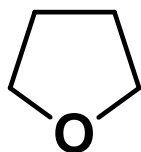
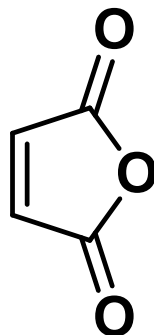


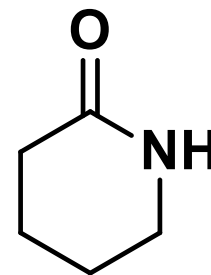
第十五章 杂环化合物



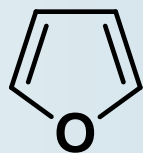
THF



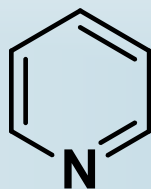
顺丁烯二酸酐



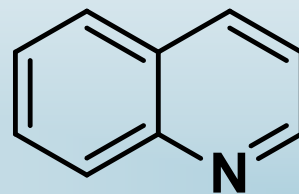
戊内酰胺



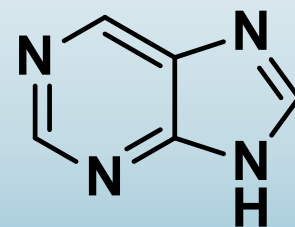
呋喃



吡啶



喹啉



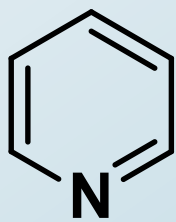
嘌呤

——芳香杂环化合物

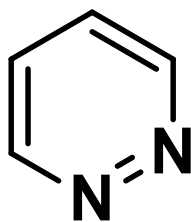
第十五章 杂环化合物

第一节 六元杂环化合物

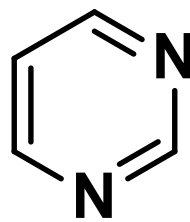
常见的六元含氮杂环



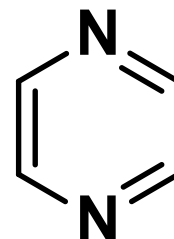
吡啶



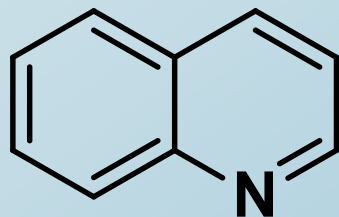
哒嗪



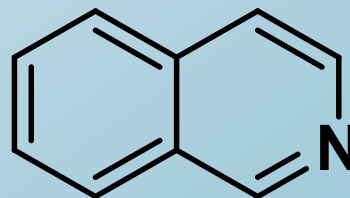
咪唑



吡嗪

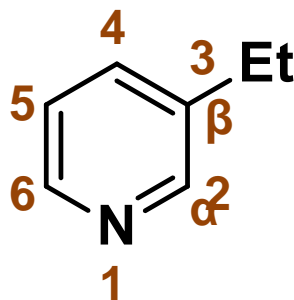


喹啉

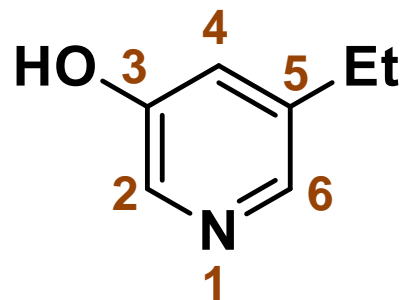


异喹啉

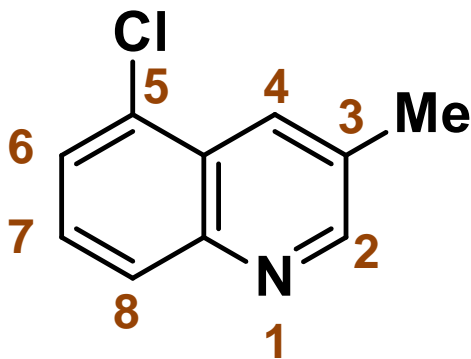
单氮六元杂环的命名



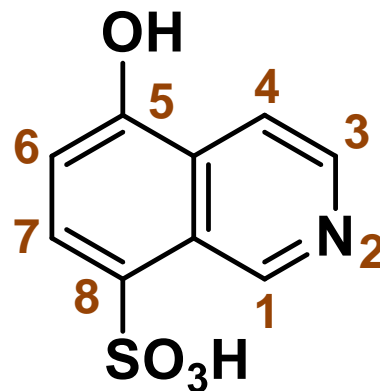
3-乙基吡啶 β -乙基吡啶
3-ethylpyridine



5-乙基吡啶-3-醇
5-ethylpyridin-3-ol




5-氯-3-甲基喹啉
5-chloro-3-methylquinoline



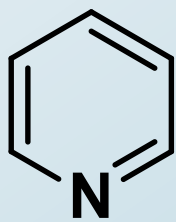
5-羟基异喹啉-8-磺酸

5-hydroxyisoquinoline-8-sulfonic acid

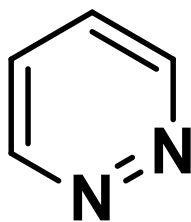
杂化化合物命名基本原则

- 杂环本体
 - 通常使用习惯名称呼
- 环外基团
 - -OR、-R、-X、-NO₂、-NO等优先级较低基团视作取代基
 - 其它基团视作特性基团 
- 编号
 - 编号时尽可能使杂原子位次较小，再依次考虑主特性基团、取代基
 - 稠合边上原子通常不参与编号

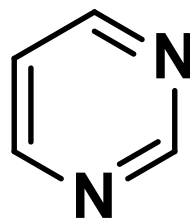
常见的六元含氮杂环



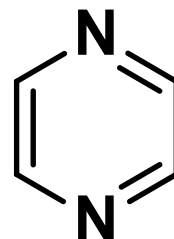
吡啶



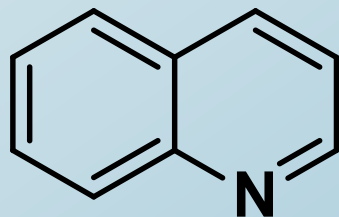
哒嗪



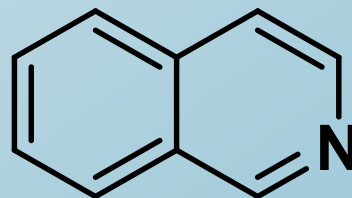
咪唑



吡嗪

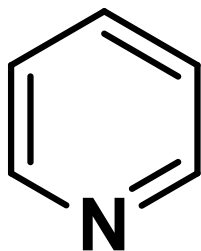


喹啉

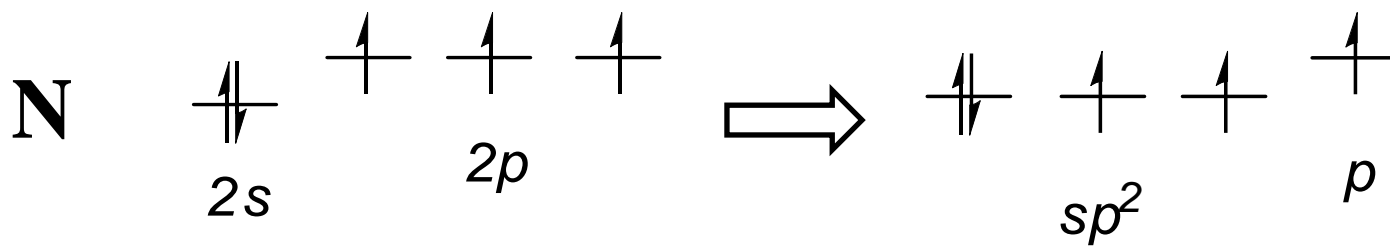
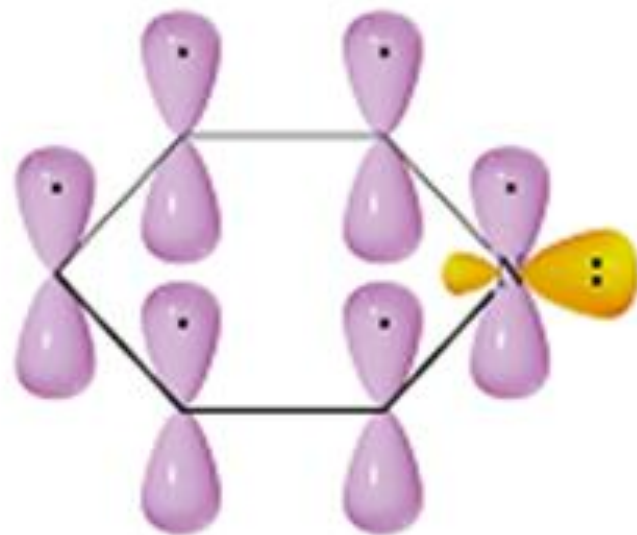


异喹啉

吡啶的结构

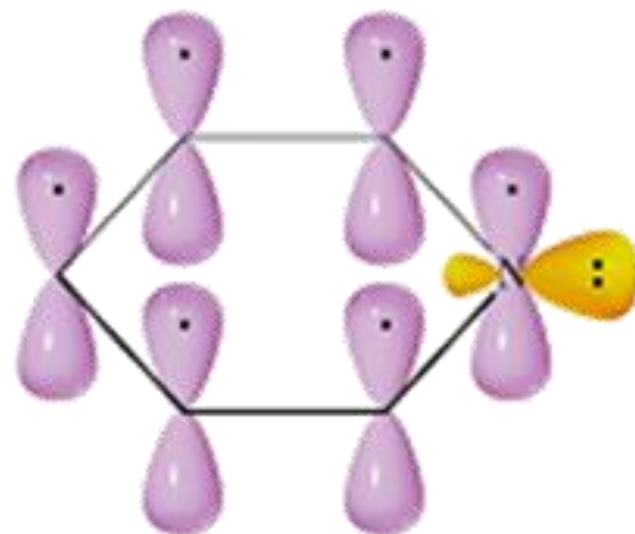
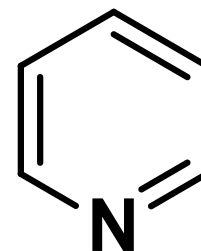


吡啶



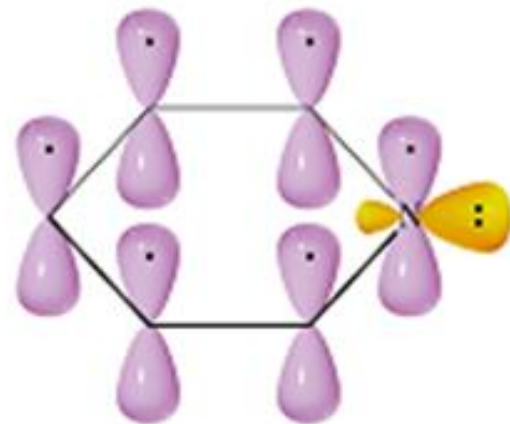
吡啶型氮原子

- 经典结构式上存在与其它原子间的双键
- 单个电子参与共轭
- 一对电子伸向环外，具有碱性
- 吸电子，使芳环上电子云密度下降，类似于硝基对苯环的作用



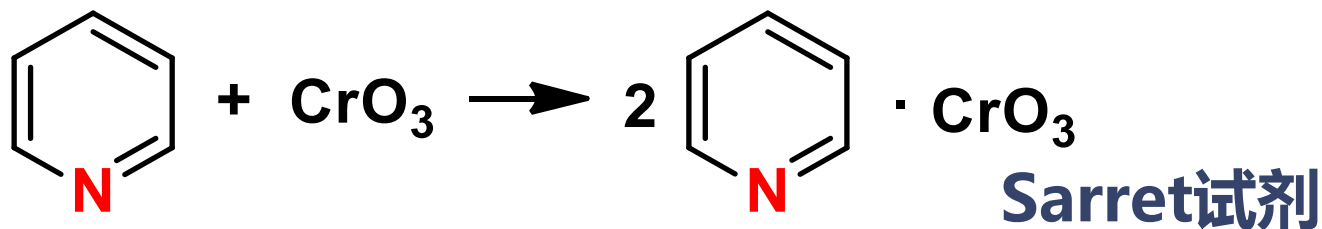
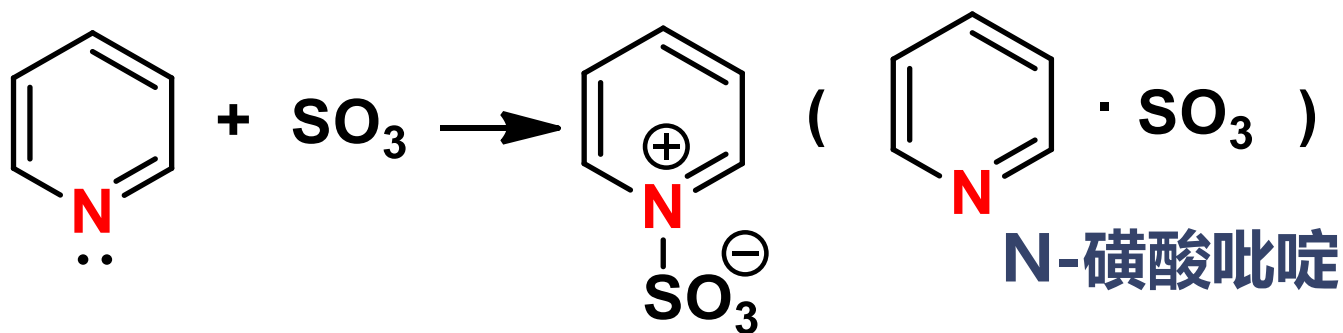
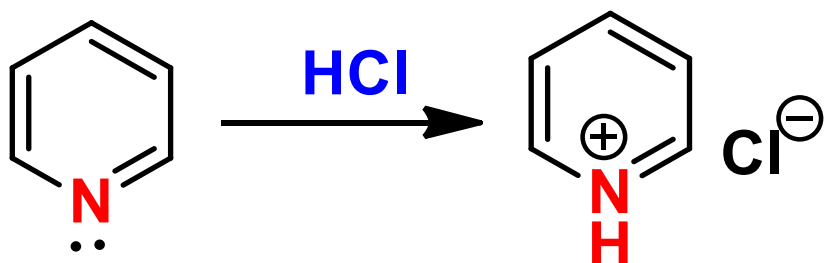
吡啶的化学性质

- N上孤对电子
——碱性 with 亲核性
- 芳香环
——亲电取代
- 缺 π 芳杂环
——亲核取代
- 氧化与还原

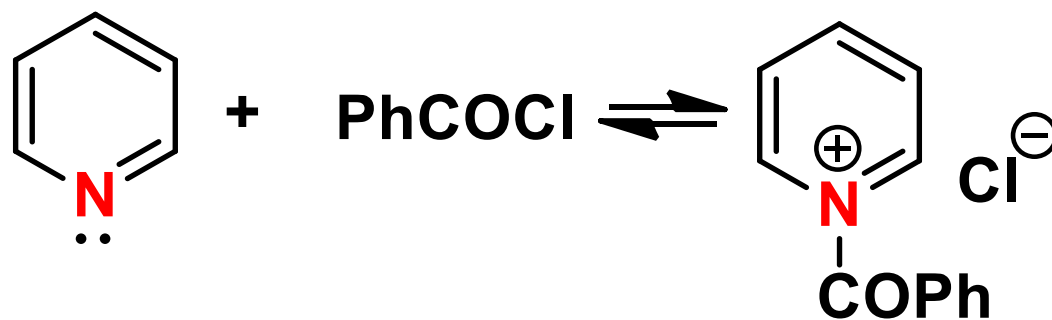
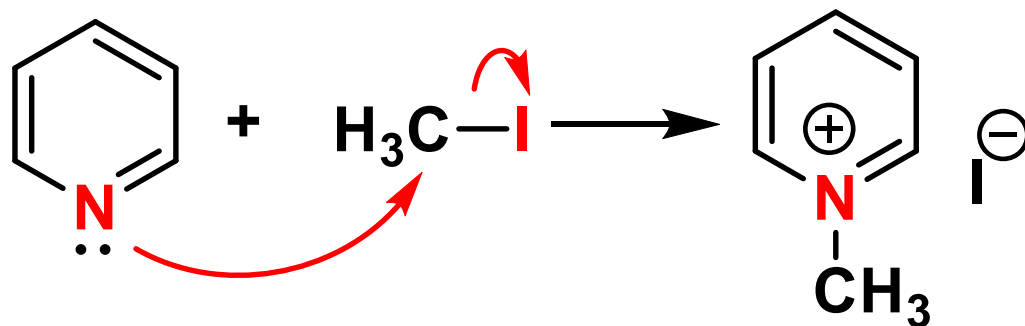


