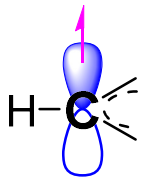
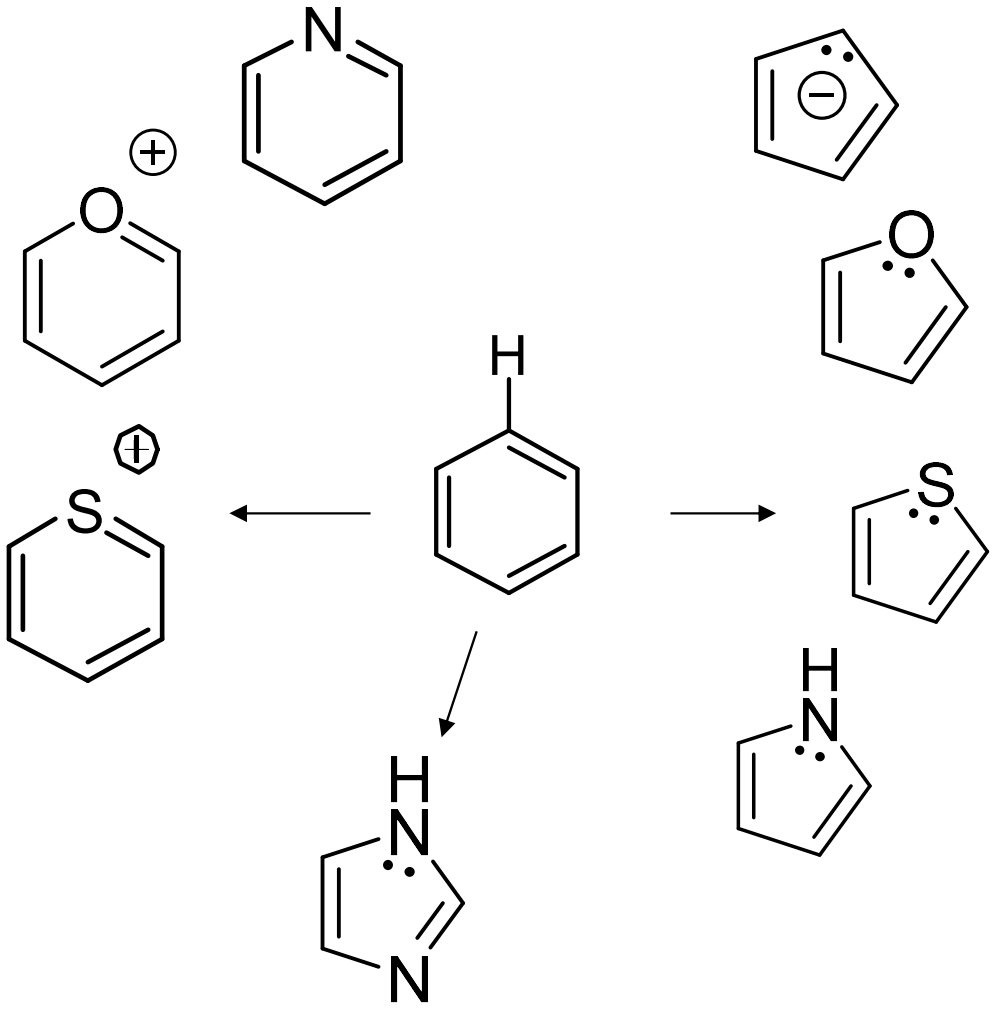
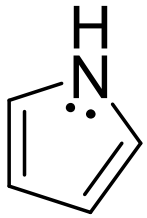
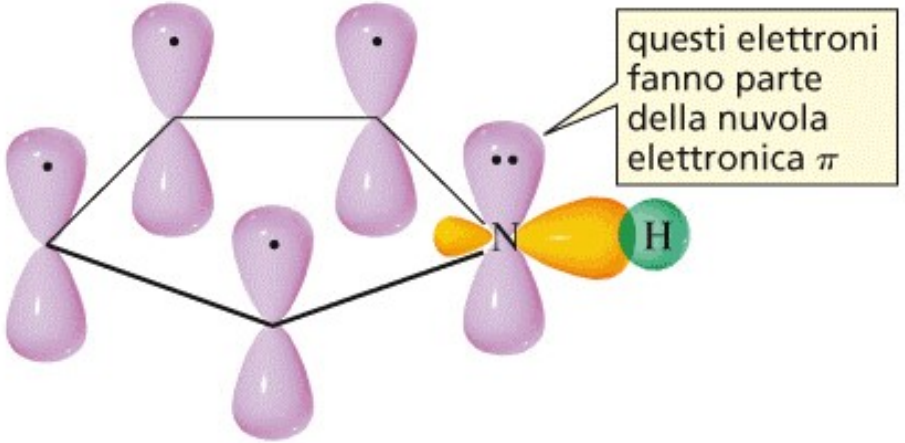
Composti eteroaromatici: quali sono?



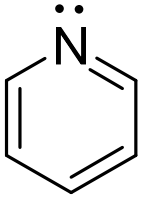


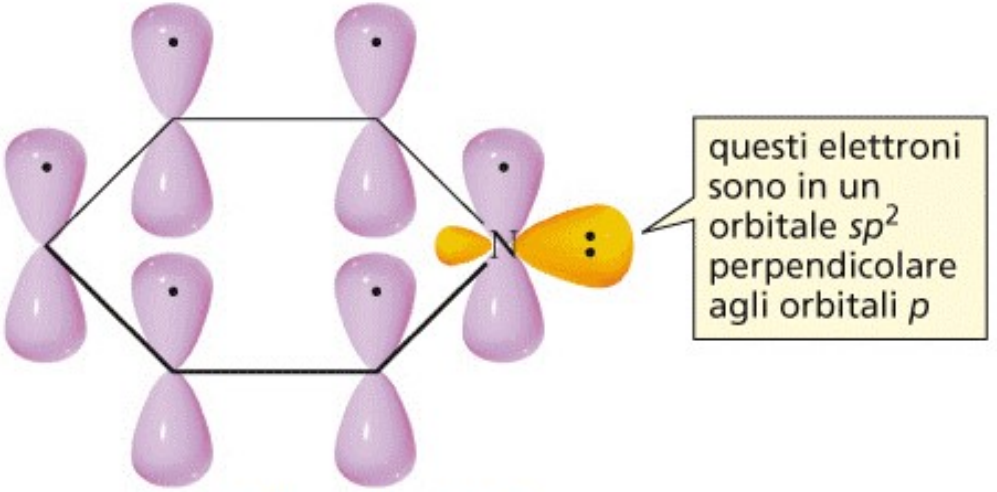
Composti eteroaromatici: quali sono?





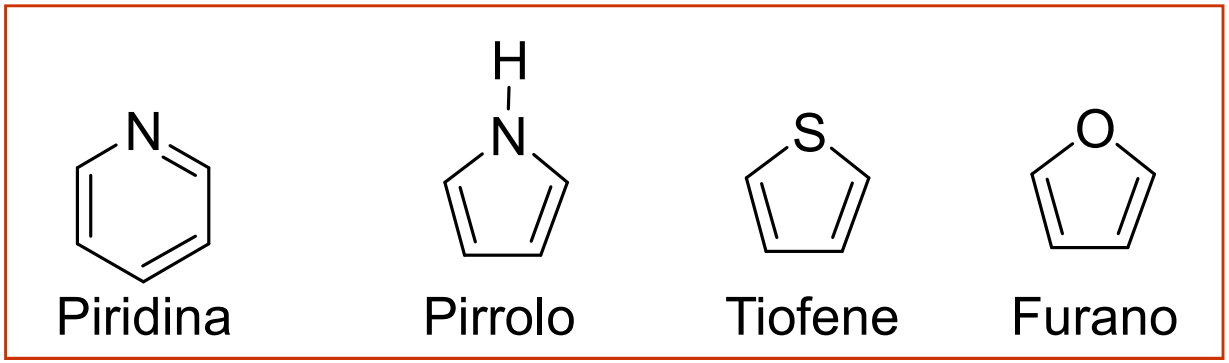
struttura orbitalica del pirrolo

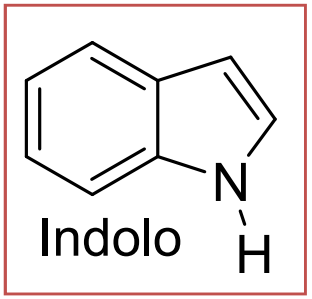




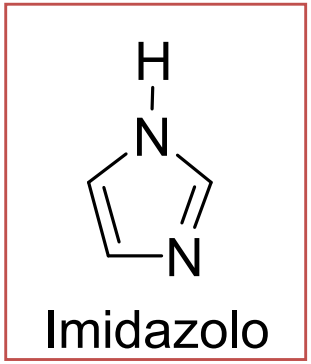
struttura orbitalica della piridina

Composti eteroaromatici

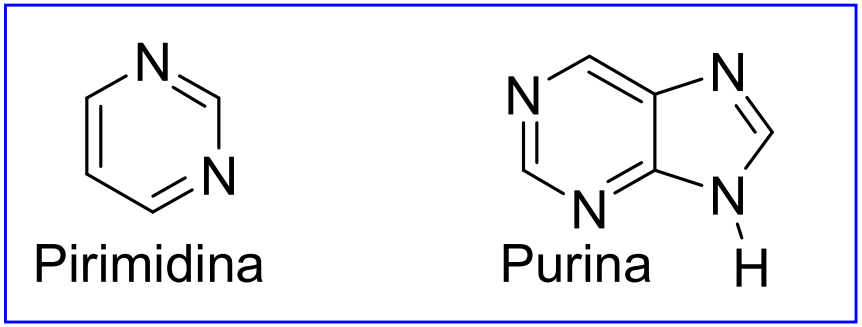




Amminoacidi
(Trp)



