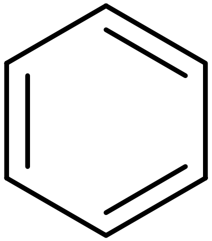
Composti Aromatici: Benzene

C_6H_6 (1825)

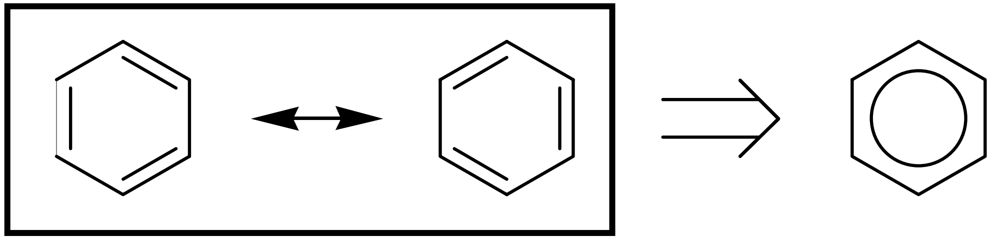


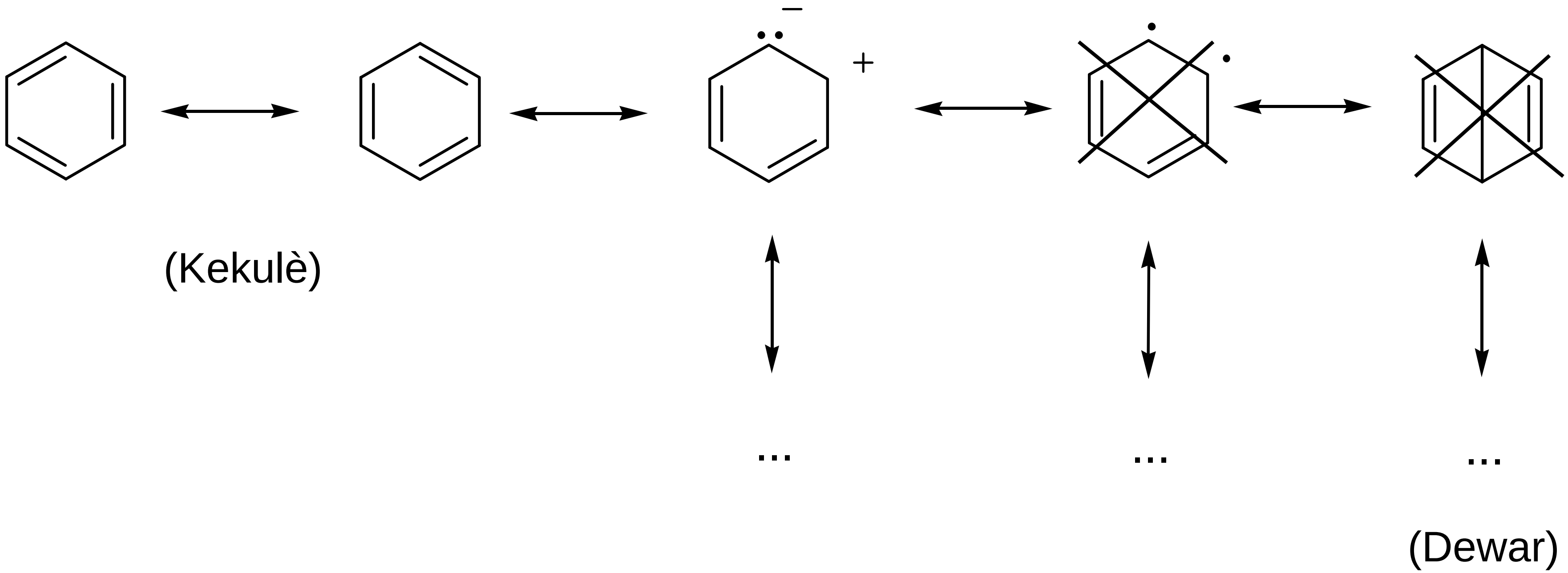
(1865)

Friedrich August Kekulé

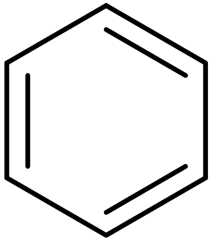
La reattività del benzene è differente dalla reattività tipica delle olefine, anche se coniugate