吡啶的化学性质：碱性

苯胺 < 吡啶 < 氨 < 脂肪胺

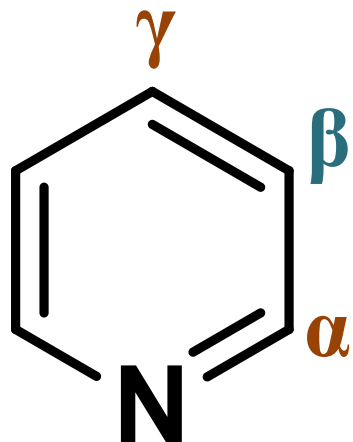


吡啶的化学性质：亲核性



吡啶的碱性与亲核性类同于芳香叔胺

吡啶的化学性质：环的电性反应

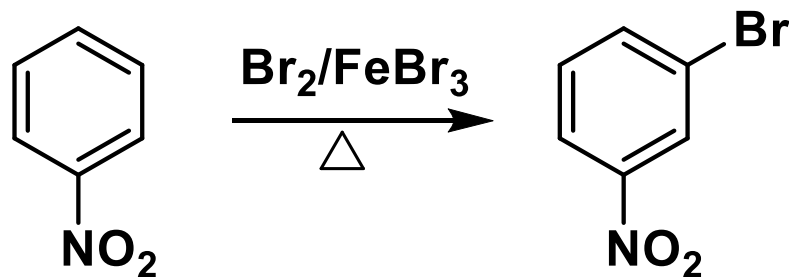
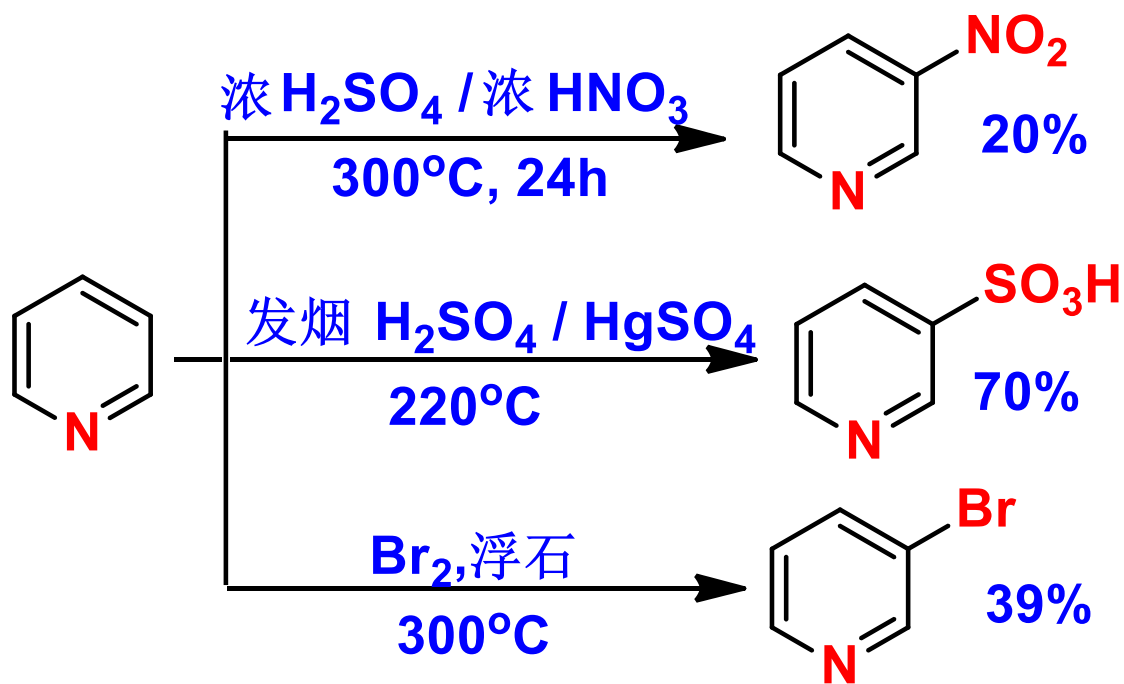


$$e: \beta > \gamma > \alpha$$

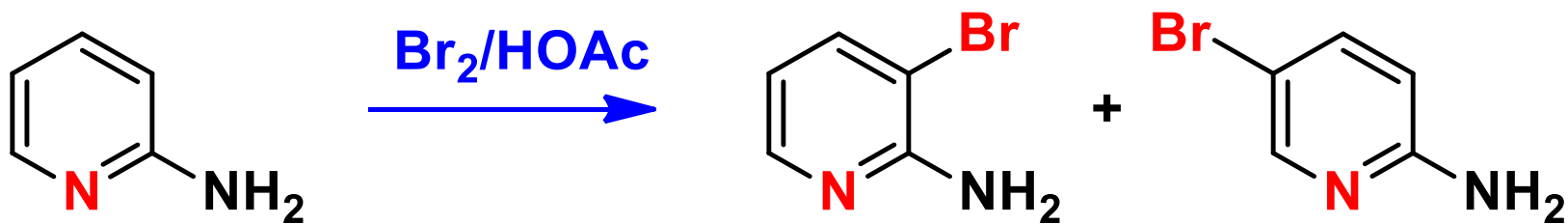
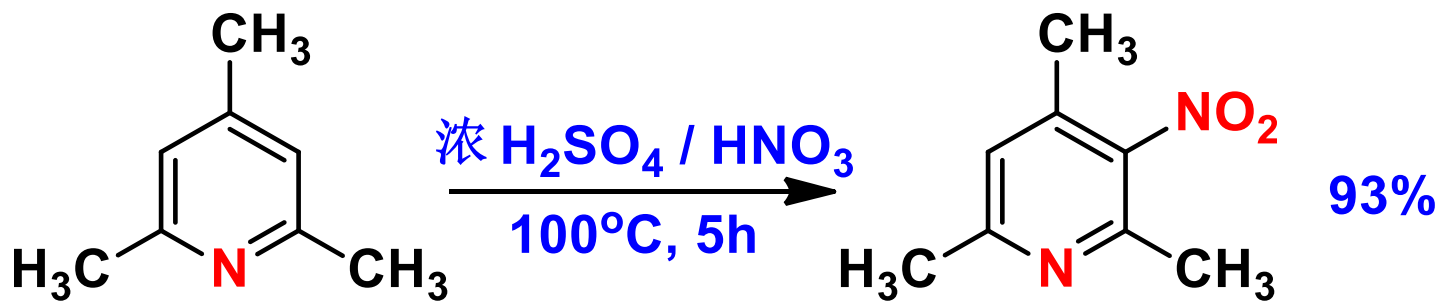
亲电取代： β 位

亲核取代： α 、 γ 位

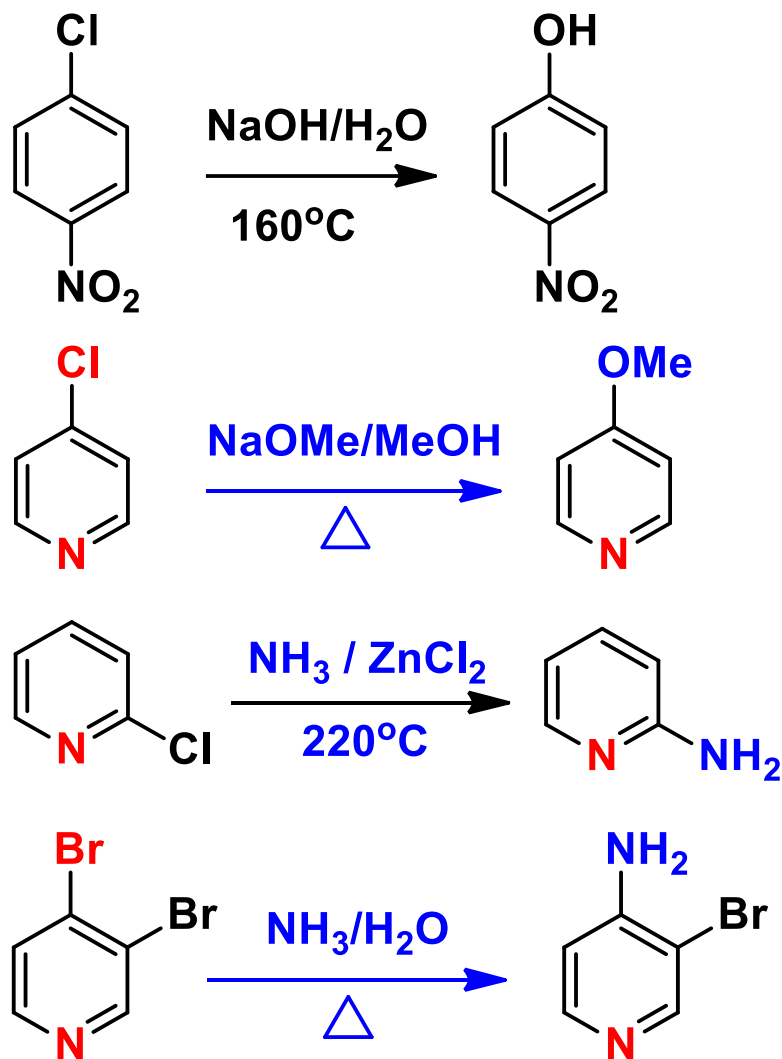
吡啶的化学性质：亲电取代



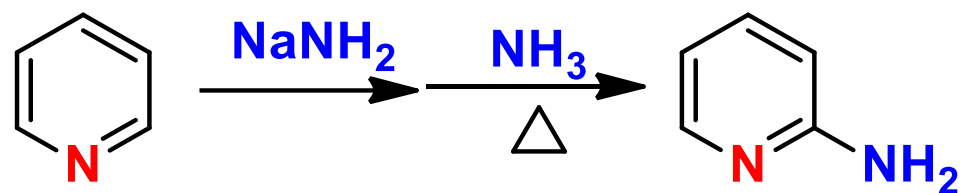
吡啶的化学性质：亲电取代



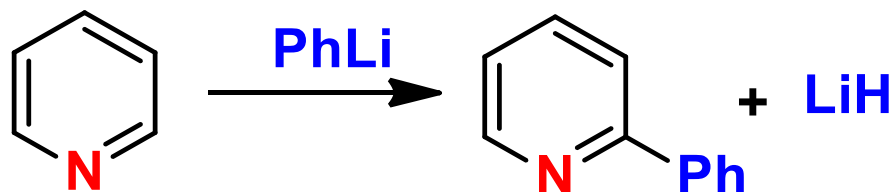
吡啶的化学性质：亲核取代



吡啶的化学性质：亲核取代

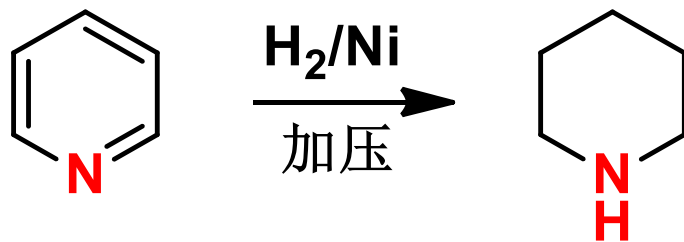


(Chichibabin反应)



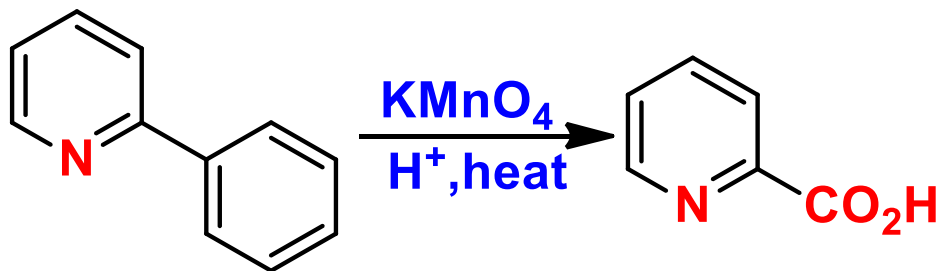
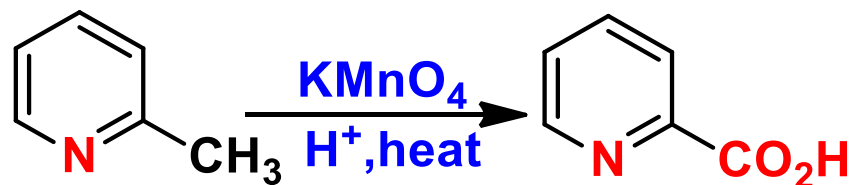
吡啶的化学性质：还原