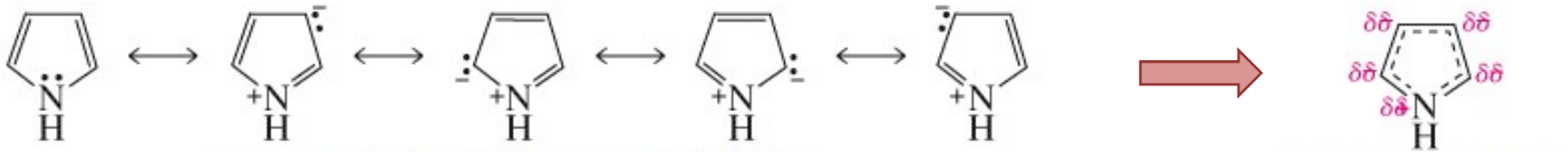
Amminoacidi
(His)



Nucleobasi,
caffeina

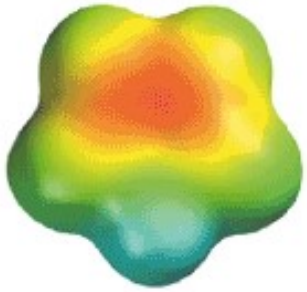
Composti eteroaromatici a 5 atomi

pirrolo furano tiofene

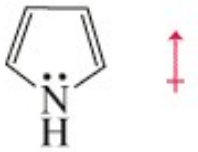


strutture limite di risonanza del pirrolo

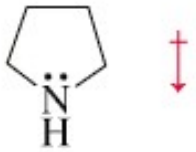
ibrido di risonanza



pirrolo



μ = 1.80 D

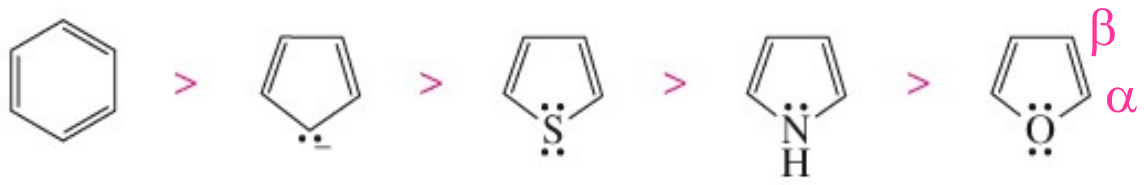


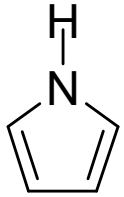
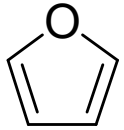
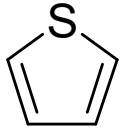
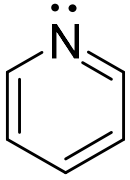
μ = 1.57 D

pirrolidina

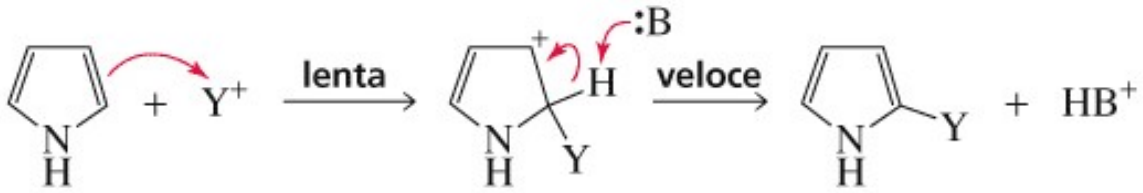
Eterocicli aromatici a 5 atomi: struttura e proprietà

energie relative di delocalizzazione di alcuni composti aromatici

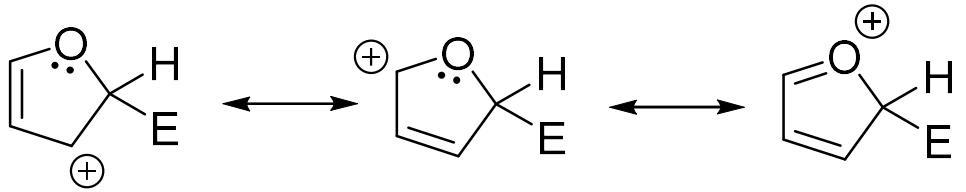


	**Pirrolo**	**89 KJ/mol**
	**Furano**	**66 KJ/mol**
	**Tiofene**	**120 KJ/mol**
	**Piridina**	**134 KJ/mol**

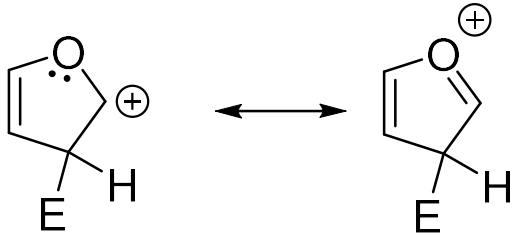
Eterocicli aromatici a 5 atomi: reattività



L'energia di coniugazione è inferiore rispetto al benzene: gli eterocicli aromatici a 5 atomo sono **attivati** verso le sostituzioni.



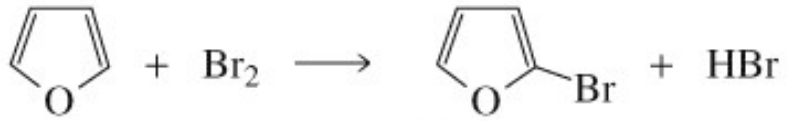
Sostituzione in α



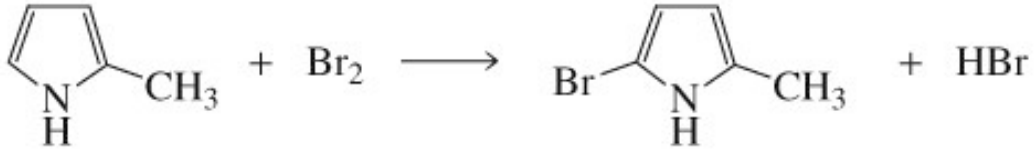
Sostituzione in β

La sostituzione avviene preferenzialmente in **posizione** α: intermedio arenio di questo cammino di reazione è più stabile.

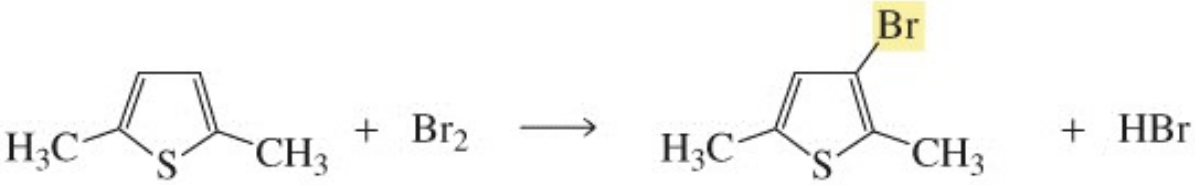
Eterocicli aromatici a 5 atomi: reattività



