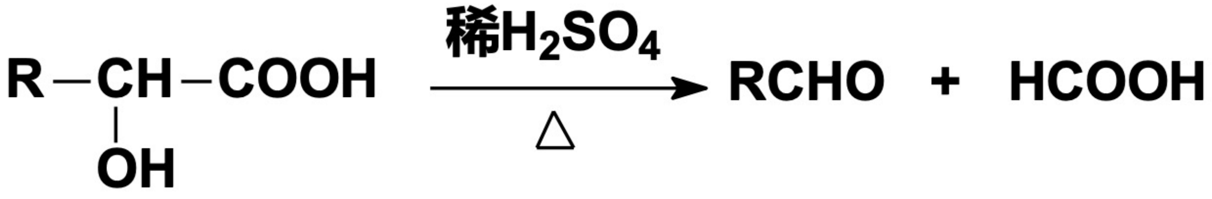
氧化反应



$$R-\underset{}{\overset{OH}{\overset{|}{C}H}}-COOH \xrightarrow[\text{吐伦试剂}]{[O]} R-\overset{O}{\overset{\|}{C}}-COOH \xrightarrow[\text{加热}]{-CO_2} RCHO$$

$$R-\overset{OH}{\overset{|}{C}H}-CH_2-COOH \xrightarrow{[O]} R-\overset{O}{\overset{\|}{C}}-CH_2-COOH \xrightarrow[\text{加热}]{-CO_2} R\overset{O}{\overset{\|}{C}}CH_3$$

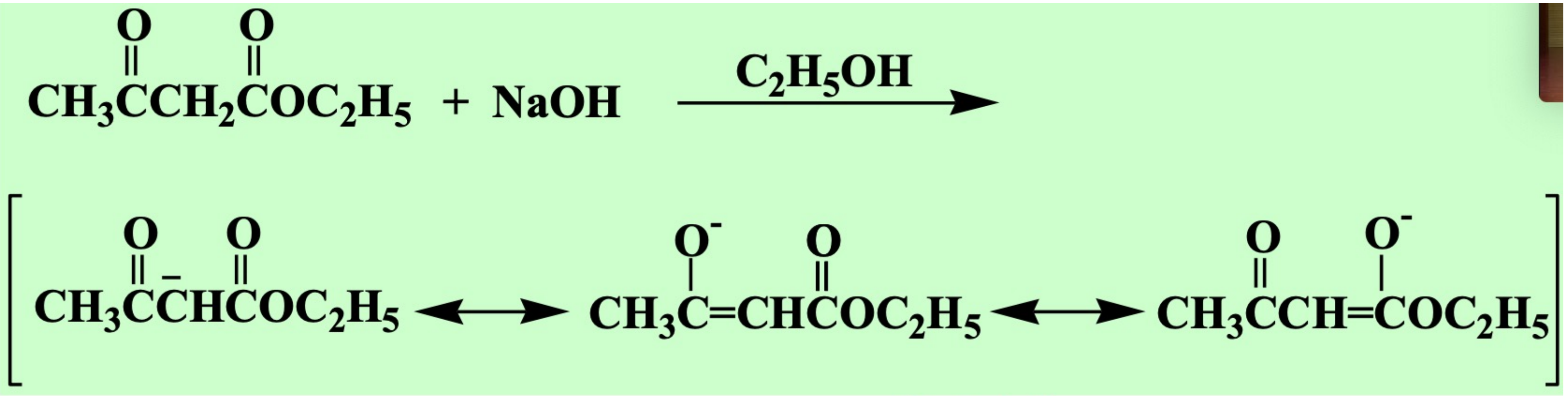
脱羧



$$R-\underset{OH}{\underset{|}{C}H}-COOH \xrightarrow[\triangle]{\text{稀}H_2SO_4} RCHO + HCOOH$$

羰基酸、酯

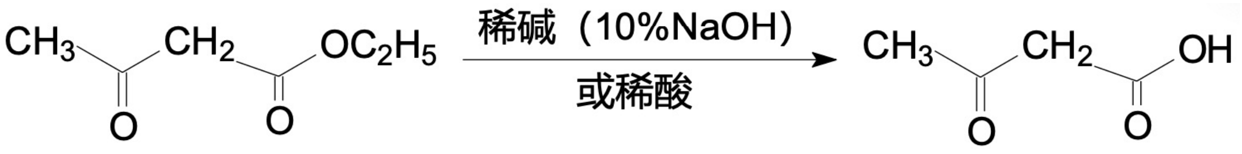
- 乙酰乙酸乙酯



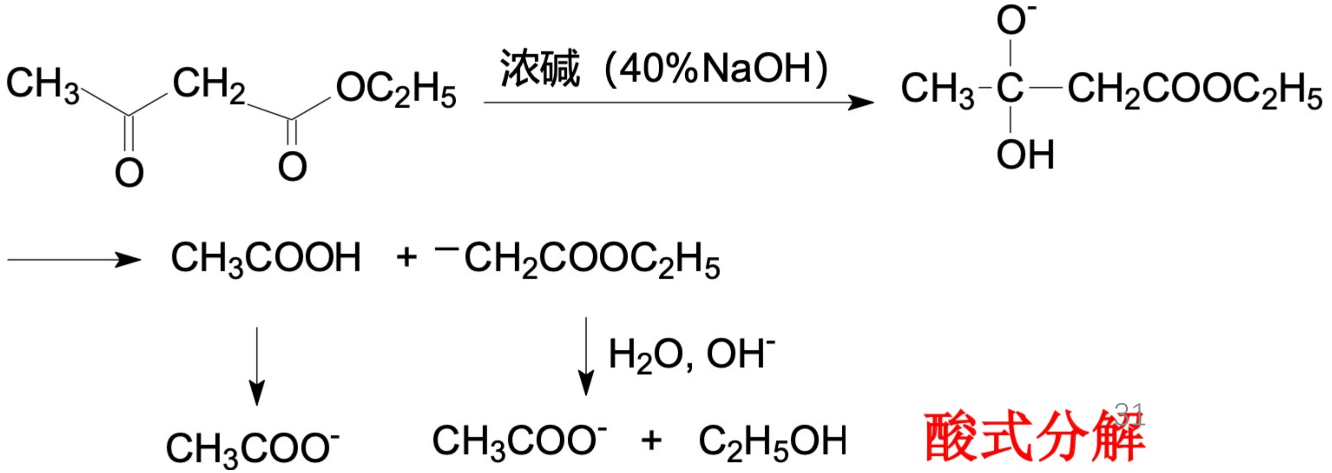
$$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5 + NaOH \xrightarrow{C_2H_5OH}$$

$$\left[CH_3\overset{O}{\overset{\|}{C}}\overset{-}{C}H\overset{O}{\overset{\|}{C}}OC_2H_5 \longleftrightarrow CH_3\overset{O^-}{\overset{|}{C}}=CH\overset{O}{\overset{\|}{C}}OC_2H_5 \longleftrightarrow CH_3\overset{O}{\overset{\|}{C}}CH=\overset{O^-}{\overset{|}{C}}OC_2H_5 \right]$$

(1) (2)（贡献最大） (3)



$\xrightarrow{加热} CH_3COCH_3$ 酮式分解

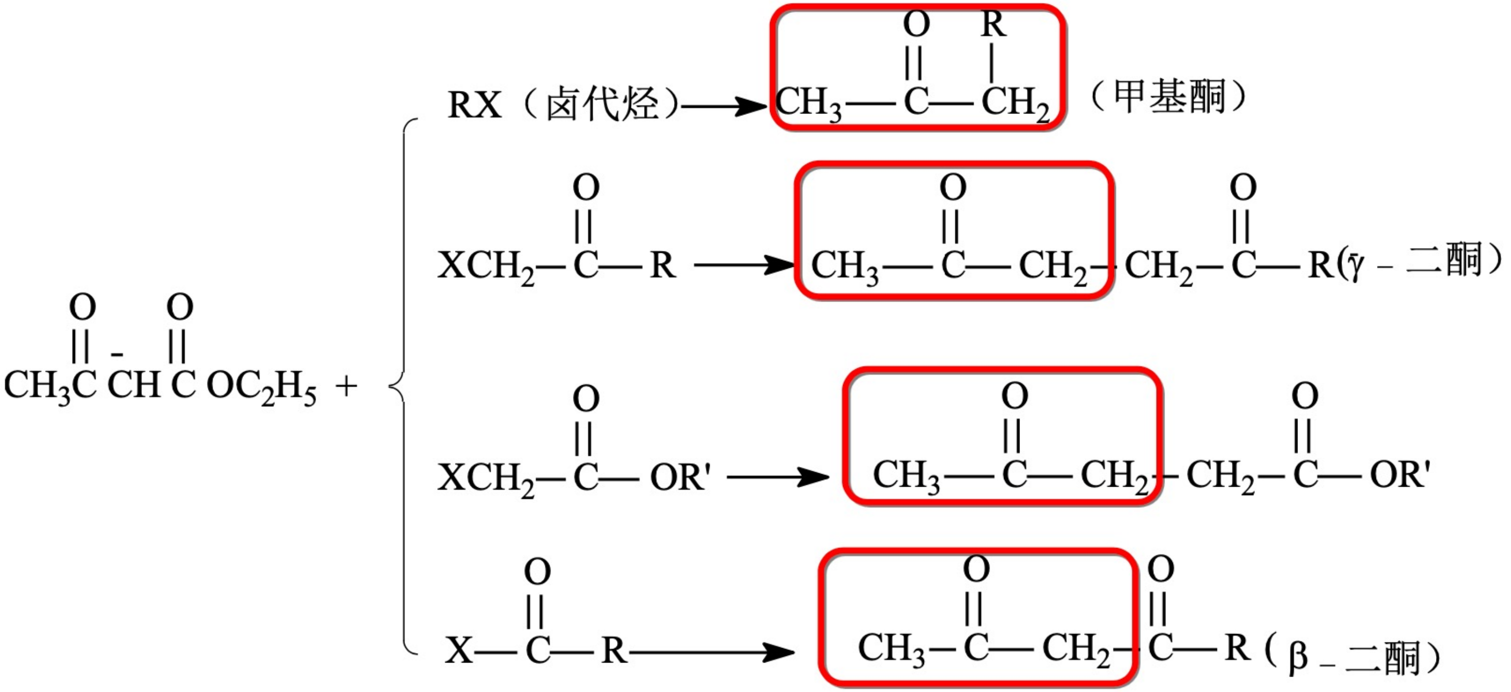


酸式分解

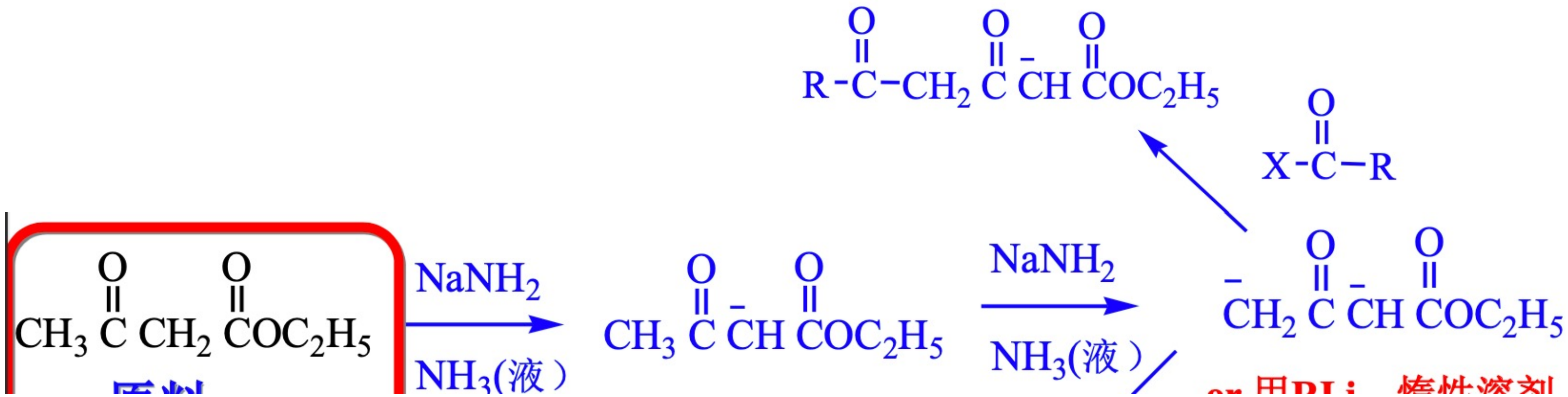
羰基酸、酯

- 乙酰乙酸乙酯

α-烷基化、 α-酰基化



γ-烷基化或酰基化2mol强碱

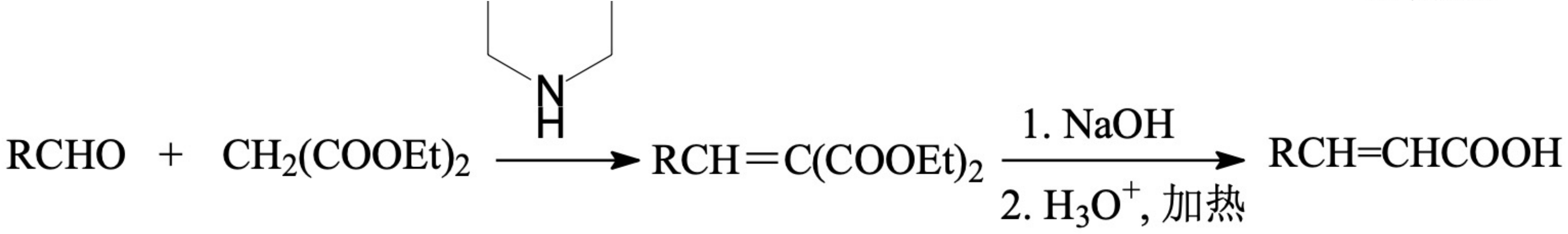


羰基酸、酯

- 丙二酸酯

$$\mathrm{CH_2(COOC_2H_5)_2} \xrightarrow[\text{2. RX}]{\text{1. NaOC}_2\text{H}_5} \mathrm{RCH(COOC_2H_5)_2} \xrightarrow[\text{2. H}_3\text{O}^+ \text{ 3. 加热}]{\text{1. NaOH}} \boxed{\mathrm{RCH_2COOH}}$$

取代乙酸



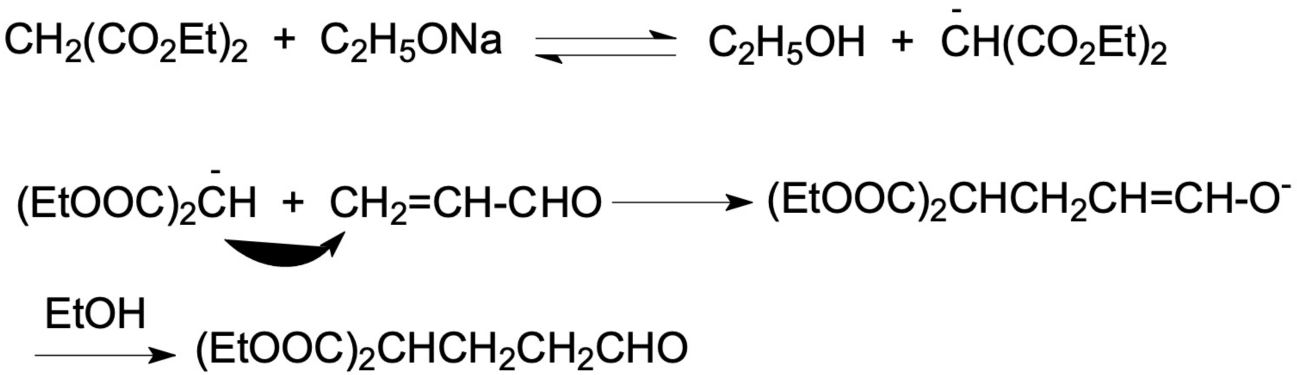
$$\mathrm{RCHO} + \mathrm{CH_2(COOEt)_2} \longrightarrow \mathrm{RCH{=}C(COOEt)_2} \xrightarrow[\text{2. H}_3\text{O}^+\text{, 加热}]{\text{1. NaOH}} \mathrm{RCH{=}CHCOOH}$$

Knoevenagel反应

$$\mathrm{CH_2{=}CHCHO} + \mathrm{CH_2(COOEt)_2} \xrightarrow[\text{EtOH}]{\text{EtONa}} \mathrm{(EtOOC)_2CHCH_2CH_2CHO}$$

Michael反应

1，5-二羰基化合物



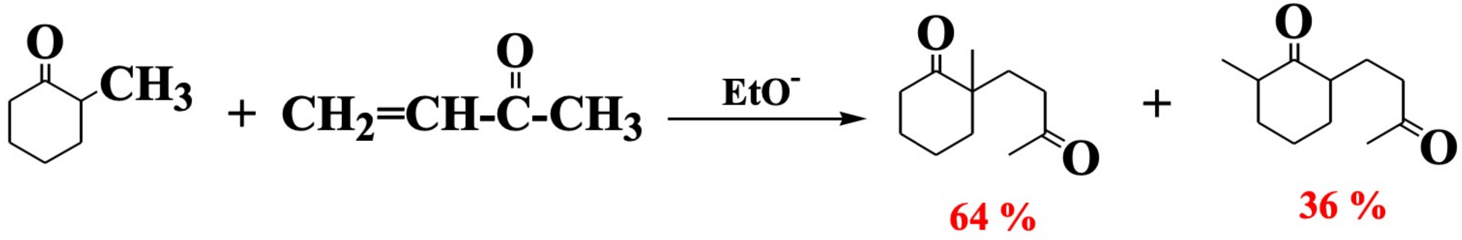
$$\mathrm{CH_2(CO_2Et)_2} + \mathrm{C_2H_5ONa} \rightleftharpoons \mathrm{C_2H_5OH} + \overset{-}{\mathrm{C}}\mathrm{H(CO_2Et)_2}$$

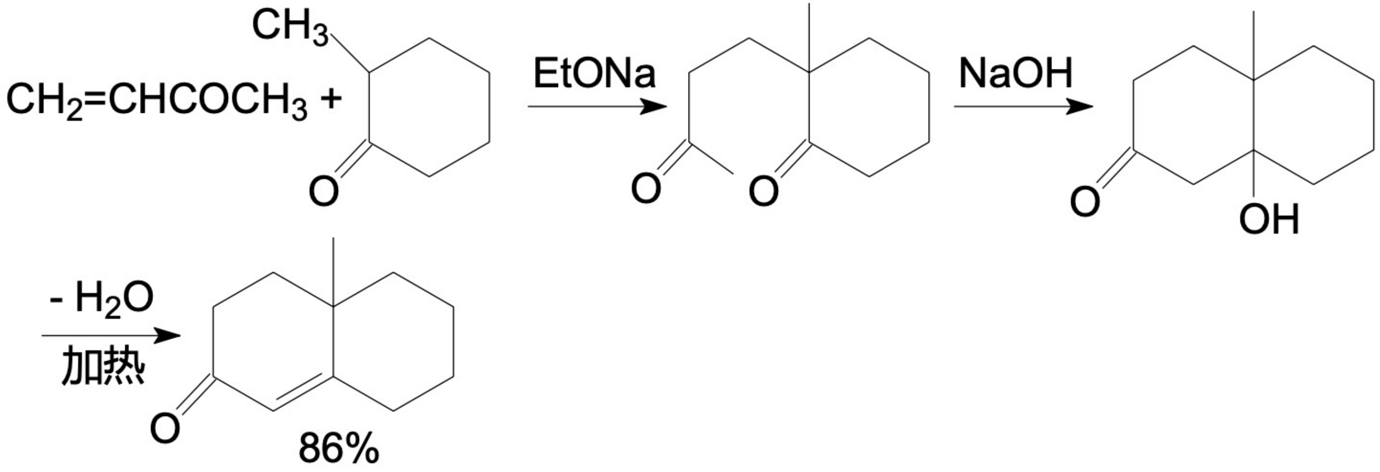
$$\mathrm{(EtOOC)_2}\overset{-}{\mathrm{C}}\mathrm{H} + \mathrm{CH_2{=}CH\text{-}CHO} \longrightarrow \mathrm{(EtOOC)_2CHCH_2CH{=}CH\text{-}O^-}$$

$$\xrightarrow{\text{EtOH}} \mathrm{(EtOOC)_2CHCH_2CH_2CHO}$$

羰基酸、酯

不对称酮进行麦克尔加成时，反应总是在多取代α -C上发生。



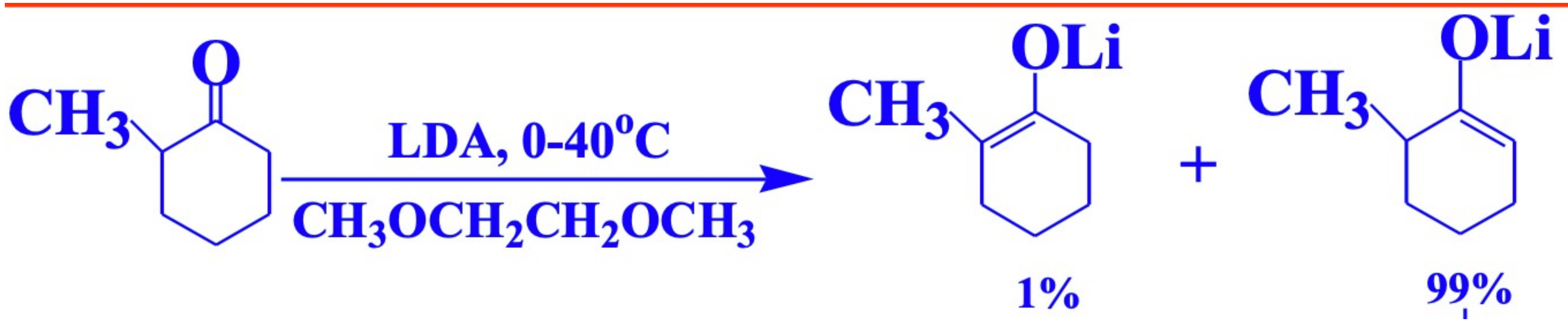


Robinson关环反应

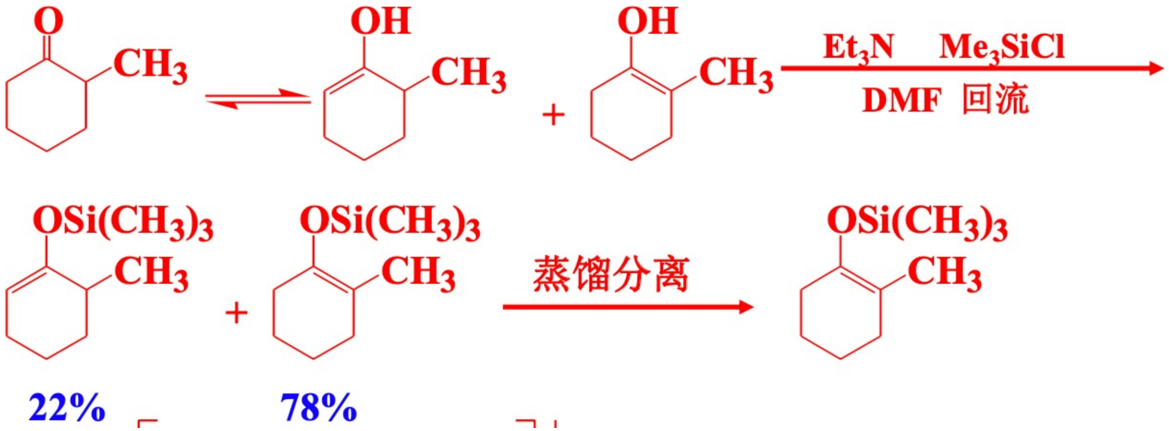
羰基酸、酯

- 酮的烃基化反应

用**LDA**处理，得动力学控制产物 **LDA：(i-Pr)$_2$NLi**



用三甲基氯硅烷和锂盐处理，得热力学控制产物



羰基酸、酯

- 醛的烃基化反应

在反应前将醛基保护，可以发生烷基化反应。

$$\mathrm{RCH_2CHO} \xrightarrow{\mathrm{R'NH_2}} \mathrm{RCH_2CH{=}NR'} \xrightarrow[\text{or LDA}]{\mathrm{C_2H_5MgX}}$$

$$\mathrm{R\overset{-}{CH}CH{=}NR'} \xrightarrow{\mathrm{R''X}} \mathrm{RR''CHCH{=}NR'}$$

$$\xrightarrow{\mathrm{H^+}} \mathrm{RR''CHCHO}$$

胺

- 碱性

碱性强弱顺序：脂肪胺 > NH_3 > 芳香胺

pK_b　3~4.5　4.75　9~10

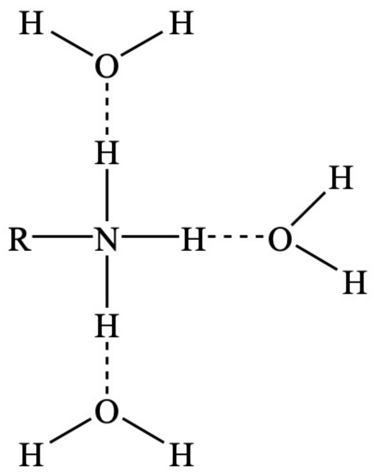
在脂肪胺中：RNH_2 < R_2NH > R_3N

一级　二级　三级

电子效应：R给电子，N上电子云密度增加

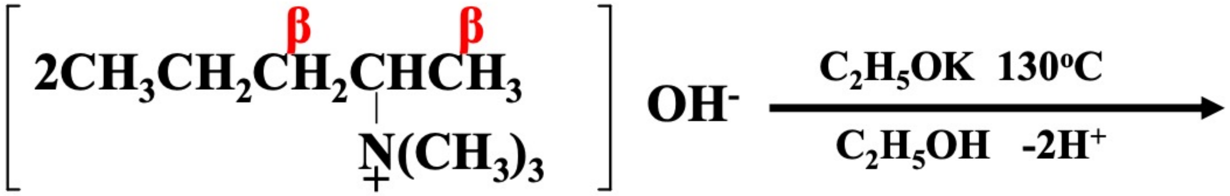
溶剂效应：N上取代基多，与质子性溶剂形成氢键少，与H^+结合形成铵离子后，溶剂化稳定作用弱，碱性减弱

空间位阻：N上取代基多，空阻不利于N接受H^+



胺

霍夫曼消除规律: 四级铵碱热解时，若有两个β-H可发生消除, 总是优先消去取代较少的碳上的β-H.