- 电子云密度低：易还原



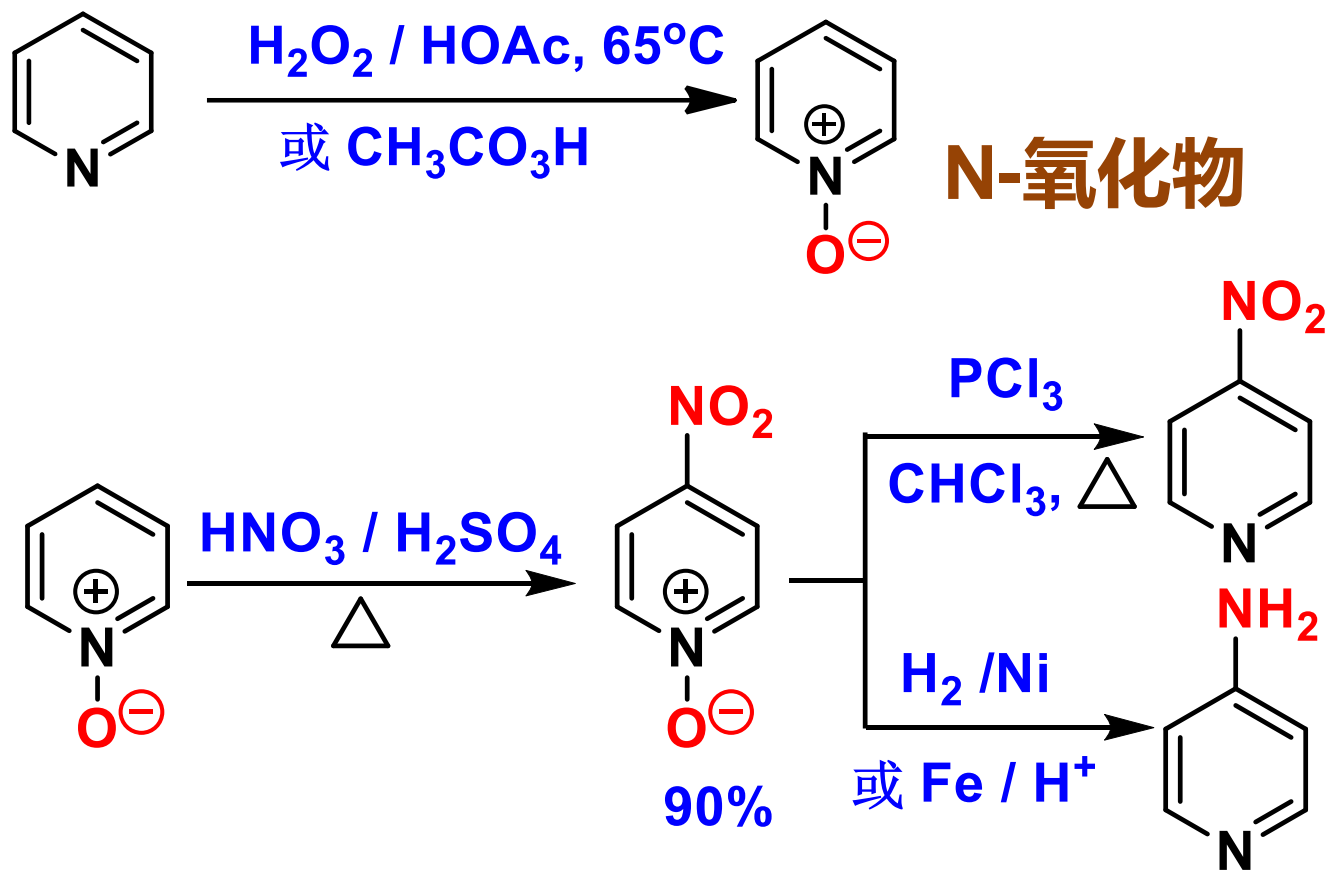
吡啶的化学性质：氧化

- 电子云密度低：吡啶环难以被氧化



吡啶的化学性质：氧化

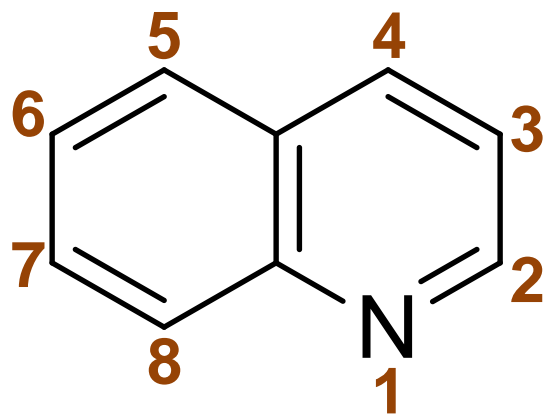
- 特殊氧化条件



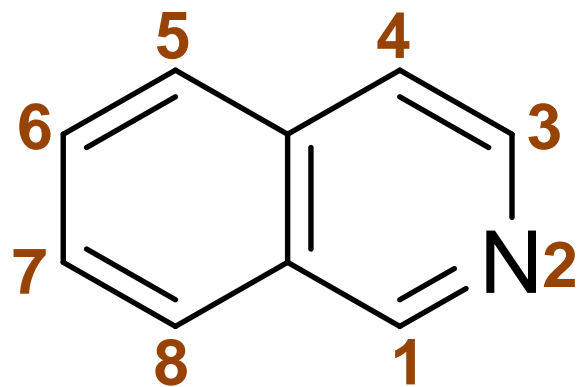
吡啶的化学性质：总结

- 缺 π 芳杂环，性质类似硝基苯
 - 亲核取代易，亲电取代难
 - 还原易，氧化难
- 吡啶型N原子：有亲核性与碱性

喹啉与异喹啉



喹啉

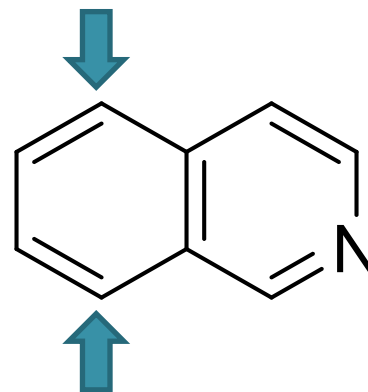
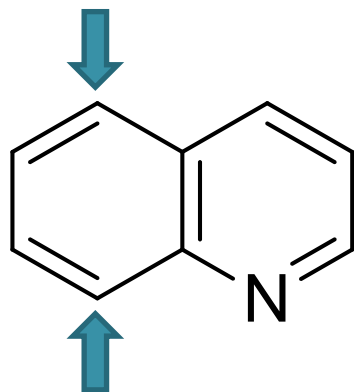


异喹啉

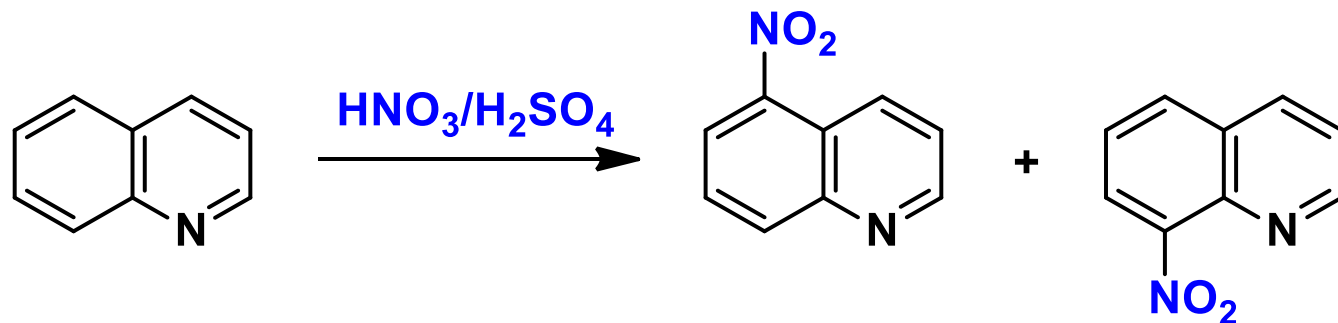
化学性质与吡啶及萘有相当密切的关联

喹啉与异喹啉的化学性质

- 亲电取代



(发生在富电子苯环类似萘的 α -位)

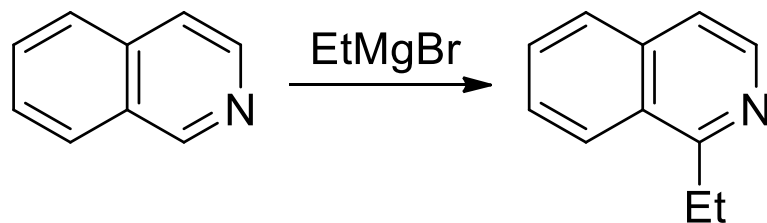
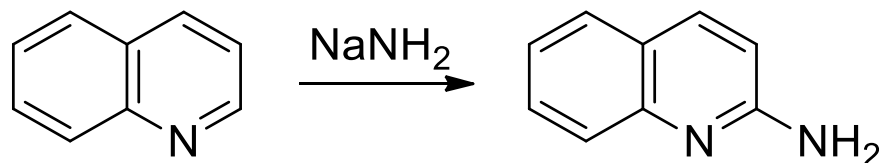
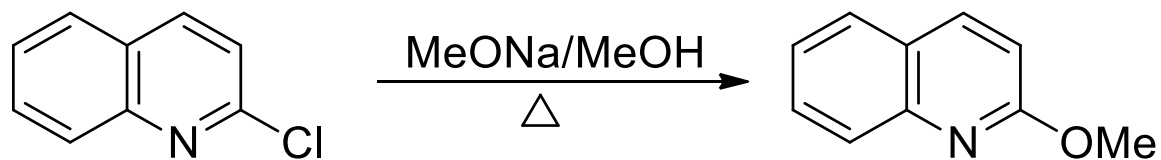


喹啉与异喹啉的化学性质

- 亲核取代

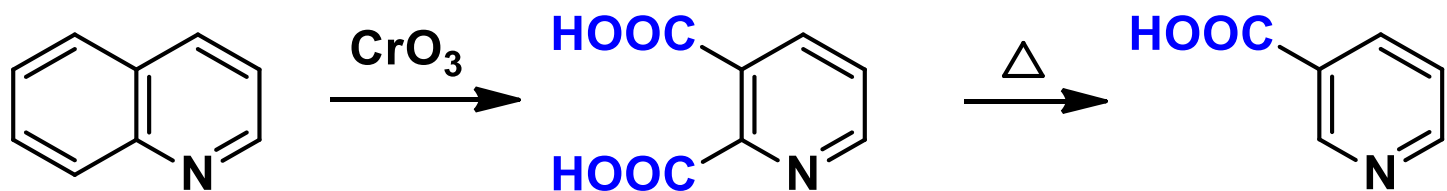


(易发生在缺电子吡啶N原子 α -位)