2-bromofurano



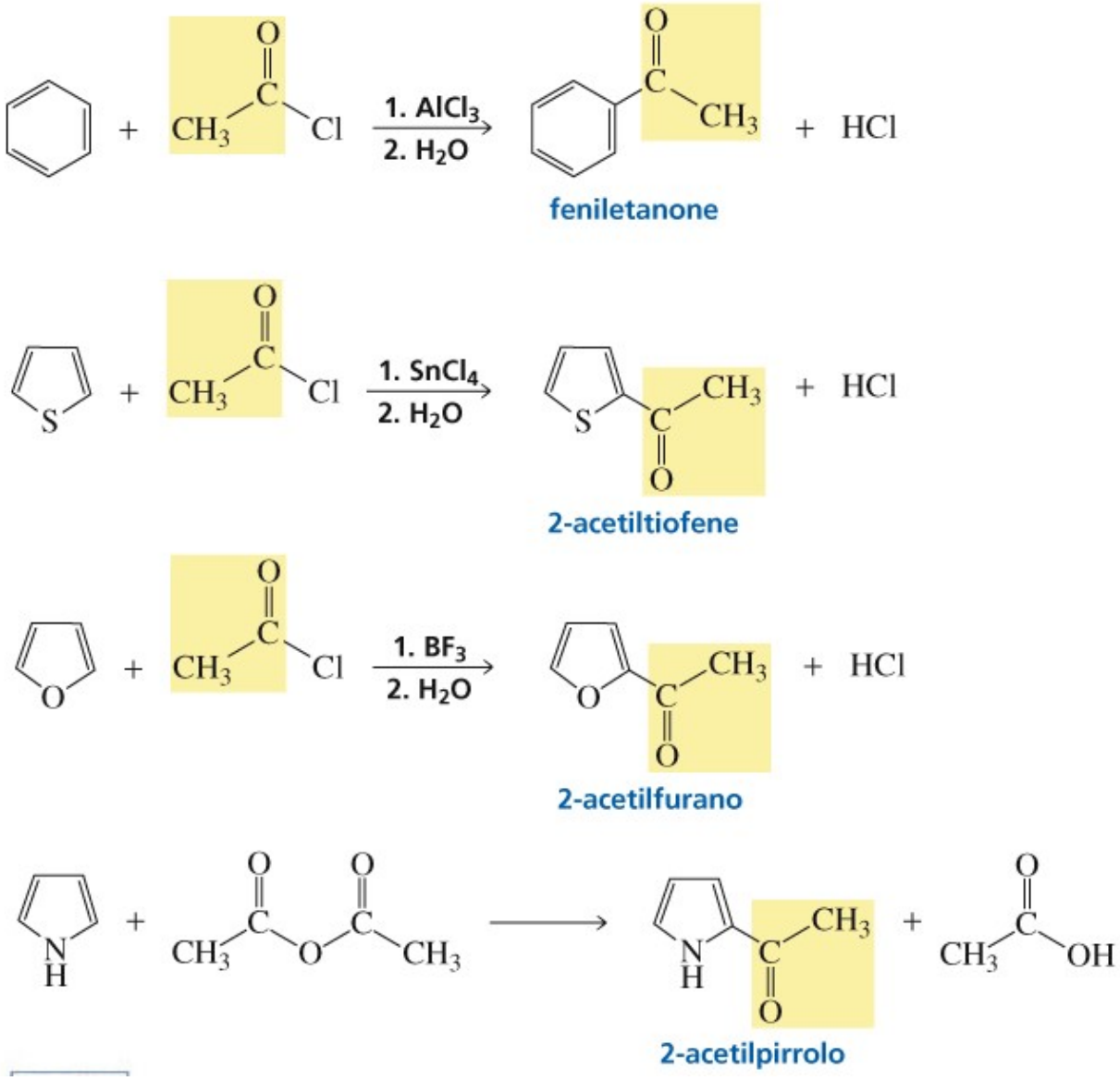
2-bromo-5-metilpirrolo



3-bromo-2,5-dimetiltiofene

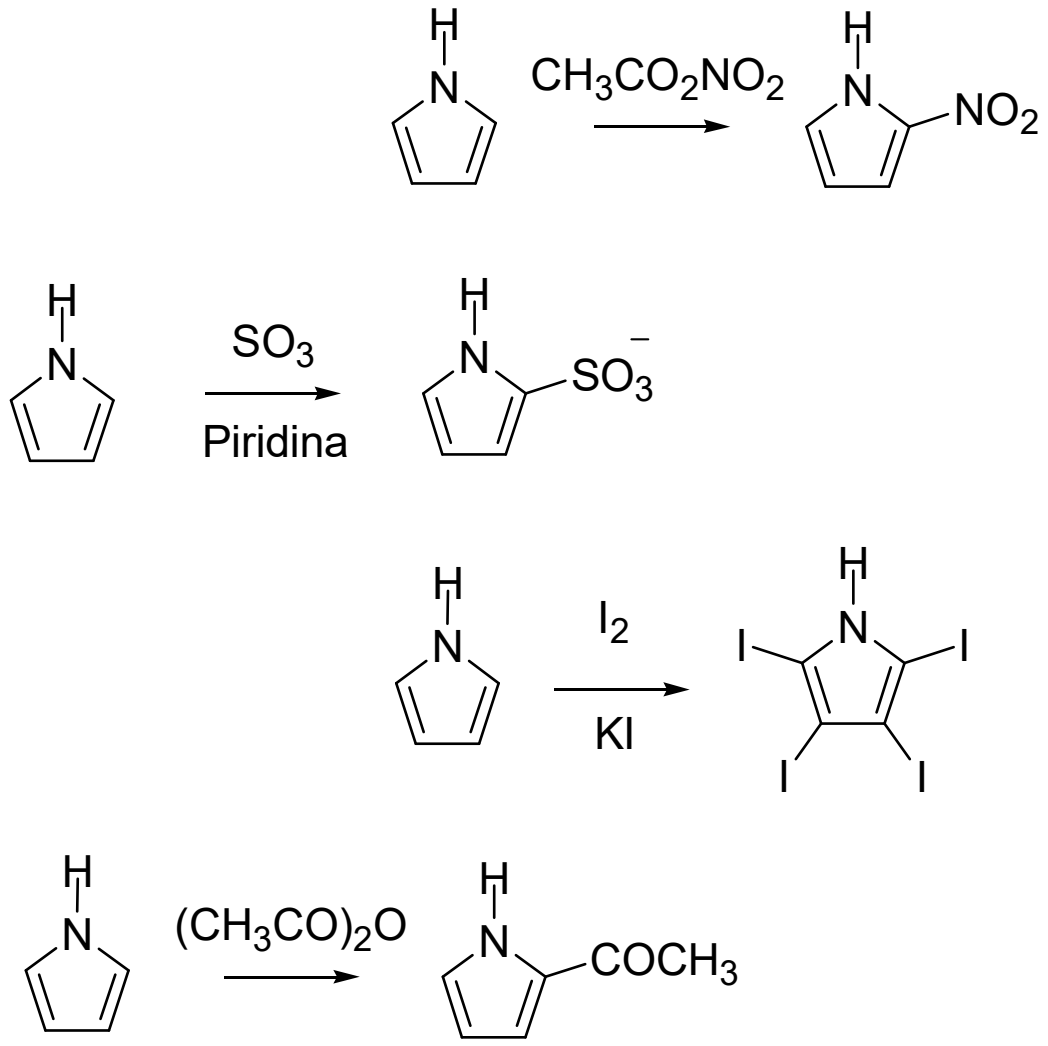
pirrolo furano tiofene benzene

Eterocicli aromatici a 5 atomi: reattività



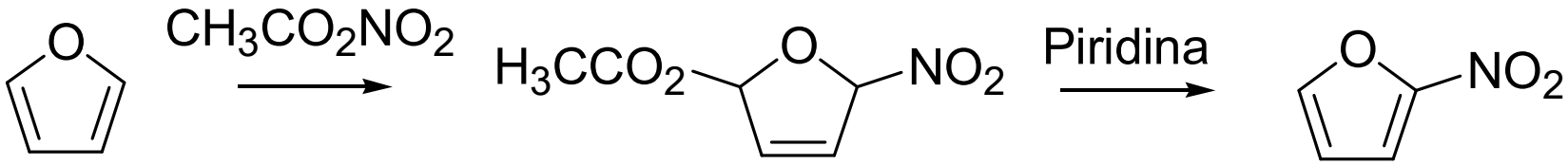
Pirrolo: reattività

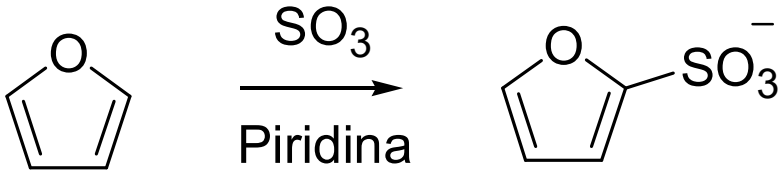
Il pirrolo è molto più reattivo del benzene. Non si possono usare acidi forti o acidi di Lewis.

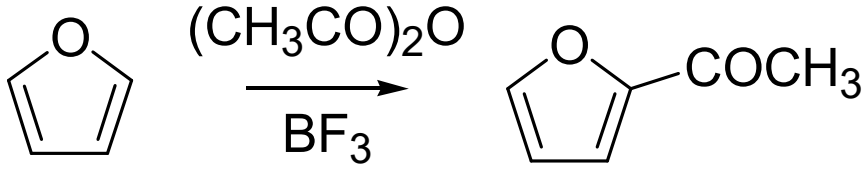


Furano: proprietà e reattività

Il furano è molto più reattivo del benzene. Non si possono usare acidi forti o acidi di Lewis. Si osservano facilmente prodotti di addizione

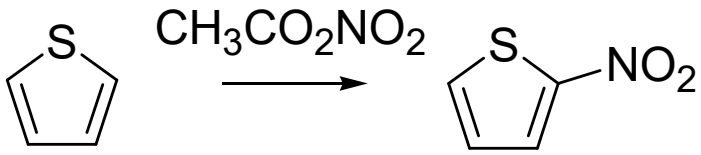


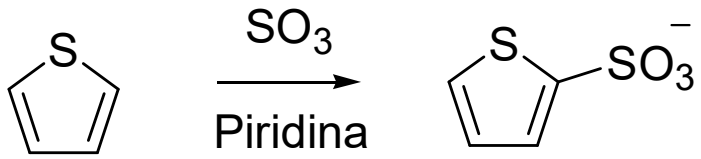


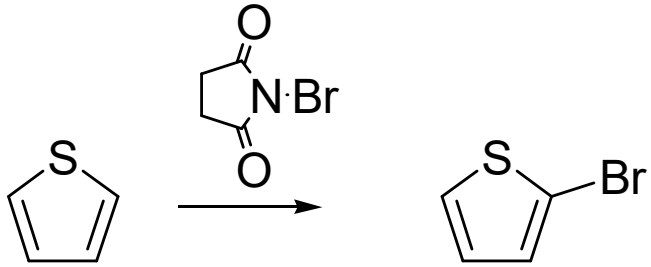


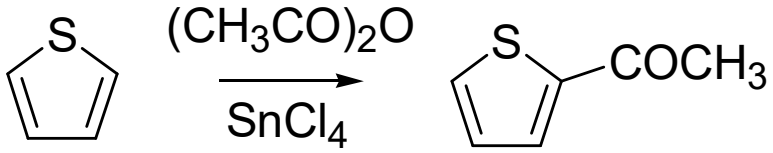
Tiofene: proprietà e reattività

Il tiofene è molto più del benzene. Più stabile agli acidi di pirrolo e furano ma polimerizza con acidi fortissimi e $AlCl_3$.