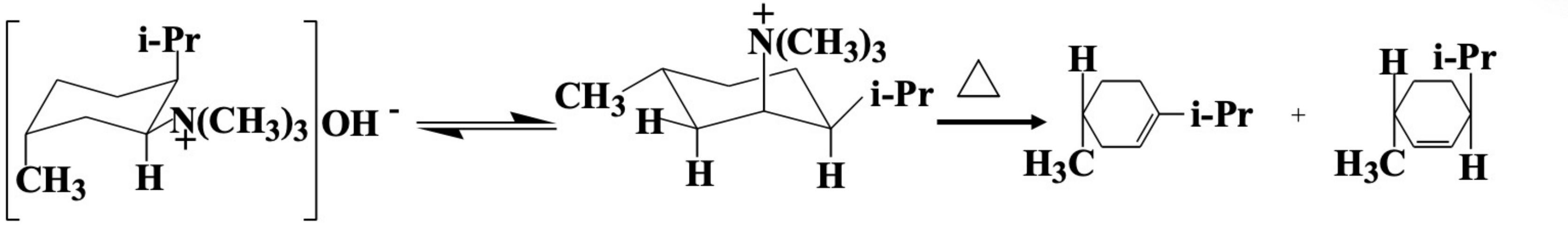


$$\left[2CH_3CH_2\overset{\beta}{C}H_2\underset{\overset{+}{N}(CH_3)_3}{C}H\overset{\beta}{C}H_3\right]OH^- \xrightarrow[C_2H_5OH\ \ -2H^+]{C_2H_5OK\ \ 130^{o}C}$$

E1cb

$2CH_3CH_2CH_2CH{=}CH_2 + CH_3CH_2CH{=}CHCH_3 + 2N(CH_3)_3$

55.7% 1.3%



有两种β-H，均在环上。

89.5 % -93 %

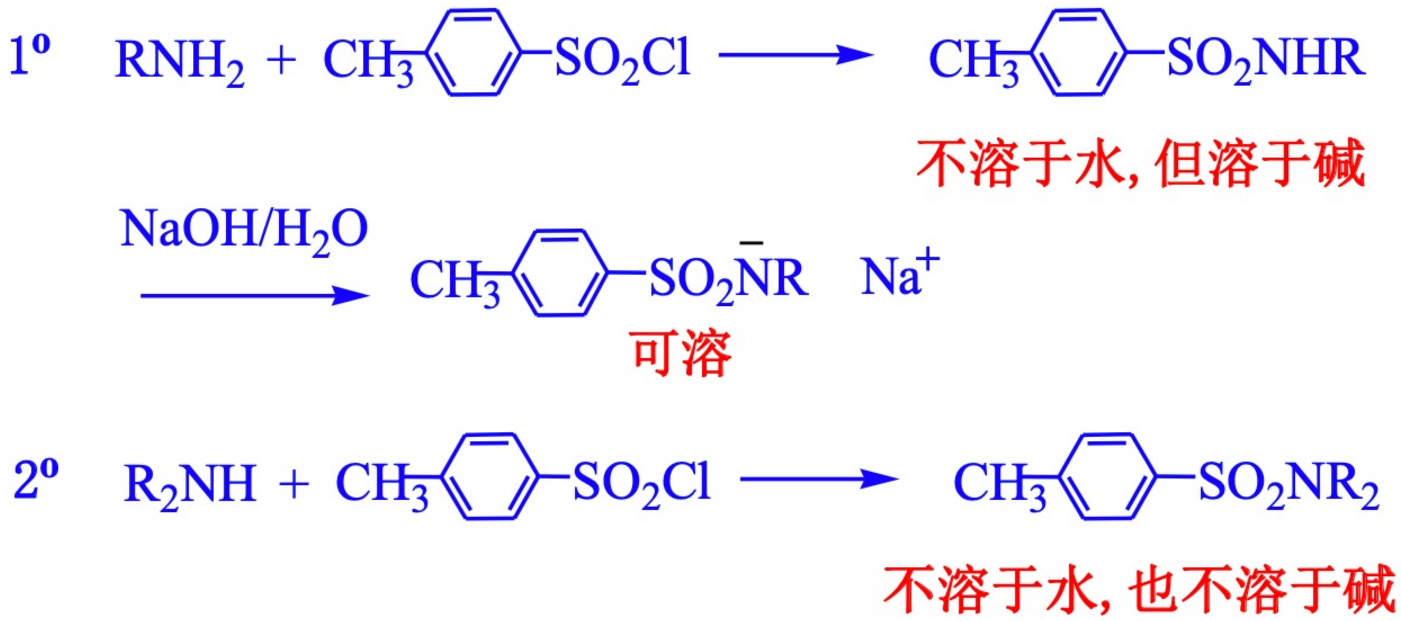
扎依采夫产物

10.5 % -7 %

霍夫曼产物

胺

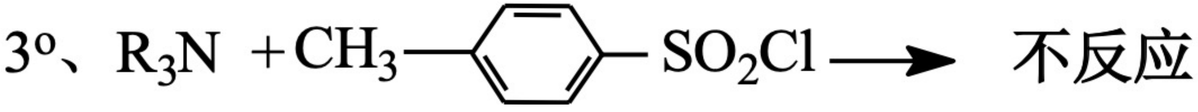
兴斯堡(Hinsberg)反应——用于鉴别1°、2 °、3 °胺



不溶于水, 但溶于碱

可溶

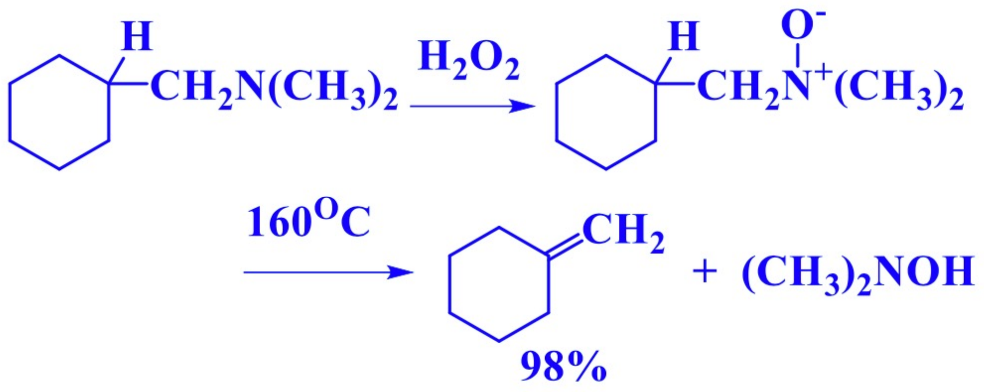
不溶于水, 也不溶于碱

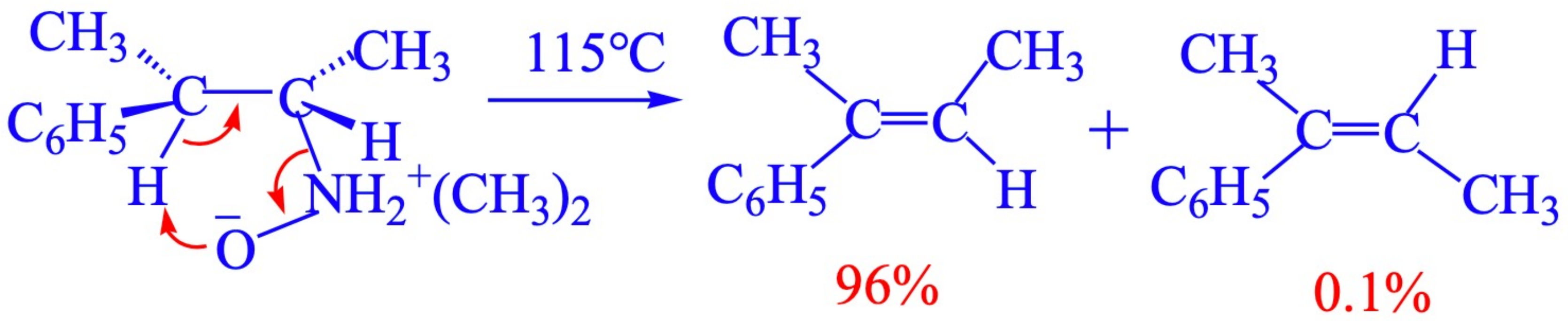


不反应

胺

- Cope消除





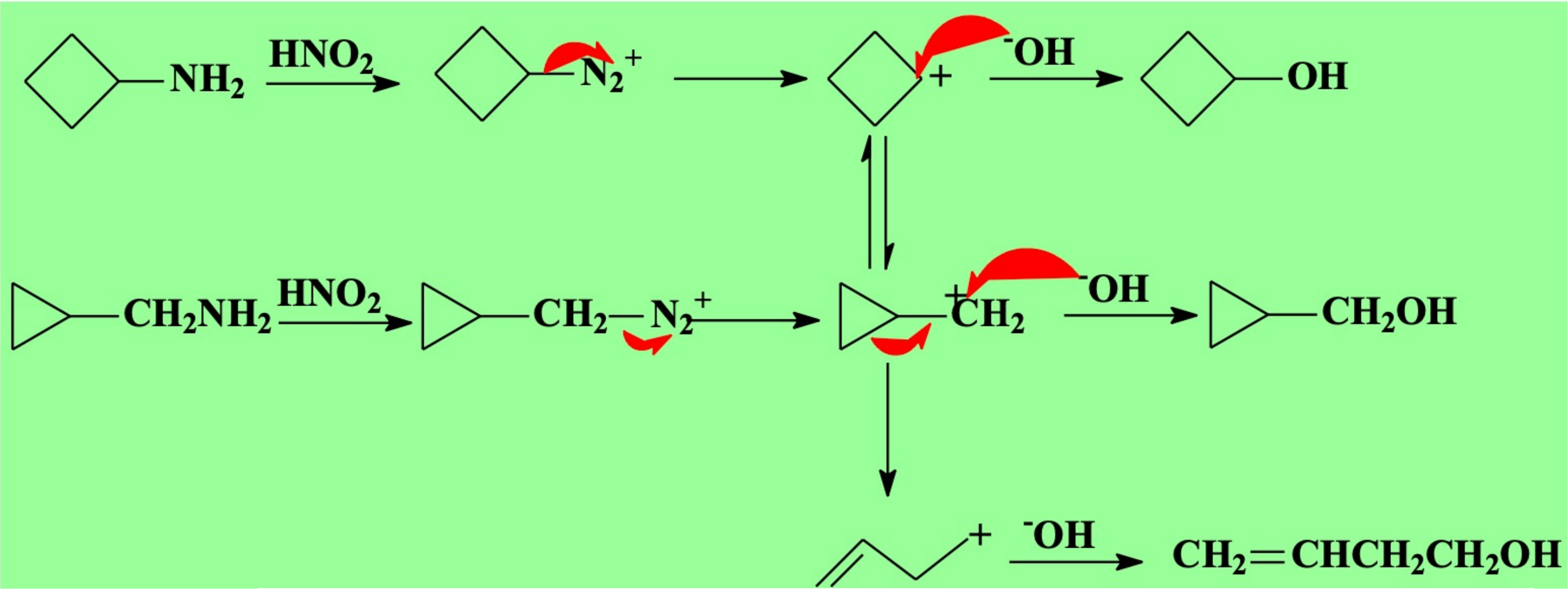
E2顺式消除

重氮化反应：一级胺与亚硝酸作用生成重氮盐的反应

$$CH_3CH_2CH_2CH_2NH_2 \xrightarrow[HCl]{NaNO_2} CH_3CH_2CH_2CH_2N_2^+Cl^-$$

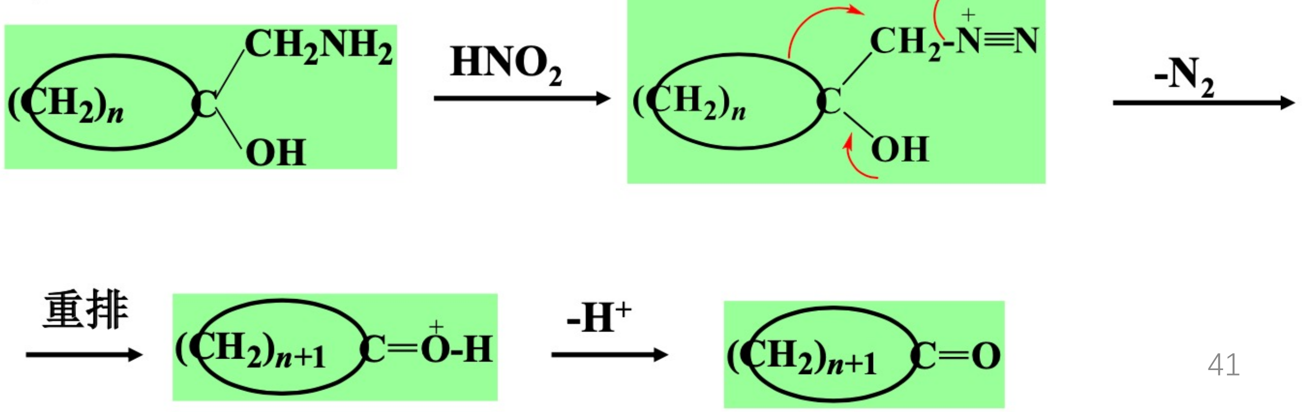
胺

- 捷姆扬诺夫反应



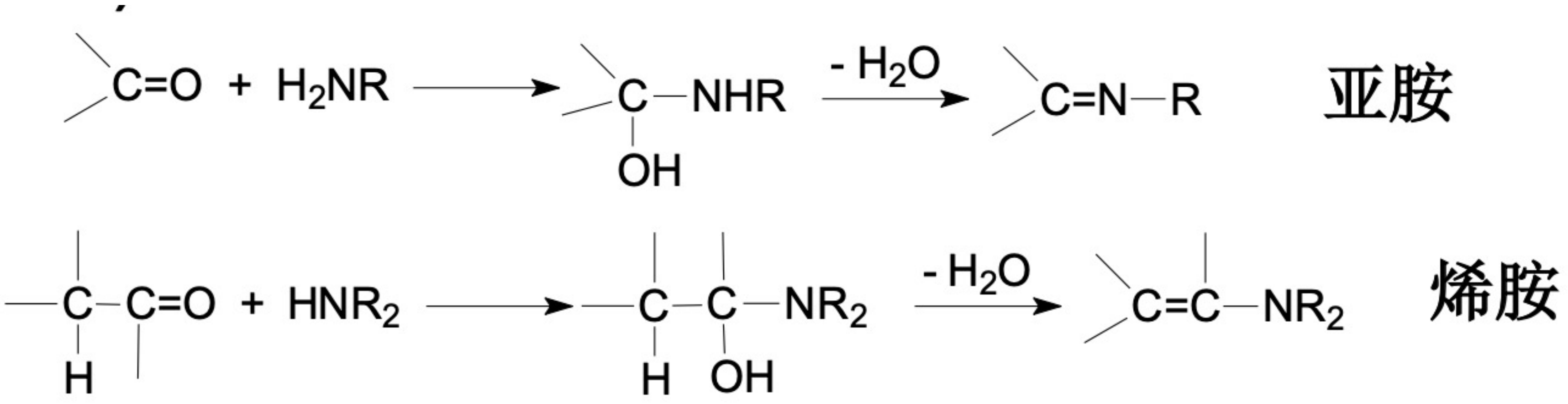
- 蒂芬欧--捷姆杨诺夫反应

机理：

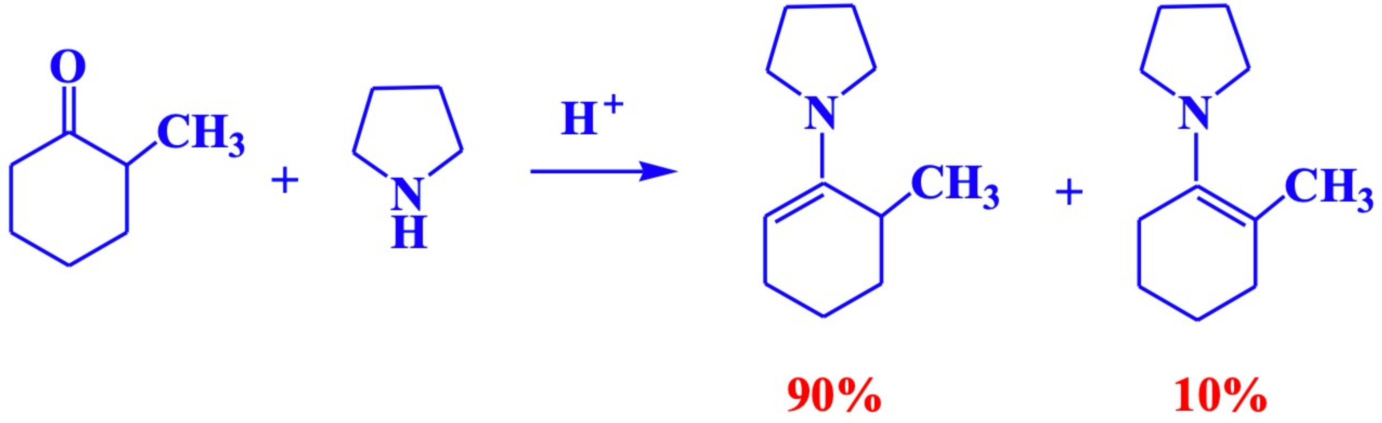


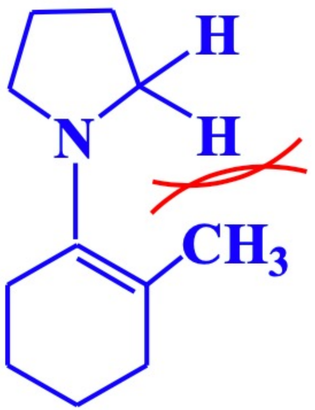
胺

- 烯胺



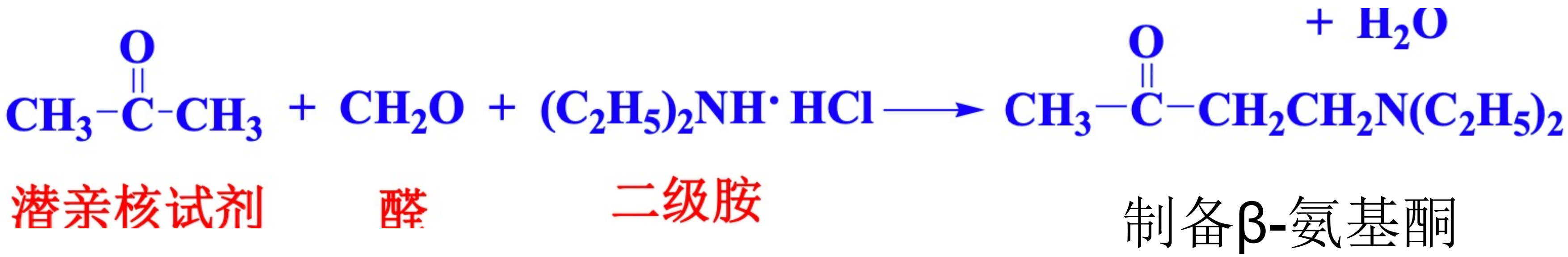
不对称酮主要生成双键碳上取代较少的烯胺：





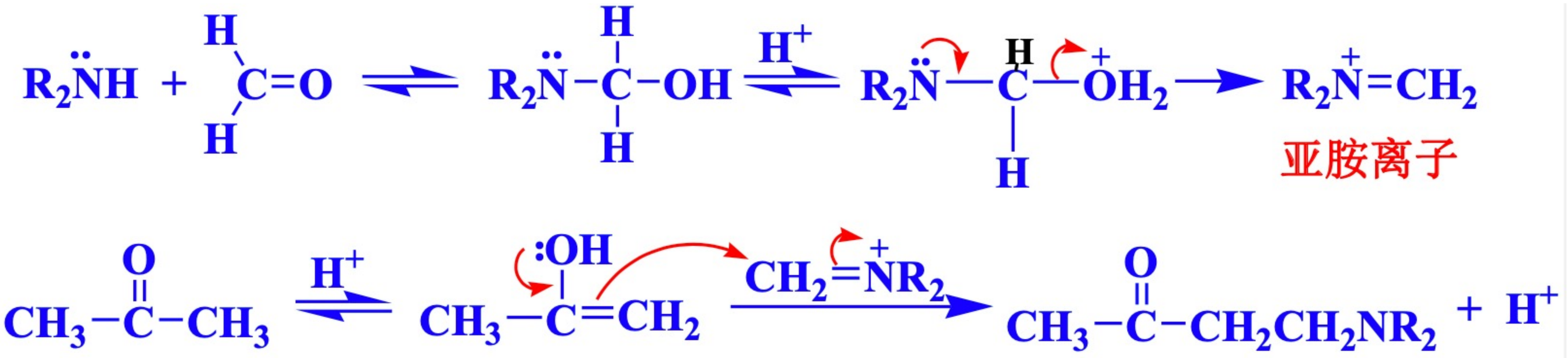
胺

- Mannich反应



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CH_2O + (C_2H_5)_2NH\cdot HCl \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2N(C_2H_5)_2 + H_2O$$

制备β-氨基酮



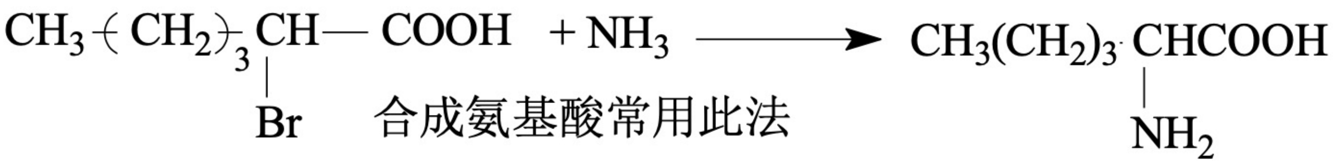
$$R_2\ddot{N}H + \begin{matrix}H\\ \diagdown \\ \end{matrix}C=O \rightleftharpoons R_2\ddot{N}-\underset{H}{\overset{H}{C}}-OH \xrightleftharpoons{H^+} R_2\ddot{N}-\underset{H}{\overset{H}{C}}-\overset{+}{O}H_2 \longrightarrow R_2\overset{+}{N}=CH_2$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightleftharpoons{H^+} CH_3-\overset{:OH}{C}=CH_2 \xrightarrow{CH_2=\overset{+}{N}R_2} CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2NR_2 + H^+$$

胺

- 制备

氨的烷基化



$$CH_3\text{+}(CH_2)_3\underset{\substack{|\\ Br}}{CH}\text{—}COOH + NH_3 \longrightarrow CH_3(CH_2)_3\underset{\substack{|\\ NH_2}}{CH}COOH$$

合成氨基酸常用此法

硝基化合物的还原

1 酸性还原剂：酸+金属

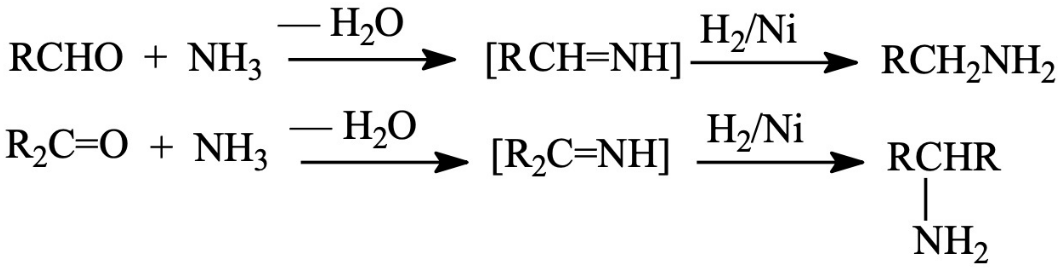
（Fe+HCl, Zn+HCl, Sn+HCl, $SnCl_2$+HCl)

2 中性还原剂：催化氢化，常用的催化剂有 Ni, Pt, Pd.

3 碱性还原剂：Na_2S, NaSH, $(NH_4)_2S$, NH_4SH, $LiAlH_4$

($NaBH_4$ 和 B_2H_6 不能还原硝基）

醛酮的还原胺化

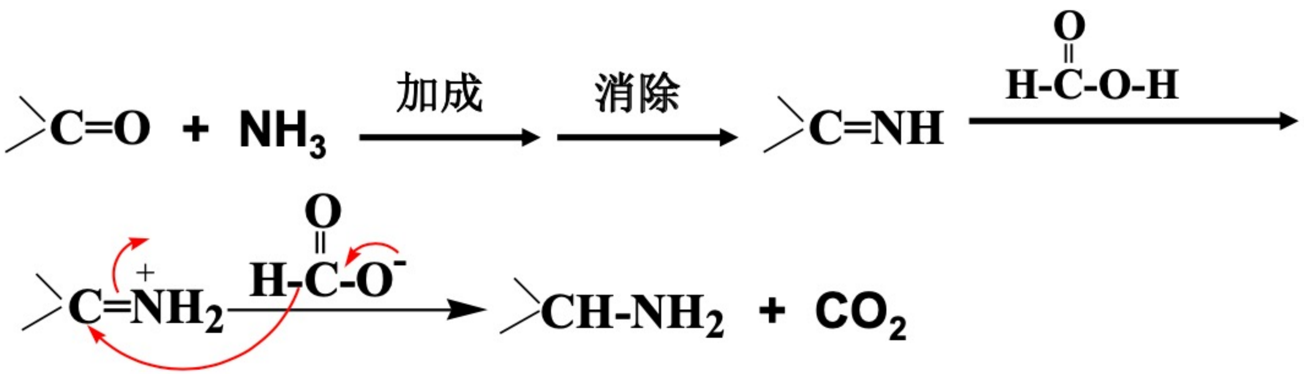


$$RCHO + NH_3 \xrightarrow{-H_2O} [RCH{=}NH] \xrightarrow{H_2/Ni} RCH_2NH_2$$

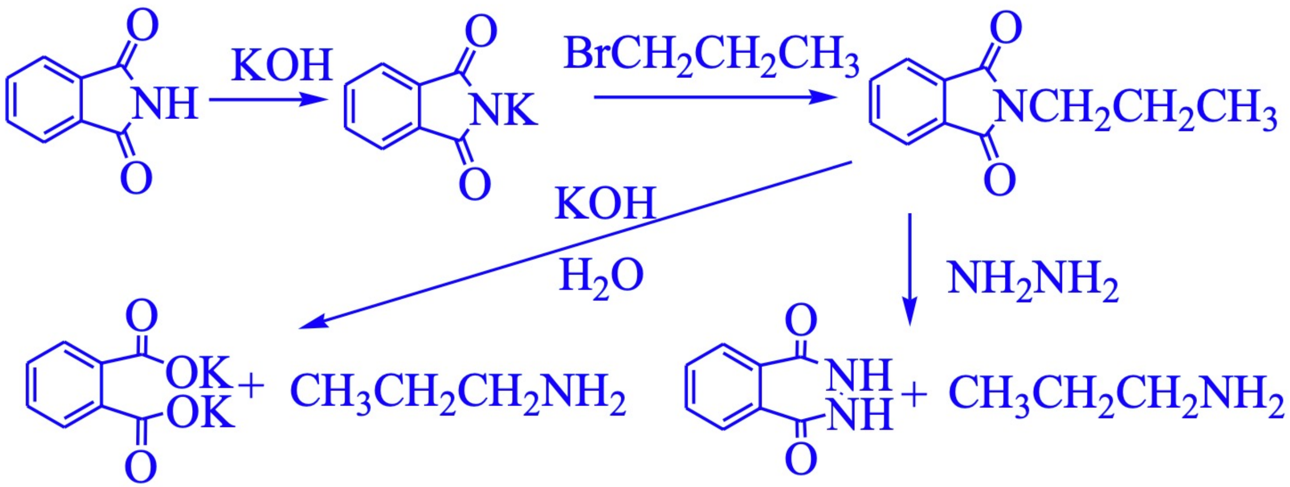
$$R_2C{=}O + NH_3 \xrightarrow{-H_2O} [R_2C{=}NH] \xrightarrow{H_2/Ni} R\underset{\substack{|\\ NH_2}}{CH}R$$

胺

Leukart反应



Gabriel (盖布瑞尔)合成法



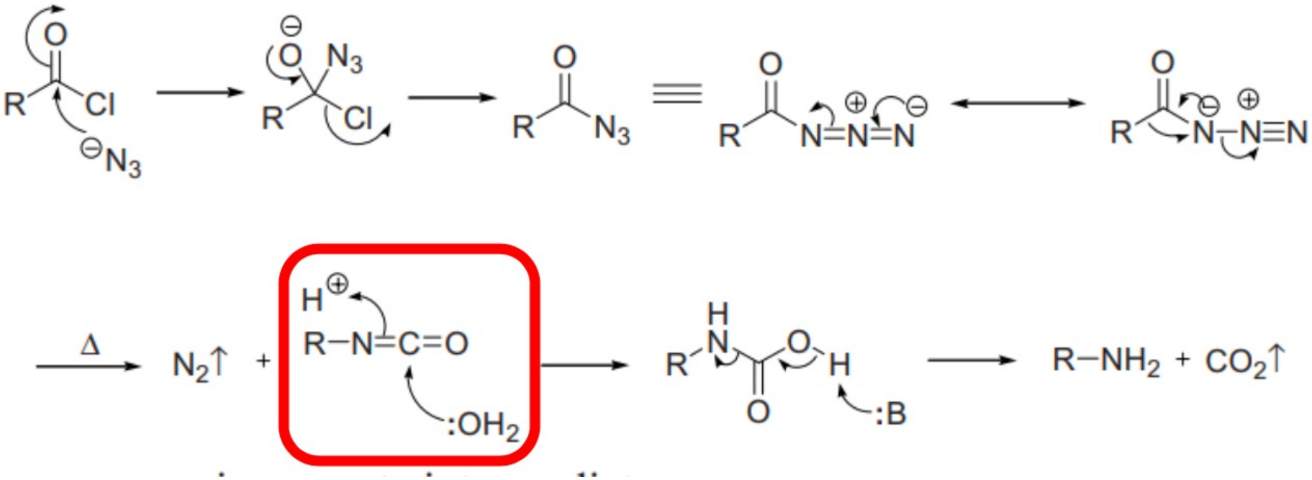
胺

从羧酸衍生物合成

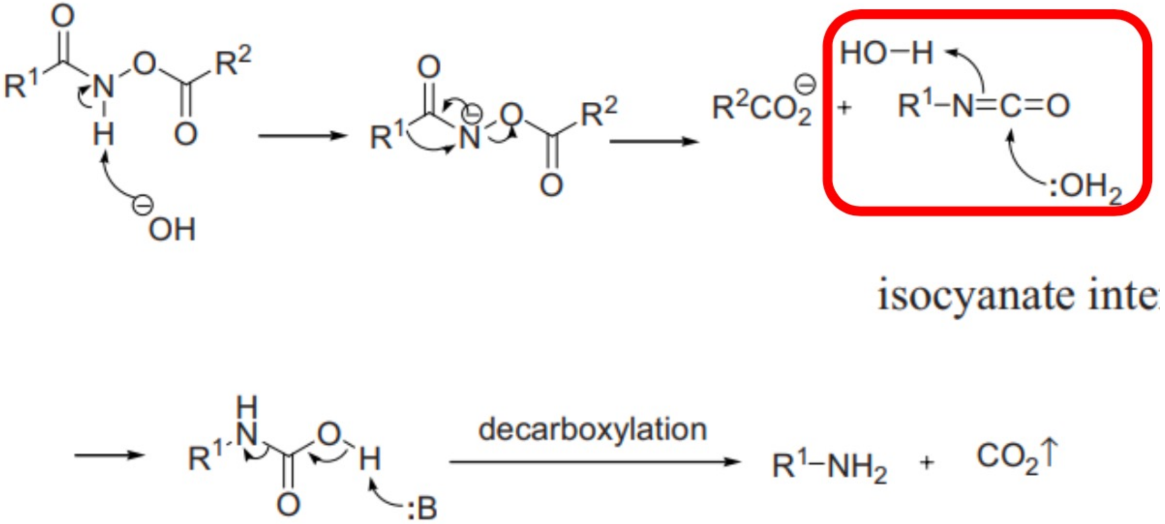
霍夫曼重排

$$\overset{\overset{\displaystyle O}{\|}}{RC}NH_2 + Br_2 + NaOH \xrightarrow{H_2O} RNH_2 + CO_2 + 2NaBr$$