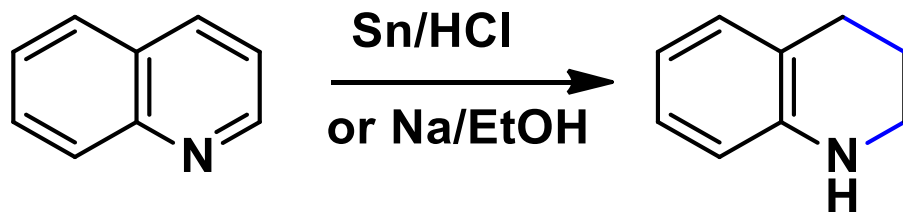


喹啉与异喹啉的化学性质

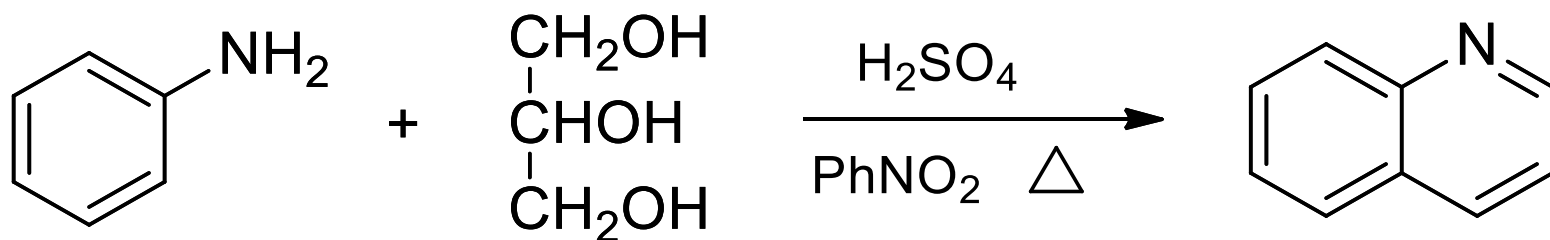
- 氧化：优先氧化富电子苯环



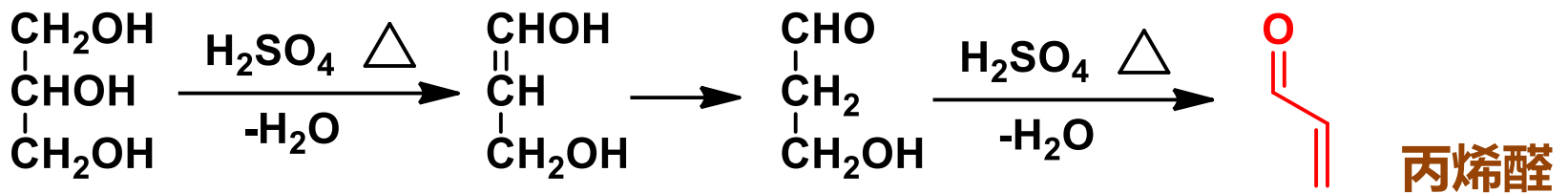
- 还原：优先还原缺电子吡啶环



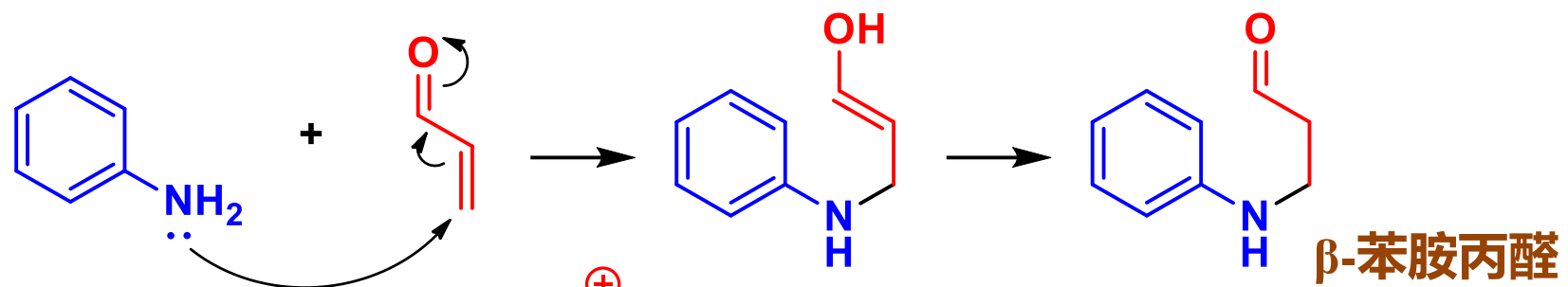
喹啉的合成：Skraup法



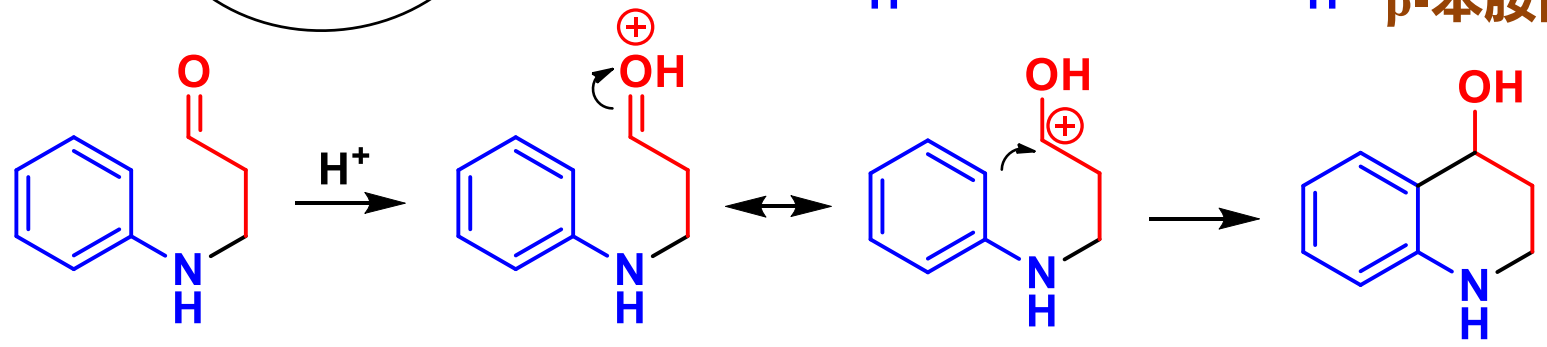
1°



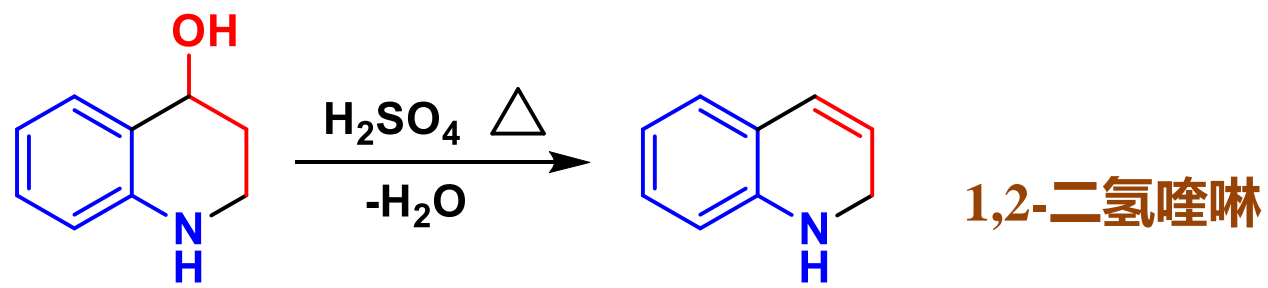
2°



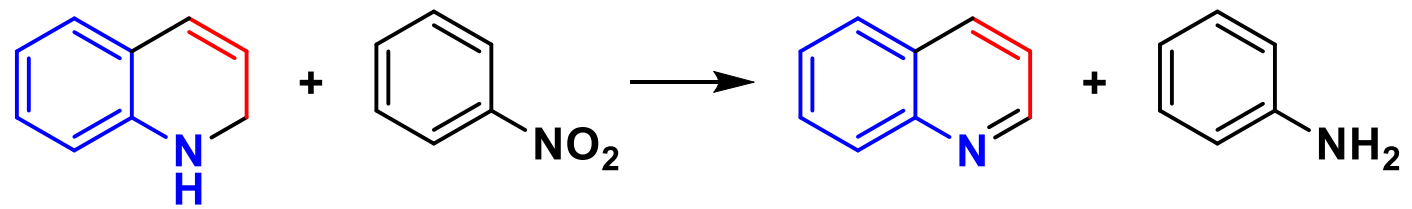
3°



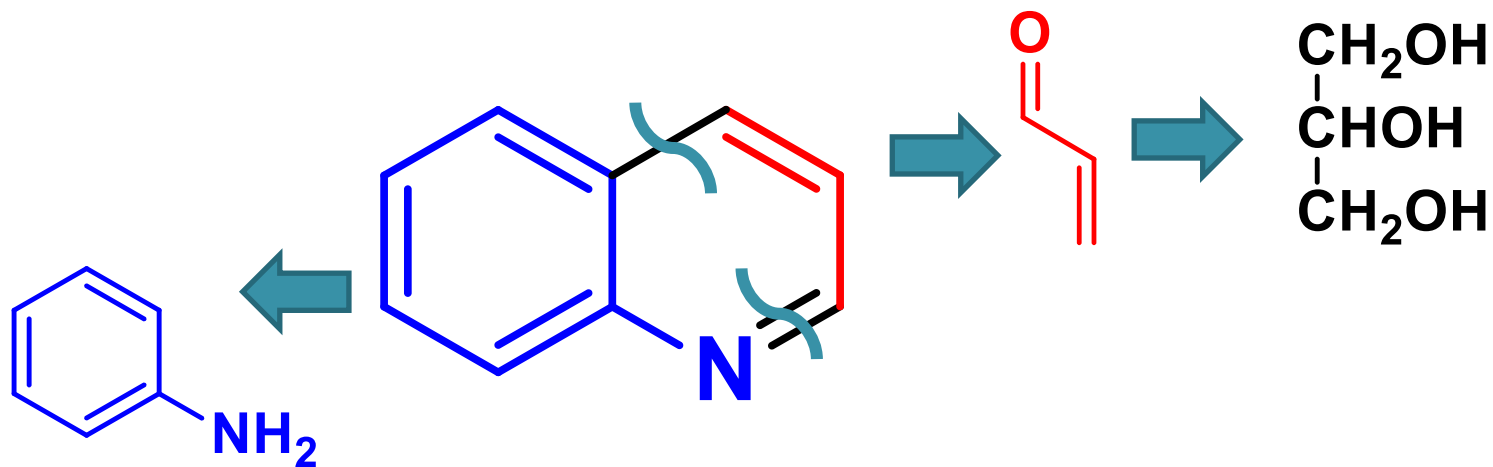
4°



5°

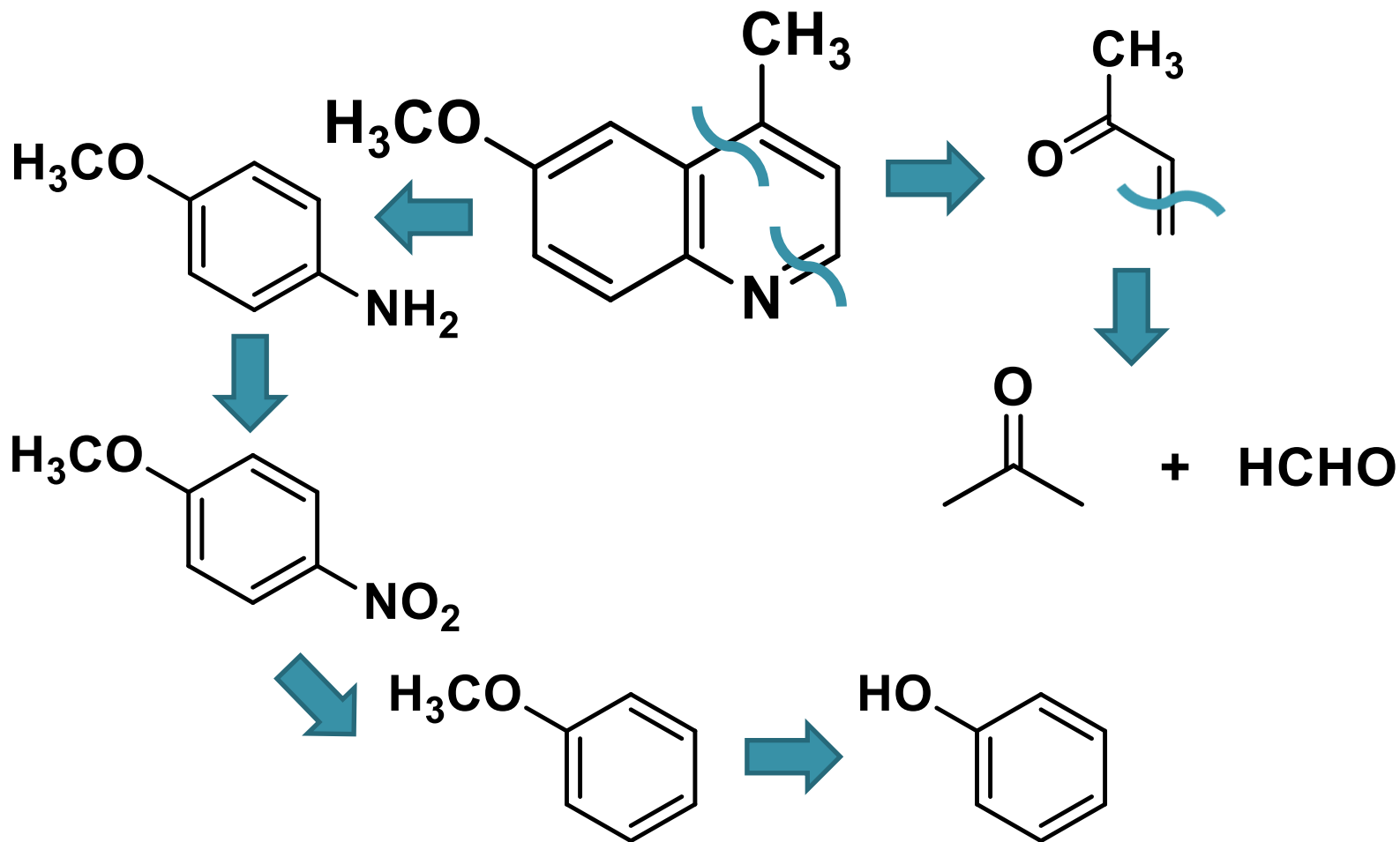


Skraup法逆合成思路



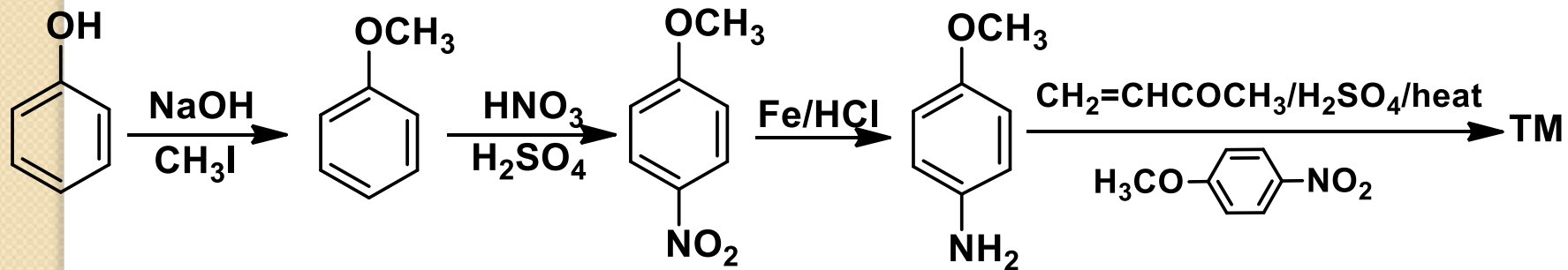
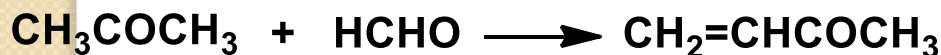
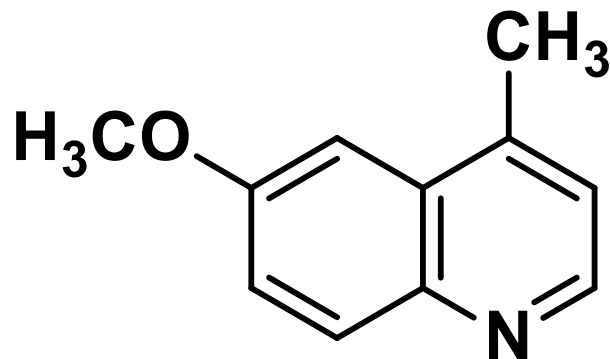
Skraup法实例

- 以苯酚和不超过三碳的有机试剂合成

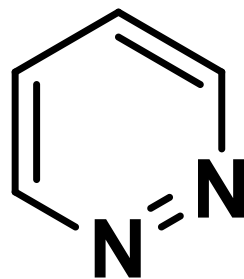


Skraup法实例

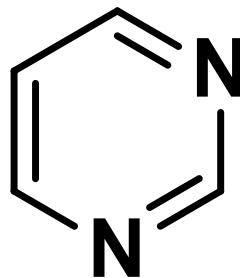
- 以苯酚和不超过三碳的有机试剂合成



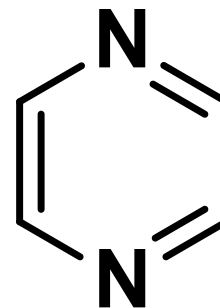
含两个氮原子的六元杂环



哒嗪



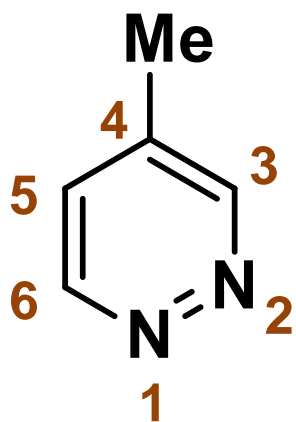
嘧啶



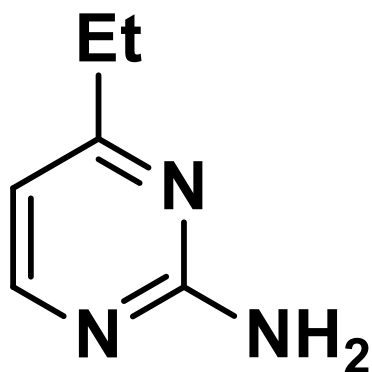
吡嗪

——二嗪类化合物

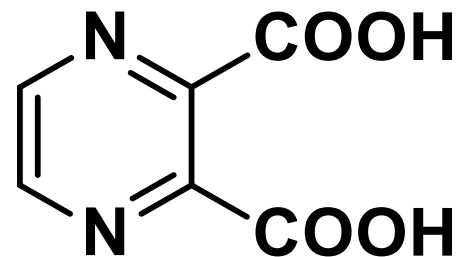
二嗪类化合物的命名



4-甲基吡嗪
4-methylpyridazine

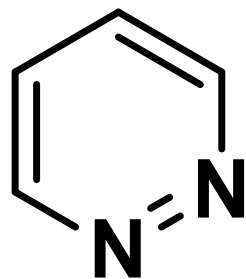


4-乙基嘧啶-2-胺
4-ethylpyrimidin
-2-amine

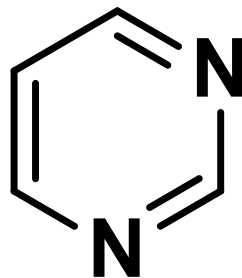


吡嗪-2,3-二甲酸
pyrazine
-2,3-dicarboxylic acid

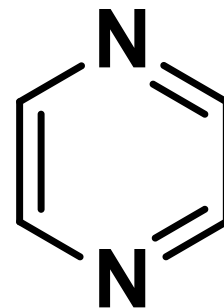
含两个氮原子的六元杂环



咪嗪



咪啉

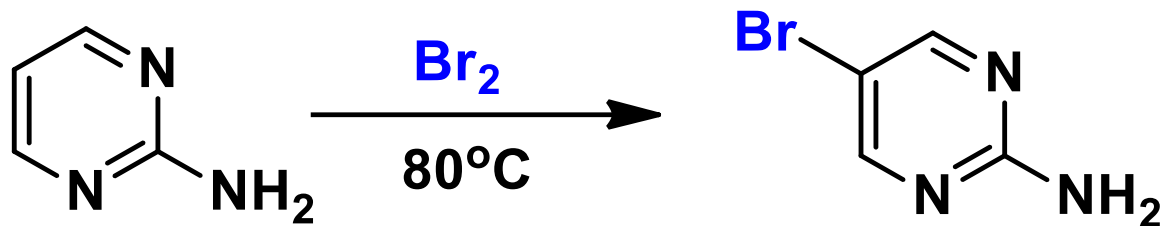
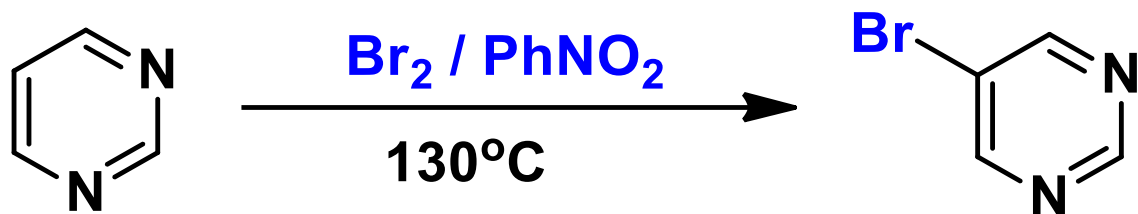