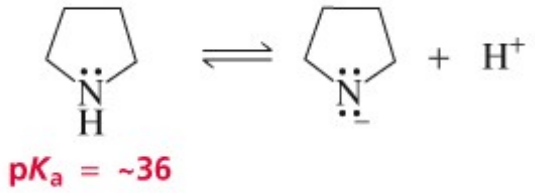


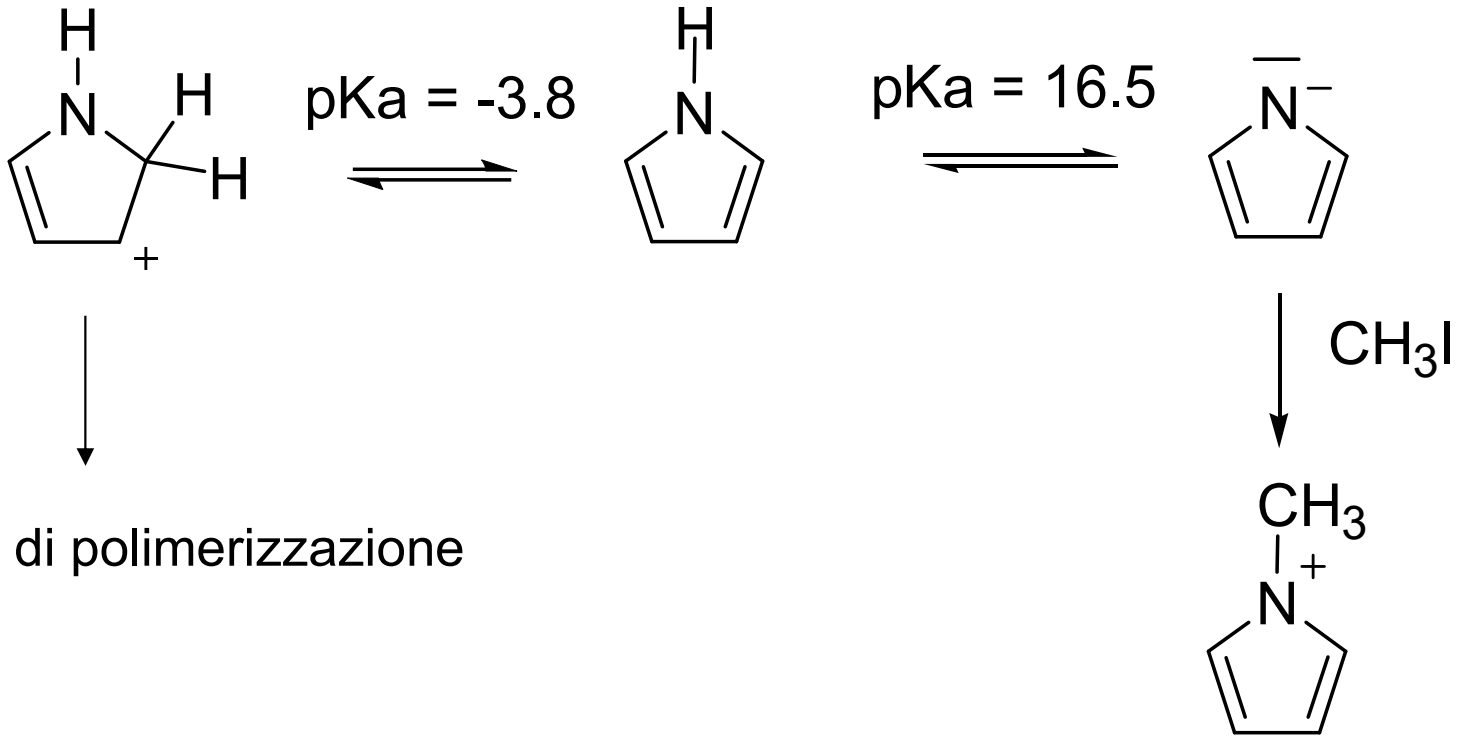


Pirrolo: proprietà e reattività

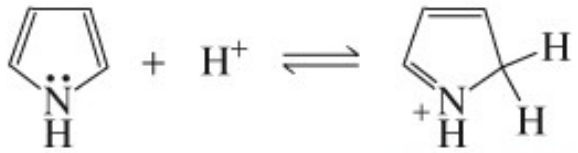
Il doppietto elettronico non condiviso fa parte del sistema aromatico: il pirrolo è base debolissima ed il sito di protonazione è il carbonio α

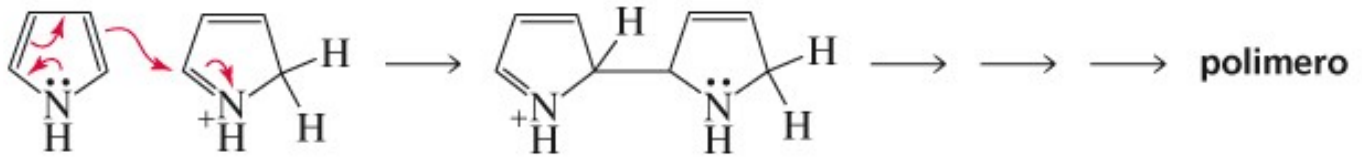
L'azoto sp^2 è più elettronegativo e l'anione è stabilizzato per risonanza: il pirrolo è un acido debolissimo.