Curtius重排

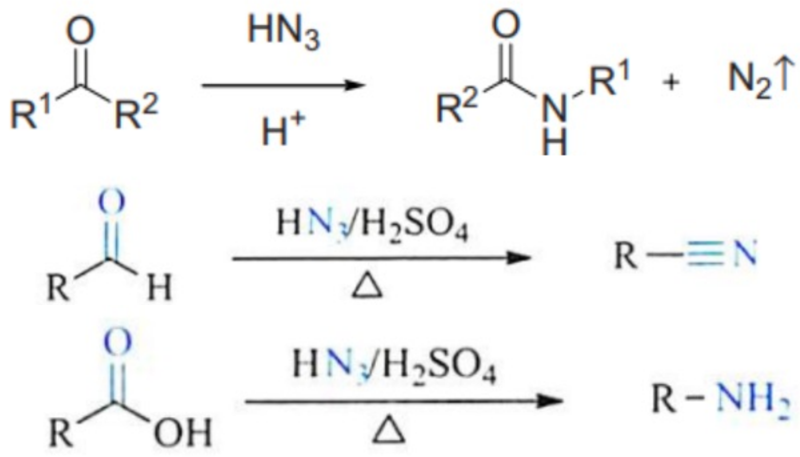


Lossen 重排

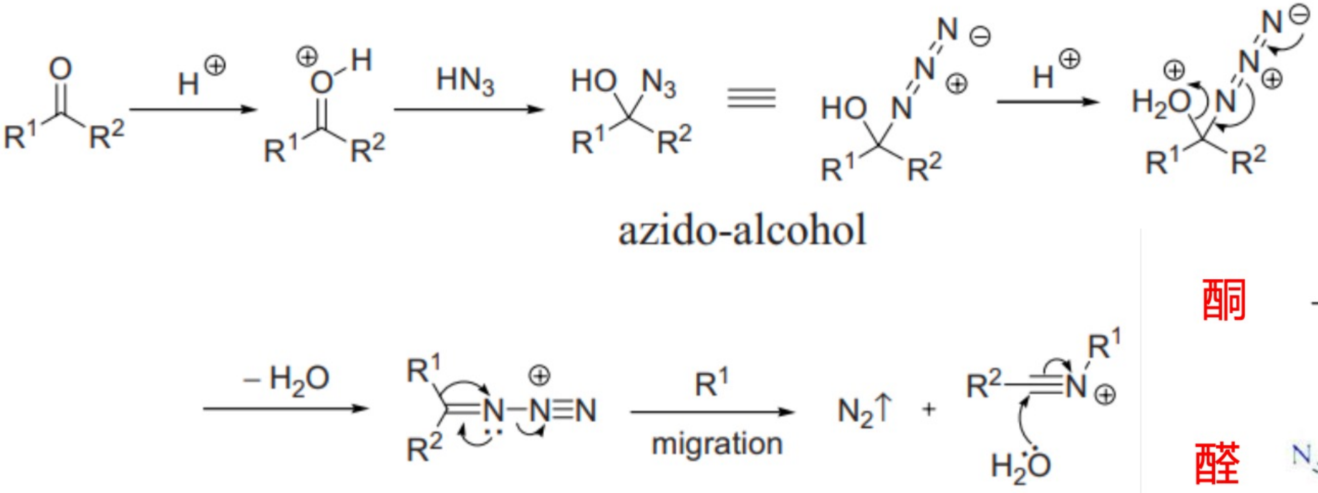


胺

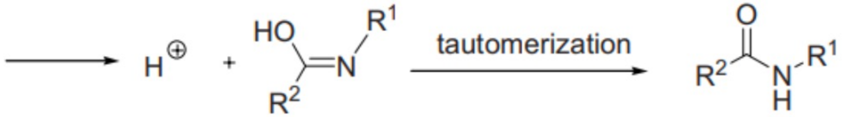
从羧酸衍生物合成



Schmidt重排

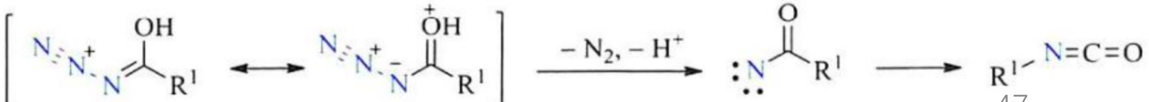


酮



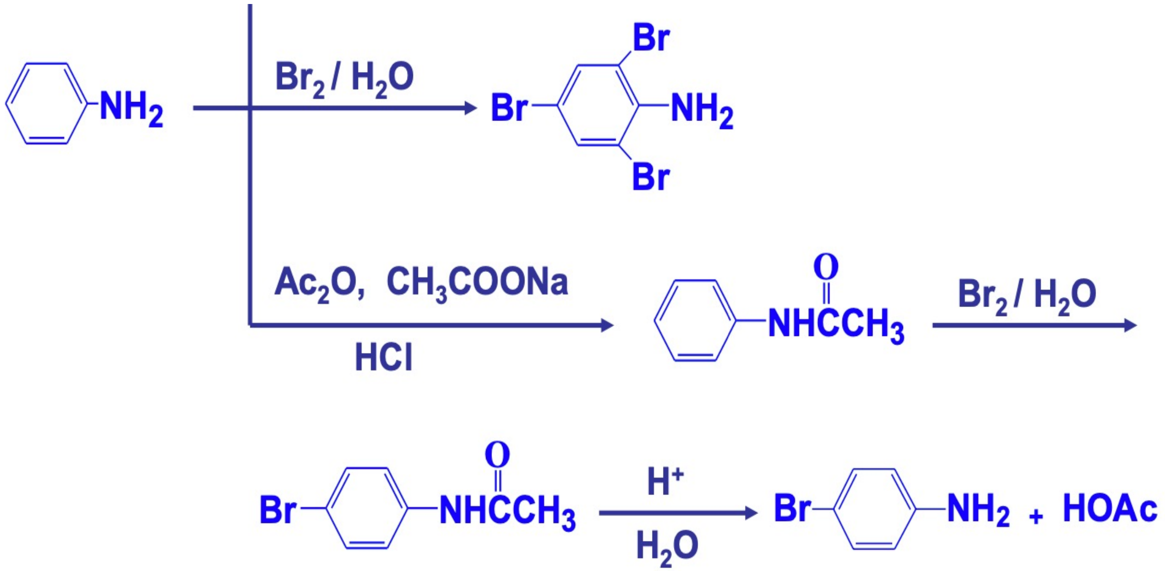
醛

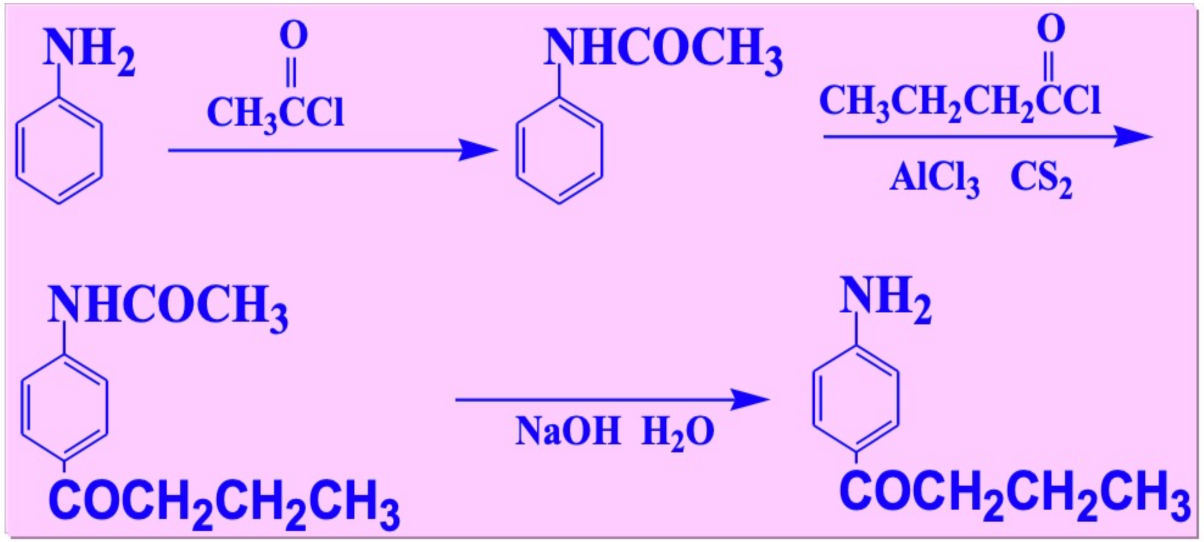
羧酸



胺

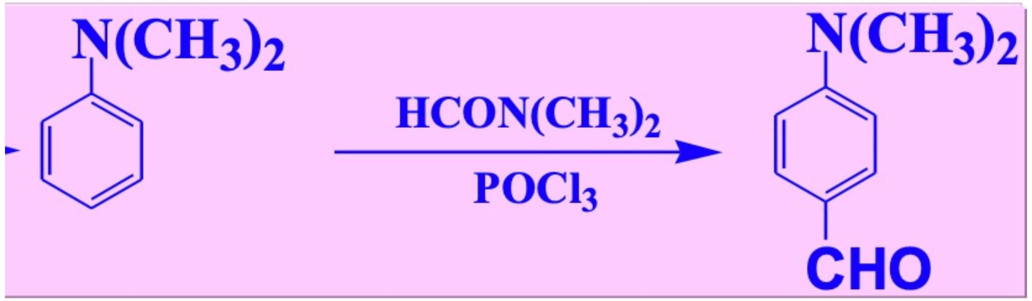
- 芳香胺芳环上的亲电取代反应

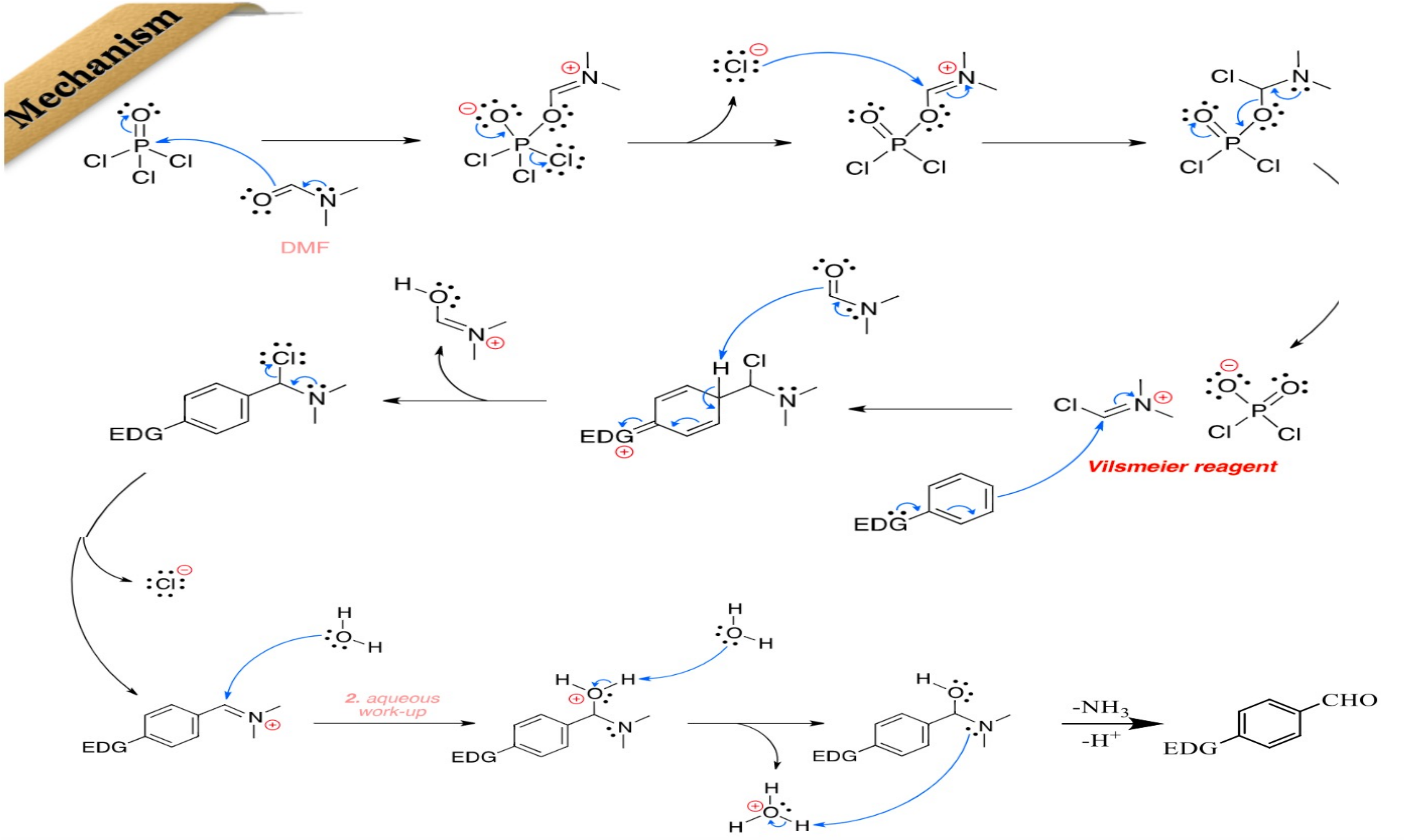




胺

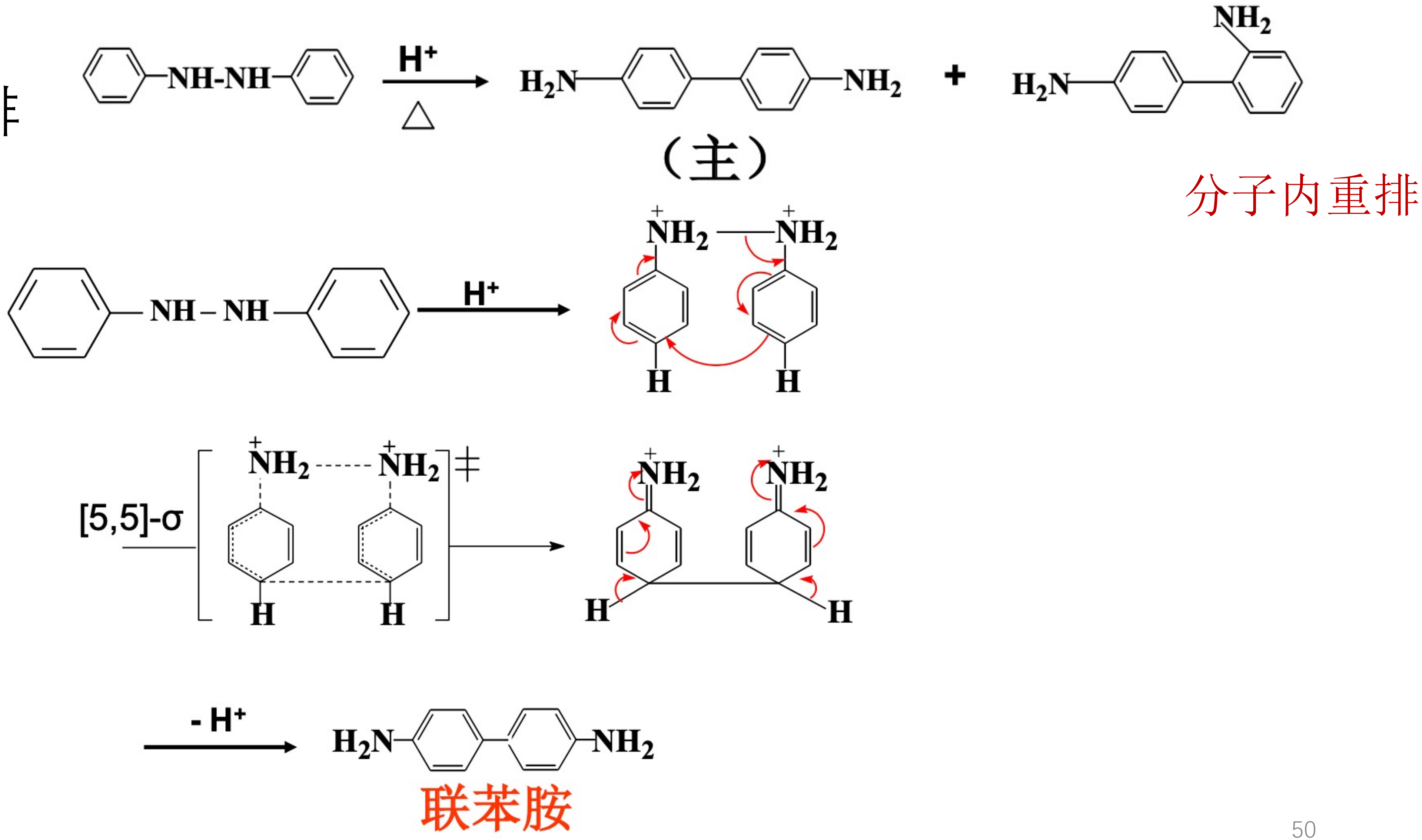
- 威尔斯麦尔反应


N(CH3)2
HCON(CH3)2
POCl3
N(CH3)2
CHO


Mechanism
DMF
Vilsmeier reagent
EDG
2. aqueous work-up
-NH3
-H+
CHO

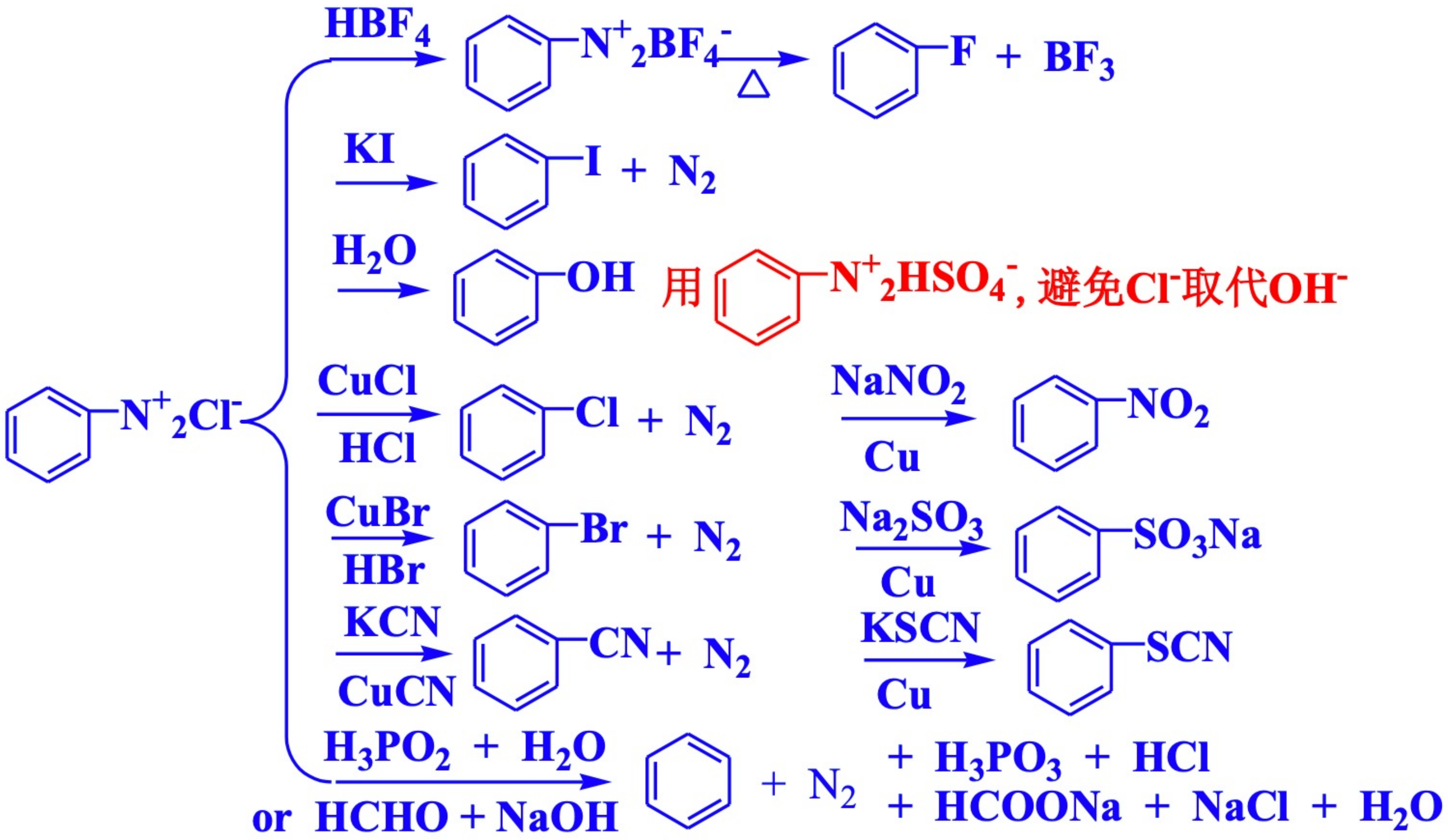
胺

- 联苯胺重排


NH-NH
H⁺
△
H₂N
NH₂
+
H₂N
NH₂
（主）
分子内重排
NH – NH
H⁺
N̊H₂
N̊H₂
H
H
[5,5]-σ
N̊H₂
N̊H₂
‡
H
H
N̊H₂
N̊H₂
H
H
- H⁺
H₂N
NH₂
联苯胺

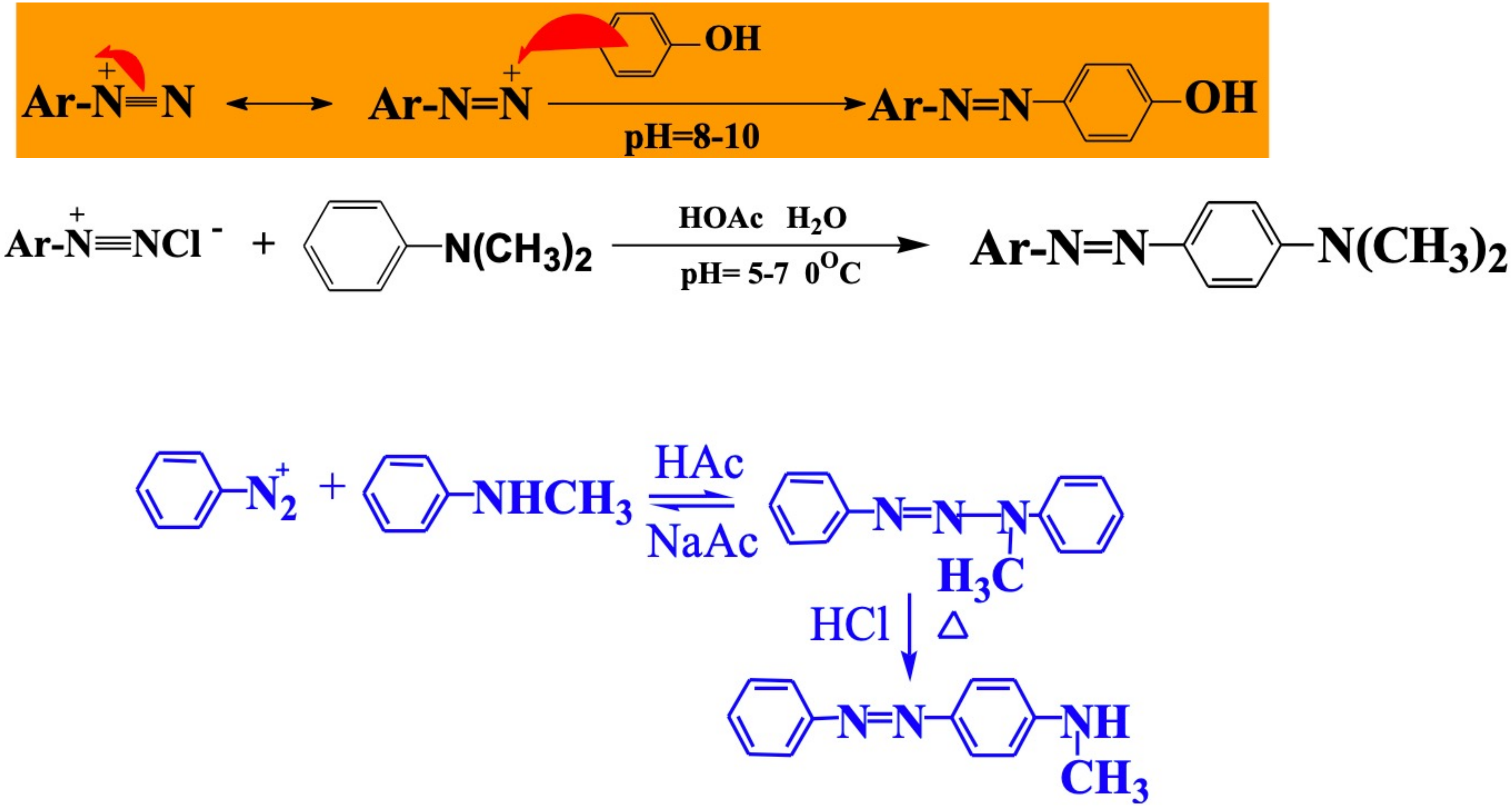
胺

- 芳香重氮盐的取代反应



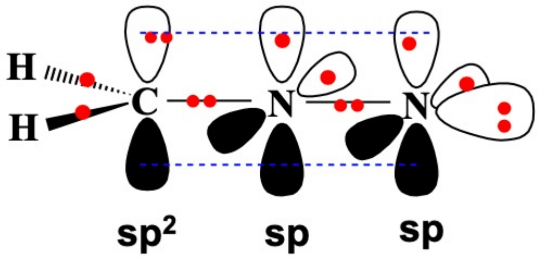
胺

- 芳香重氮盐的偶联反应



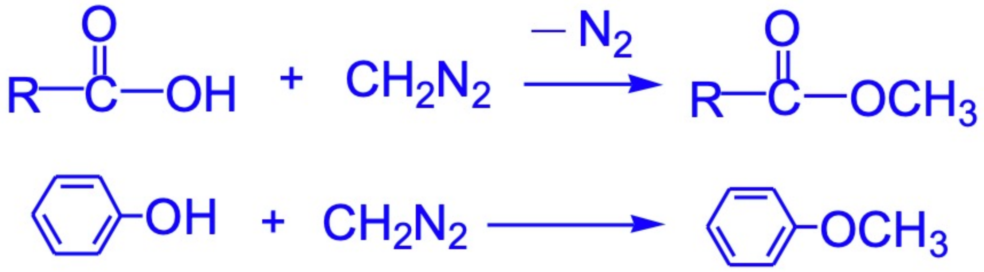
重氮甲烷

$$CH_2N_2 \equiv \left[H_2C{=}\overset{+}{N}{=}\overset{-}{N} \longleftrightarrow {}^{-}CH_2\text{-}\overset{+}{N}{\equiv}N \right]$$



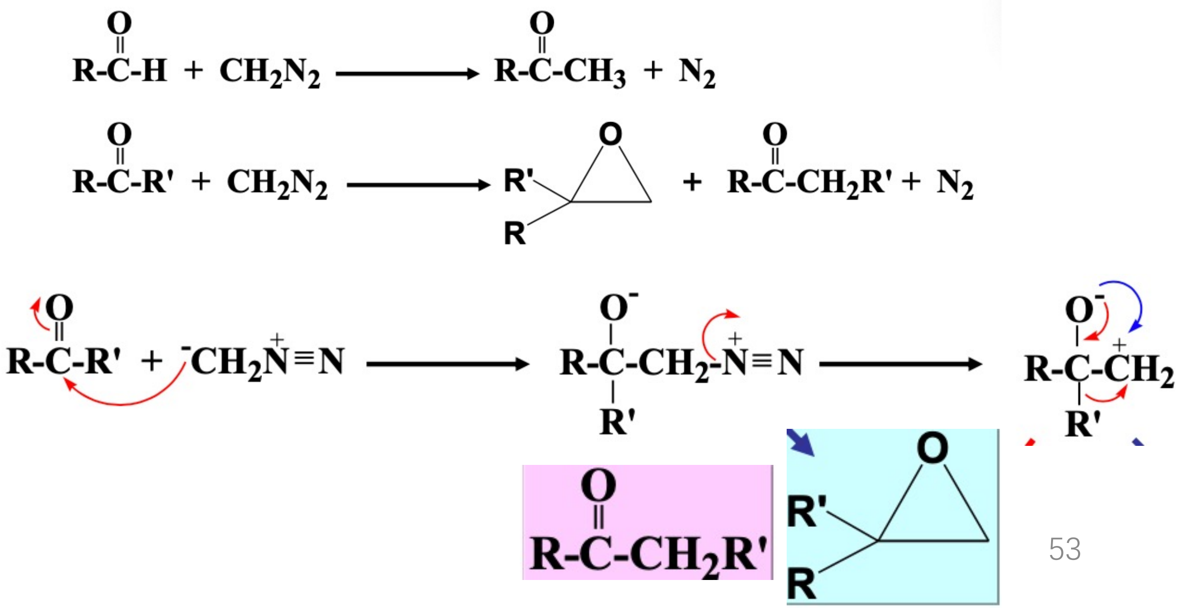
3中心4电子的大π键

- 与酸性物质的反应



$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + CH_2N_2 \xrightarrow{-N_2} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3$$

- 与醛、酮的反应

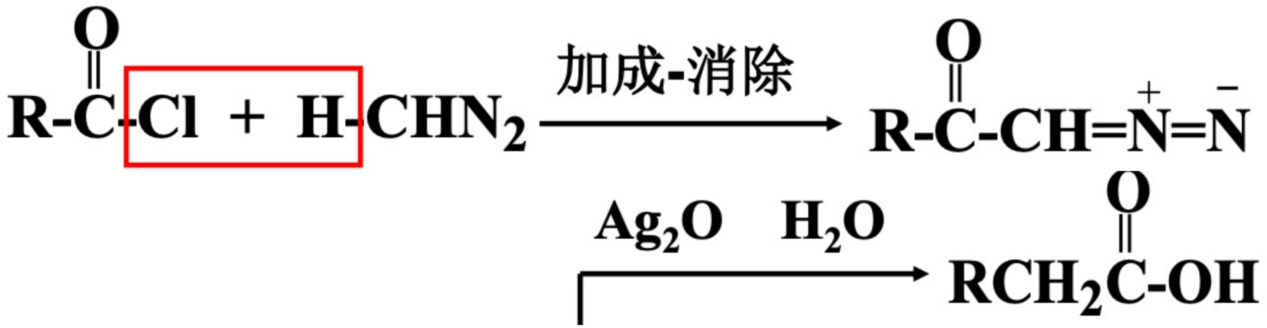


$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}H + CH_2N_2 \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + N_2$$

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}R' + CH_2N_2 \longrightarrow \text{(epoxide)} + R\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2R' + N_2$$