吡嗪

——二嗪类化合物

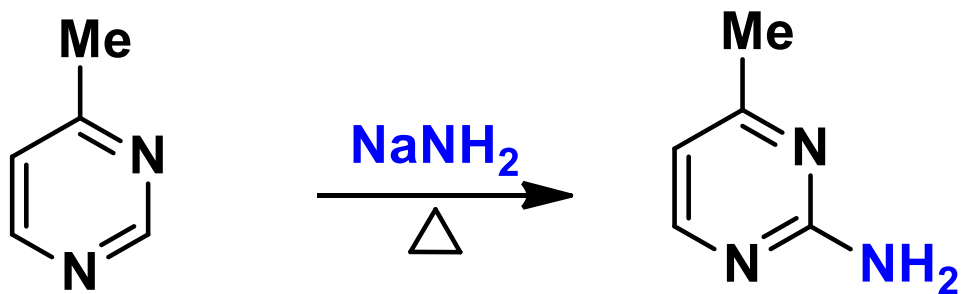
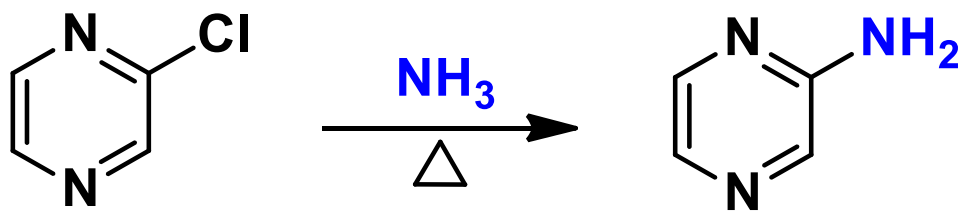
二嗪类化合物的反应

- 亲电取代——较困难



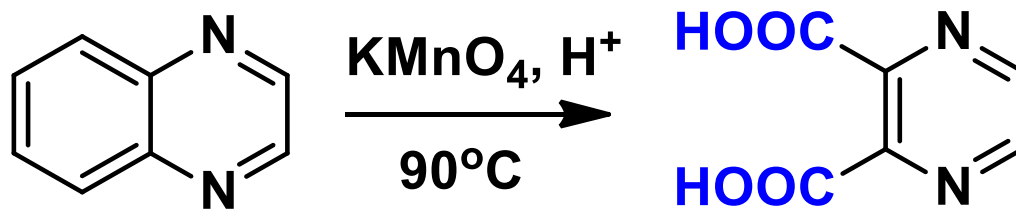
二嗪类化合物的反应

- 亲核取代——较容易

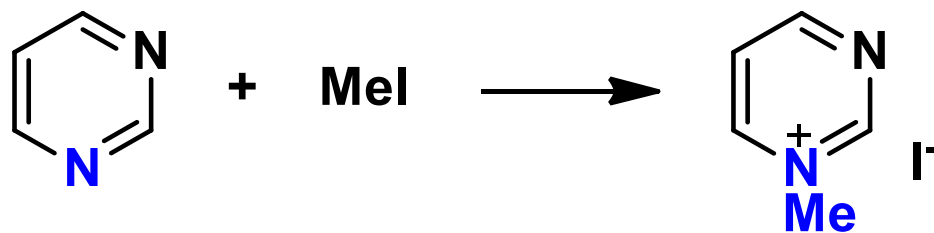
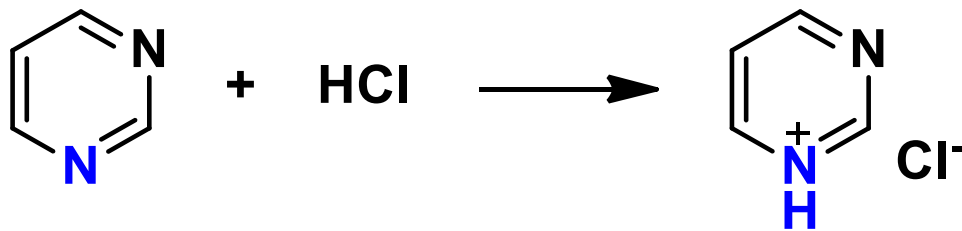


二嗪类化合物的反应

- 氧化

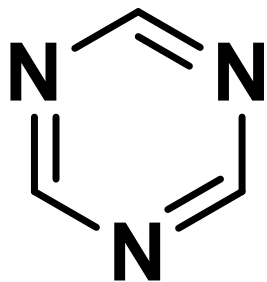


- 碱性与亲核性

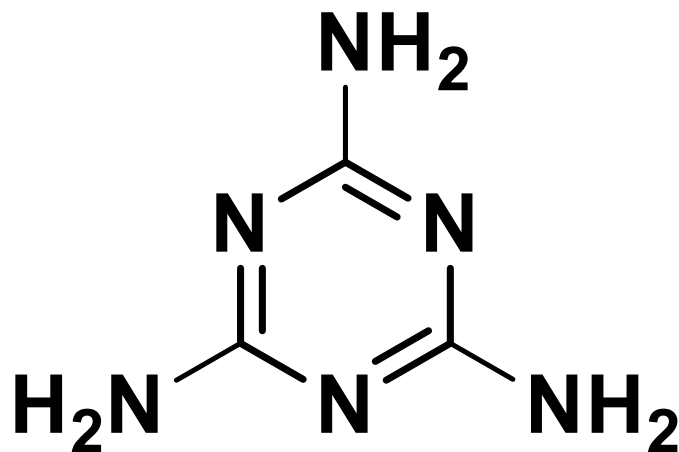


相当于一元胺

含三个氮原子的六元杂环



1,3,5-三嗪

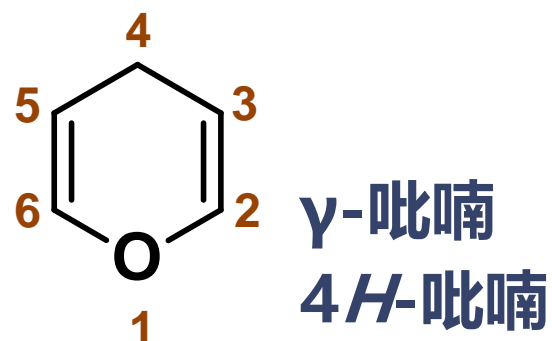
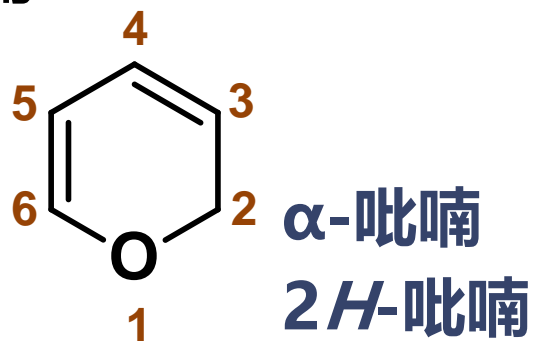


三聚氰胺

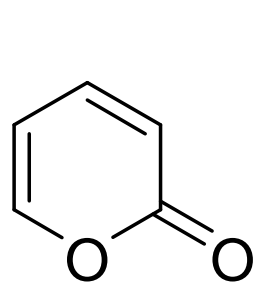
- 白色晶体，氰氨化钙法或尿素法合成
- 与甲醛缩合后聚合可得三聚氰胺树脂
- 用于塑料及涂料工业
- 也作纺织物防摺、防缩处理剂

含氧六元杂环

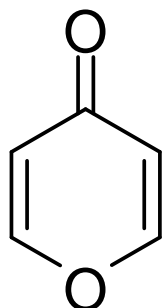
- 吡喃



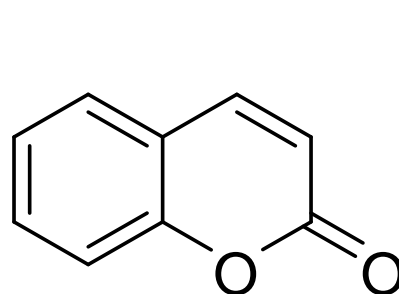
- 吡喃衍生物



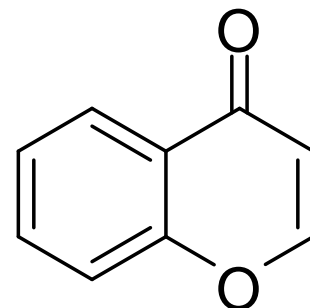
α -吡喃酮



γ -吡喃酮



香豆酮



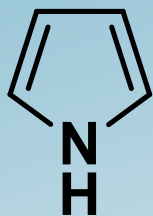
色酮

第十五章 杂环化合物

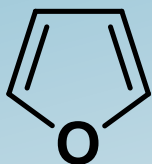
第二节 五元杂环化合物

常见的五元杂环化合物

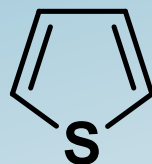
- 含单个杂原子的五元杂环



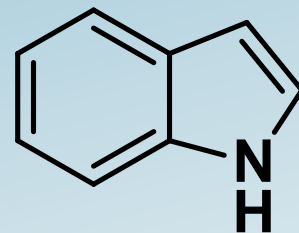
吡咯



呋喃

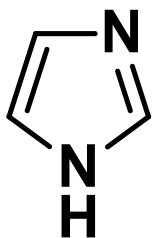


噻吩

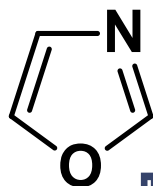


吲哚

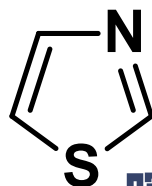
- 含多个杂原子的五元杂环



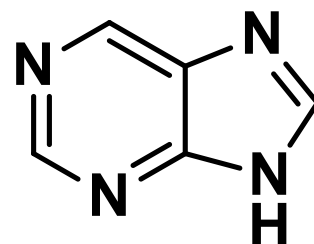
咪唑



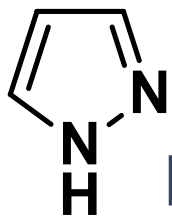
噁唑



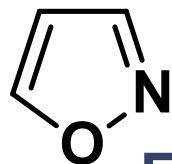
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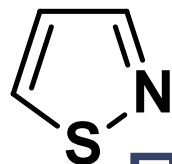
嘌呤



吡唑

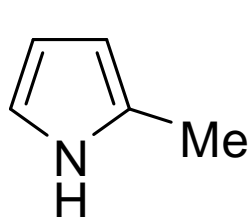


异噁唑

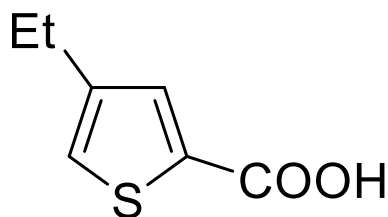


异噻唑

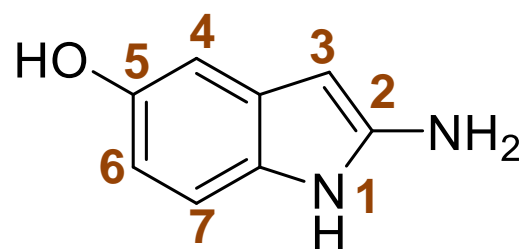
含单个杂原子五元杂环的命名



2-甲基吡咯
2-methylpyrrole

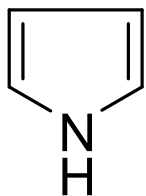


4-乙基噻吩-2-甲酸
4-ethylthiophene
-2-carboxylic acid

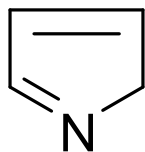


2-氨基吲哚-5-醇
2-aminoindol-5-ol

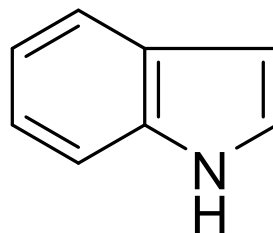
• 吡咯位置异构体的命名



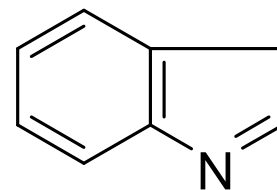
1H-吡咯



2H-吡咯



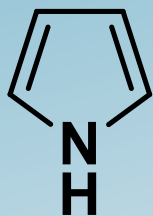
1H-吲哚



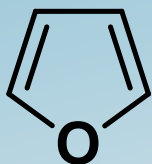
3H-吲哚

常见的五元杂环化合物

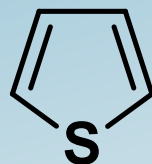
- 含单个杂原子的五元杂环



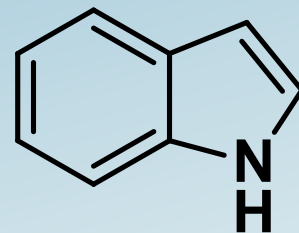
吡咯



呋喃

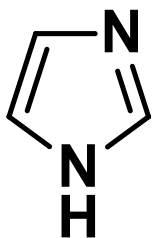


噻吩

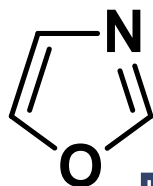


吲哚

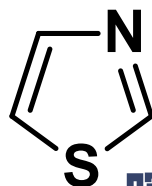
- 含多个杂原子的五元杂环



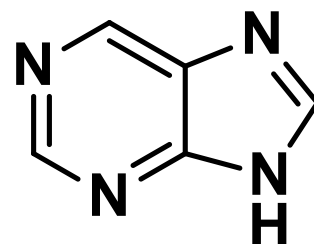
咪唑



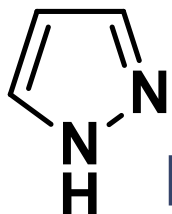
噁唑



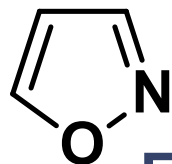
噻唑



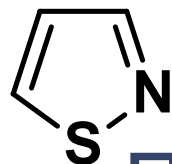
嘌呤



吡唑

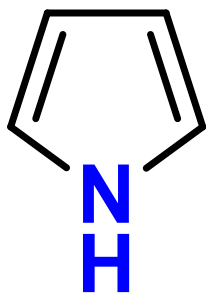


异噁唑

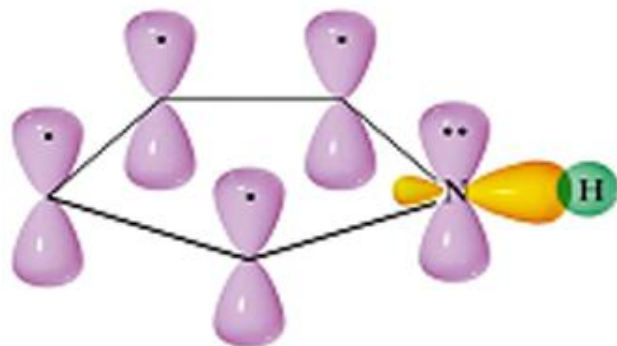


异噻唑

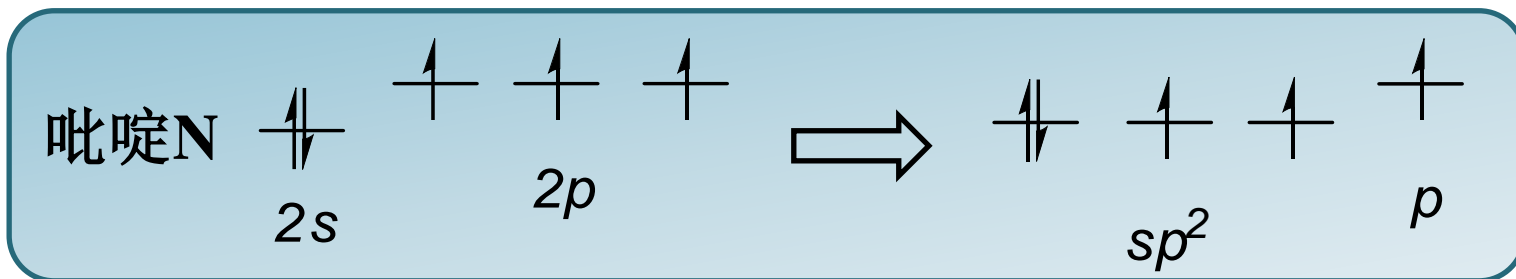
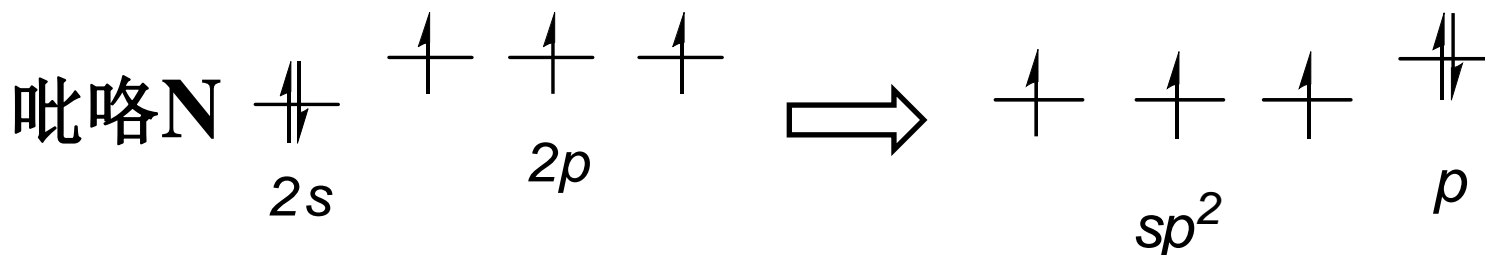
吡咯的结构