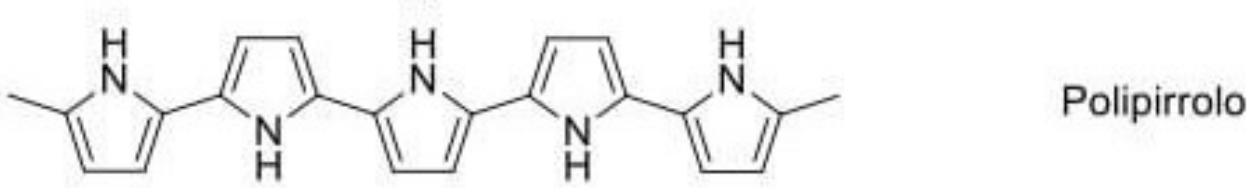




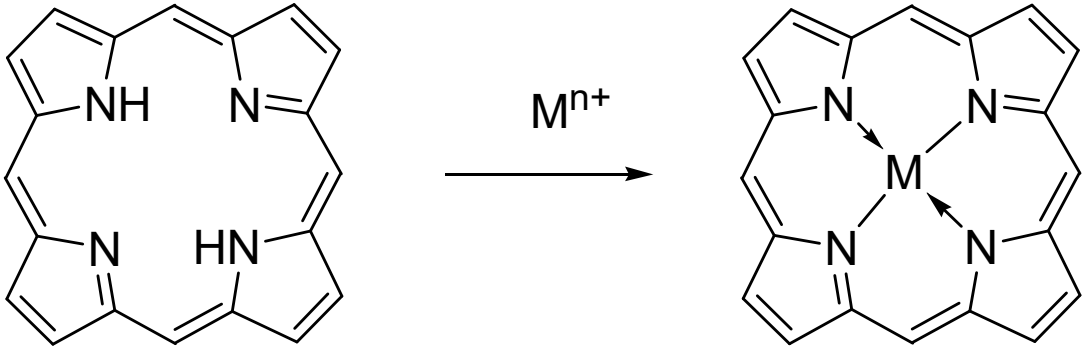
Pirrolo: proprietà e reattività



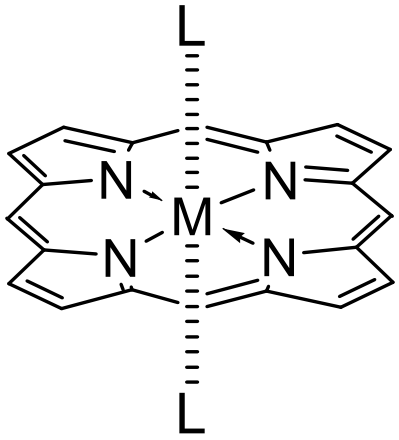




Porfine



porfina



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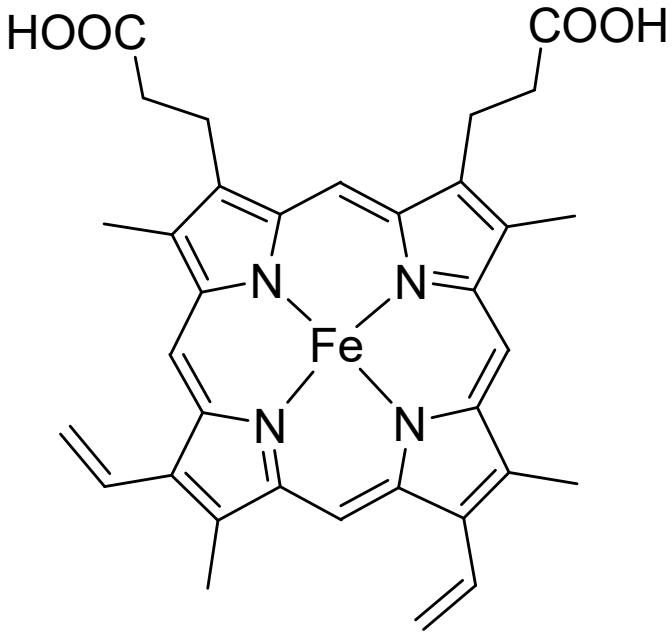
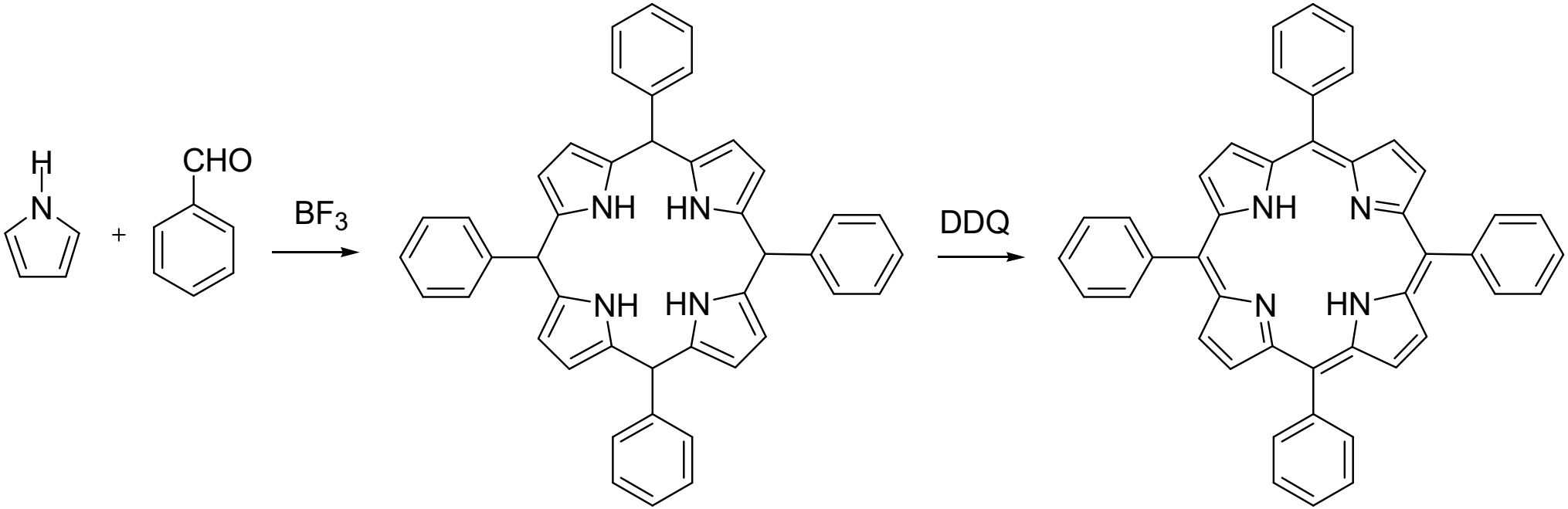


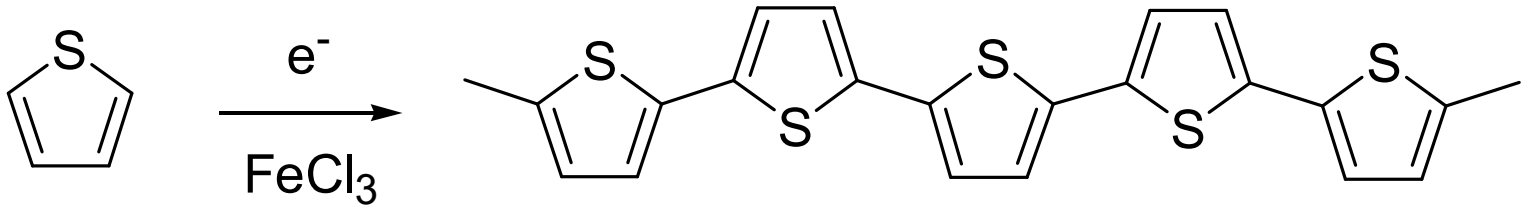
- Trasporto ossigeno
- Fotosintesi
- Ossidazione (citocromi)
- Decomposizione H_2O_2 (catalasi)

Porfirine

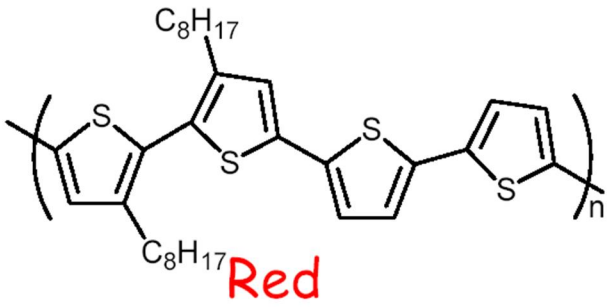


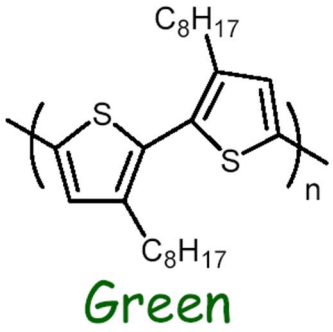
- Catalizzatori di reazioni di ossidazione
- Recettori supramolecolari
- Coloranti e fluorofori

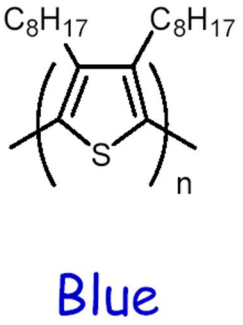
Politiofeni: polimeri coniugati



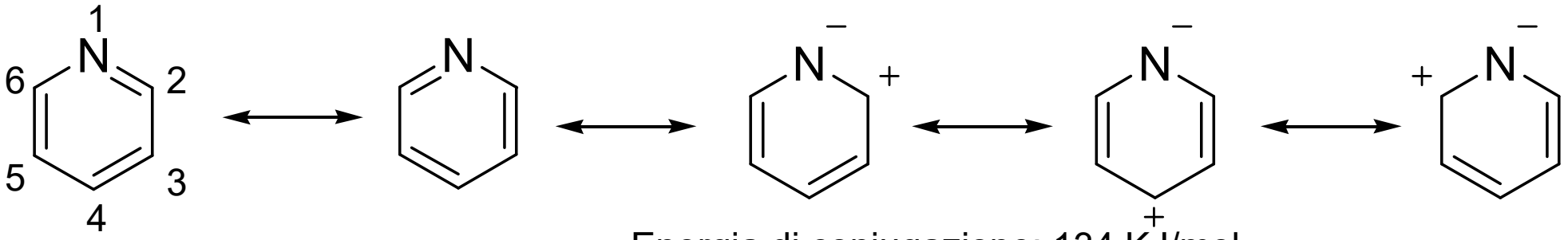
- **Organic Light Emitting Diodes (OLED)**
- **Plastic Solar Cells**
- **Organic Field Effect Transistors**