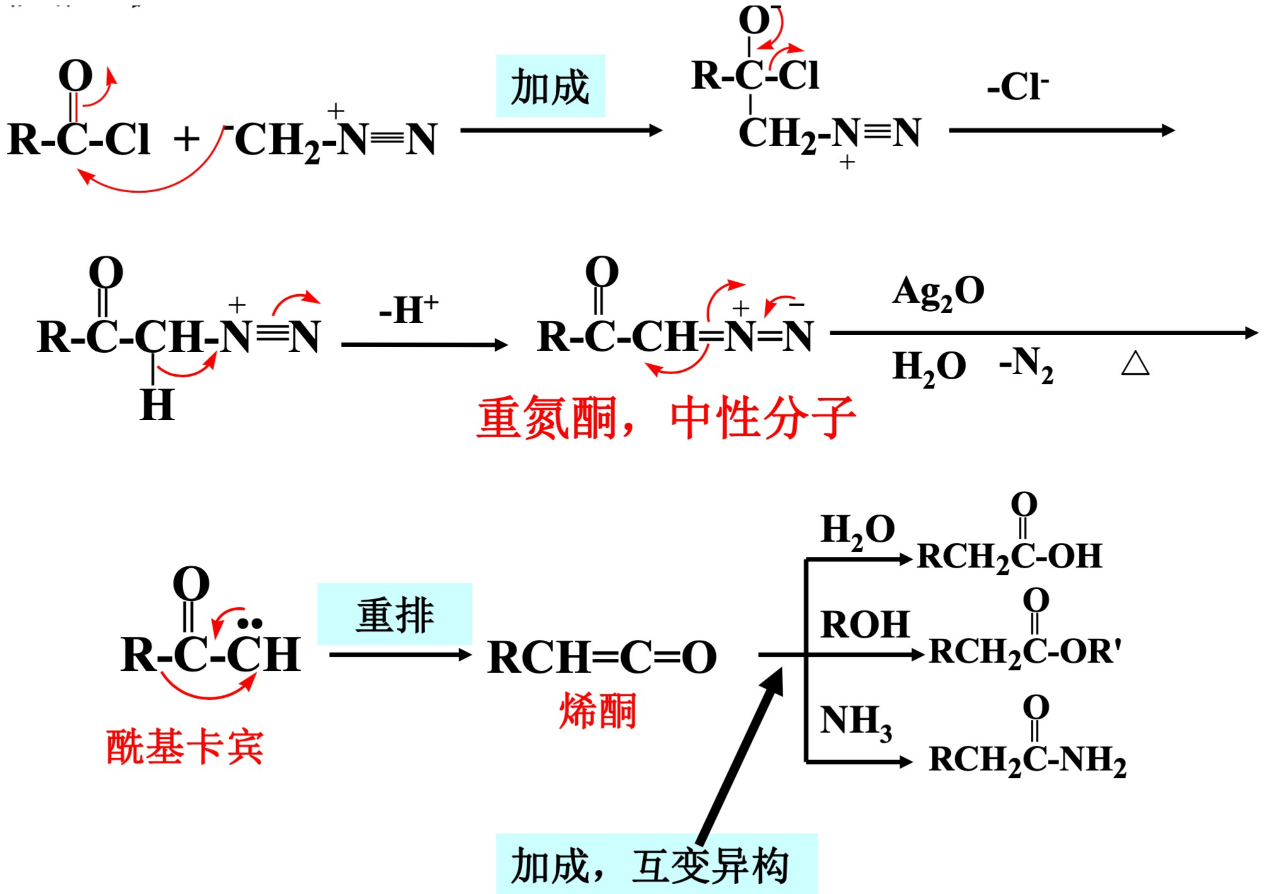
重氮甲烷

- 与酰氯反应



$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + H\text{-}CHN_2 \xrightarrow{\text{加成-消除}} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH=\overset{+}{N}=\overset{-}{N} \xrightarrow{Ag_2O\quad H_2O} RCH_2\overset{O}{\overset{\|}{C}}\text{-}OH$$

Wolff重排



$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + {}^{-}CH_2\text{-}\overset{+}{N}\equiv N \xrightarrow{\text{加成}} R\text{-}\underset{CH_2\text{-}\overset{+}{N}\equiv N}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}\text{-}Cl \xrightarrow{-Cl^-}$$

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{H}{\underset{|}{CH}}\text{-}\overset{+}{N}\equiv N \xrightarrow{-H^+} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH=\overset{+}{N}=\overset{-}{N} \xrightarrow[H_2O\quad -N_2\quad \triangle]{Ag_2O}$$

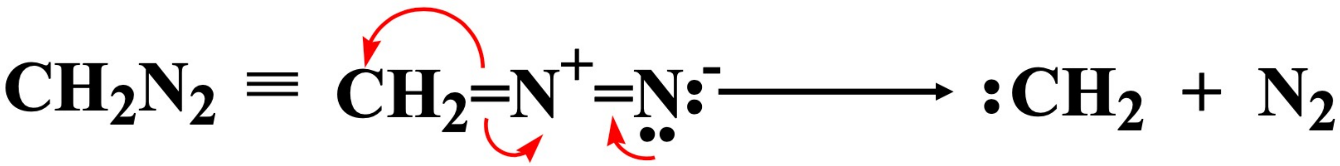
$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\ddot{C}H \xrightarrow{\text{重排}} RCH=C=O$$

$$RCH=C=O \xrightarrow{H_2O} RCH_2\overset{O}{\overset{\|}{C}}\text{-}OH$$

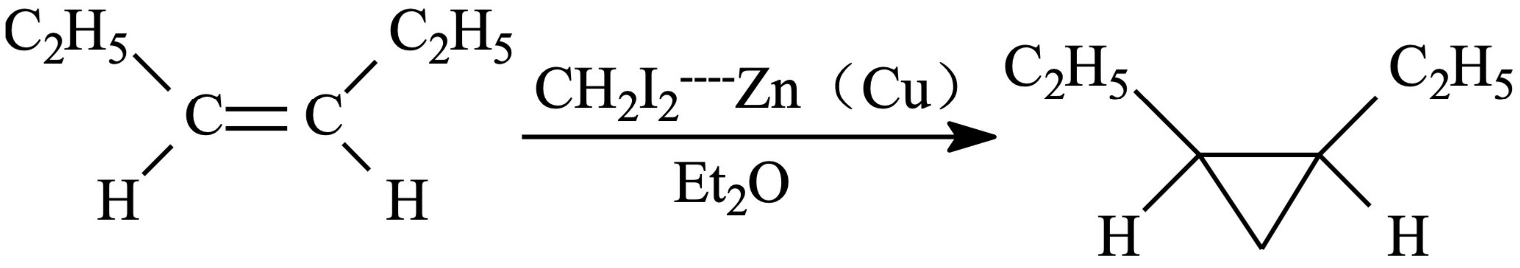
$$RCH=C=O \xrightarrow{ROH} RCH_2\overset{O}{\overset{\|}{C}}\text{-}OR'$$

$$RCH=C=O \xrightarrow{NH_3} RCH_2\overset{O}{\overset{\|}{C}}\text{-}NH_2$$

重氮甲烷

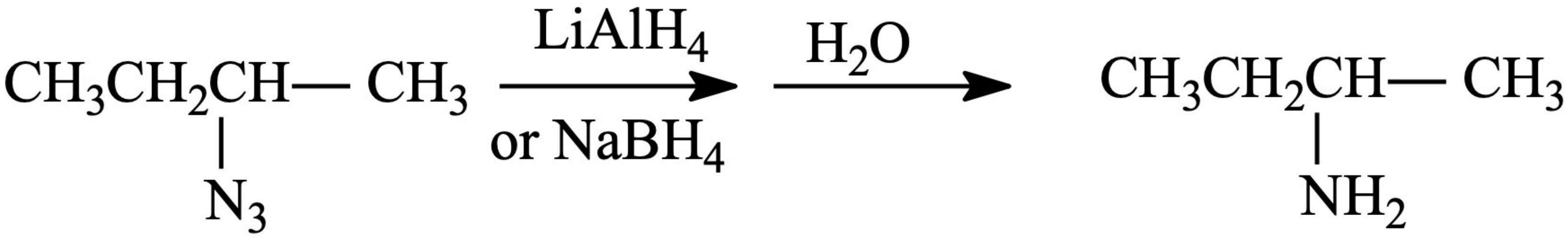


$$CH_2N_2 \equiv CH_2{=}N^+{=}N{:}^- \longrightarrow {:}CH_2 + N_2$$

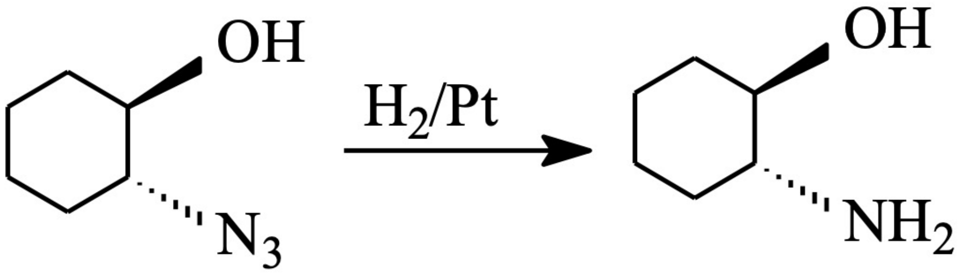


Simmons-Simth反应

叠氮化合物



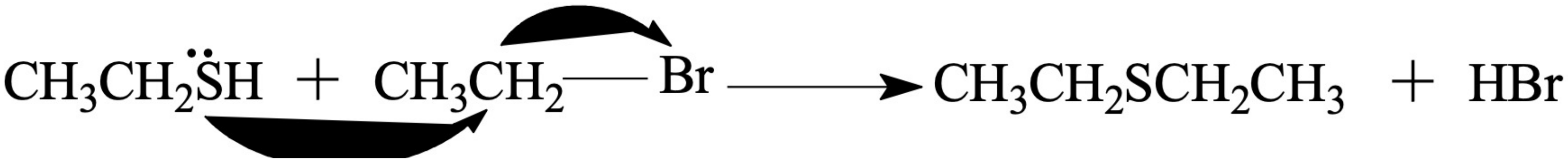
$$CH_3CH_2\underset{\displaystyle N_3}{\underset{|}{C}H}-CH_3 \xrightarrow[\text{or } NaBH_4]{LiAlH_4} \xrightarrow{H_2O} CH_3CH_2\underset{\displaystyle NH_2}{\underset{|}{C}H}-CH_3$$



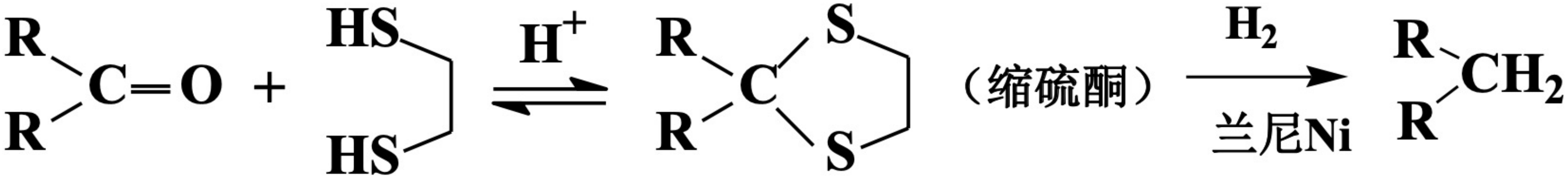
硫醇

- 硫醇酸性大于相应醇

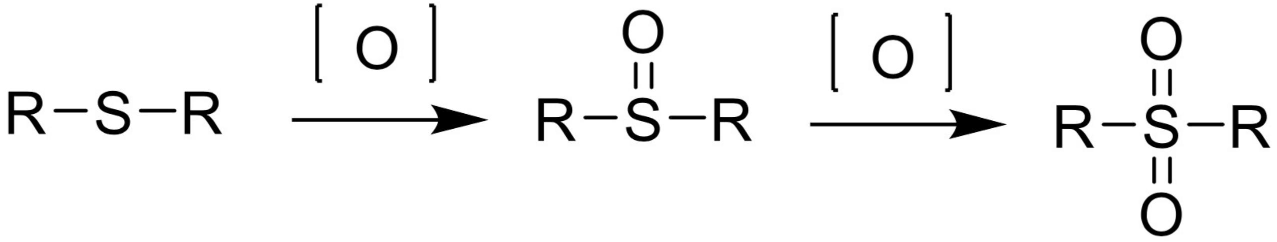
- 亲核取代



$$CH_3CH_2\ddot{S}H + CH_3CH_2—Br \longrightarrow CH_3CH_2SCH_2CH_3 + HBr$$

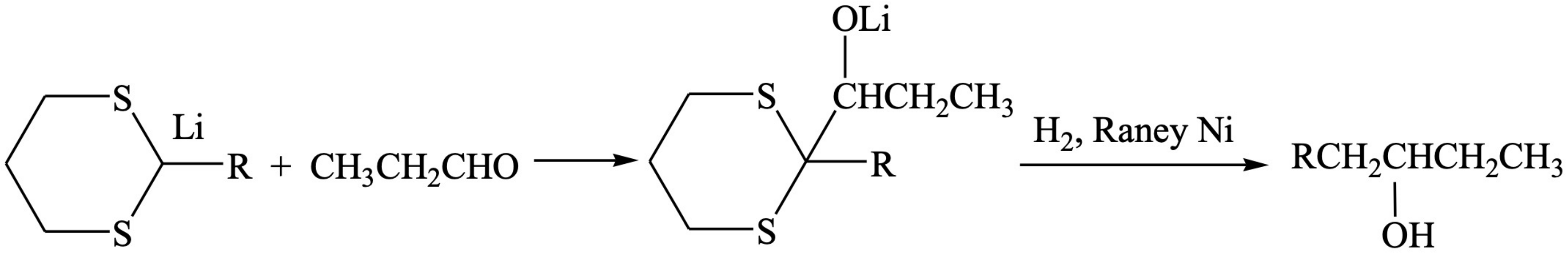


硫醚

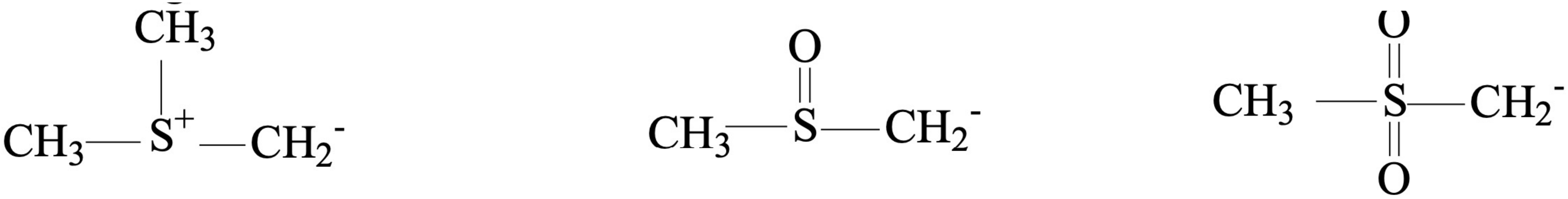


$$R-S-R \xrightarrow{[O]} R-\overset{O}{\overset{\|}{S}}-R \xrightarrow{[O]} R-\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}-R$$

α-碳负离子的反应

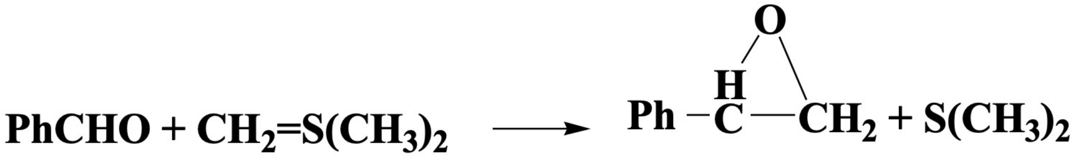


硫原子使相邻的碳负离子稳定化(通过**p - d** π 反馈键 ）



硫叶立德与醛酮的加成反应

$$\mathbf{(CH_3)_2S + CH_3I \longrightarrow (CH_3)_2SCH_3I \xrightarrow{LDA} (CH_3)_2S{=}CH_2 \longleftrightarrow (CH_3)_2\overset{+}{S}-\overset{-}{C}H_2}$$

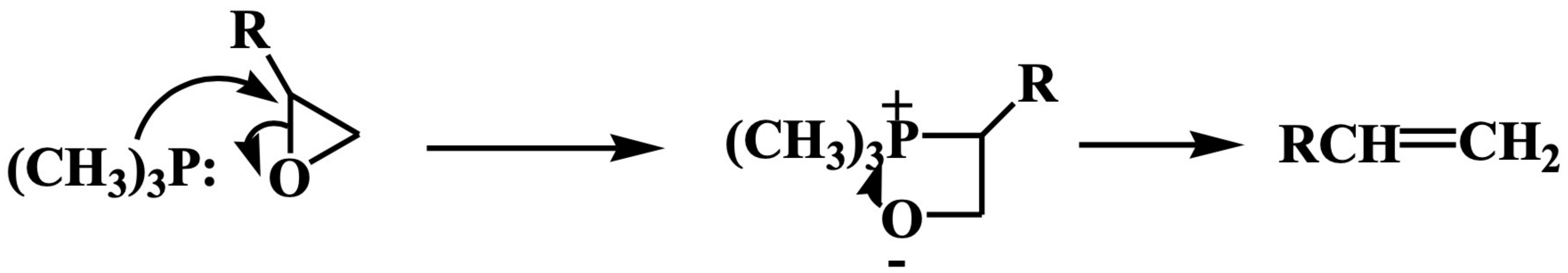


含磷化合物

$$(C_6H_5)_3\ddot{P} + CH_3Br \longrightarrow (C_6H_5)_3P^{+}{-}CH_3Br^{-} \xrightarrow{nC_4H_9Li} (C_6H_5)_3P^{+}{-}CH_2^{-} \xrightarrow{>C=O} >C=CH_2$$

Wittig 反应

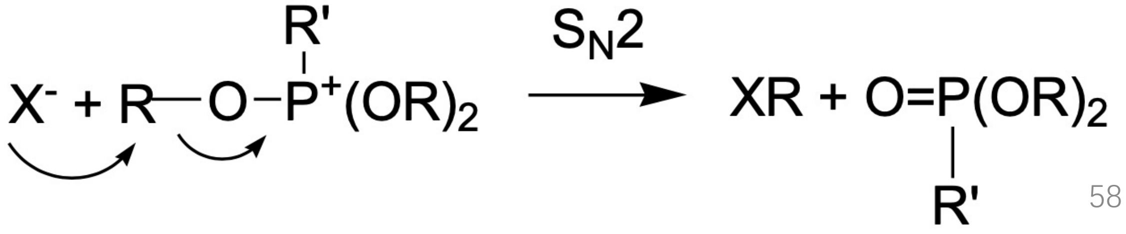
亲核反应



Arbuzov反应 由醇制备卤代烷 $3ROH + PCl_3 \longrightarrow (RO)_3P$

$$(C_2H_5O)_3P + BrCH_2CO_2C_2H_5 \longrightarrow CH_3CH_2OOCCH_2\overset{O}{\overset{\|}{P}}(OC_2H_5)_2 + C_2H_5Br$$

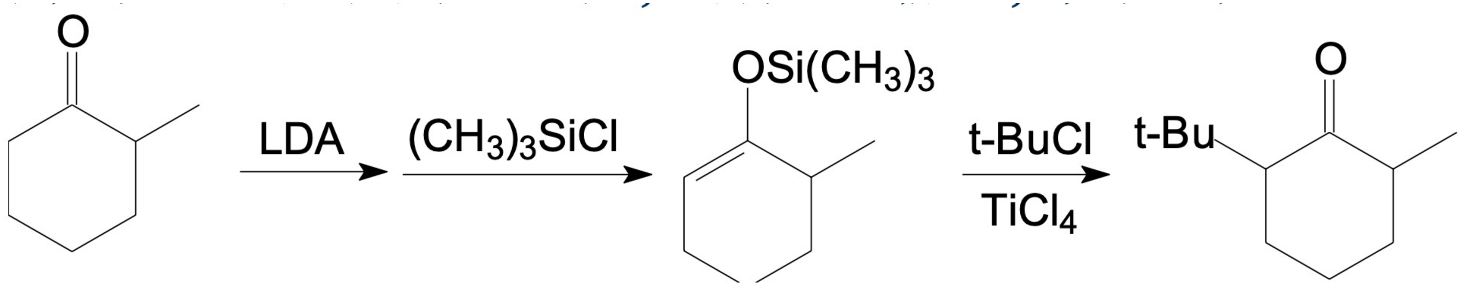
$$(RO)_3P + R'X \xrightarrow{S_N2} (RO)_3P^{+}R'X^{-}$$

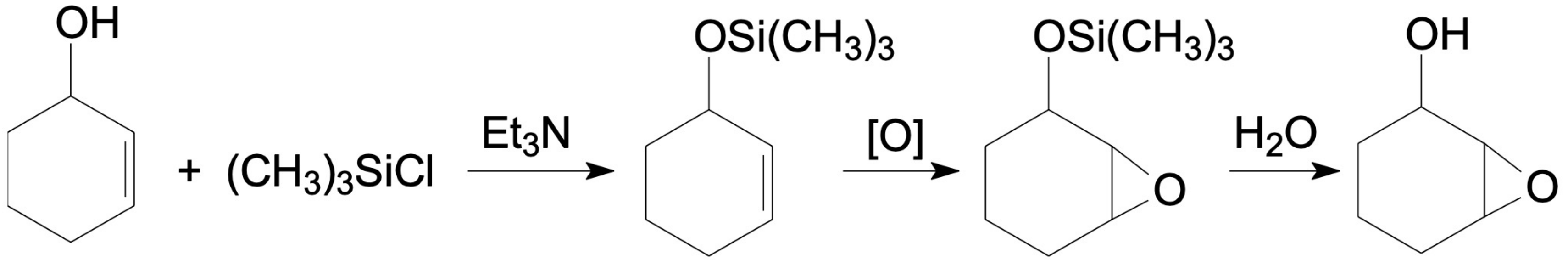


$$X^{-} + R{-}O{-}\overset{R'}{\overset{|}{P}}{}^{+}(OR)_2 \xrightarrow{S_N2} XR + O{=}\underset{R'}{\underset{|}{P}}(OR)_2$$

含硅化合物

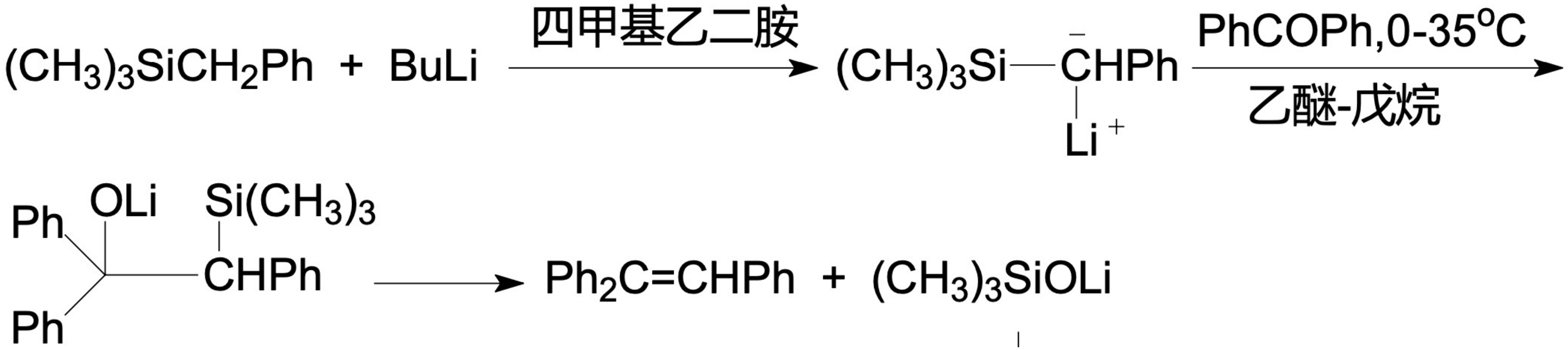
烯醇硅醚





保护羟基

硅叶立德

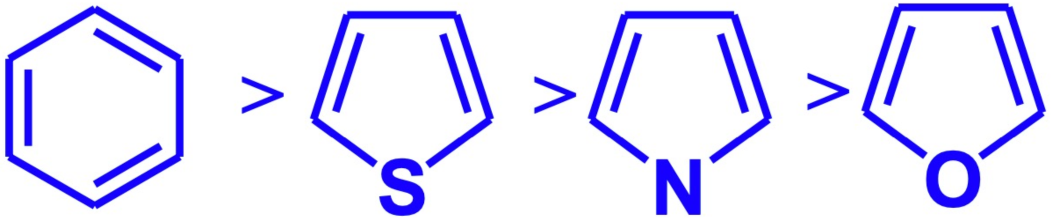


$$(CH_3)_3SiCH_2Ph + BuLi \xrightarrow{\text{四甲基乙二胺}} (CH_3)_3Si-\underset{Li^+}{\overset{-}{C}}HPh \xrightarrow[\text{乙醚-戊烷}]{PhCOPh,0\text{-}35^{o}C}$$

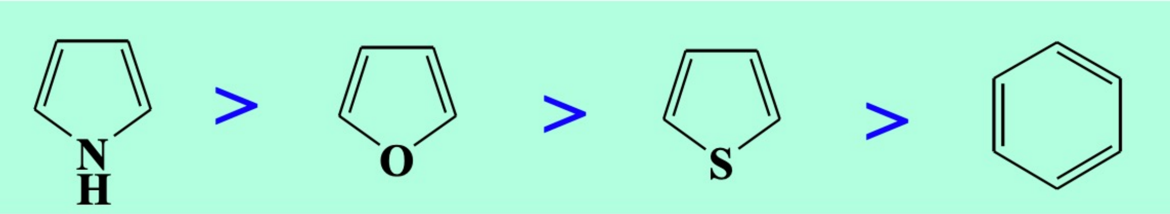
$$Ph_2C(OLi)-CH(Si(CH_3)_3)Ph \longrightarrow Ph_2C{=}CHPh + (CH_3)_3SiOLi$$

五元杂环

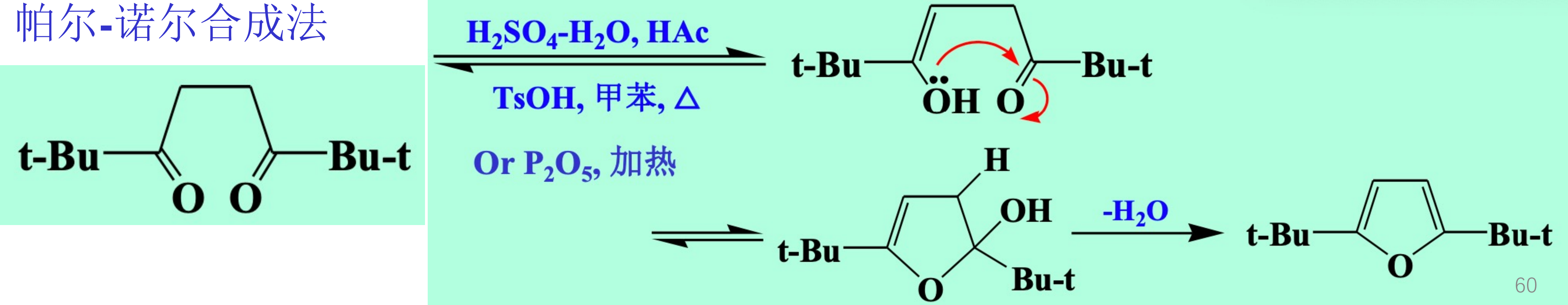
- 芳香性



亲电取代反应的活性顺序为：

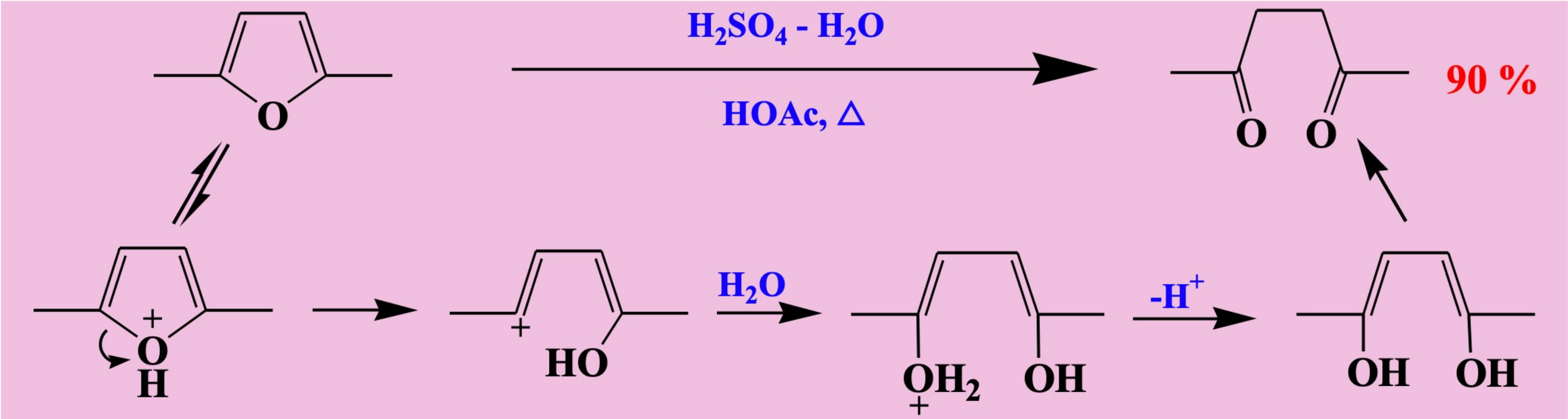


帕尔-诺尔合成法



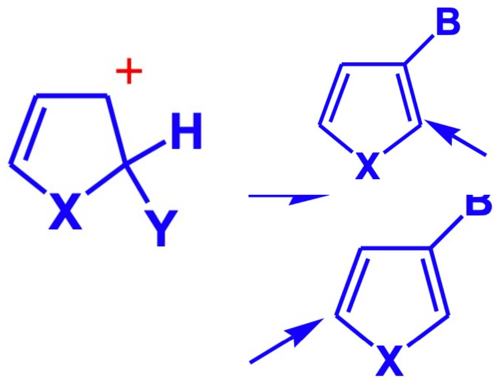
五元杂环

- 稀酸溶液 开环



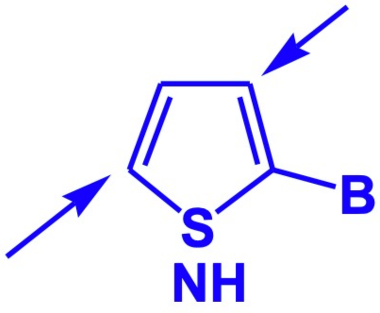
杂原子的定位效应——邻位定位效应

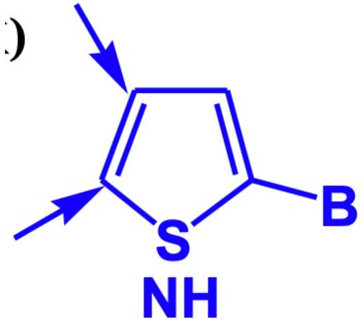
α-位取代:



B为邻对位定位基

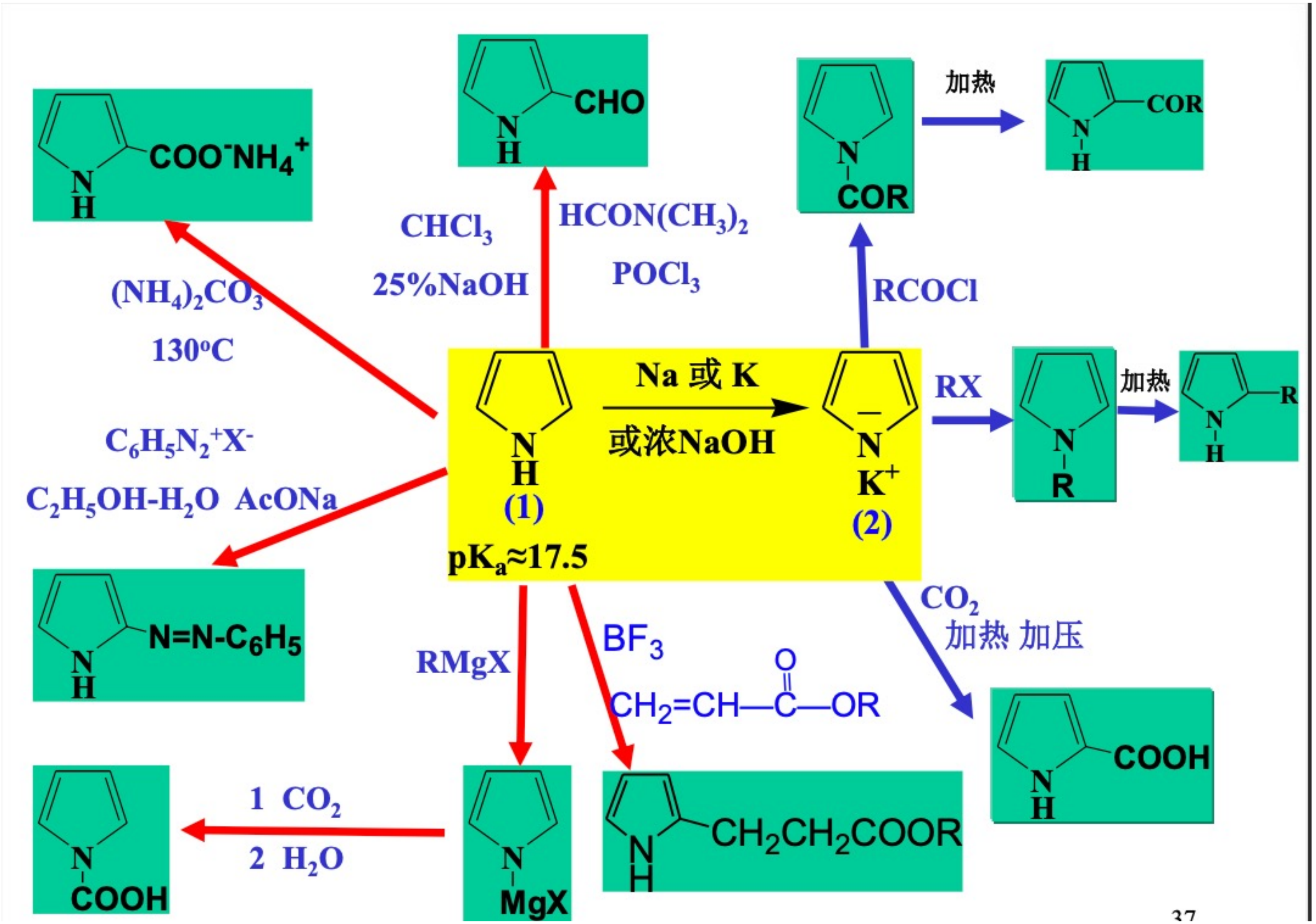
B为间位定位基





B为邻对位定位基 3为间位定位基

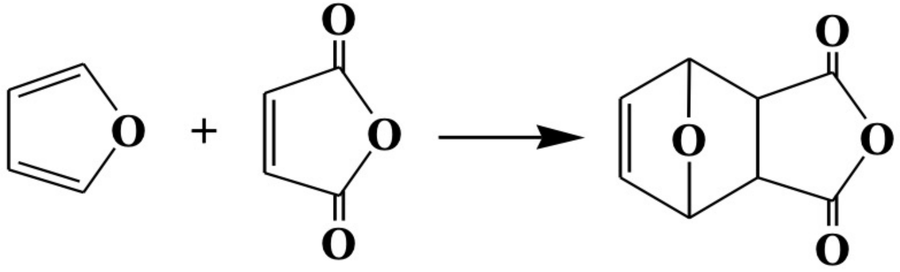
五元杂环

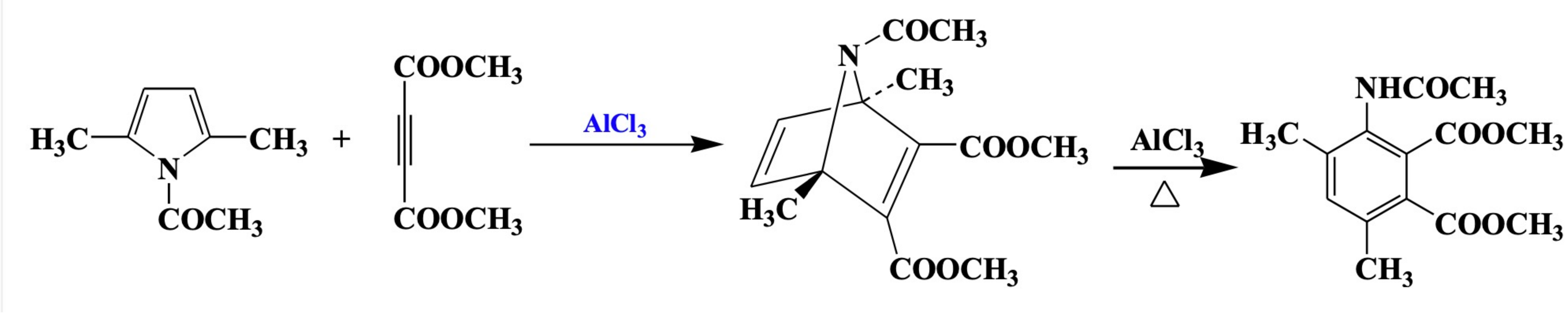


$COO^-NH_4^+$
CHO
N
H
$(NH_4)_2CO_3$
130°C
$CHCl_3$
25%NaOH
$HCON(CH_3)_2$
$POCl_3$
COR
加热
COR
RCOCl
Na 或 K
或浓NaOH
(1)
$pK_a≈17.5$
K^+
(2)
RX
R
加热
R
$C_6H_5N_2^+X^-$
C_2H_5OH-H_2O AcONa
$N=N-C_6H_5$
CO_2
加热 加压
COOH
RMgX
BF_3
$CH_2=CH-C(=O)-OR$
CH_2CH_2COOR
1 CO_2
2 H_2O
COOH
MgX
37