吡咯

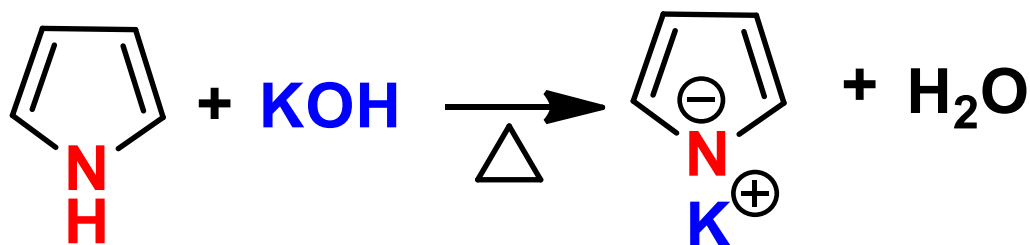
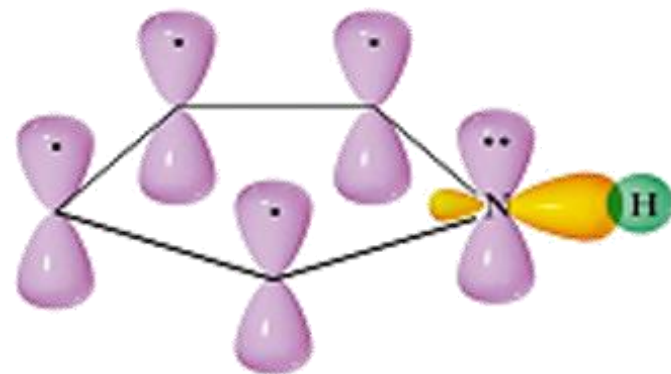
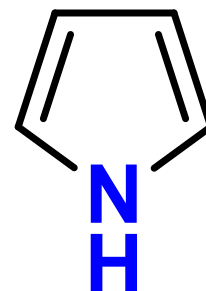


“吡咯”型N原子

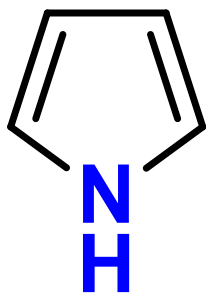


吡咯型氮原子

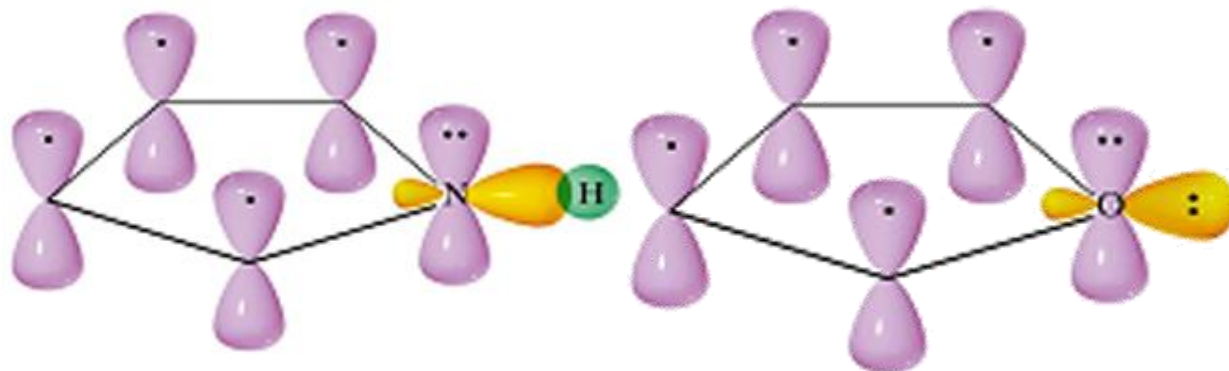
- 一对电子参与共轭，
- 结构式上与C、H以单键相连
- 给电子，使芳环上电子云密度升高，类似于氨基对苯环的作用
- 不具有碱性，相反有一定酸性



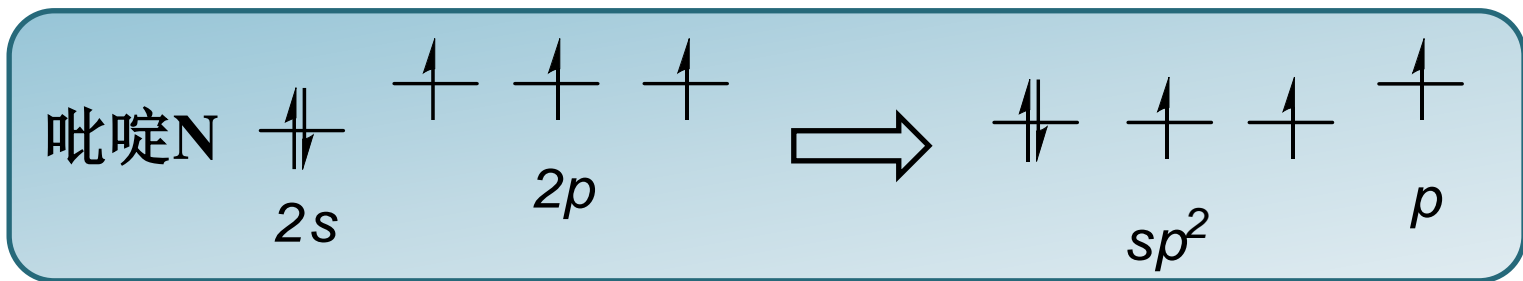
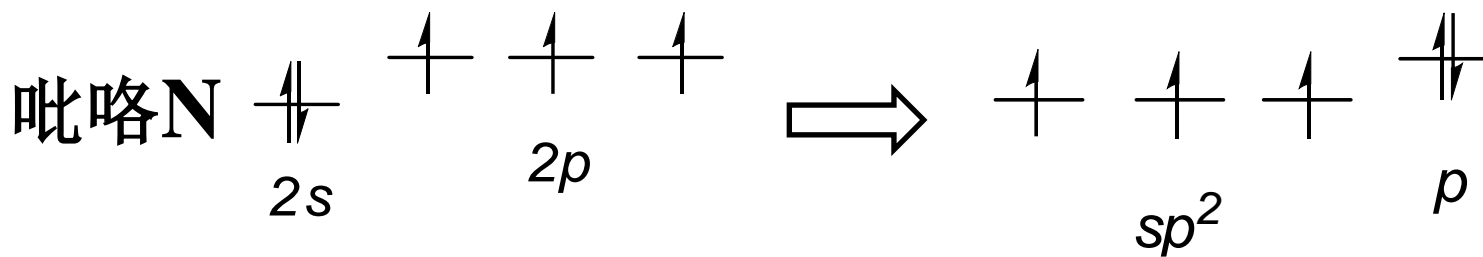
吡咯的结构



吡咯



“吡咯”型N原子

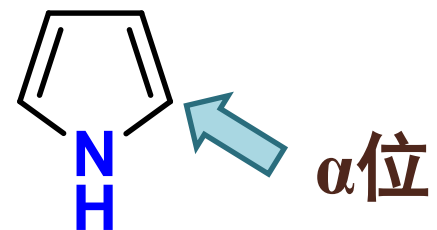
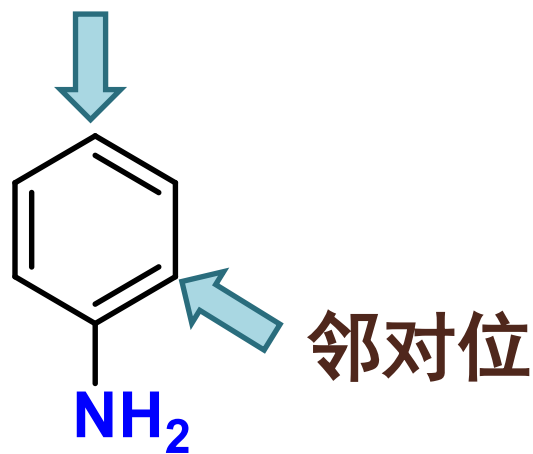


吡咯、呋喃、噻吩的化学性质

- 多 π 芳杂环
 - 亲电取代活性高
 - 易被氧化
 - 对酸敏感
 - 易开环
- 芳香性略差
 - 易被还原

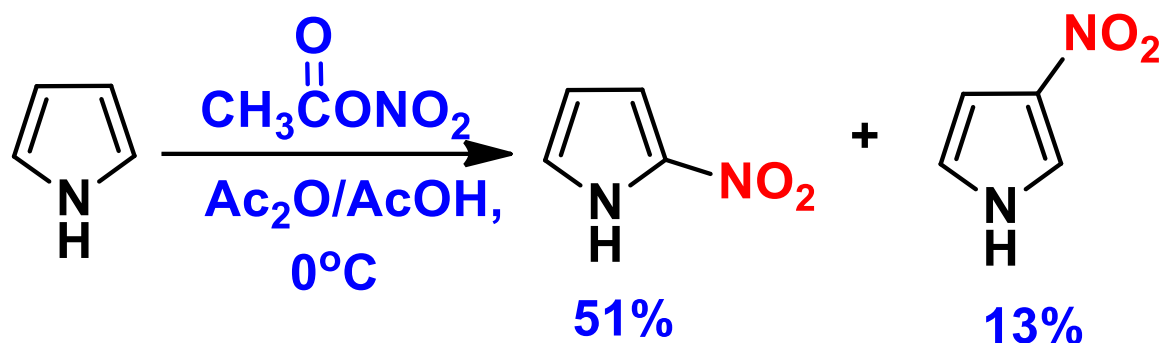
吡咯等的化学性质：亲电取代

- 活性高，类似苯胺
- 吡咯 > 呋喃 > 噻吩 > 苯
- 需采用温和条件和试剂

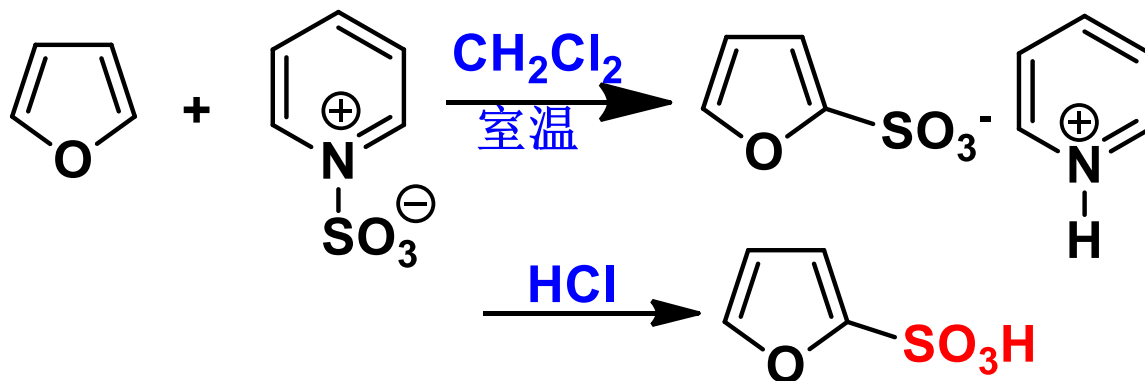


吡咯等的化学性质：亲电取代

- 硝化：一般使用温和硝化剂硝乙酰

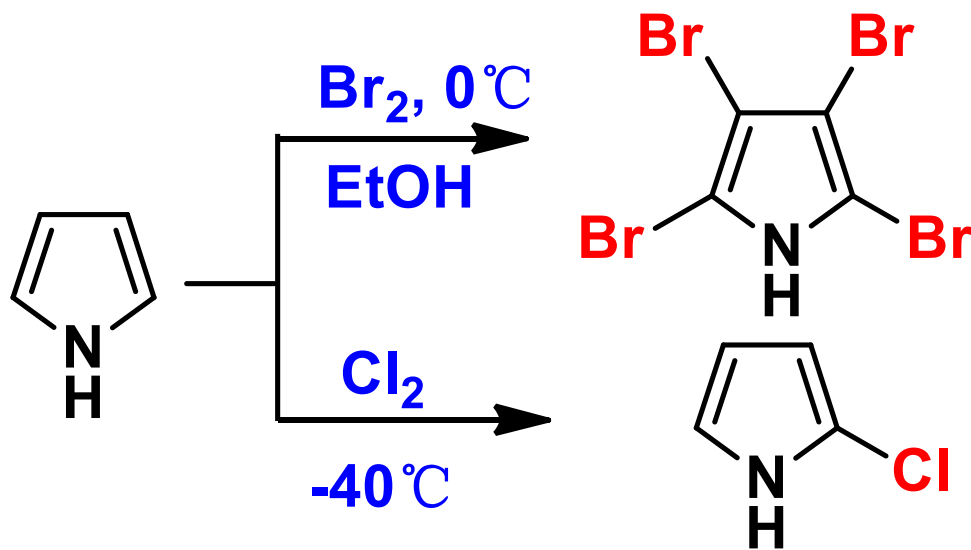


- 磺化：同样使用温和磺化剂



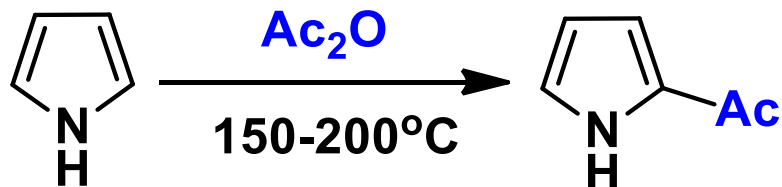
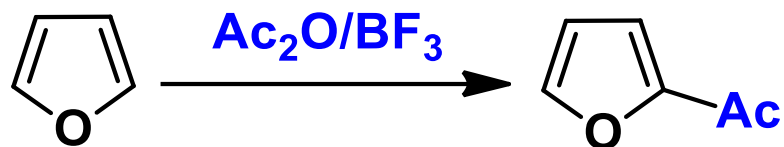
吡咯等的化学性质：亲电取代