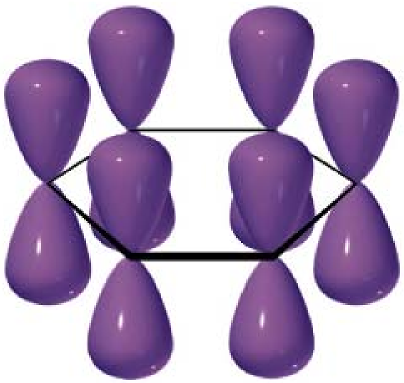
Composti Aromatici: formule di risonanza





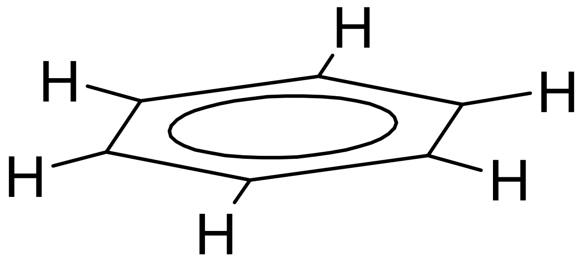
Composti Aromatici: Benzene, orbitali molecolari





6 orbitali atomici *p*

Orbitale π a più bassa energia

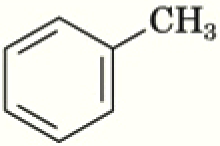
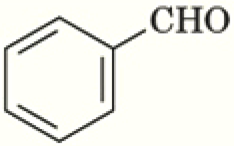
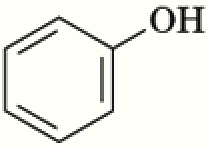
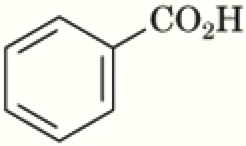
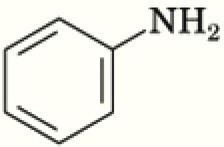
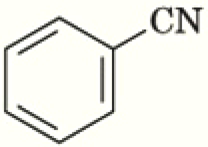
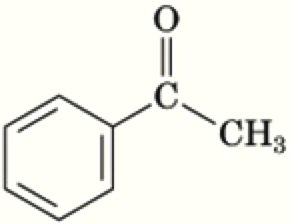
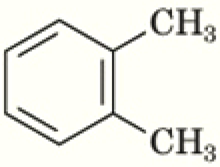
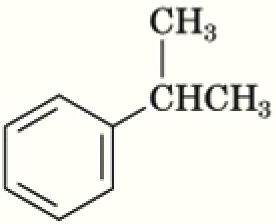
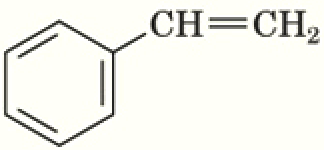


Distanza di legame C-C: 1.40 A

(C-C: 1.48 A, C=C: 1.32 A)

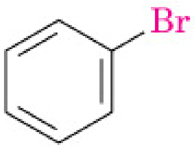
Nomenclatura dei derivati benzene: nomi comumi

TABELLA 15.1 Nomi comuni di alcuni composti aromatici

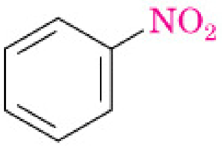
Formula	Nome	Formula	Nome
	Toluene (p.e. 111°C)		Benzaldeide (p.e. 178°C)
	Fenolo (p.f. 43°C)		Acido benzoico (p.f. 122°C)
	Anilina (p.e. 184°C)		Benzonitrile (p.e. 191°C)
	Acetofenone (p.f. 21°C)		*orto*-Xilene (p.e. 144°C)
	Cumene (p.e. 152°C)		Stirene (p.e. 145°C)