五元杂环

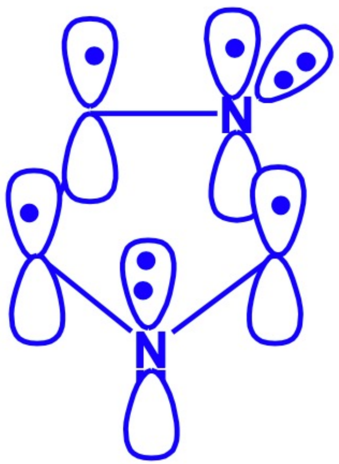
- 呋喃最易发生Diels-Alder反应

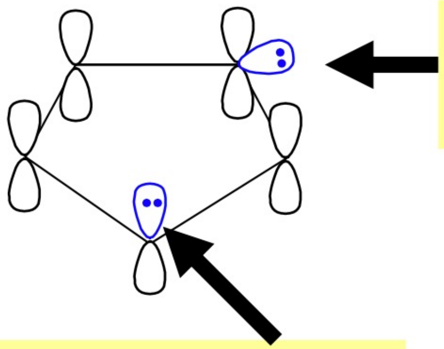




五元杂环

- 唑





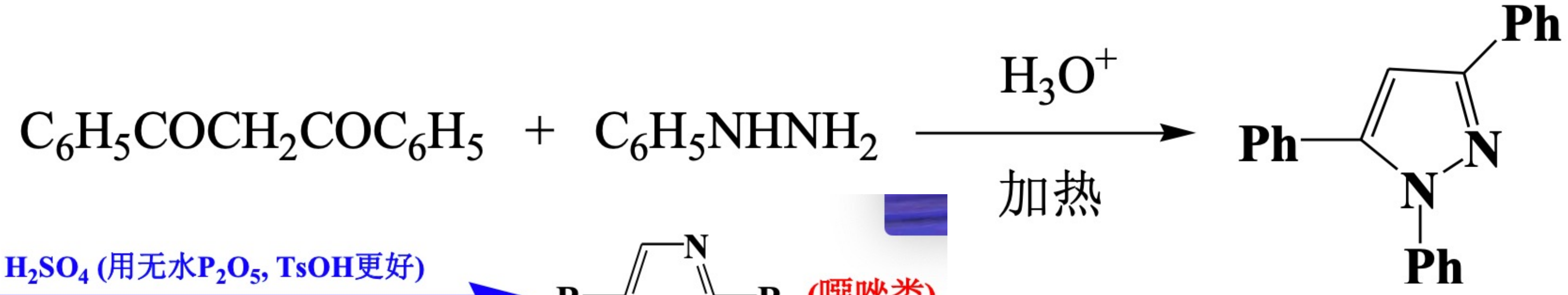
N 的孤电子对处于sp²杂化轨道

吡咯N的孤电子对处于*p*轨道

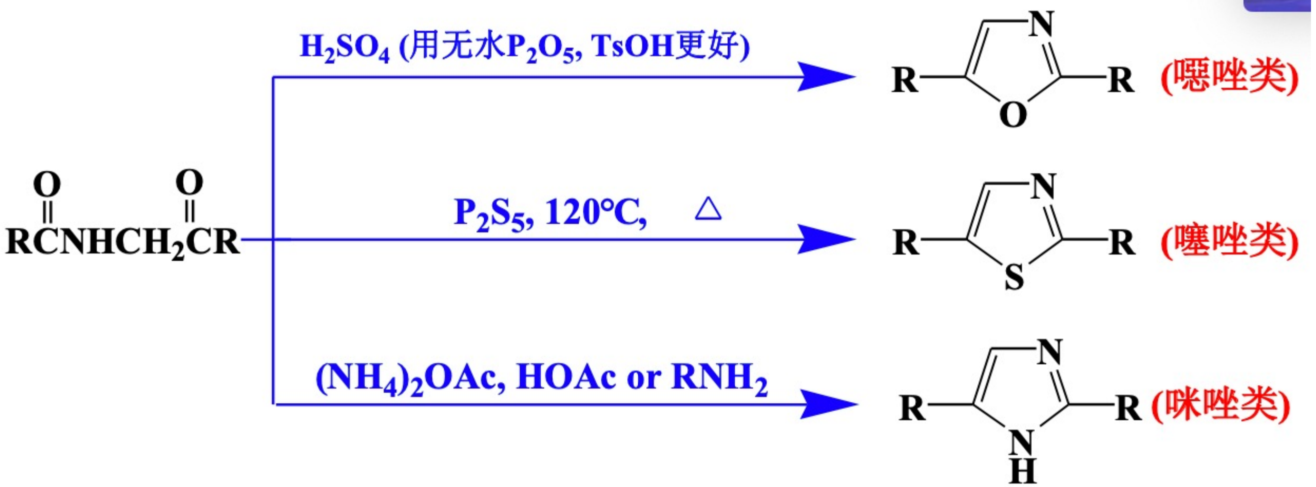
吡啶N与吡咯N均为sp²杂化。

- 合成

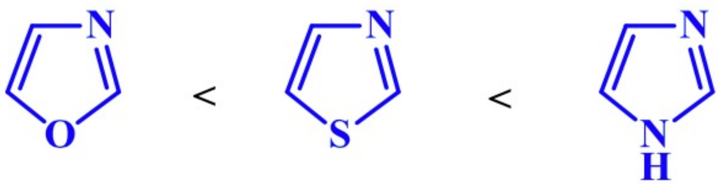
1,3-二羰基化合物合成吡唑和异噁唑



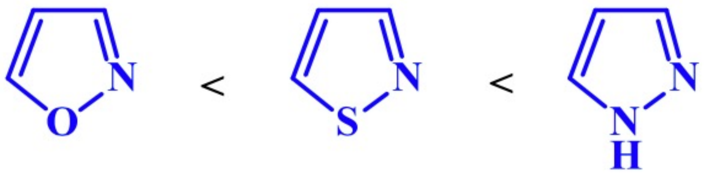
1,3-唑



五元杂环



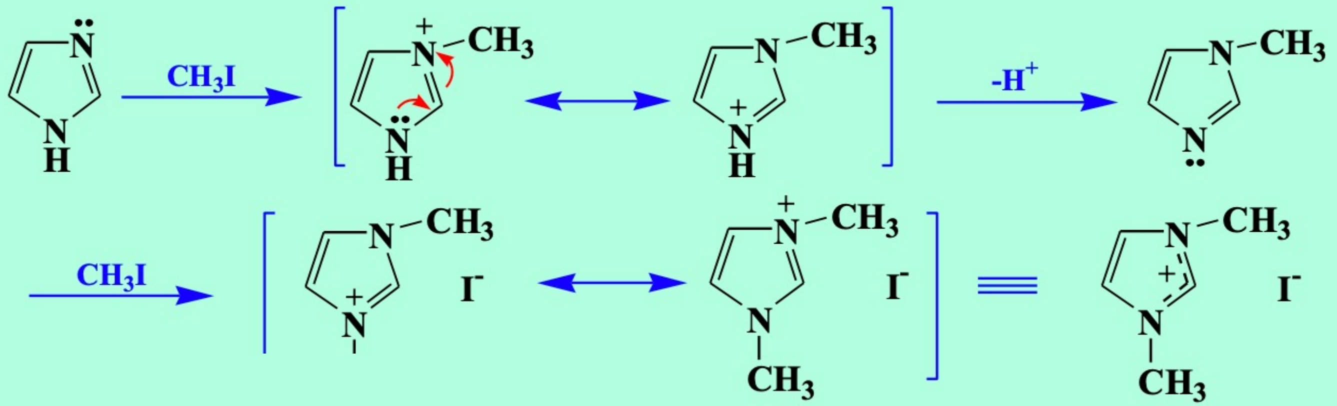
- 唑的亲电取代活性顺序

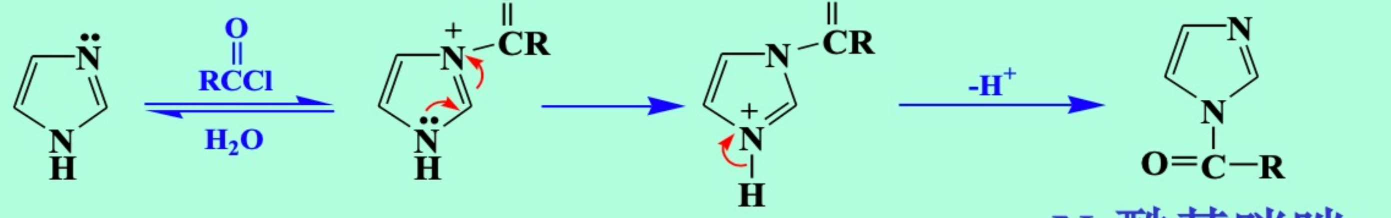


1,2-唑　主要得到**4-**位取代产物
1,3-唑　主要得到**4-**位或**5-**位取代产物

- 傅克反应

总是先吡啶N上发生



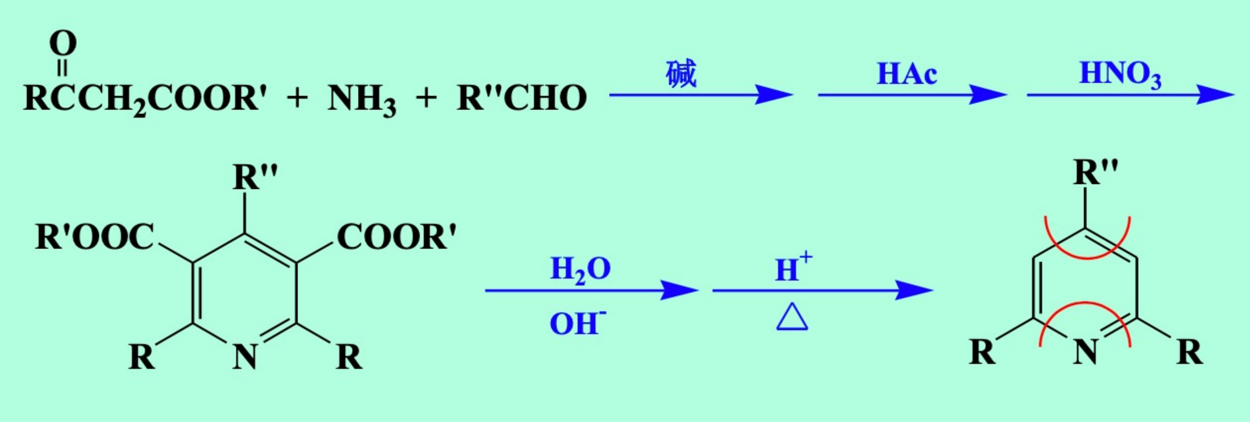


N-酰基咪唑

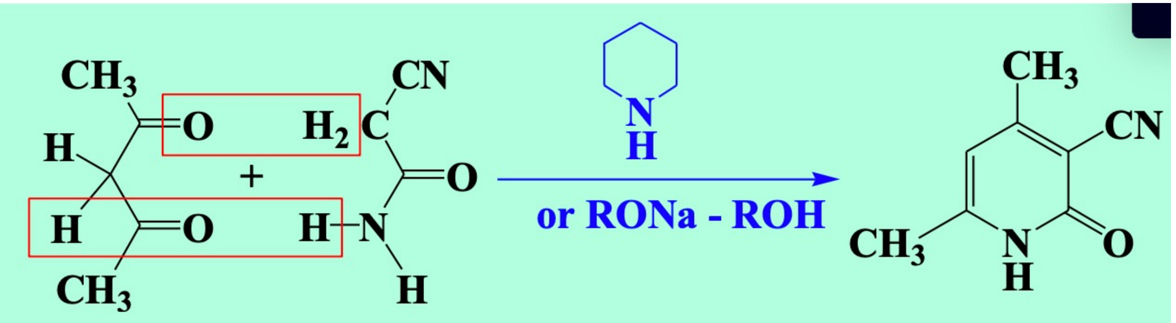
六元杂环

- 合成

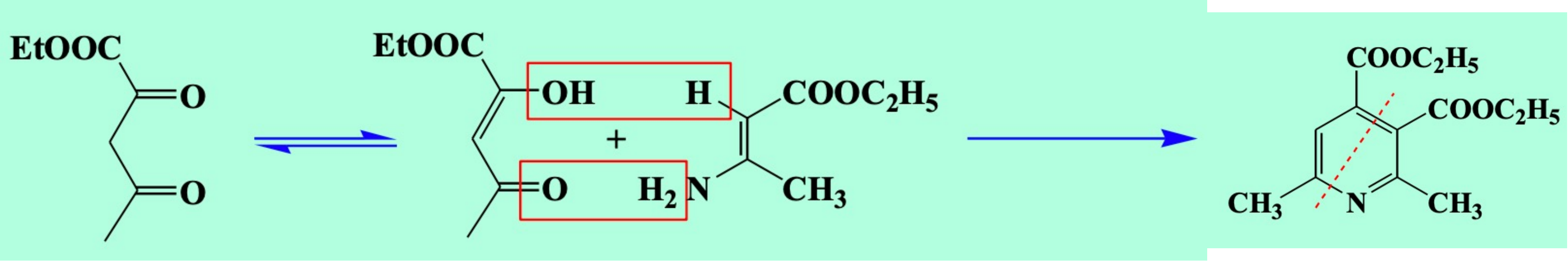
韩奇合成法



β-二羰基化合物与氰乙酰胺合成法



β-二羰基化合物和β-氨基-α,β-不饱和羰基化合物合成法

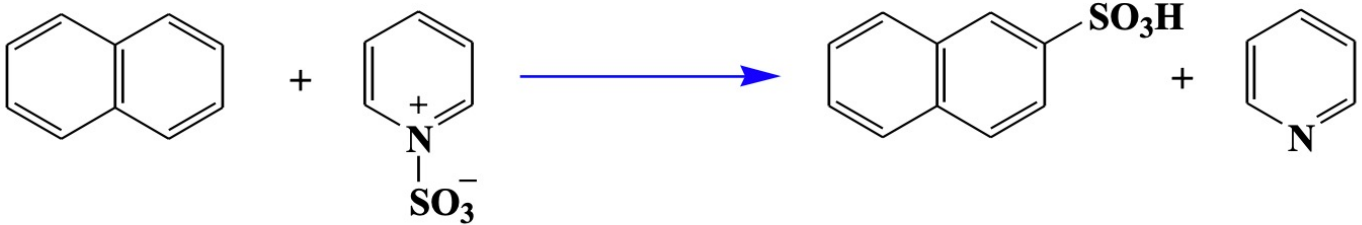


六元杂环

- 亲电反应

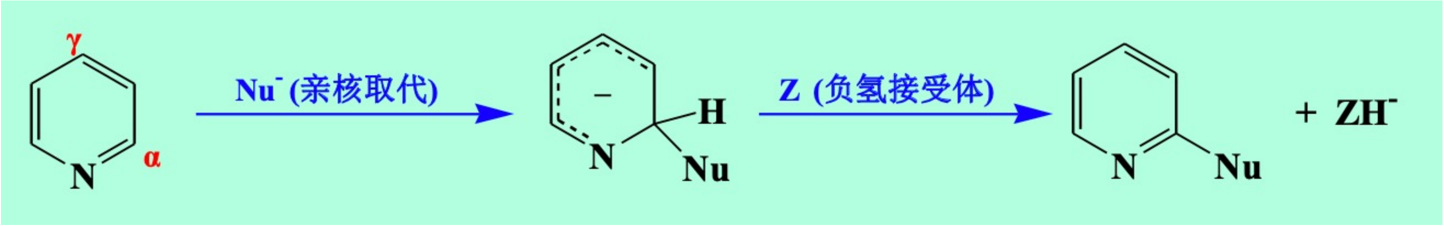
温和条件，亲电试剂主要与N反应；强烈条件，C取代为主

做温和的磺化、硝化、卤化、烷基化、酰基化的试剂



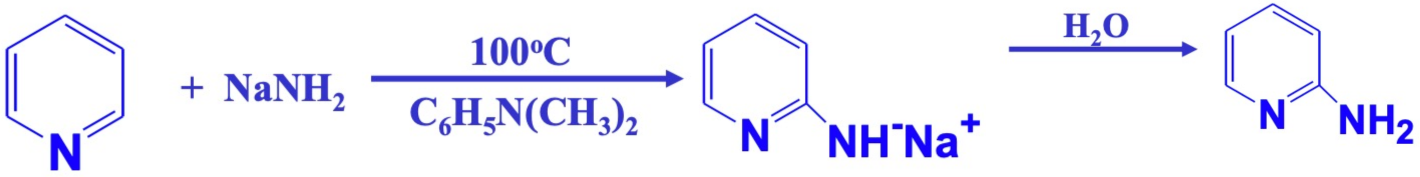
C取代反应主要发生在**3-**位

- 亲核反应



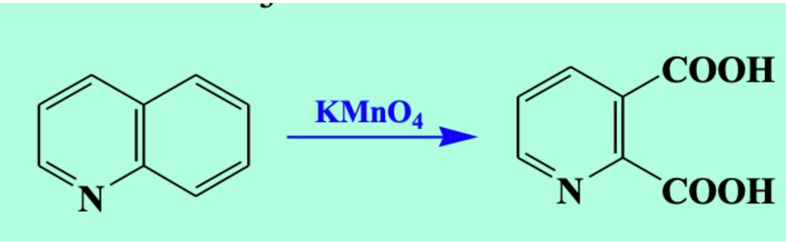
优先在**α**位上发生

齐齐巴宾反应



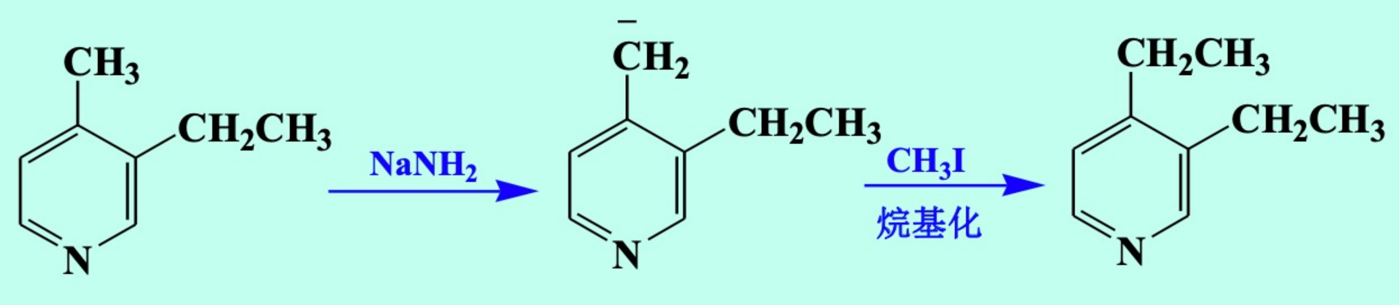
六元杂环

- 氧化还原



- 侧链α-H的反应

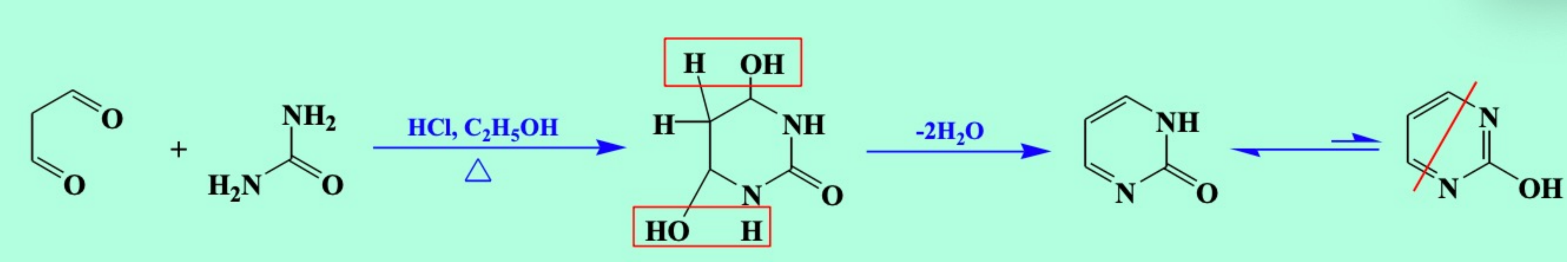
2,4,6-位烷基的α **-H**与羰基α **-H**相似，具有一定酸性。

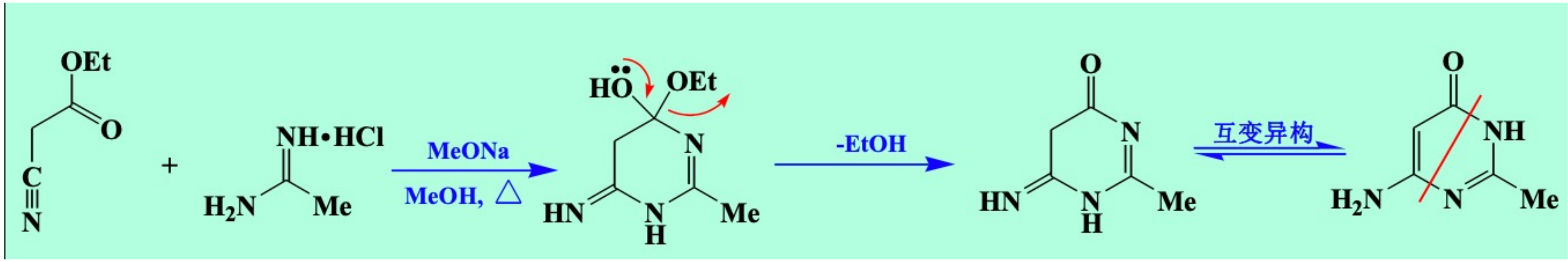


六元杂环

- 嘧啶合成

由β-二羰基化合物（或类似物）与1,1-二胺类化合物合成

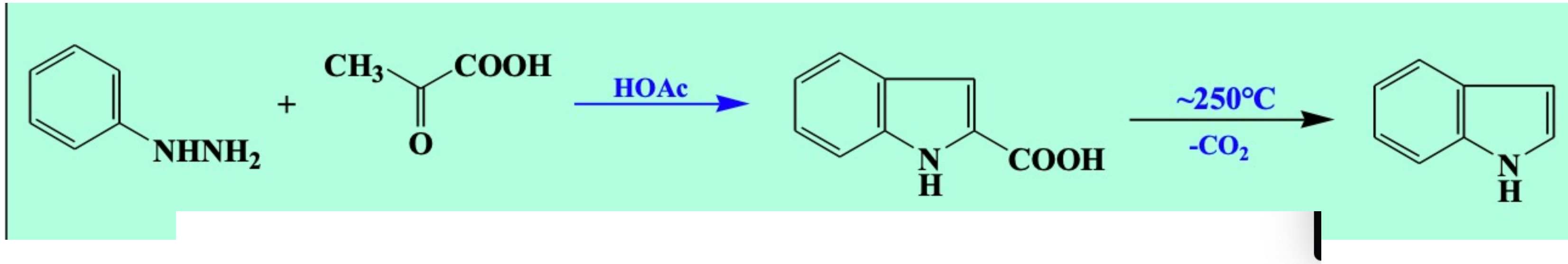


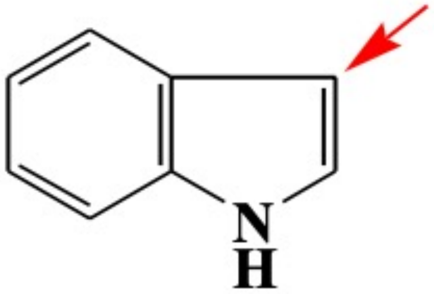


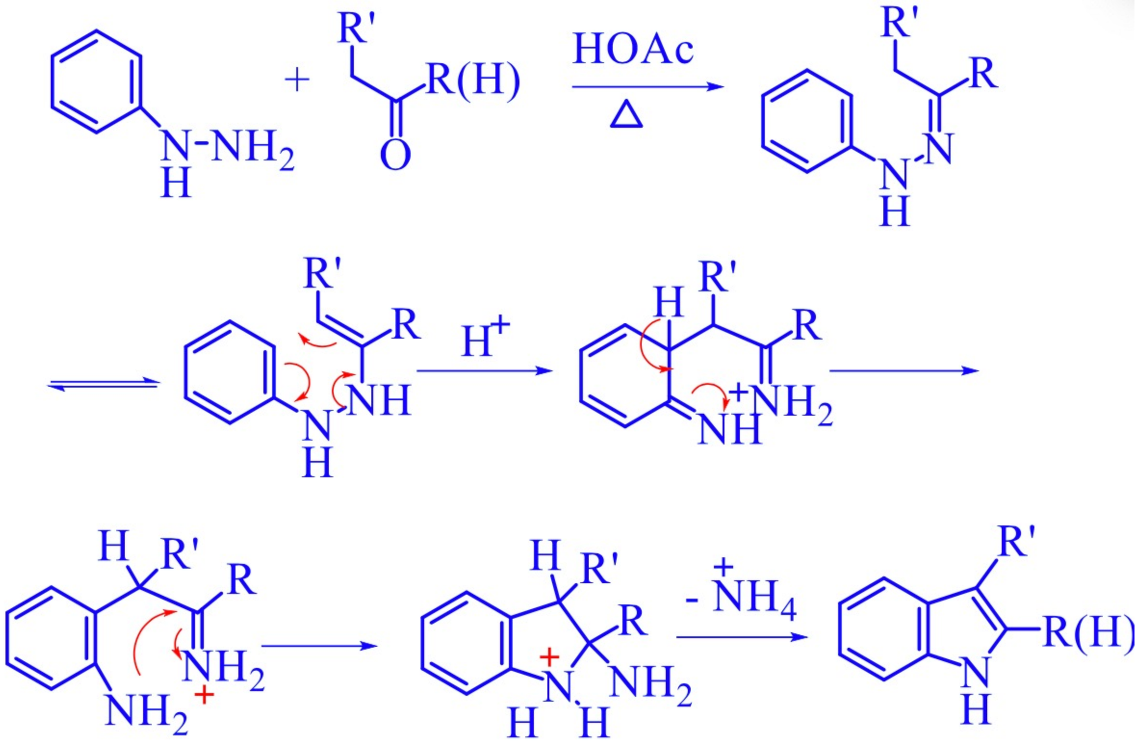
苯并杂环

- 吲哚

费歇尔(Fischer)合成法



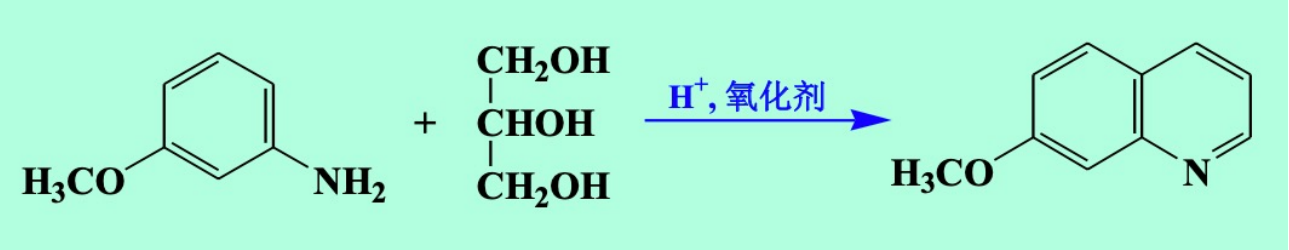


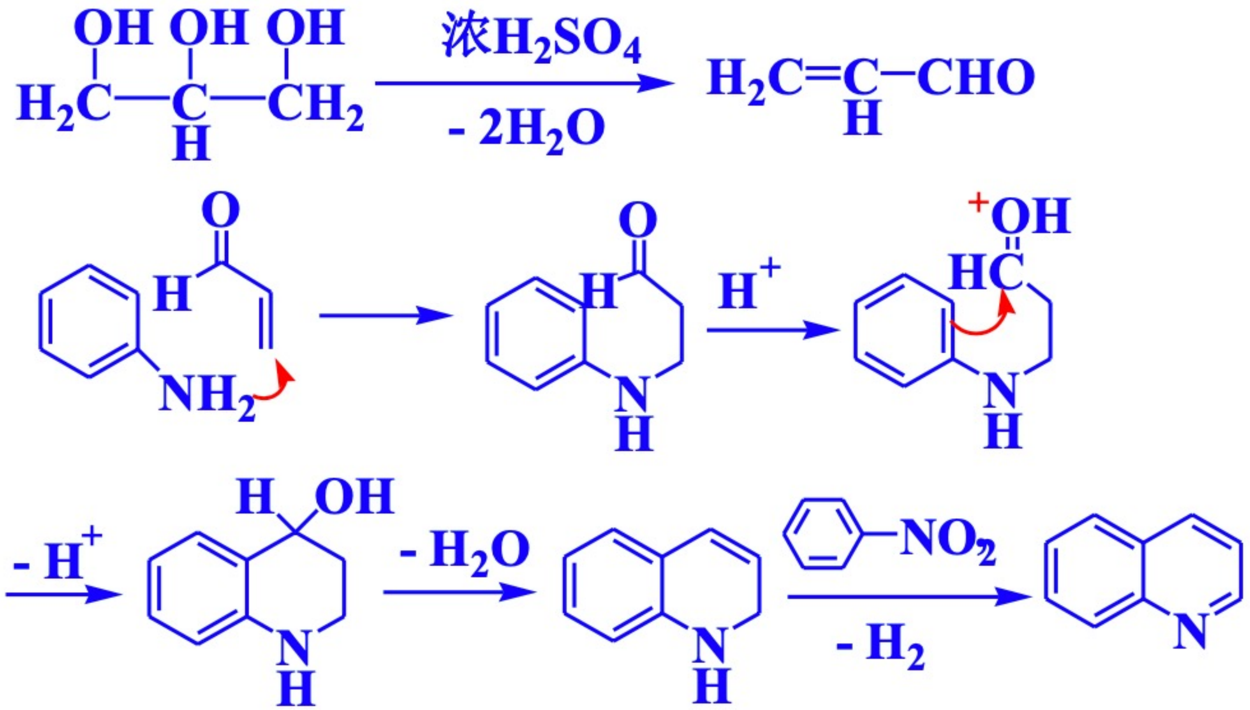


苯并杂环

- 喹啉和异喹啉

斯克劳普(Skraup)反应

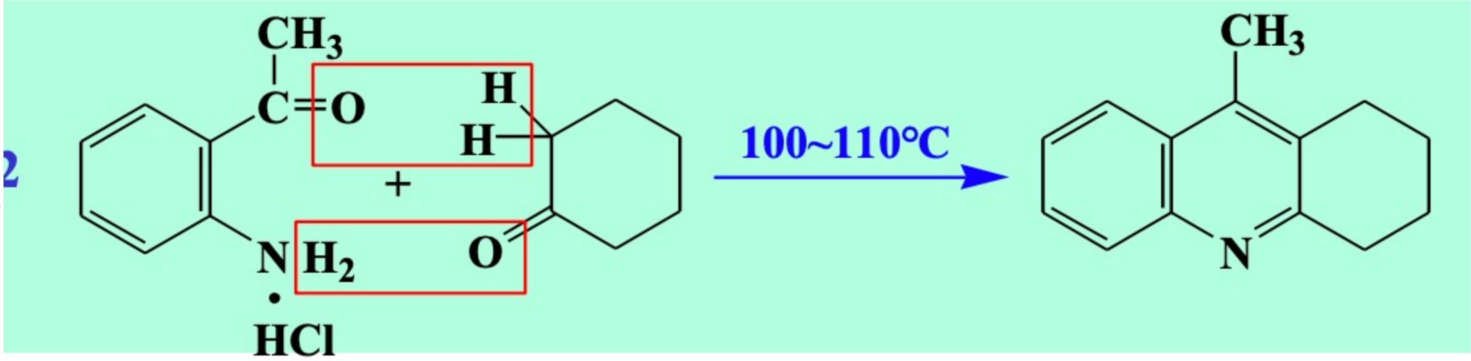




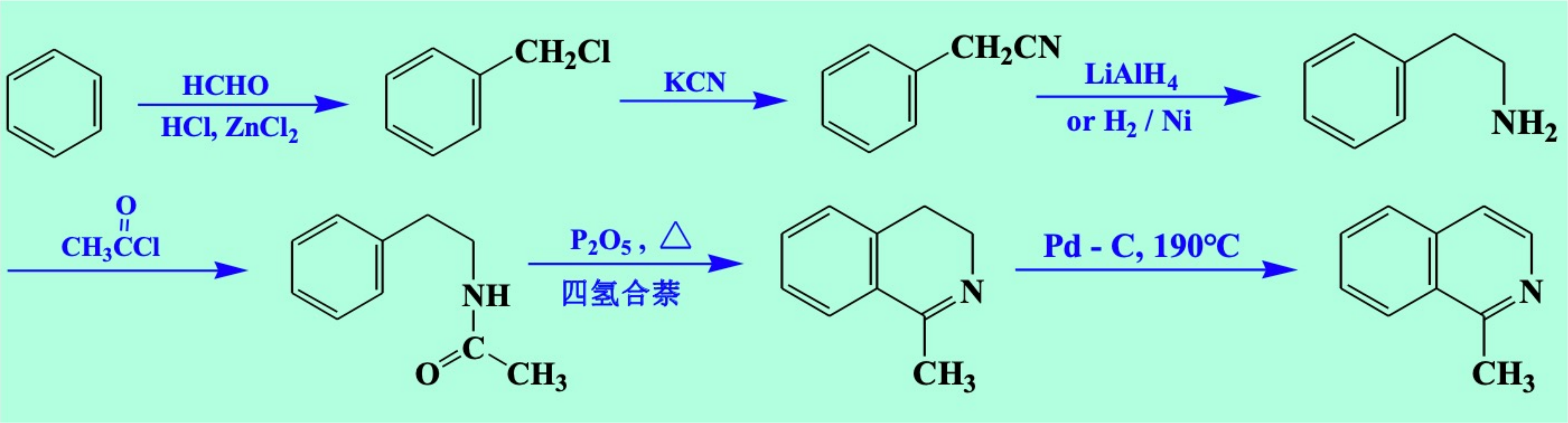
苯并杂环

- 喹啉和异喹啉

弗里德伦德(Friedlander)反应



毕歇尔-纳皮尔拉斯基(Bischler–Napieralski)反应

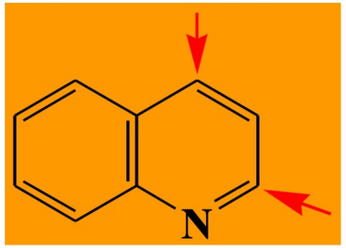


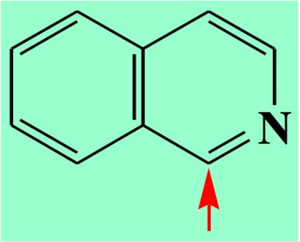
苯并杂环

- 喹啉和异喹啉

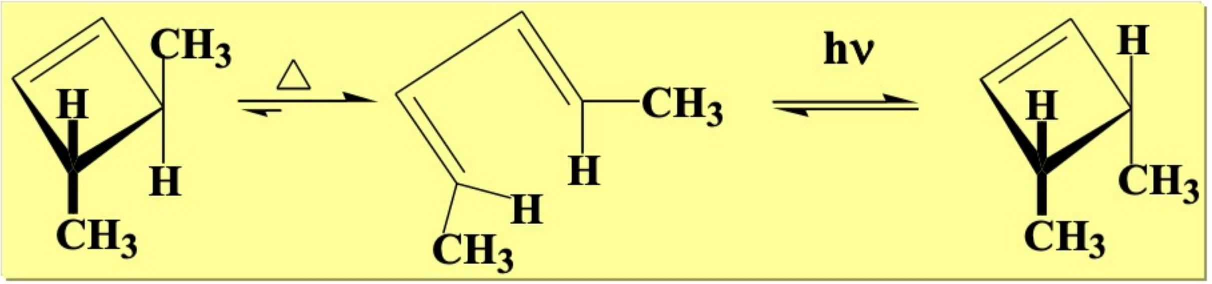
亲电取代 5-位和8-位

亲核取代 喹啉在2位和4位(2位为主)，异喹啉在1位





电环化反应



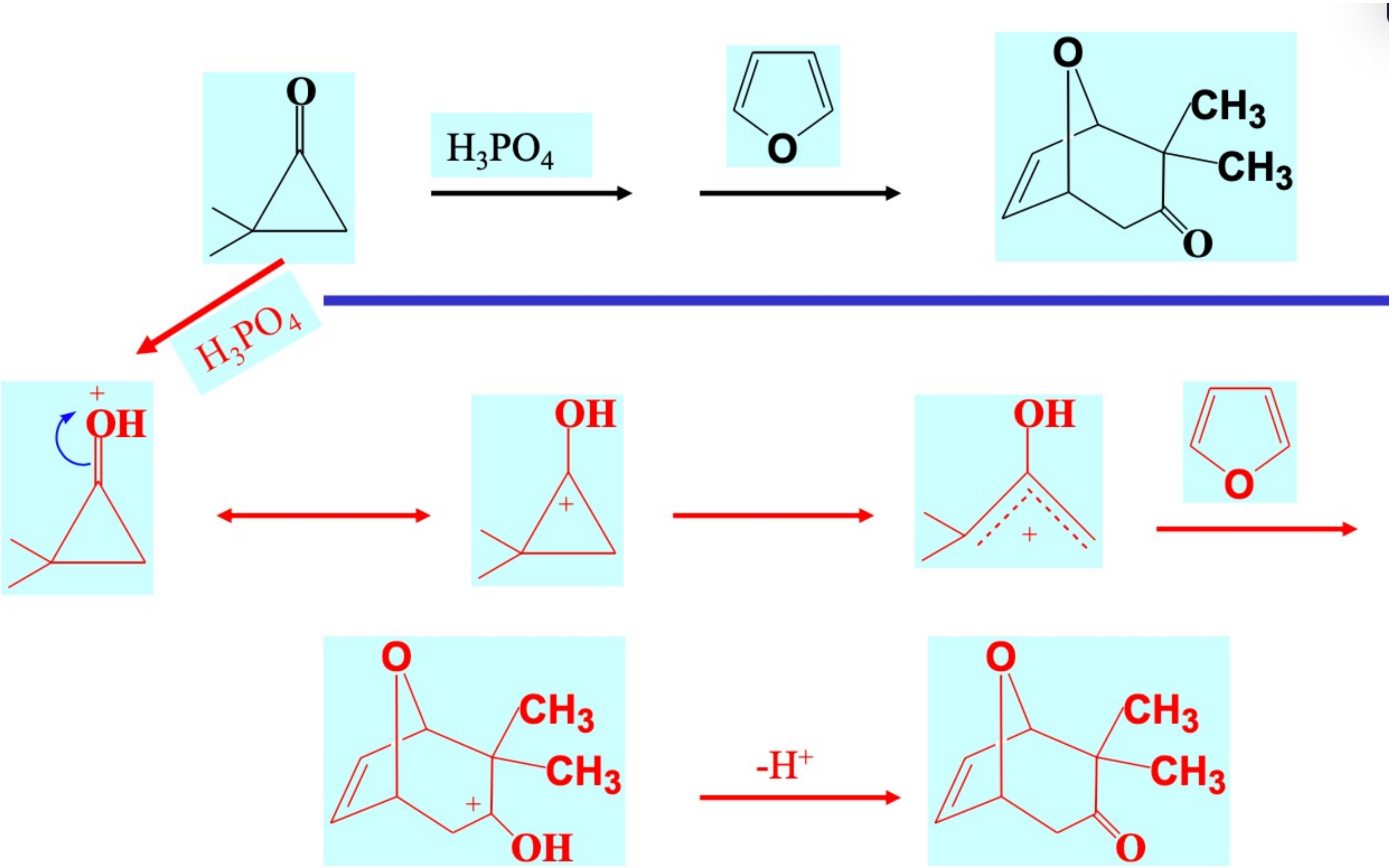
共轭体系π电子数	$4n+2$		$4n$	
顺　　旋	▲	$h\nu$	▲	$h\nu$
	禁阻	允许	允许	禁阻
对　　旋	▲	$h\nu$	▲	$h\nu$
	允许	禁阻	禁阻	允许

电环合与开环是逆反应，遵守同一规则

环加成反应

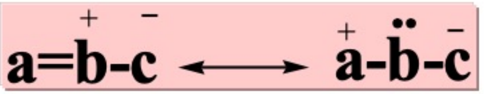
参与反应的π电子数	$4n+2$		$4n$	
同面----同面	▲	$h\nu$	▲	$h\nu$
	允许	禁阻	禁阻	允许
同面----异面	▲	$h\nu$	▲	$h\nu$
	禁阻	允许	允许	禁阻

环加成反应

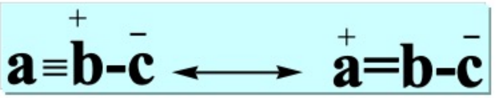


环加成反应

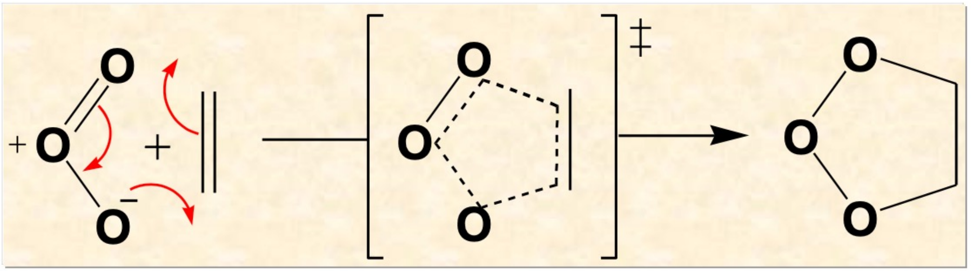
- 1,3-偶极环加成反应

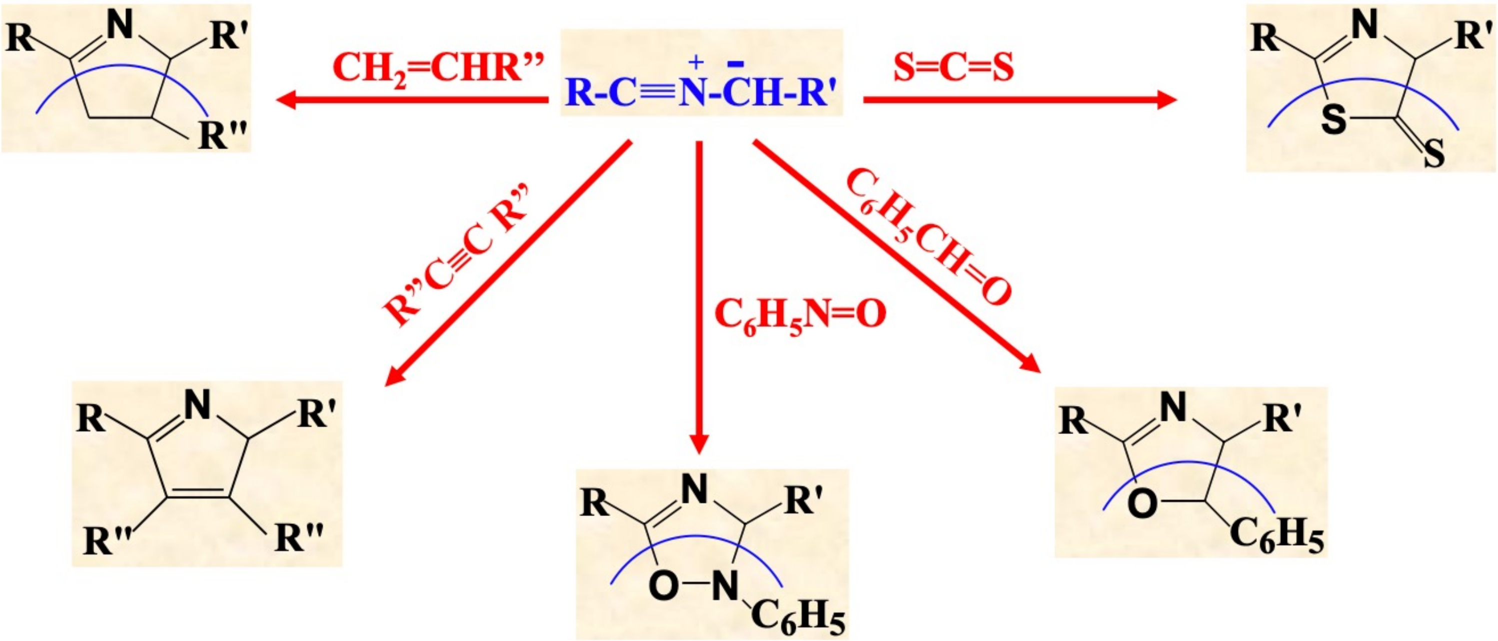


$a=\overset{+}{b}-\overset{-}{c} \longleftrightarrow \overset{+}{a}-\ddot{b}-\overset{-}{c}$

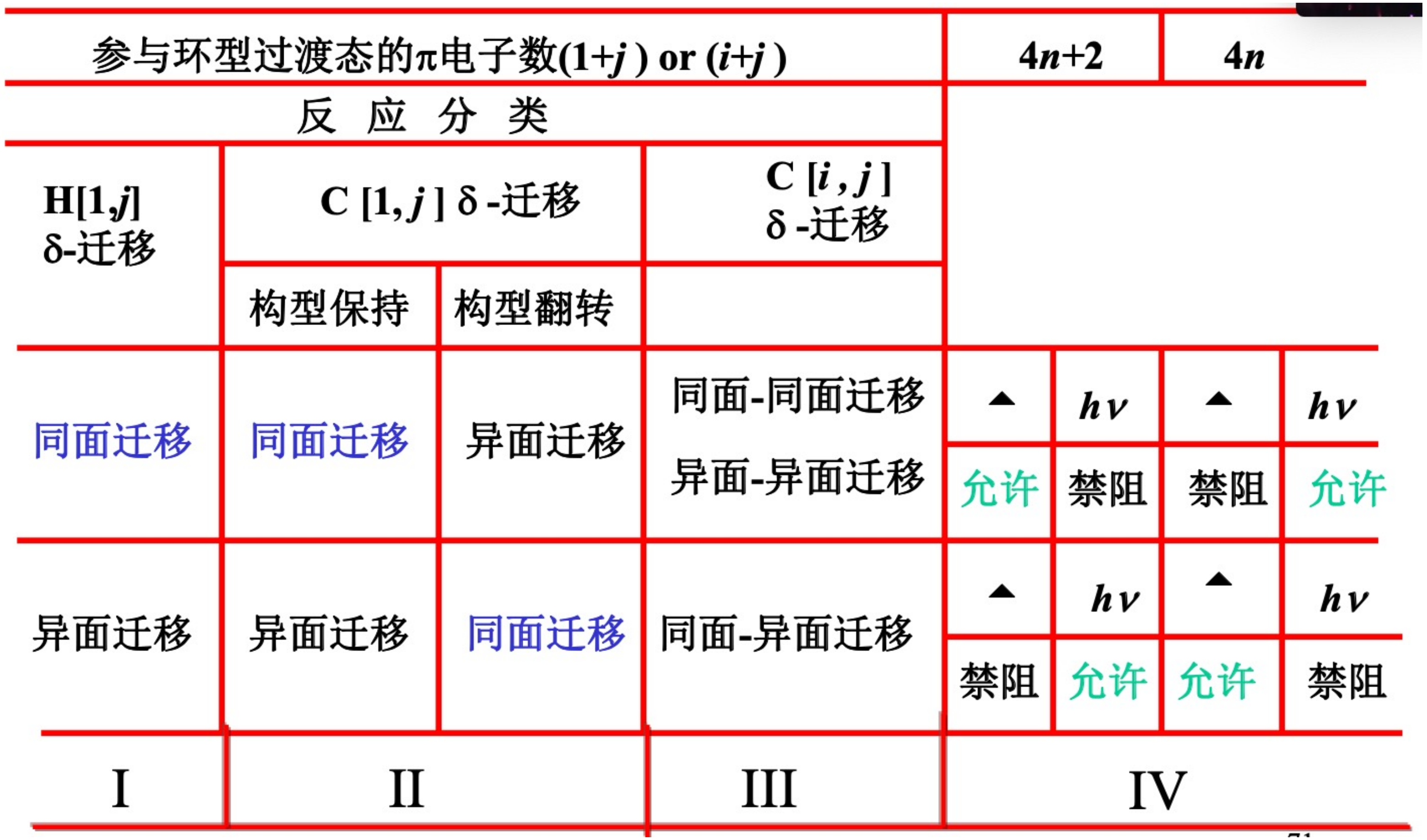


$a\equiv\overset{+}{b}-\overset{-}{c} \longleftrightarrow \overset{+}{a}=b-\overset{-}{c}$





σ-迁移反应



<table>
<tr><td colspan="4">参与环型过渡态的π电子数(1+j) or (i+j)</td><td colspan="2">4n+2</td><td colspan="2">4n</td></tr>
<tr><td colspan="4">反应分类</td><td colspan="4" rowspan="3"></td></tr>
<tr><td rowspan="2">H[1,j]
δ-迁移</td><td colspan="2">C [1, j] δ -迁移</td><td rowspan="2">C [i , j]
δ -迁移</td></tr>
<tr><td>构型保持</td><td>构型翻转</td></tr>
<tr><td rowspan="2">同面迁移</td><td rowspan="2">同面迁移</td><td rowspan="2">异面迁移</td><td rowspan="2">同面-同面迁移
异面-异面迁移</td><td>▲</td><td>hν</td><td>▲</td><td>hν</td></tr>
<tr><td>允许</td><td>禁阻</td><td>禁阻</td><td>允许</td></tr>
<tr><td rowspan="2">异面迁移</td><td rowspan="2">异面迁移</td><td rowspan="2">同面迁移</td><td rowspan="2">同面-异面迁移</td><td>▲</td><td>hν</td><td>▲</td><td>hν</td></tr>
<tr><td>禁阻</td><td>允许</td><td>允许</td><td>禁阻</td></tr>
<tr><td>I</td><td colspan="2">II</td><td>III</td><td colspan="4">IV</td></tr>
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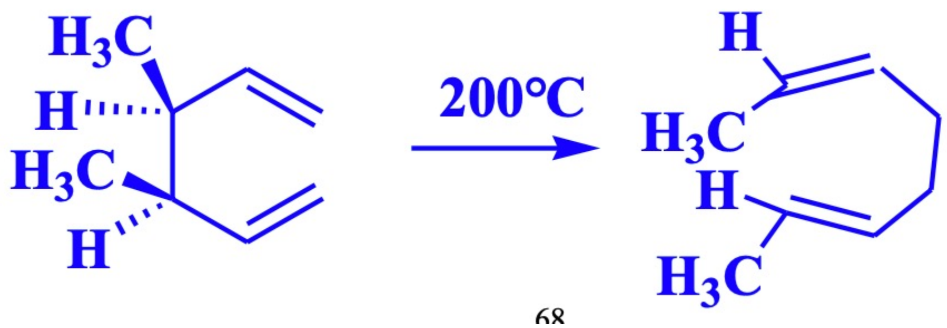
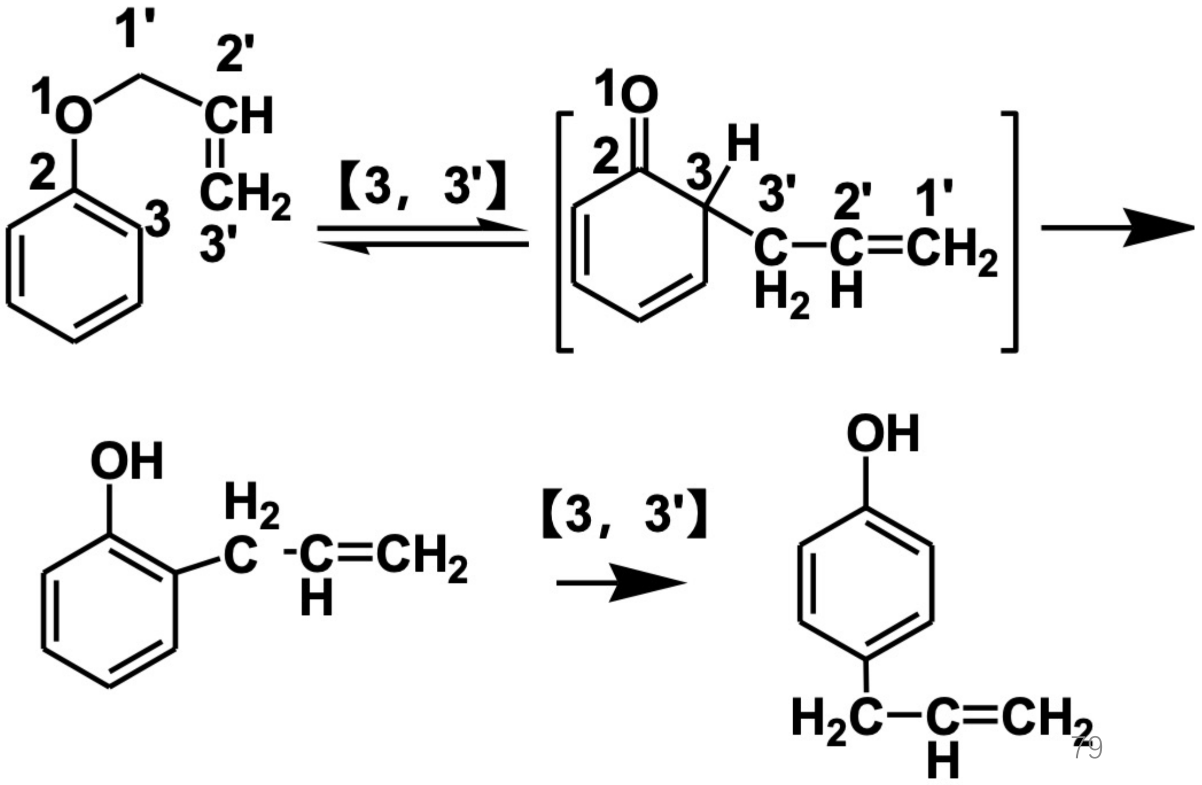
σ-迁移反应