- 卤代：反应剧烈，常得多卤代物

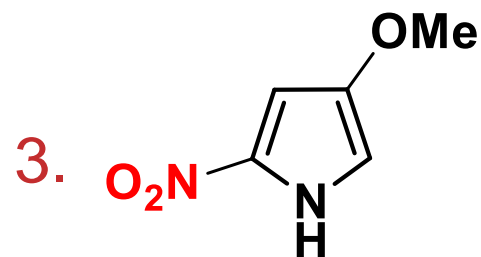
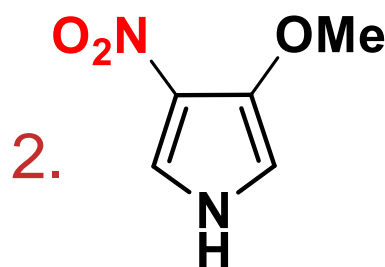
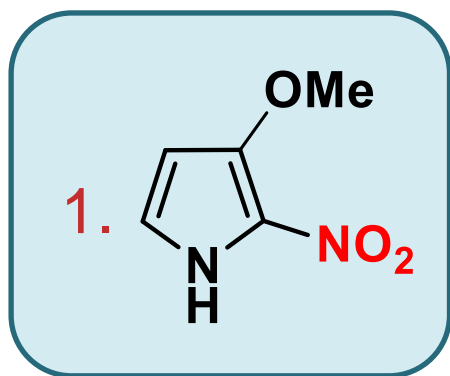
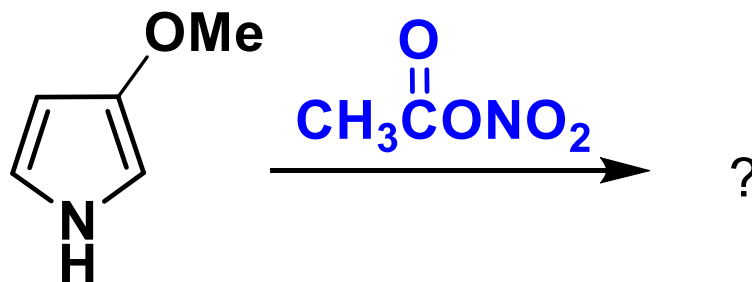


吡咯等的化学性质：亲电取代

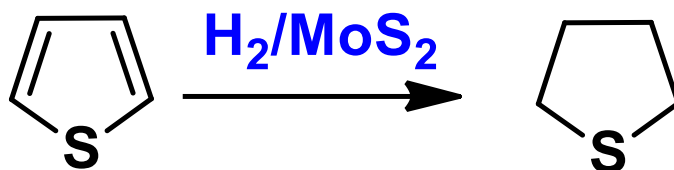
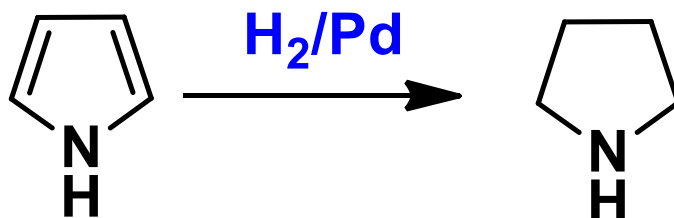
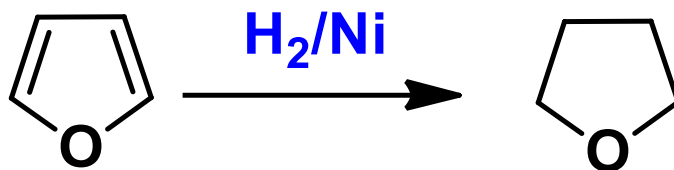
- 傅克酰化：使用温和催化剂



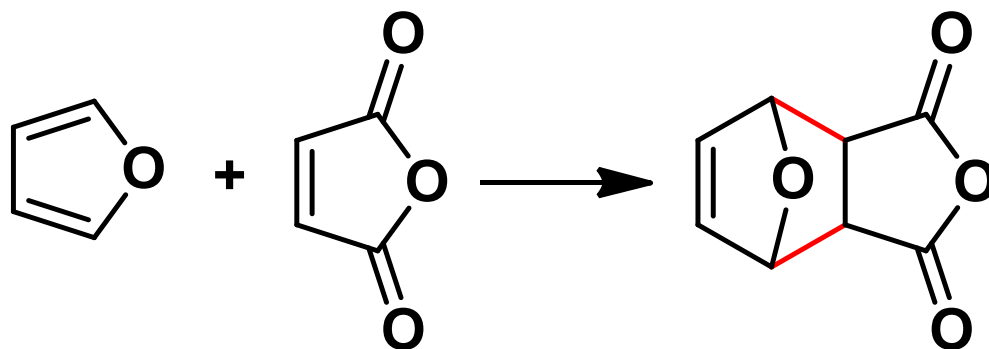
吡咯等的化学性质：亲电取代



吡咯等的化学性质：还原

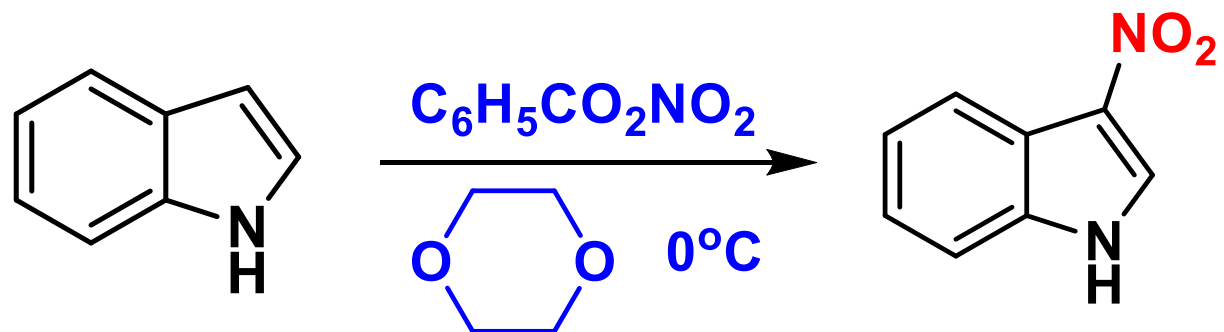


呋喃的双烯加成



呋喃芳香性较差，可体现共轭二烯的性质
吡咯、噻吩一般条件下不发生此类反应

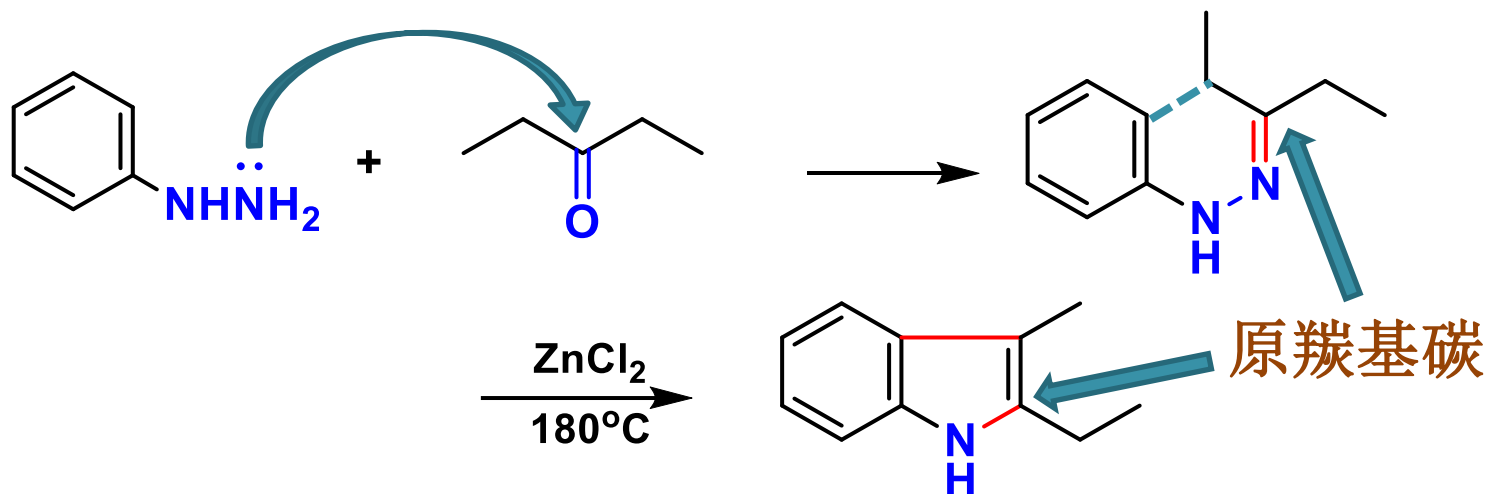
吲哚的化学性质



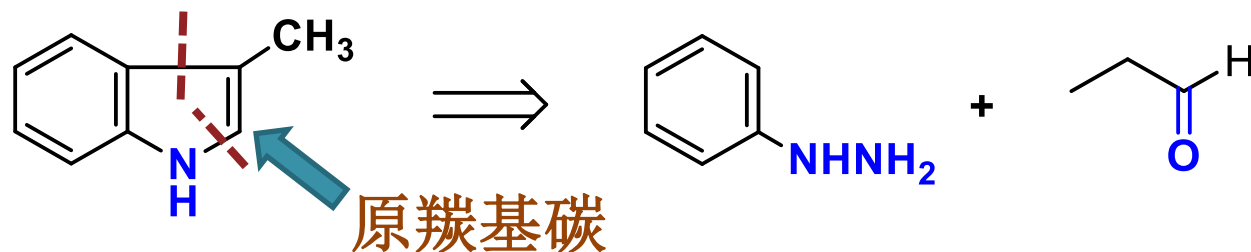
亲电取代反应性与呋喃类似
注意取代主要发生于3-位

吲哚衍生物的合成

- Fischer吲哚合成法

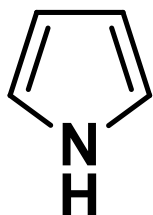


- 逆合成分析

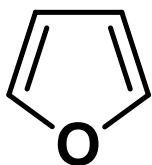


常见的五元杂环化合物

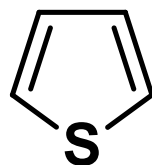
- 含单个杂原子的五元杂环



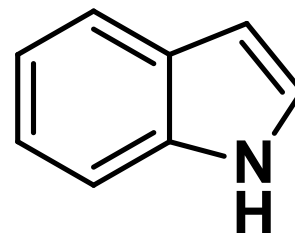
吡咯



呋喃



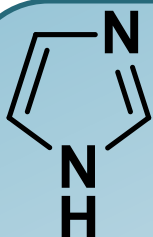
噻吩



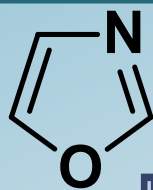
吲哚

- 含多个杂原子的五元杂环

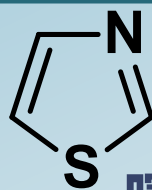
1,3-唑



咪唑

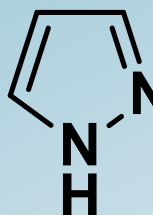


噁唑

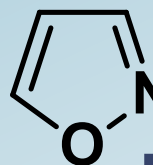


噻唑

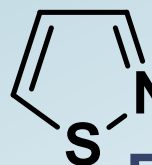
1,2-唑



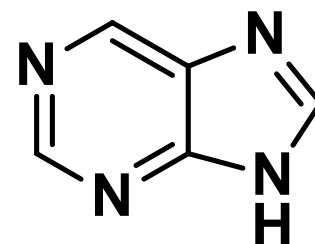
吡唑



异噁唑



异噻唑



嘌呤

唑类化合物

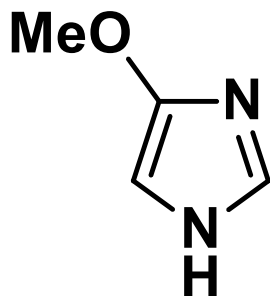
唑的命名

- 编号

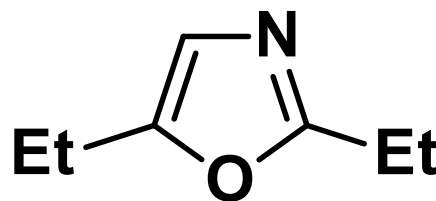
- 价数小的原子编号优先，如 $S > N$
- 价数相同，原子序数小的原子优先， $O > S$
- 若都相同，连接氢原子较多的杂原子优先