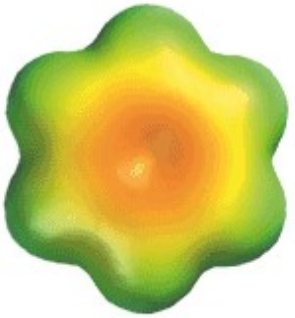




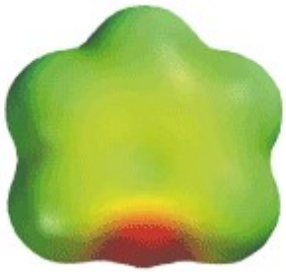
Piridina: struttura e proprietà



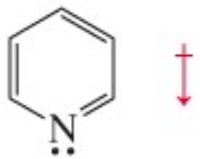
Energia di coniugazione: 134 KJ/mol

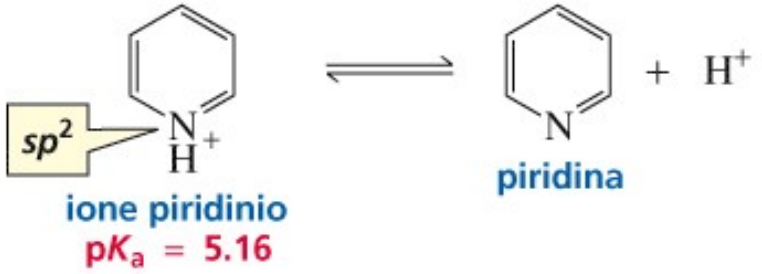


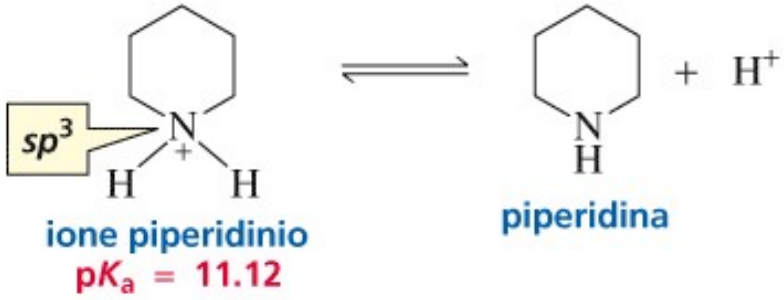
benzene



piridina

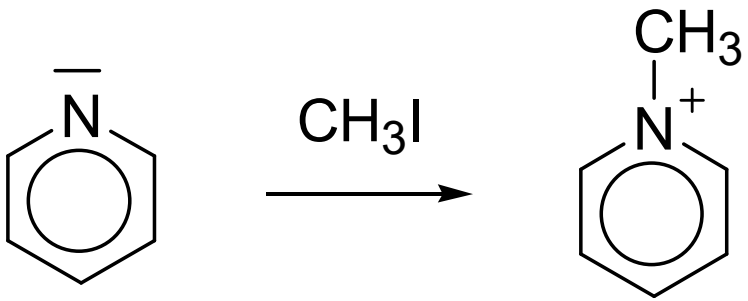




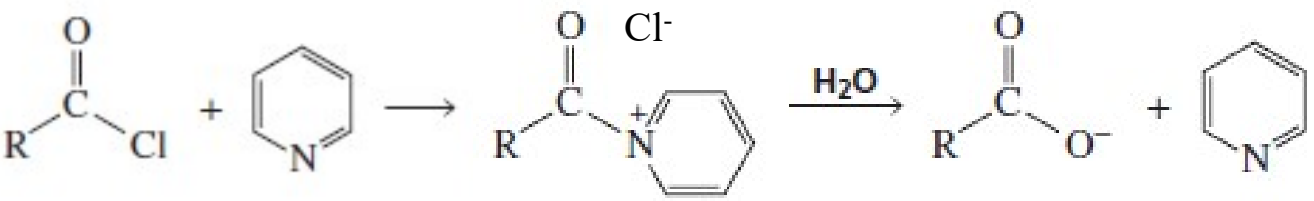


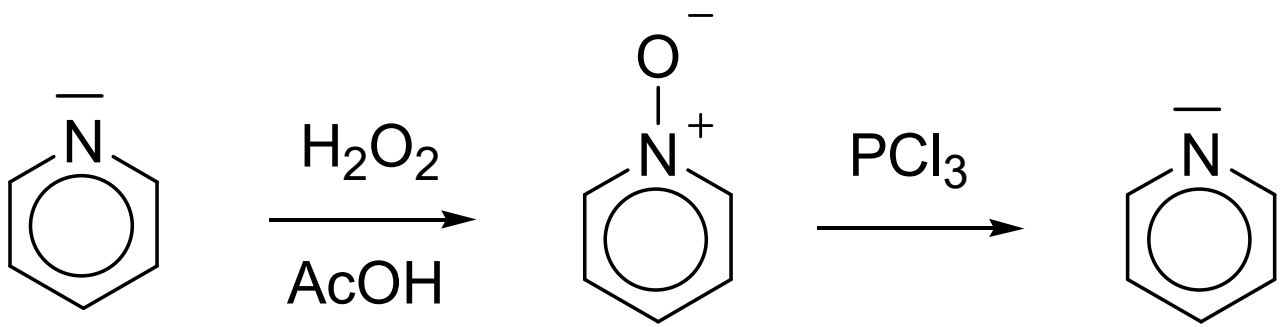
Il doppietto non condiviso si trova su un orbitale sp^2, inoltre la solvatazione del piridinio è poco efficiente: la piridina è una base debole in acqua, ma non in solventi organici!.

Piridina: reazioni all'atomo di azoto



Formazione di sali di ammonio quaternari

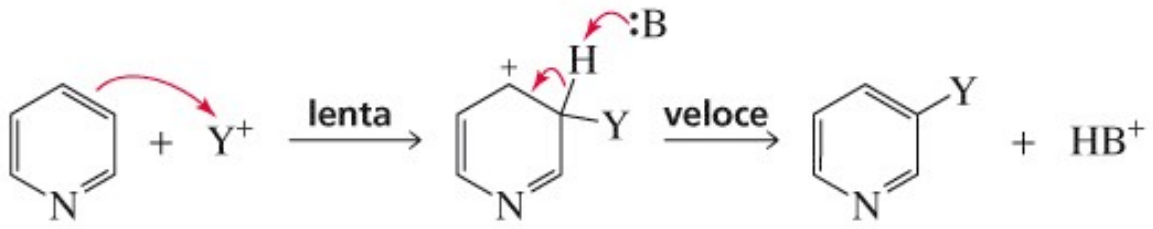




Formazione (reversibile) di N-ossidi

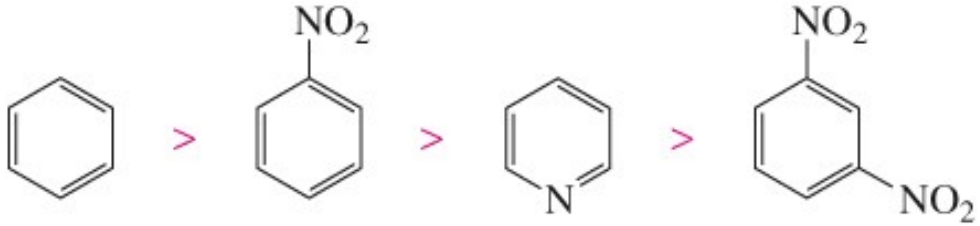
Piridina: reazioni all'anello aromatico

La presenza dell'atomo di azoto destabilizza l'intermedio carbocatione arenio: la piridina è **disattivata** verso le sostituzioni e subisce la sostituzione **preferenzialmente in posizione 3,5**.

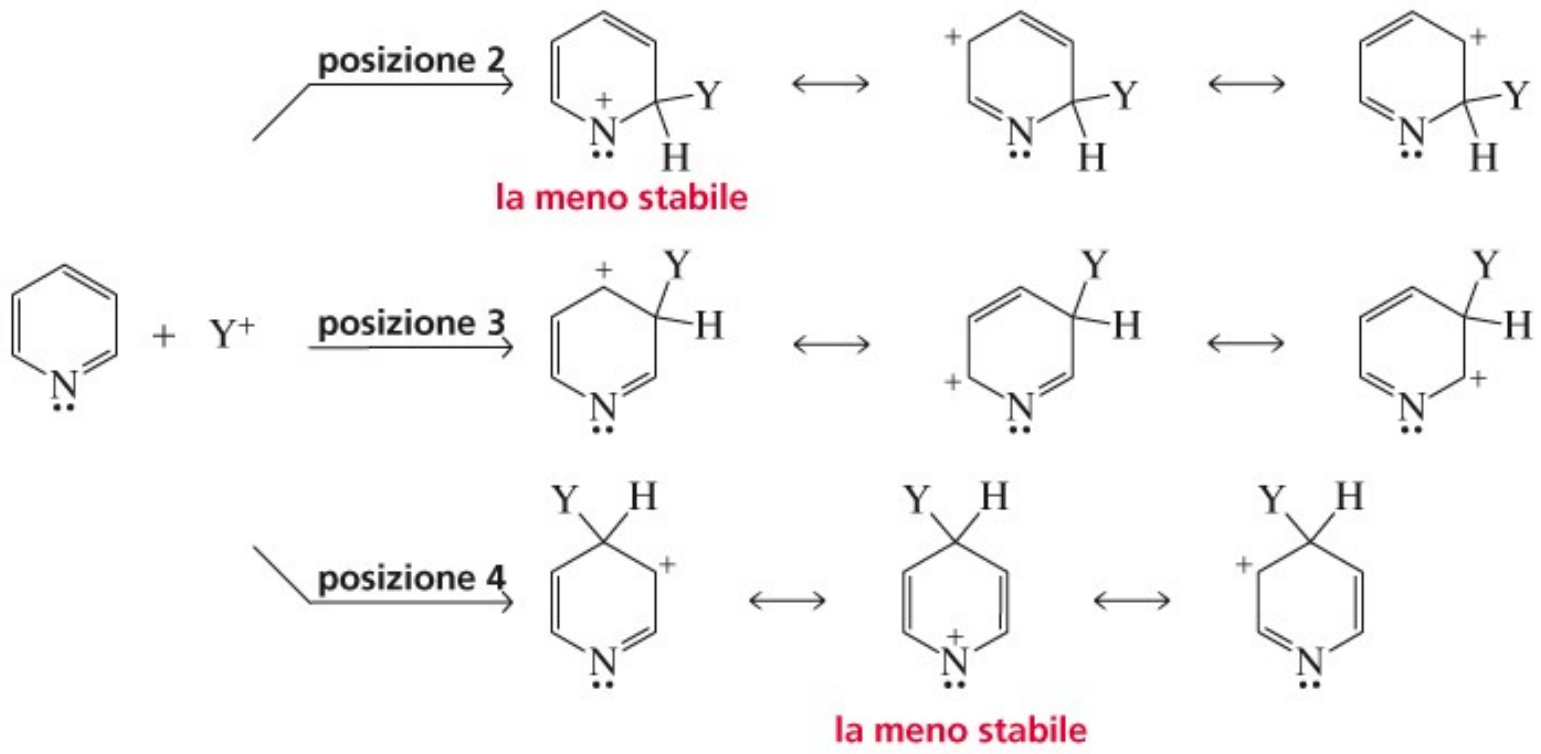


Molte reazioni di sostituzione avvengono in condizioni acide: la specie reagente non è la piridina ma il **catione piridino** (ancora più disattivato)