- [3，3] σ-迁移

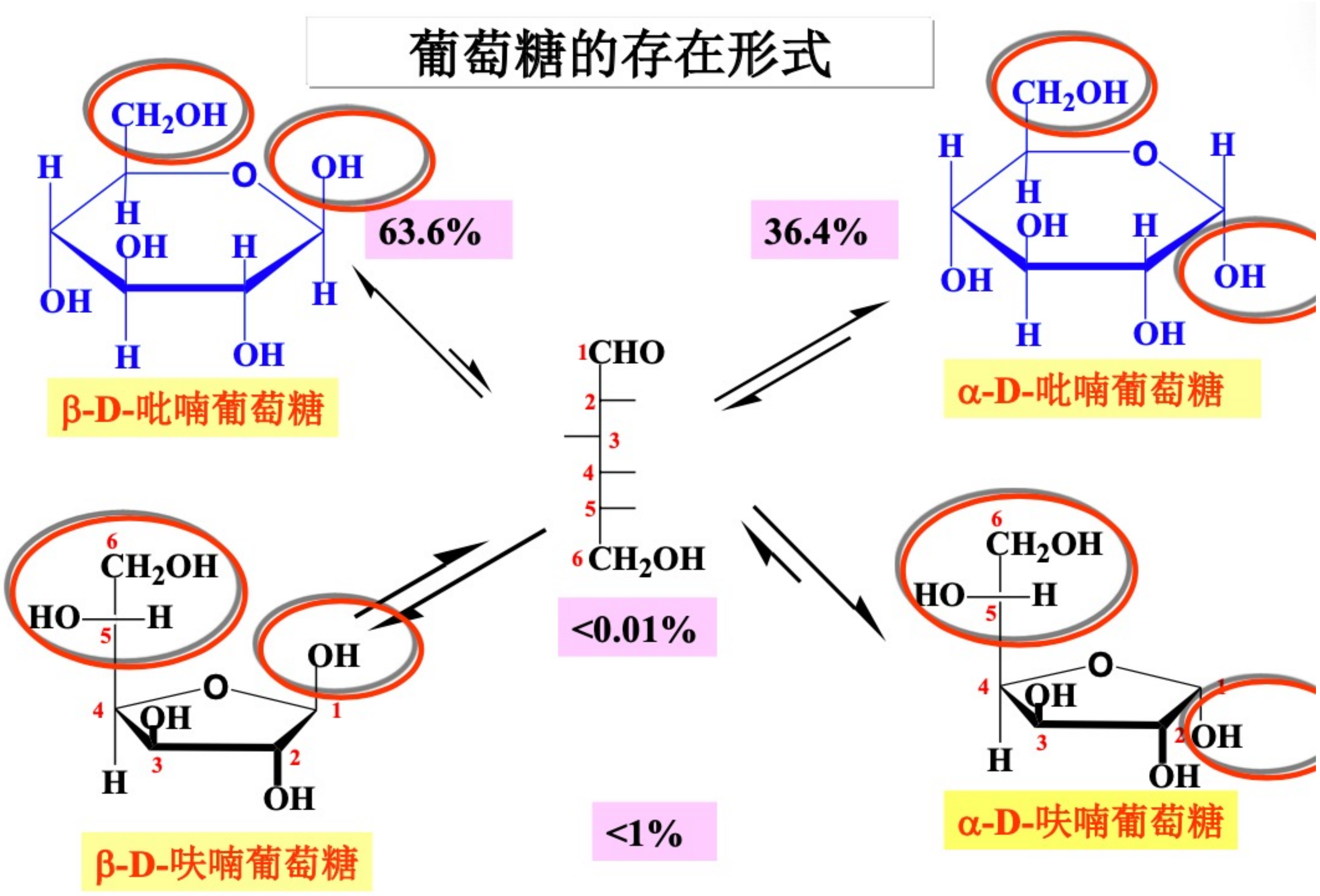
Cope重排



Claisen重排



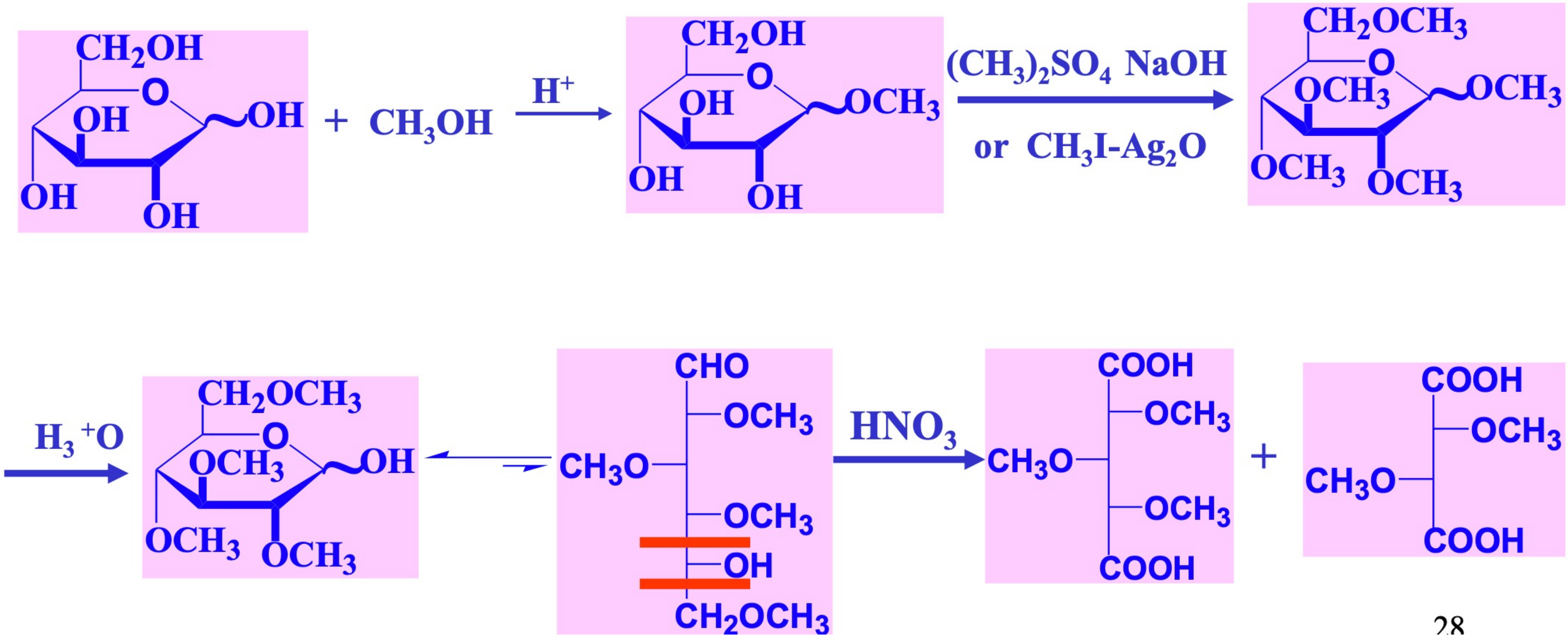
糖


葡萄糖的存在形式
63.6%
β-D-吡喃葡萄糖
36.4%
α-D-吡喃葡萄糖
<0.01%
<1%
β-D-呋喃葡萄糖
α-D-呋喃葡萄糖
1 CHO
6 CH2OH
CH2OH
OH
H
O
HO

糖

- 结构测定

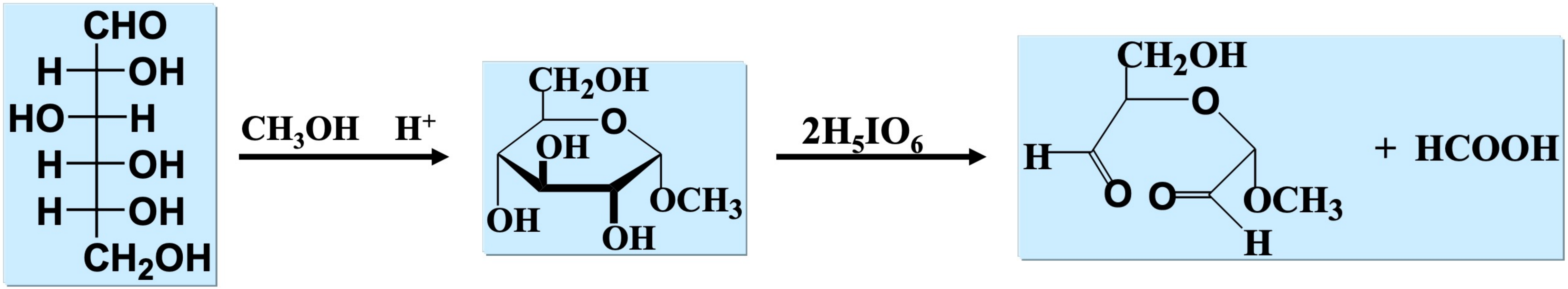
  甲基化法 （确定形成半缩醛羟基的位置）



糖

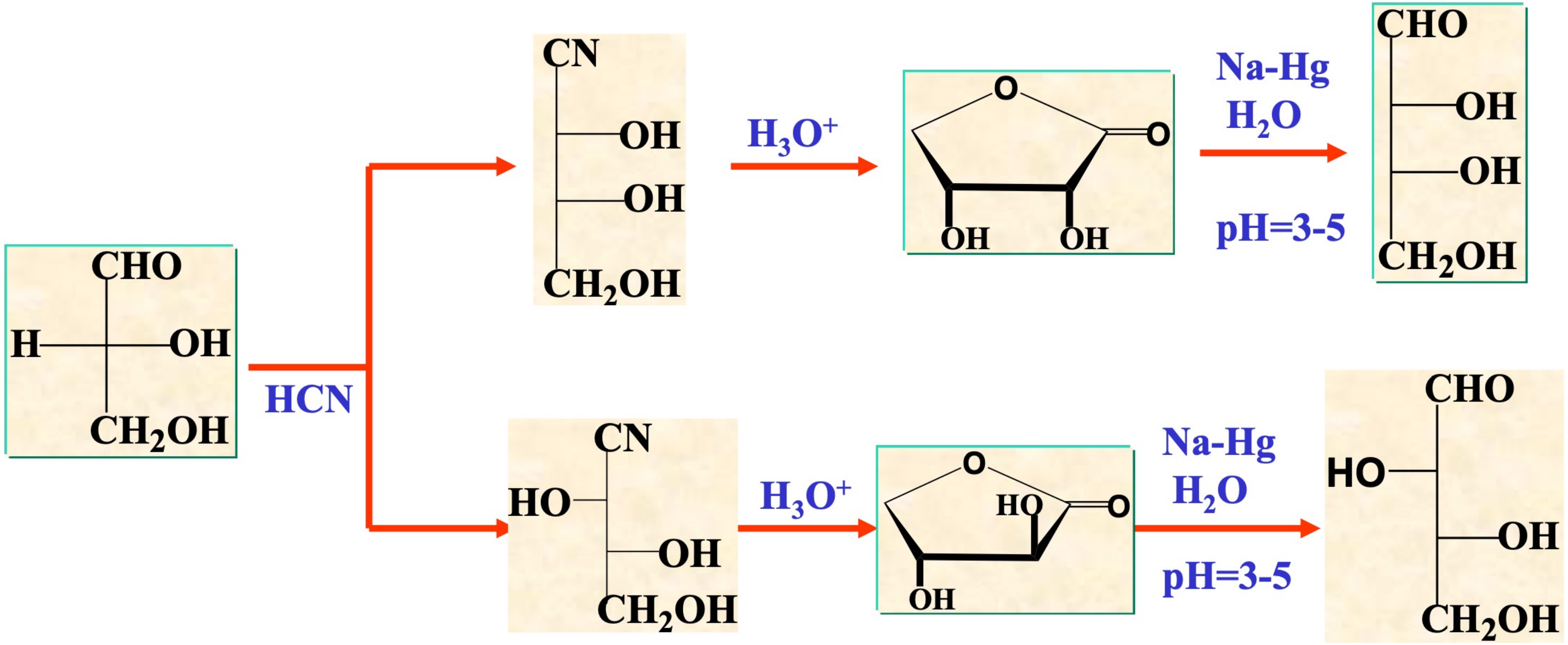
- 结构测定

高碘酸法 确定形成半缩醛羟基的位置） **打断所有α-二醇的碳碳键**



糖

- 糖的递增反应-- 克里安尼(Kiliani)氰化增碳法

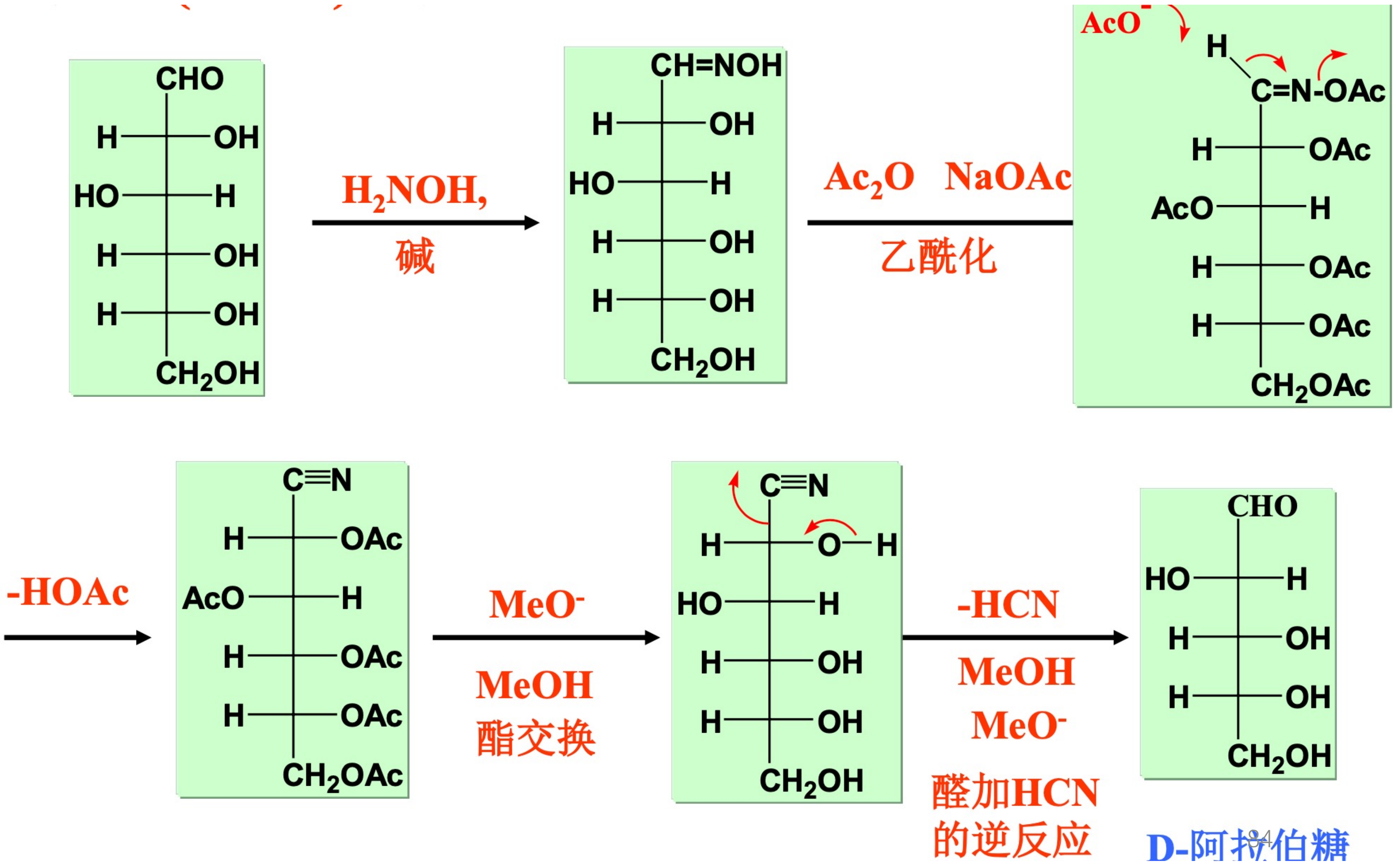


用**Na-Hg**乙醇溶液还原，则产物两端均为醇

糖

- 糖的递降反应

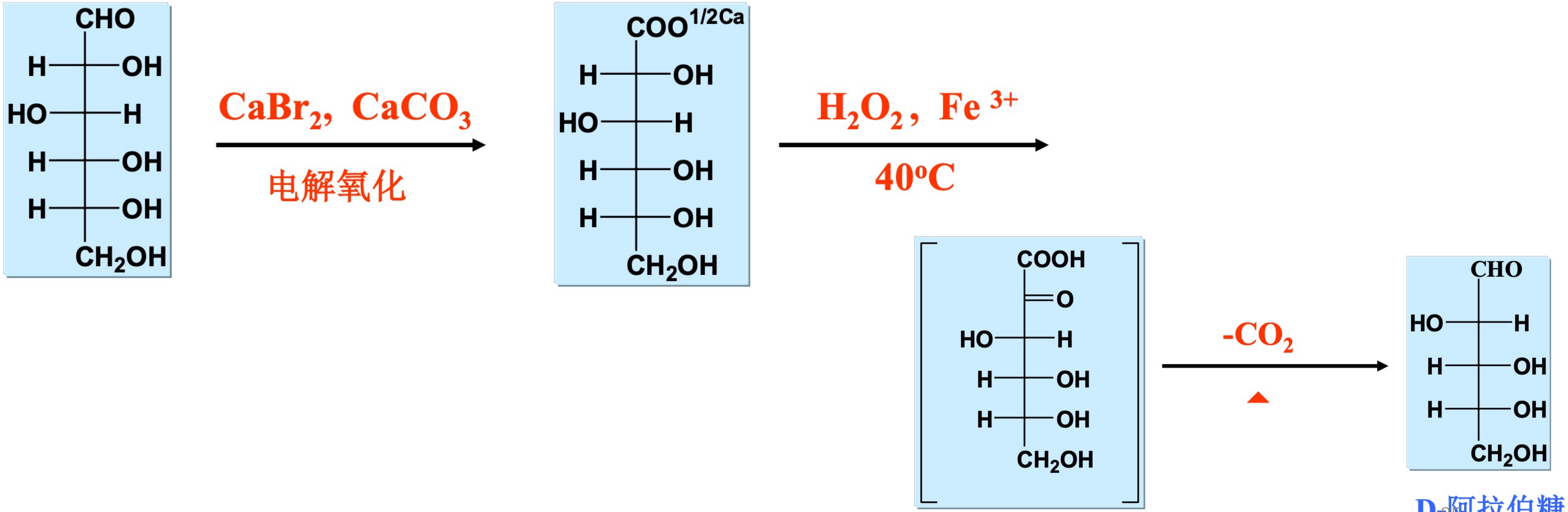
佛尔(Wohl)递降法



糖

- 糖的递降反应

芦福(Ruff)递降法

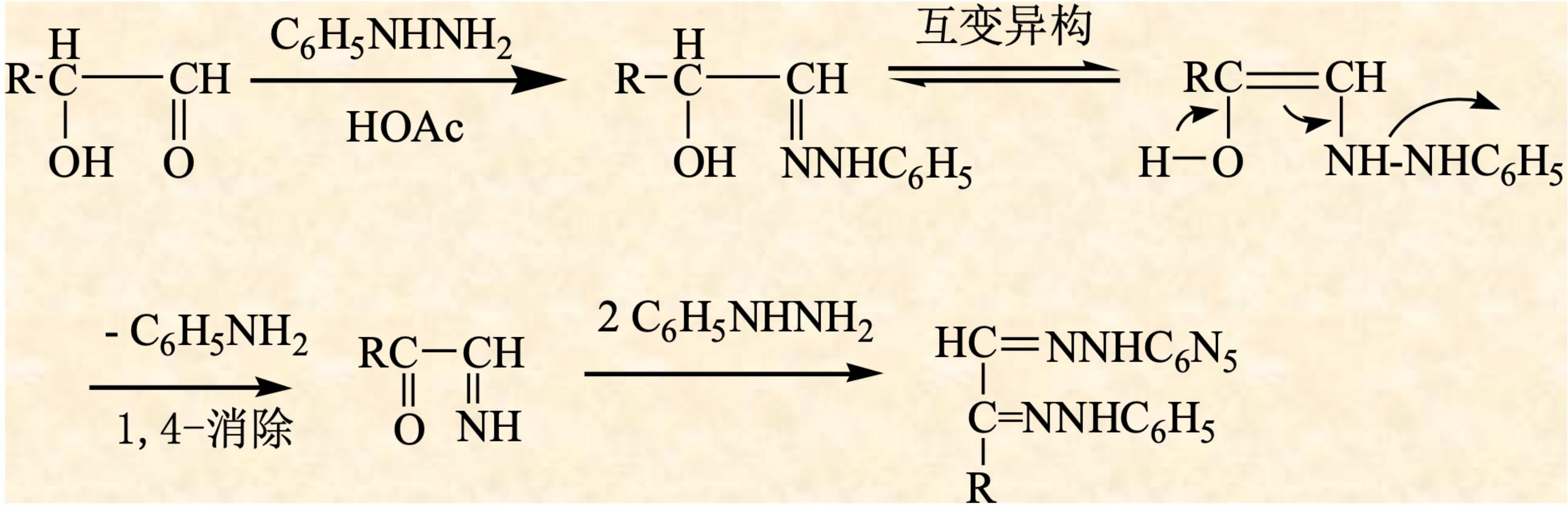


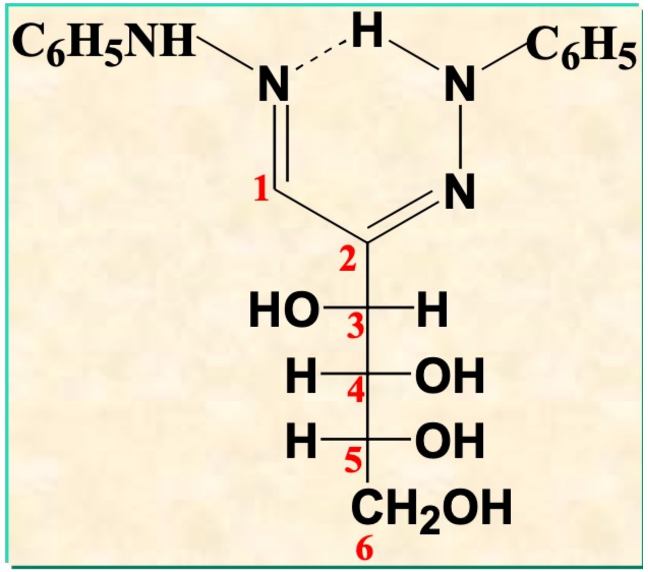
D-阿拉伯糖

糖

- 形成糖脎

一分子糖和三分子苯肼

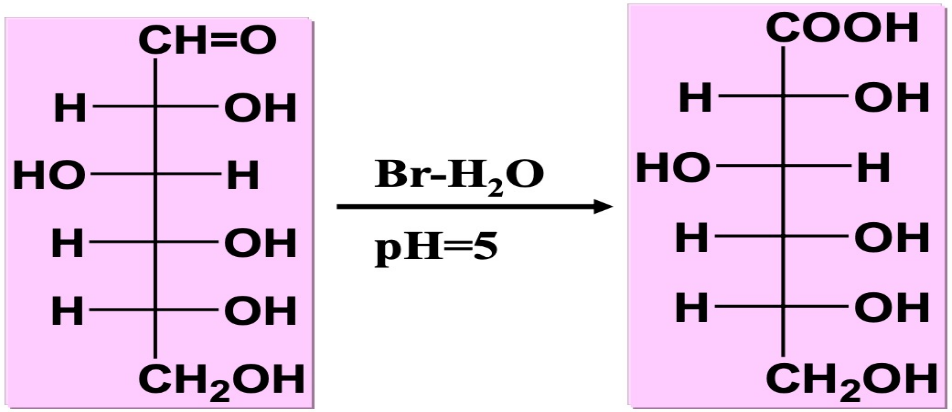




糖

- 氧化反应

溴水氧化



D-葡萄糖酸

斐林试剂、土伦试剂、本尼迪特试剂氧化(用于鉴定)