- 实例

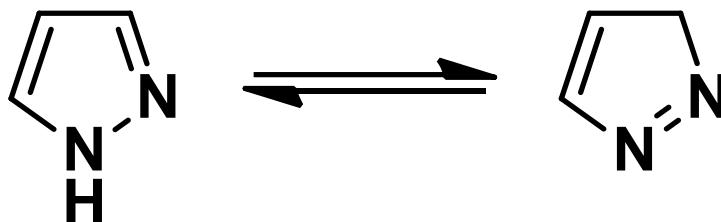


4-甲氧基咪唑



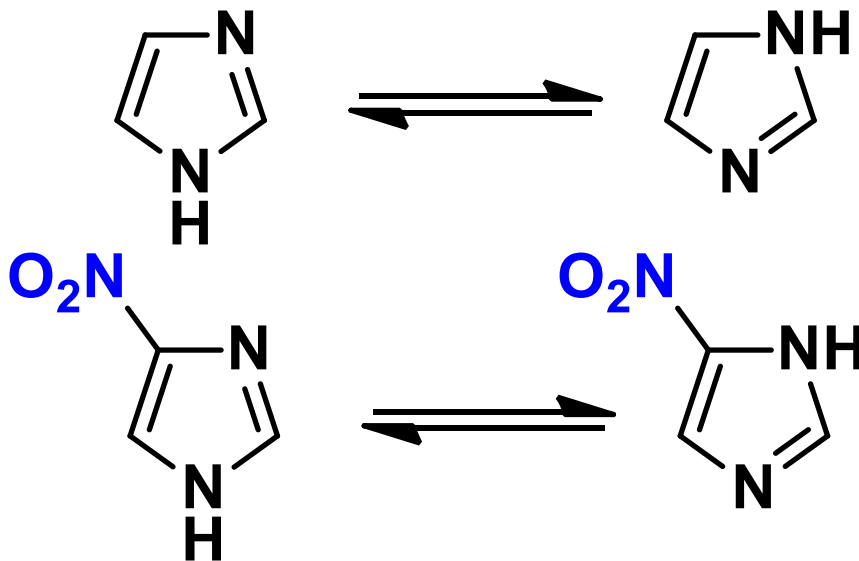
2,5-二乙基噁唑

吡唑与咪唑的互变异构



1H-吡唑

3H-吡唑



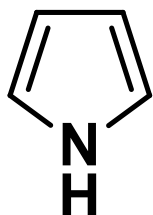
4-硝基咪唑

5-硝基咪唑

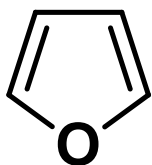
4(5)-硝基咪唑

常见的五元杂环化合物

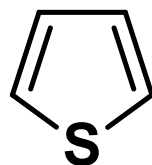
- 含单个杂原子的五元杂环



吡咯



呋喃



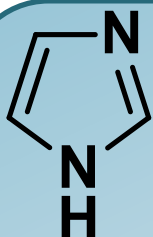
噻吩



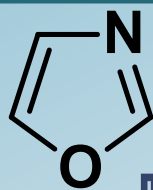
吲哚

- 含多个杂原子的五元杂环

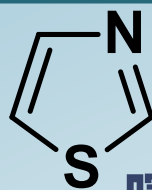
1,3-唑



咪唑

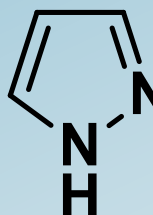


噁唑

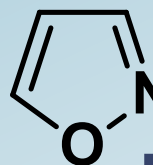


噻唑

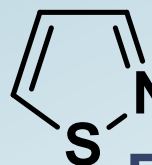
1,2-唑



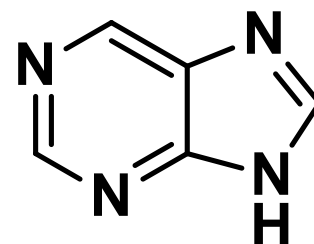
吡唑



异噁唑



异噻唑

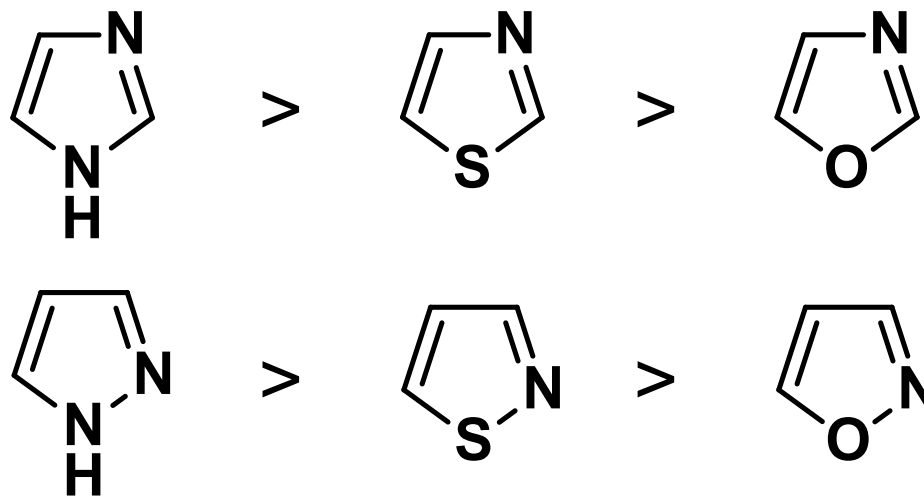


嘌呤

唑类化合物

唑的化学性质

- 碱性

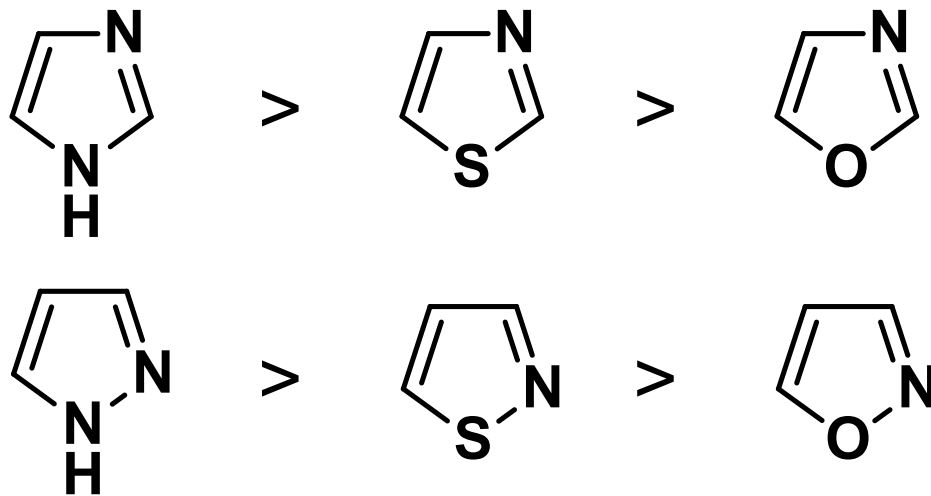


1,3-唑 > 1,2-唑

唑的化学性质

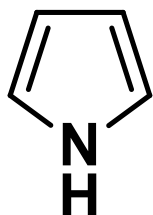
- 亲电取代活性

苯 > 唑 > 吡啶

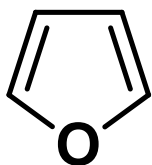


常见的五元杂环化合物

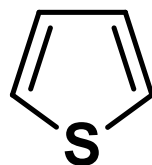
- 含单个杂原子的五元杂环



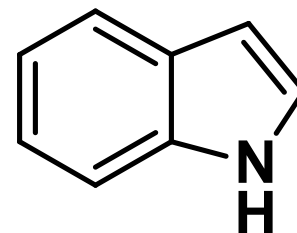
吡咯



呋喃

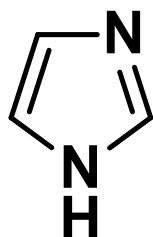


噻吩

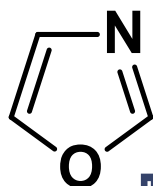


吲哚

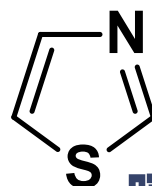
- 含多个杂原子的五元杂环



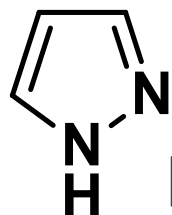
咪唑



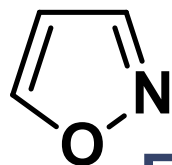
噁唑



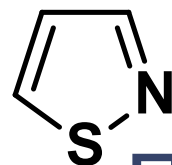
噻唑



吡唑



异噁唑

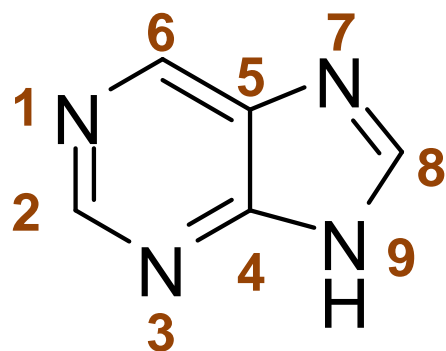


异噻唑

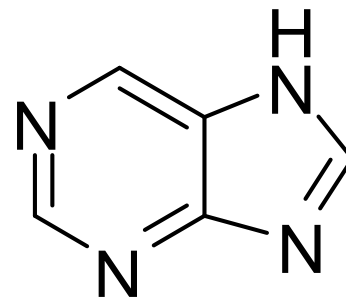
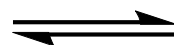


嘌呤

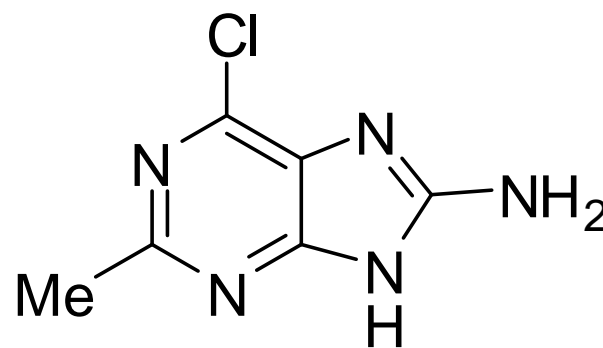
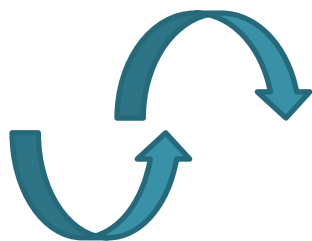
嘌呤



9H-嘌呤



7H-嘌呤



6-氯-2-甲基嘌呤-8-胺

第十五章 杂环化合物

第三节 杂环化合物的命名

杂环化合物命名的基本步骤

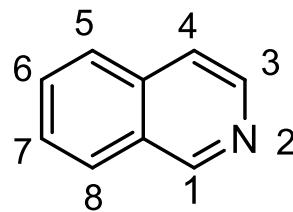
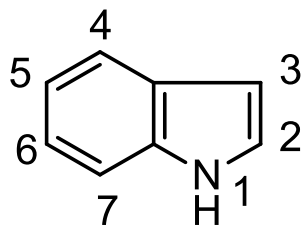
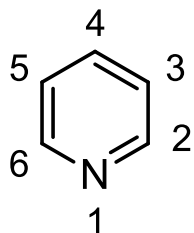
1. 杂环母核的命名
2. 杂环母核的编号
3. 根据环外基团位置写出名称

杂环母核的命名

- 习惯上采取俗名（传统名称）
 - 单个杂原子的五元单杂环
 呋喃、噻吩、吡咯、四氢呋喃
 - 两个杂原子的五元单杂环
 咪唑、噁唑、噻唑、吡唑、异噁唑、异噻唑
 - 单个杂原子的六元单杂环
 吡啶、吡喃
 - 两个杂原子的六元单杂环
 哒嗪、嘧啶、吡嗪
 - 稠杂环
 吲哚、喹啉、异喹啉、嘌呤

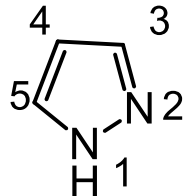
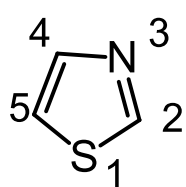
杂环母核的编号

- 通常从杂原子开始编1号



特例：异喹啉

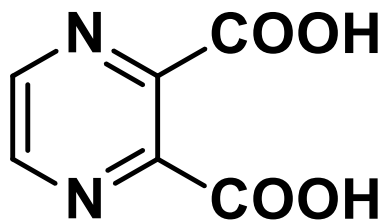
- 含多个杂原子时，按O、S、吡咯N、吡啶N的次序，优先级高的位次靠前



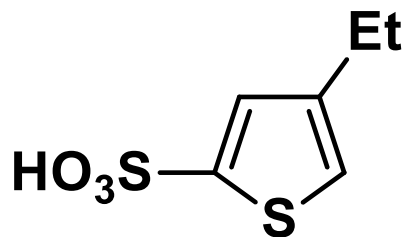
- 稠环绕大环编号，通常跳过稠合边上原子
- 个别稠杂环编号方式特殊，如嘌呤

根据环外基团位置写出名称

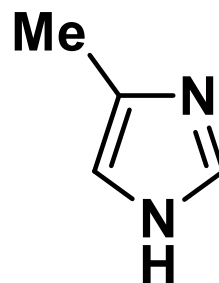
- -R、-X、-NO₂、-NO等优先级较低基团视作取代基，列于杂环名称之前
- 其它基团视作特性基团，列于杂环名称之后



吡嗪-2,3-二甲酸



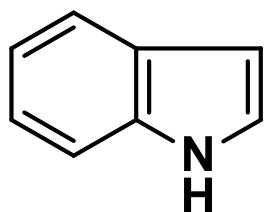
4-乙基噻吩-2-磺酸



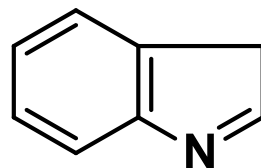
4-甲基咪唑

异构体问题

- 位置异构体的标氢

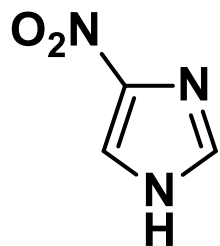


1H-吲哚

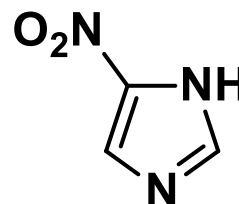
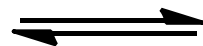


3H-吲哚

- 注意互变异构体



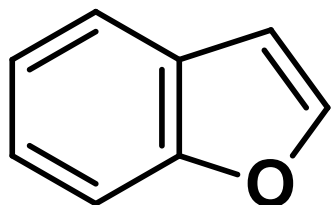
4-硝基咪唑



5-硝基咪唑

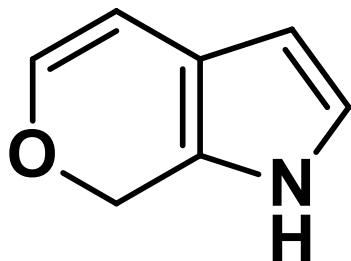
4(5)-硝基咪唑

无特定名称稠杂环母核的命名



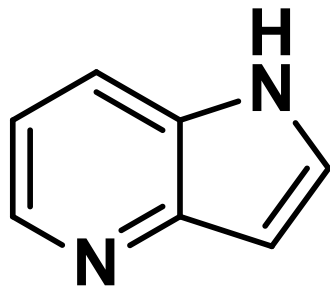
苯并[]呋喃

- 杂环+苯环，杂环为基本环



吡喃并[]吡咯

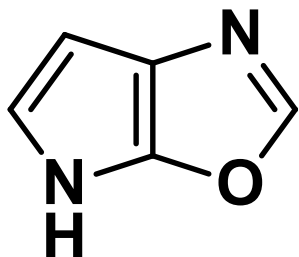
- 两环都是杂环，看环上杂原子，按N>O>S次序选择基本环



吡咯并[]吡啶

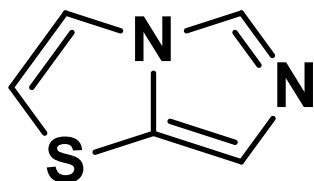
- 若两环上优先级最高的原子相同，选大环为基本环

无特定名称稠杂环母核的命名



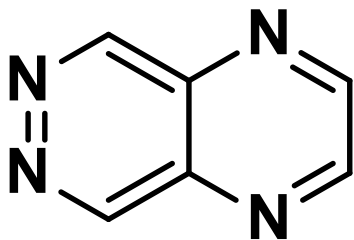
吡咯并[]噁唑

- 若环大小也相同，含杂原子数目多者优先



咪唑并[]噻唑

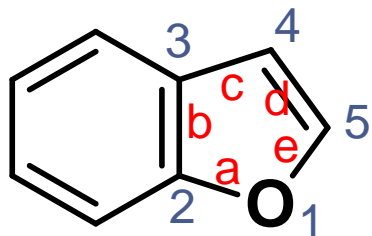
- 杂原子数目也一样，种类多者优先



吡嗪并[]哒嗪

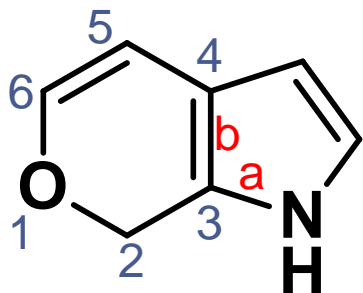
- 杂原子种类也相同，取未稠合前杂原子编号小者为基本环

无特定名称稠杂环母核的命名



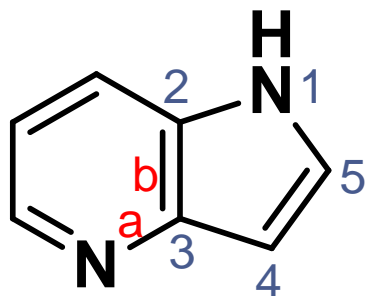
- 杂环+苯环，杂环为基本环

苯并[b]呋喃



- 两环都是杂环，看环上杂原子，按N>O>S次序选择基本环

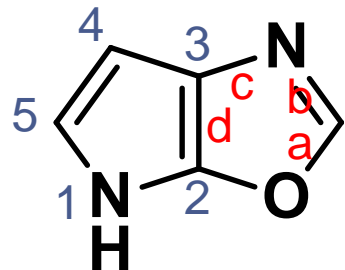
吡喃并[3,4-b]吡咯



- 若两环上优先级最高的原子相同，选大环为基本环

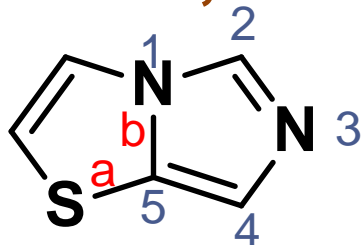
吡咯并[3,2-b]吡啶

无特定名称稠杂环母核的命名



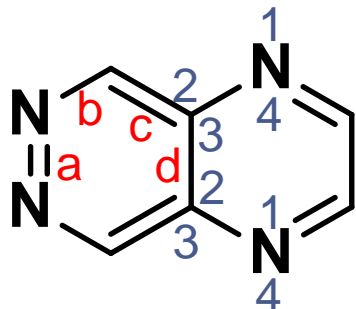
- 若环大小也相同，含杂原子数目多者优先

吡咯并[3,2-d]噁唑



- 杂原子数目也一样，种类多者优先

咪唑并[5,1-b]噻唑



- 杂原子种类也相同，取未稠合前杂原子编号小者为基本环

吡嗪并[2,3-d]哒嗪

吡嗪并[3,2-d]哒嗪 **×**