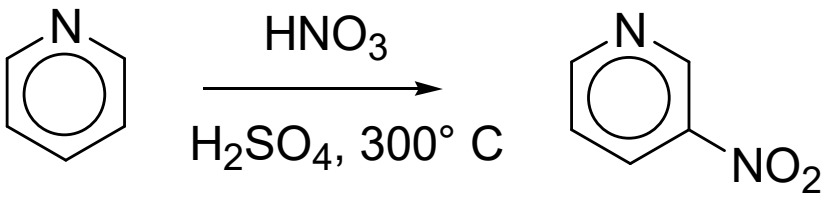
reattività relative verso la sostituzione elettrofila aromatica

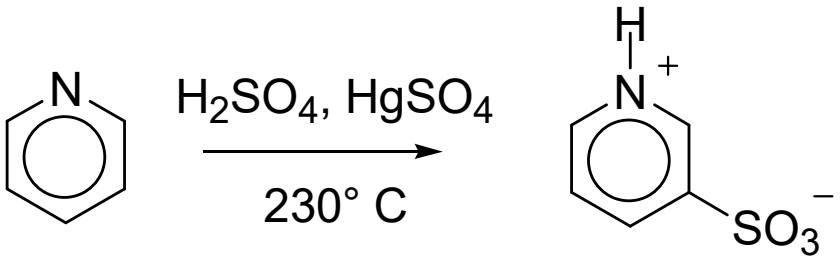


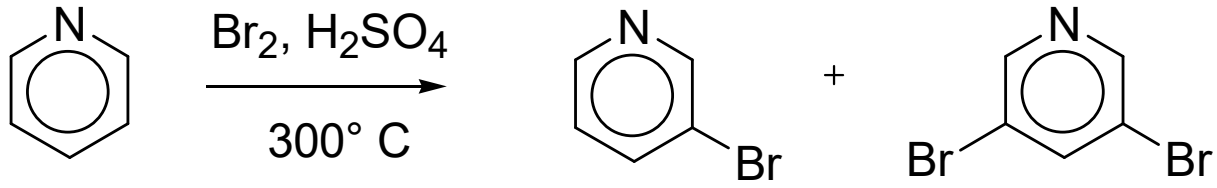
Piridina: reazione SE_{Ar}



Piridina: reazioni SE_{Ar}



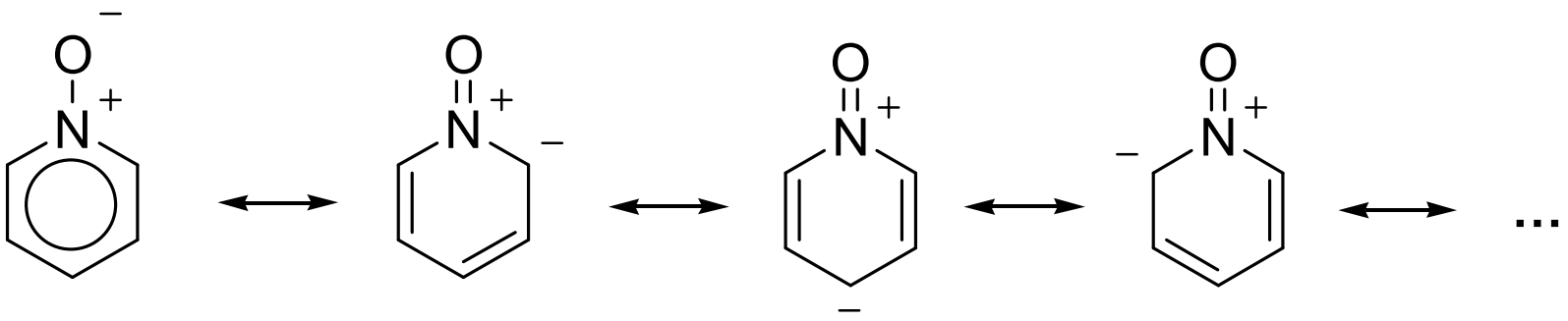




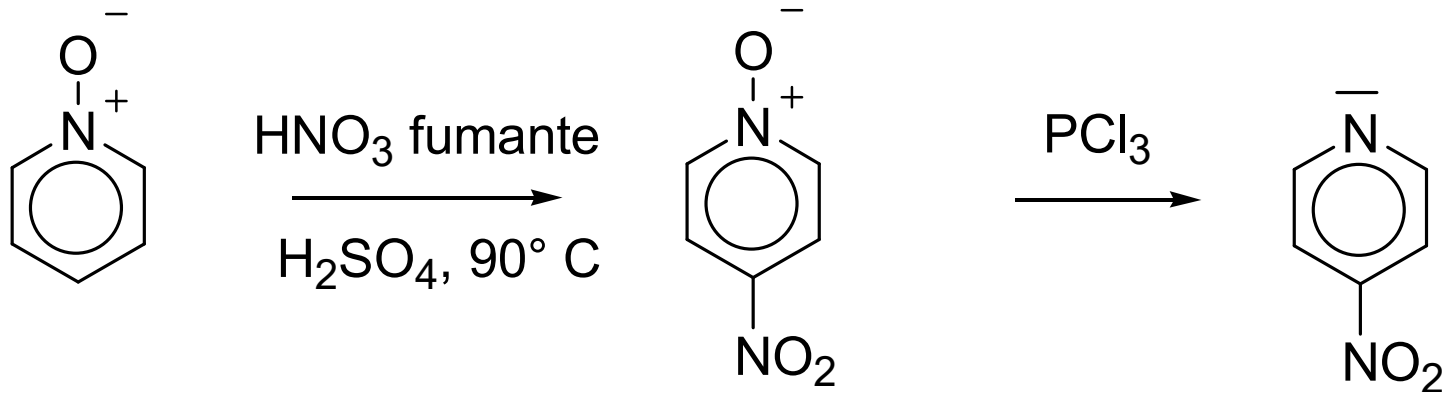
Basse rese

La reazione di Friedl-Craft non avviene sulla piridina

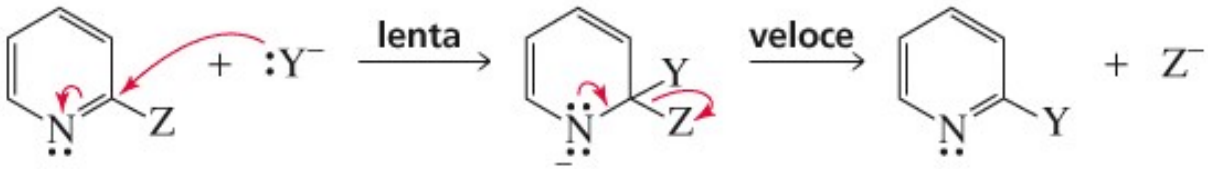
Piridina: reazioni SE_{Ar}

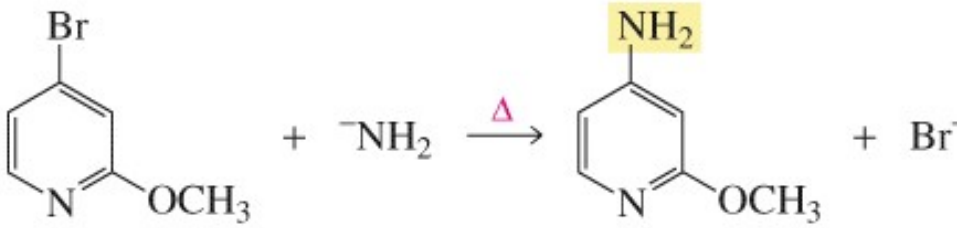


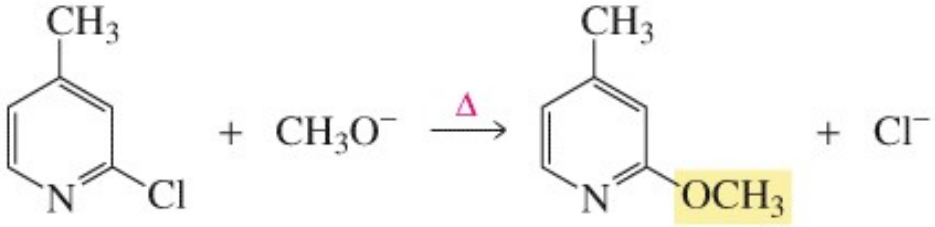
La piridina N-ossido è più attiva rispetto alla piridina (non rispetto al benzene). La sostituzione avviene preferenzialmente in posizione 2,4,6.