斐林试剂（硫酸酮和碱性酒石酸钾钠）

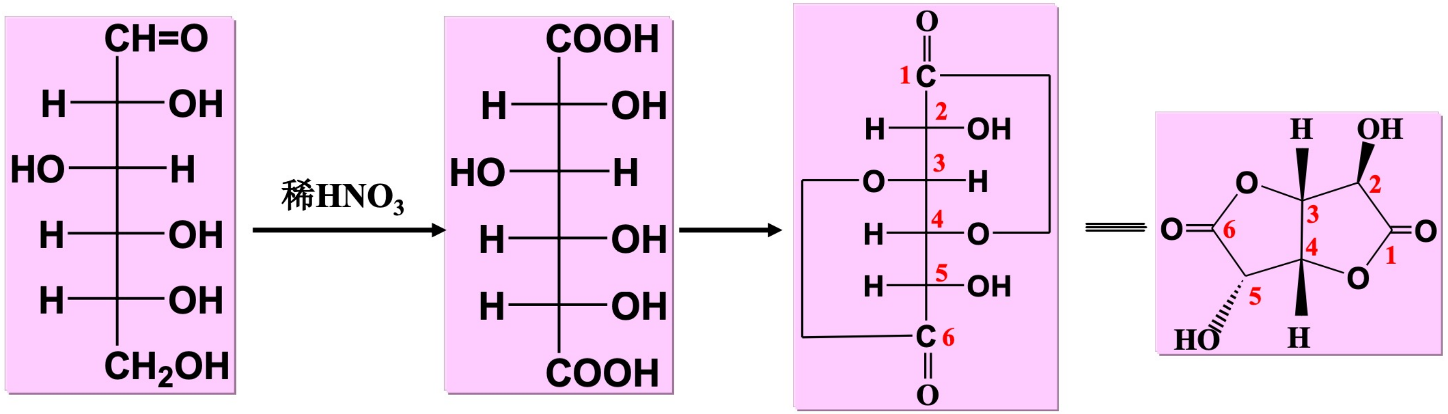
土伦试剂（硝酸银的氨水溶液）

本尼迪特试剂（柠檬酸、硫酸铜、碳酸钠配制成

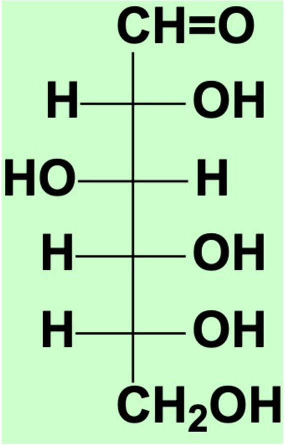
糖

- 氧化反应

硝酸氧化



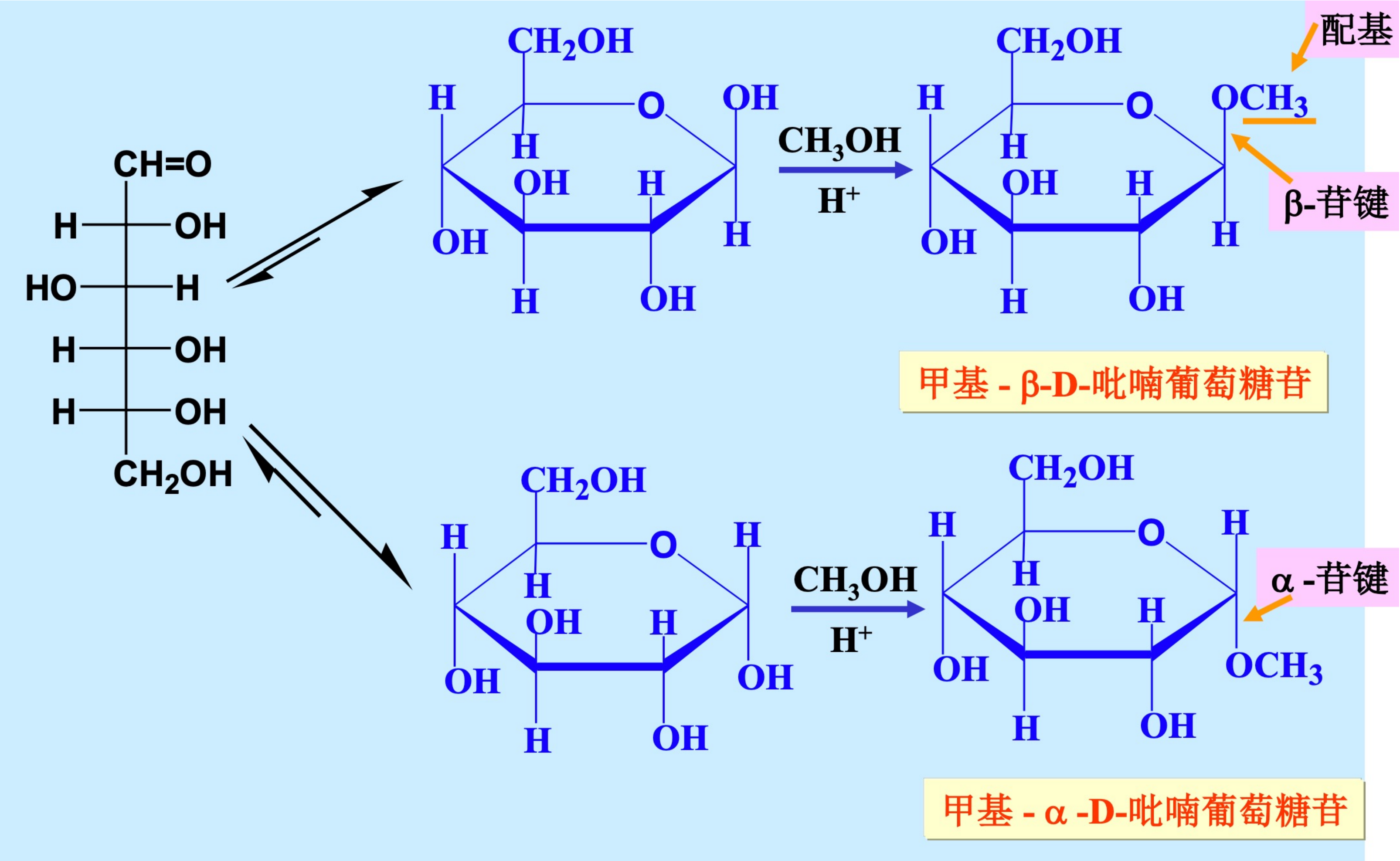
高碘酸氧化



$$+\ 5HIO_4 \longrightarrow 5\,HCOOH + CH_2O$$

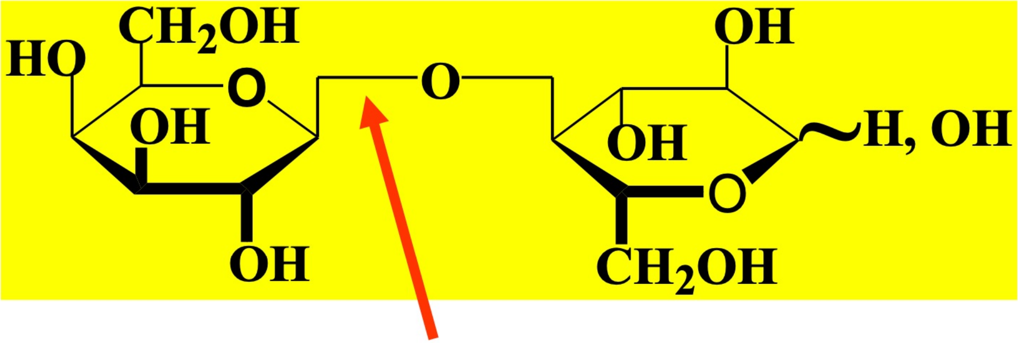
糖

- 糖苷 （配基+糖的残基+(糖)苷 ）



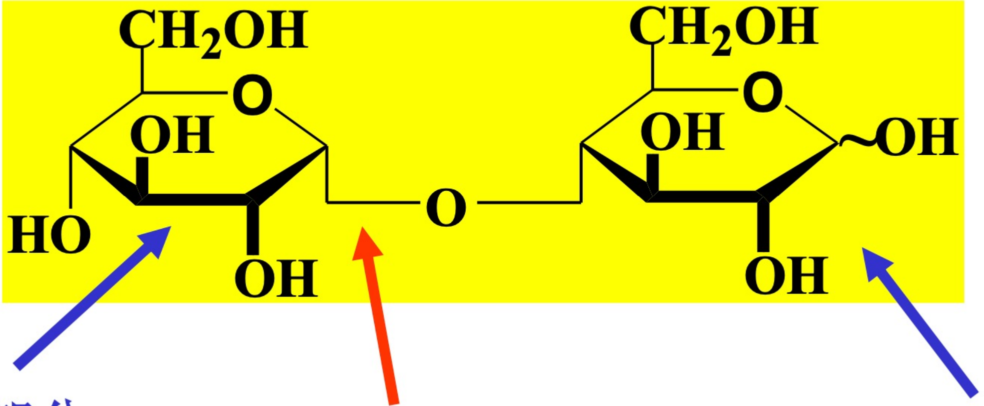
糖

- 乳糖



β-1,4 -苷键

- 麦芽糖

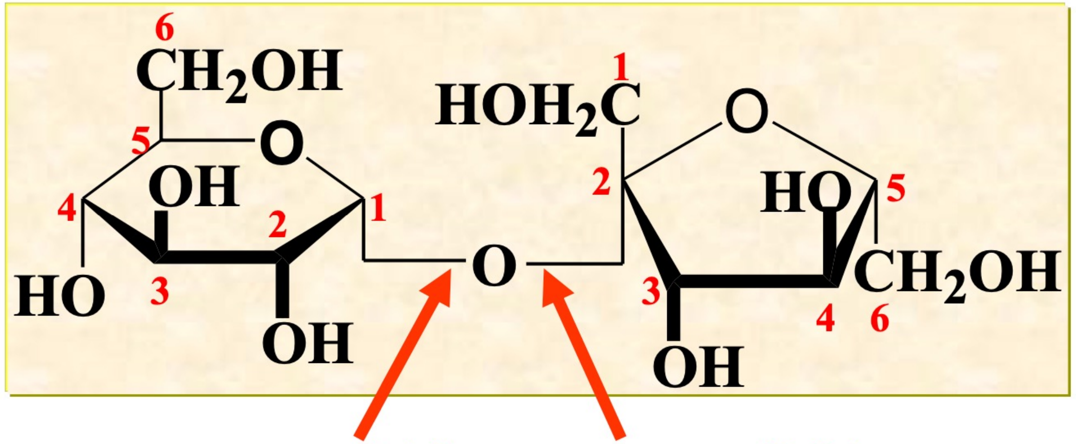


成苷部分

α-1,4 -苷键

未成苷部分

- 蔗糖



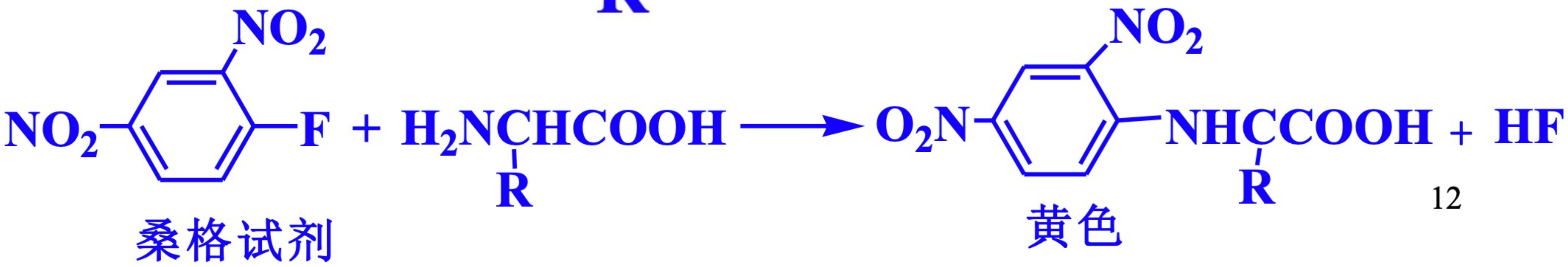
α-1,2-苷键

β-2,1-苷键

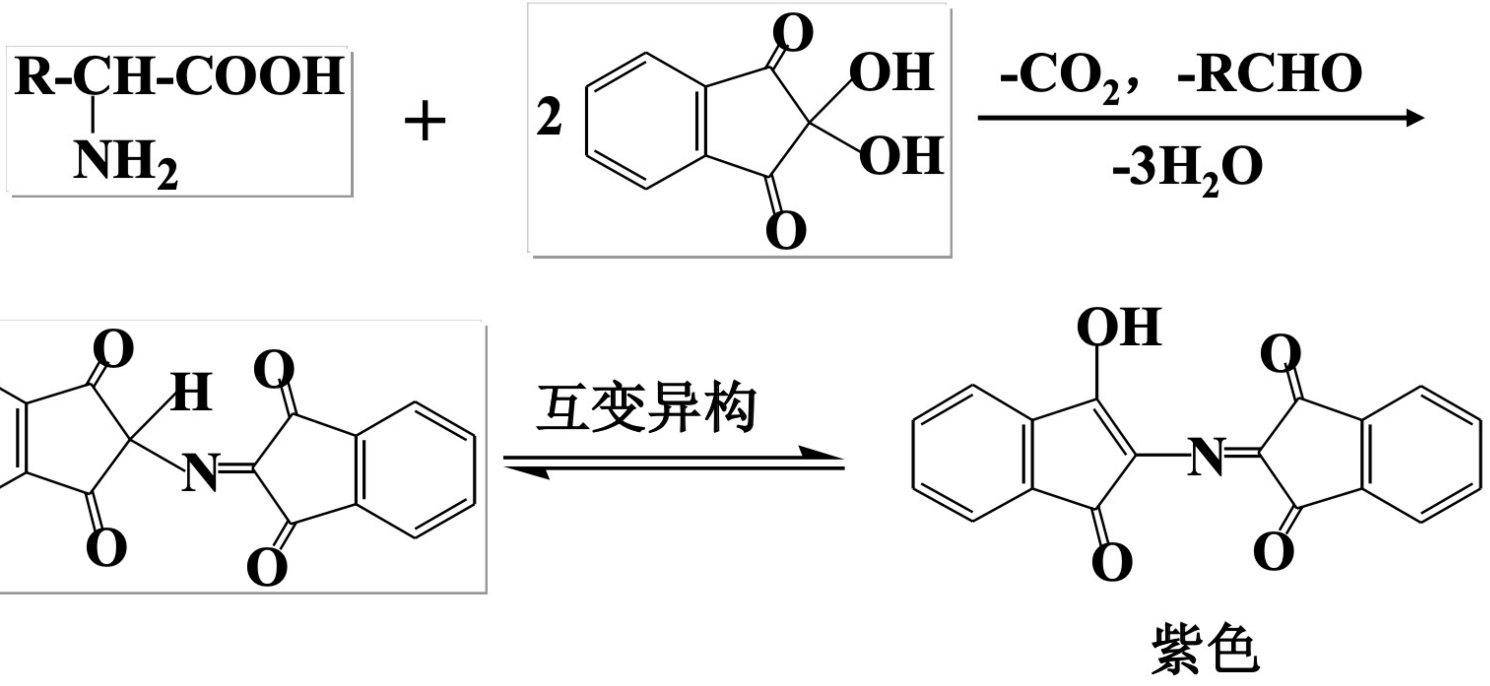
氨基酸

$$H_3\overset{+}{N}-\underset{R}{CH}COO^-$$

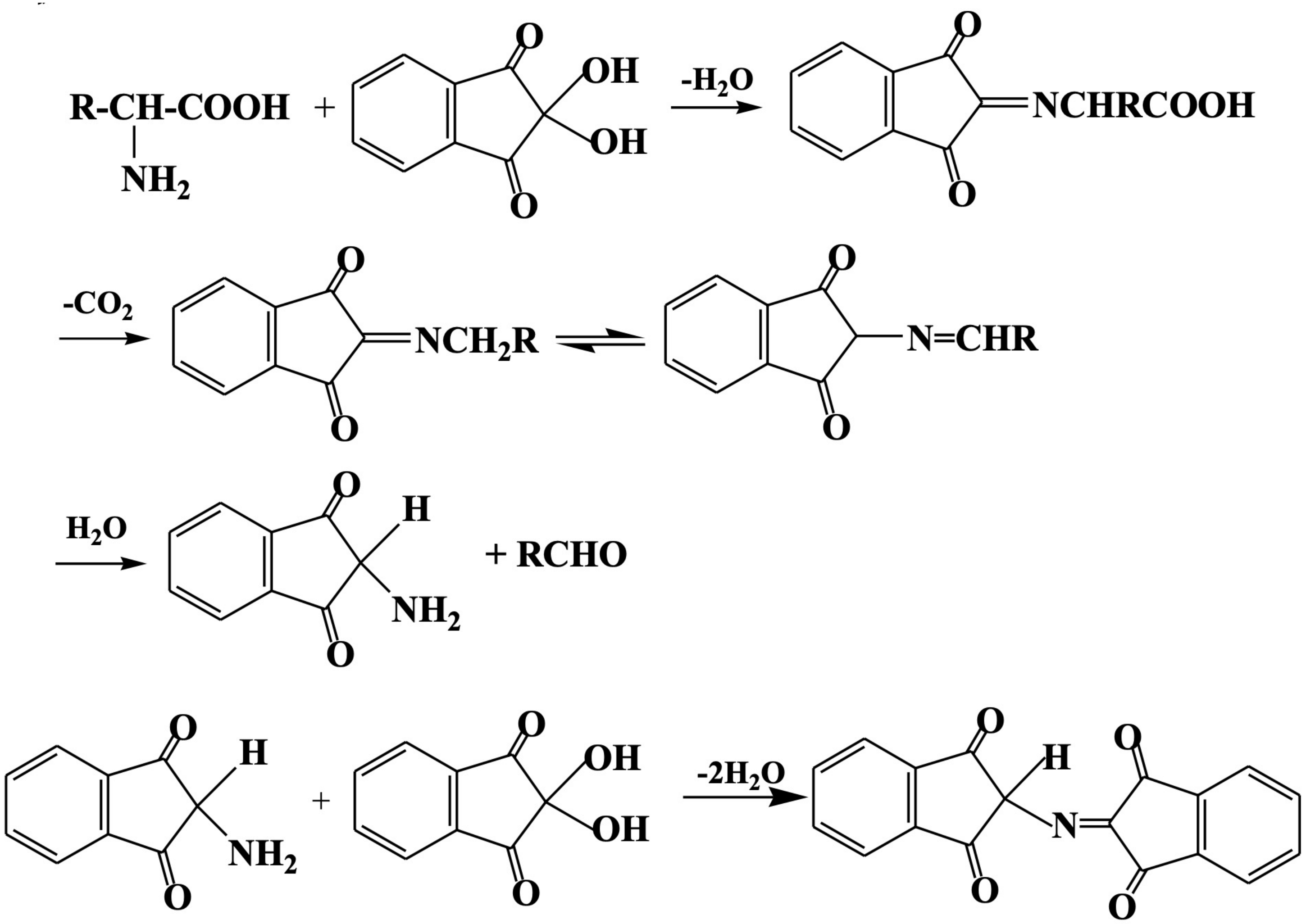
桑格试剂



与茚三酮的反应



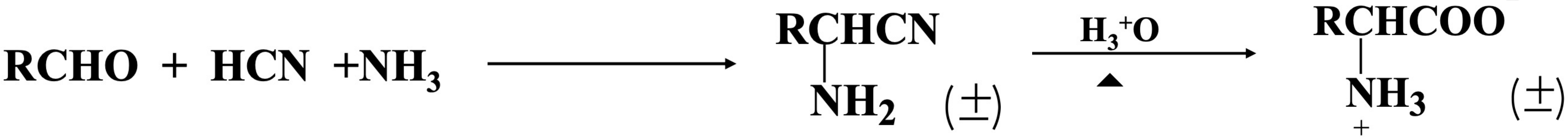
氨基酸


R-CH-COOH
NH2
+
OH
OH
O
O
-H2O
NCHRCOOH
-CO2
NCH2R
N=CHR
H2O
H
NH2
+ RCHO
+
-2H2O
N

氨基酸

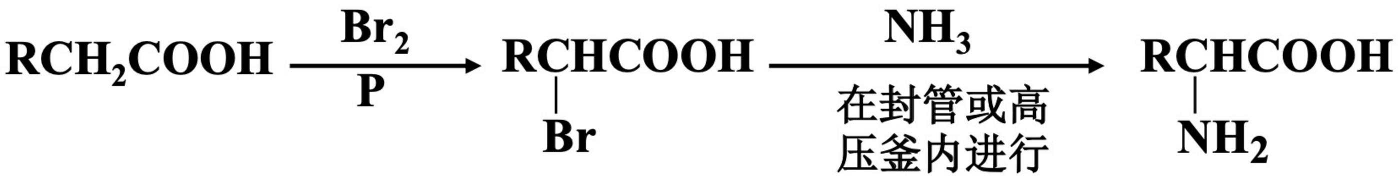
- 合成

斯瑞克合成法--醛的氨氰化



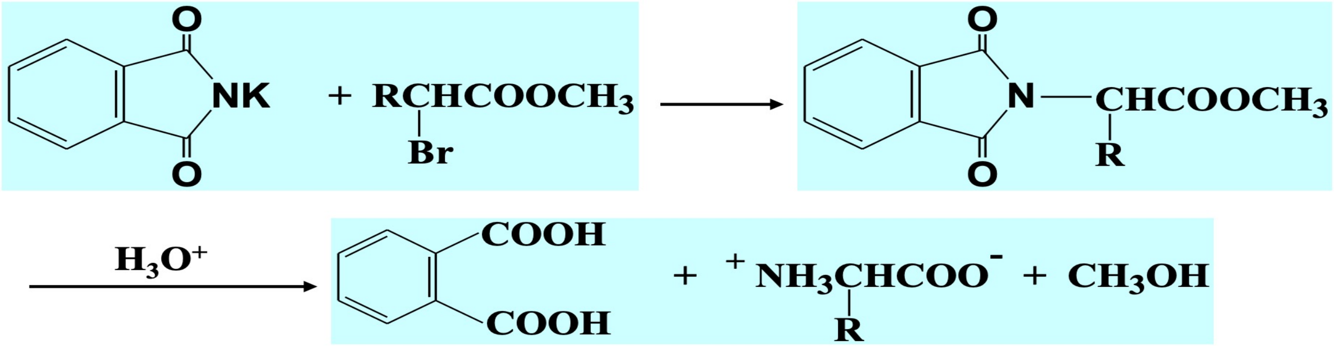
$$\mathrm{RCHO + HCN + NH_3} \longrightarrow \underset{\displaystyle \mathrm{NH_2}}{\mathrm{RCHCN}}\ (\pm) \xrightarrow[\blacktriangle]{\mathrm{H_3{}^{+}O}} \underset{\displaystyle \overset{+}{\mathrm{N}}\mathrm{H_3}}{\mathrm{RCHCOO^-}}\ (\pm)$$

赫尔--乌尔哈--泽林斯基α-溴化法



$$\mathrm{RCH_2COOH} \xrightarrow[\mathrm{P}]{\mathrm{Br_2}} \underset{\displaystyle \mathrm{Br}}{\mathrm{RCHCOOH}} \xrightarrow[\text{在封管或高压釜内进行}]{\mathrm{NH_3}} \underset{\displaystyle \mathrm{NH_2}}{\mathrm{RCHCOOH}}$$

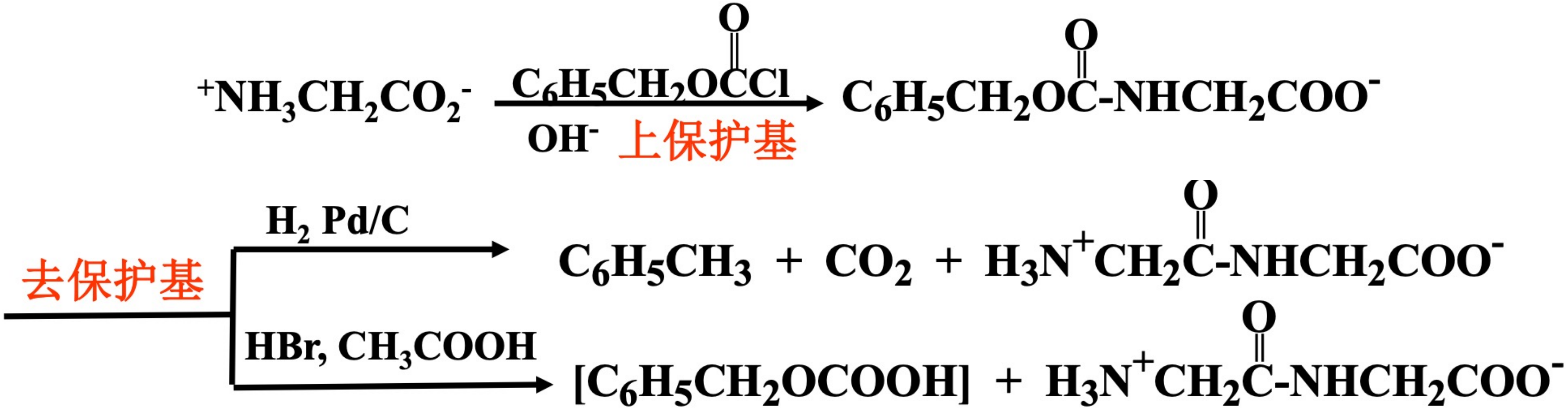
盖布瑞尔法



多肽

- 氨基的保护

氯代甲酸苯甲酯(或称苯甲氧基甲酰氯)保护 (Cbz，简写Z)



$$^{+}NH_3CH_2CO_2^- \xrightarrow[OH^-\ \text{上保护基}]{C_6H_5CH_2O\overset{O}{\overset{\|}{C}}Cl} C_6H_5CH_2O\overset{O}{\overset{\|}{C}}\text{-}NHCH_2COO^-$$

去保护基

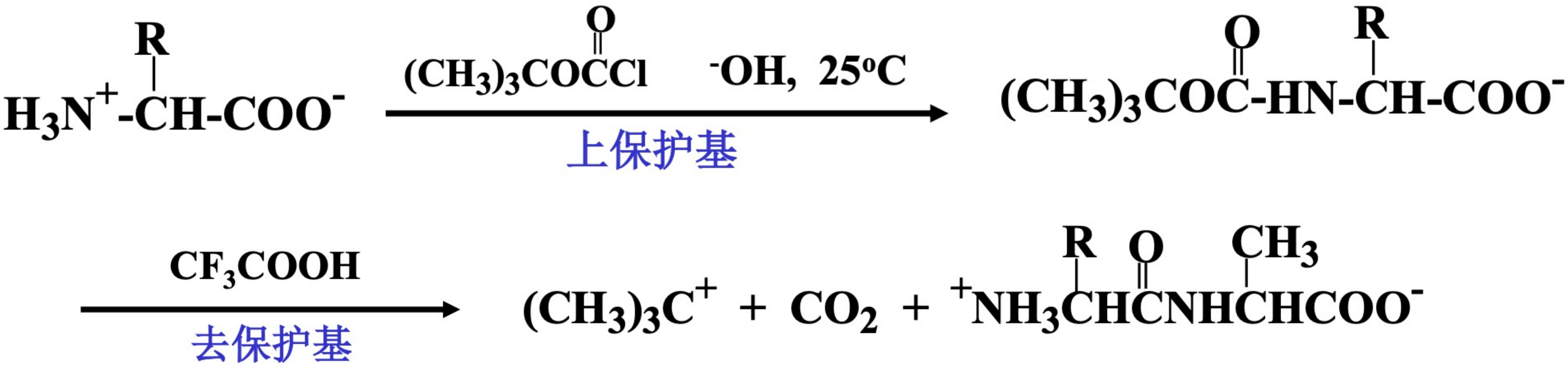
$$\xrightarrow{H_2\ Pd/C} C_6H_5CH_3 + CO_2 + H_3N^+CH_2\overset{O}{\overset{\|}{C}}\text{-}NHCH_2COO^-$$

$$\xrightarrow{HBr,\ CH_3COOH} [C_6H_5CH_2OCOOH] + H_3N^+CH_2\overset{O}{\overset{\|}{C}}\text{-}NHCH_2COO^-$$

多肽

- 氨基的保护

用氯代甲酸叔丁酯保护（Boc）

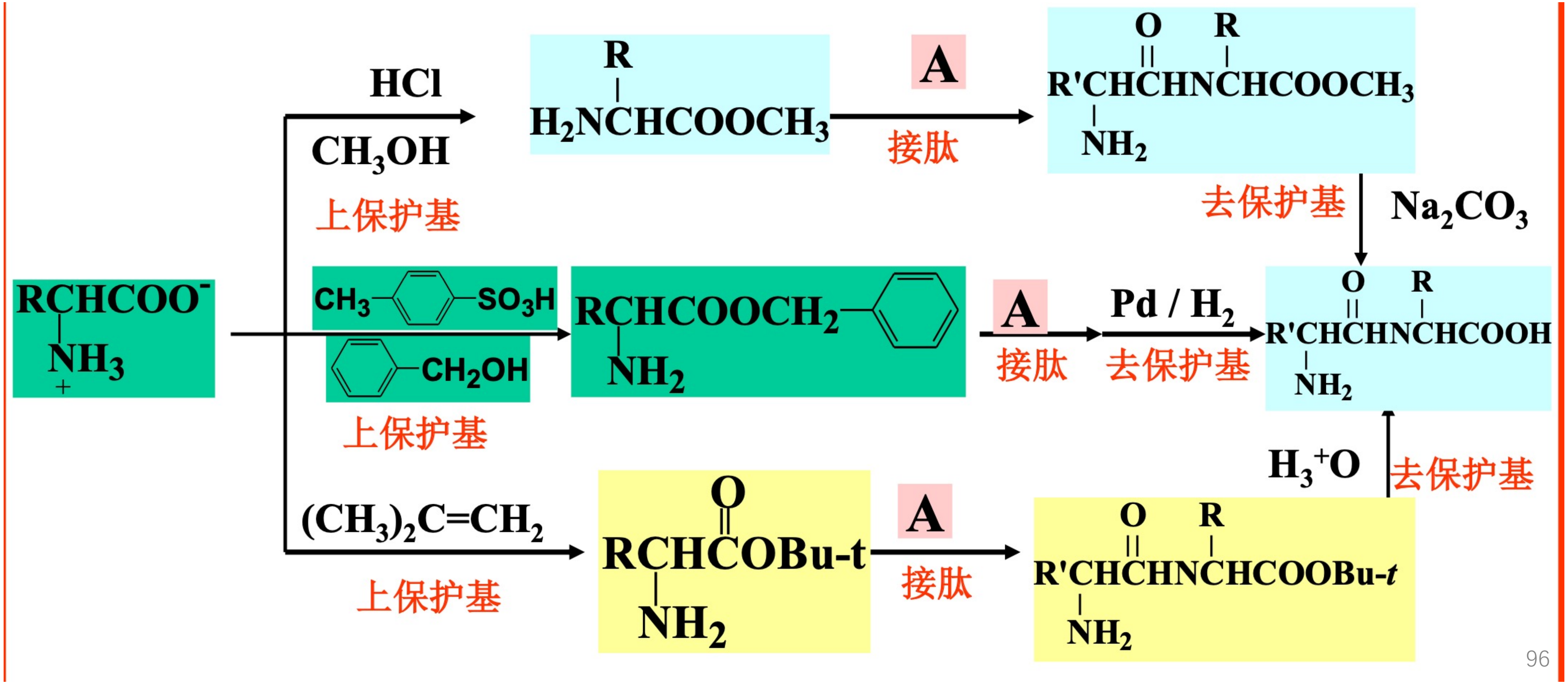


$$H_3N^+-\overset{R}{\overset{|}{C}}H-COO^- \xrightarrow[\text{上保护基}]{(CH_3)_3CO\overset{O}{\overset{\|}{C}}Cl \quad {}^-OH,\ 25^oC} (CH_3)_3CO\overset{O}{\overset{\|}{C}}-HN-\overset{R}{\overset{|}{C}}H-COO^-$$

$$\xrightarrow[\text{去保护基}]{CF_3COOH} (CH_3)_3C^+ + CO_2 + {}^+NH_3\overset{R}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}NH\overset{CH_3}{\overset{|}{C}}HCOO^-$$

多肽

- 羧基的保护



$RCH(NH_3^+)COO^-$
HCl
CH_3OH
上保护基
$H_2NCH(R)COOCH_3$
A
接肽
$R'CH(NH_2)C(=O)NHCH(R)COOCH_3$
去保护基
Na_2CO_3
$CH_3-C_6H_4-SO_3H$
$C_6H_5CH_2OH$
上保护基
$RCH(NH_2)COOCH_2C_6H_5$
A
接肽
Pd / H_2
去保护基
$R'CH(NH_2)C(=O)NHCH(R)COOH$
$(CH_3)_2C=CH_2$
上保护基
$RCH(NH_2)C(=O)OBu\text{-}t$
A
接肽
$R'CH(NH_2)C(=O)NHCH(R)COOBu\text{-}t$
H_3^+O
去保护基

谢谢！