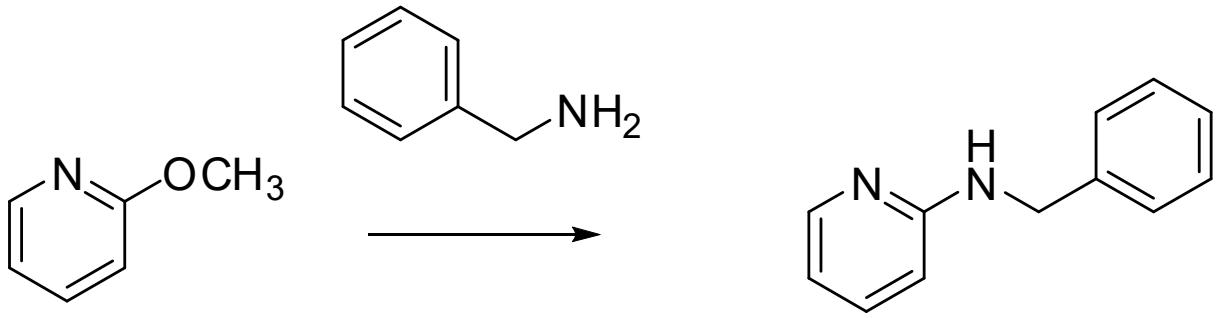


Piridina: reazioni SNAr

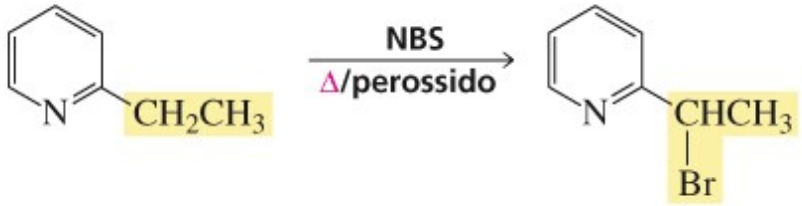


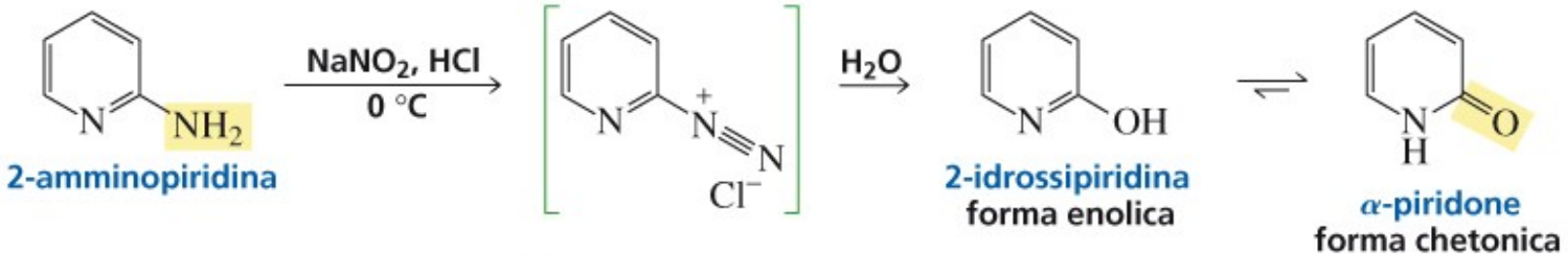


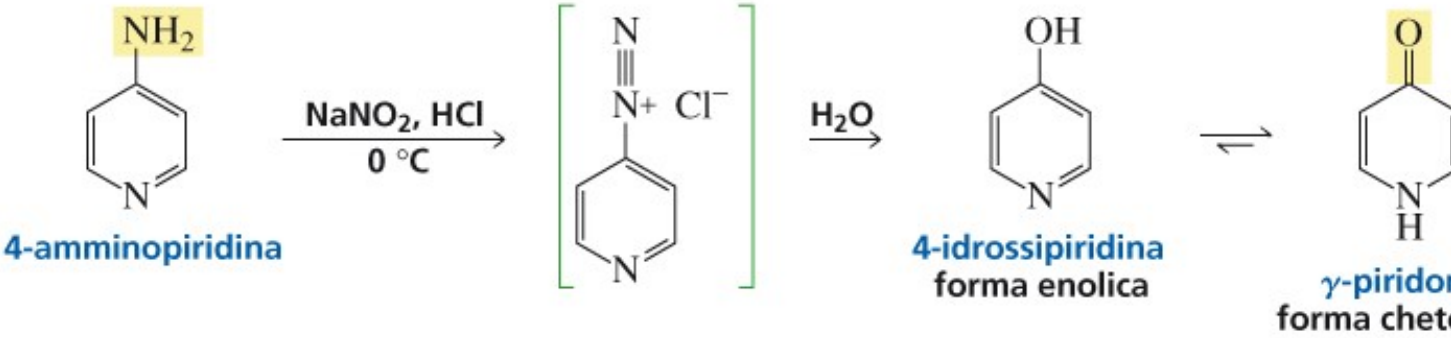




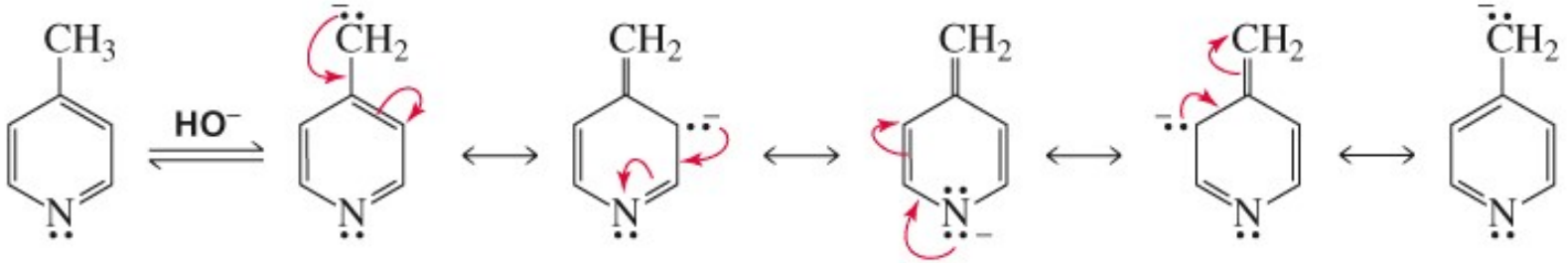
Piridina: altre reazioni

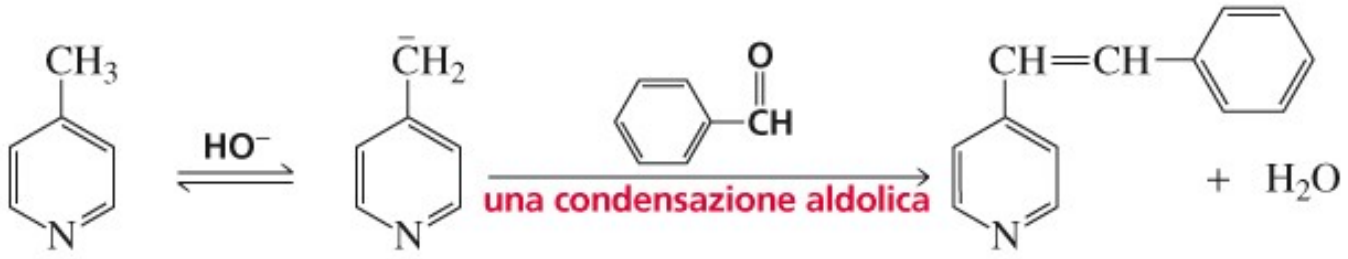




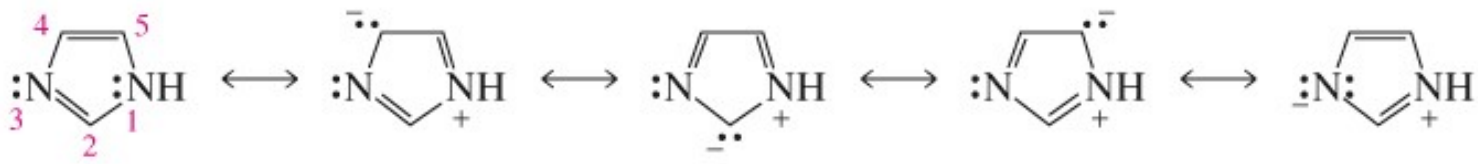


Piridina: altre reazioni

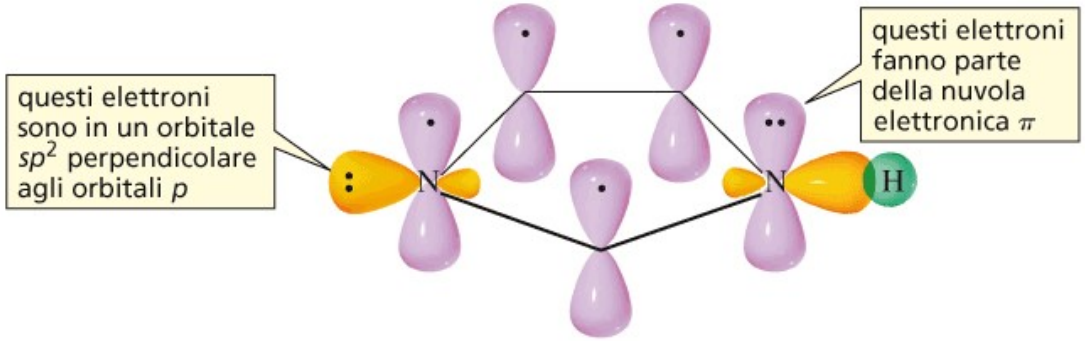




Imidazolo: altre reazioni



strutture limite di risonanza dell'imidazolo



struttura orbitalica dell'imidazolo

Imidazolo: altre reazioni