Nomenclatura dei derivati benzene: nomi IUPAC

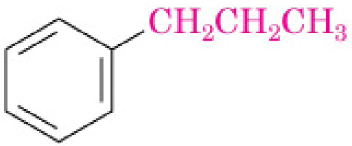
Derivati monosostituiti



Bromobenzene

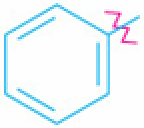


Nitrobenzene

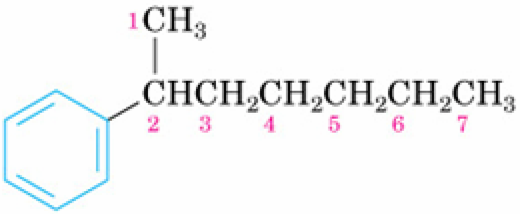


Propilbenzene

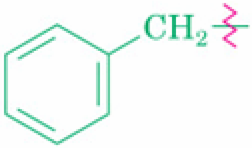
Sostituenti:



Gruppo fenilico



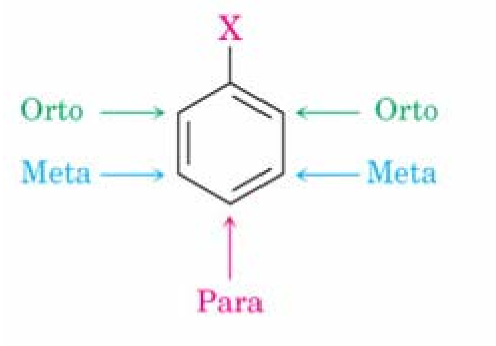
2-Fenileptano



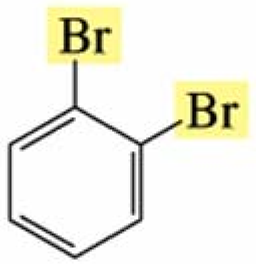
Gruppo benzilico

Nomenclatura dei derivati benzene: nomi IUPAC

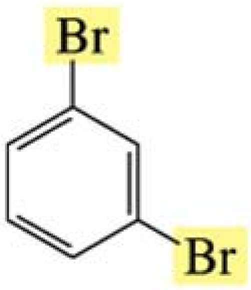
Derivati polisostituiti



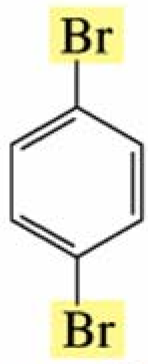
Si numera l’anello in modo che i sostituenti abbiano i numeri più bassi possibili.



1,2-dibromobenzene
***ortho*-dibromobenzene**
***o*-dibromobenzene**



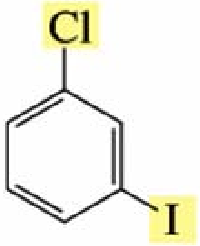
1,3-dibromobenzene
***meta*-dibromobenzene**
***m*-dibromobenzene**



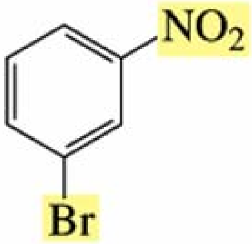
1,4-dibromobenzene
***para*-dibromobenzene**
***p*-dibromobenzene**

Nomenclatura dei derivati benzene: nomi IUPAC

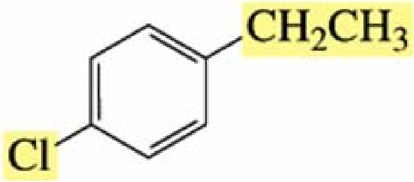
Se ci sono due sostituenti diversi, si usa l'ordine alfabetico



1-chloro-3-iodobenzene
***meta*-chloroiodobenzene**
not
1-iodo-3-chlorobenzene
***meta*-iodochlorobenzene**

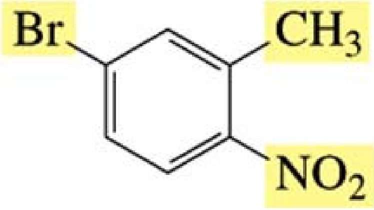


1-bromo-3-nitrobenzene
***meta*-bromonitrobenzene**

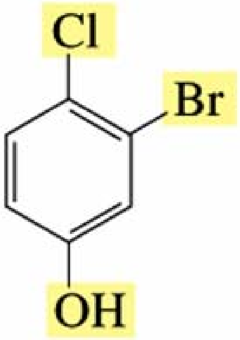


1-chloro-4-ethylbenzene
***para*-chloroethylbenzene**

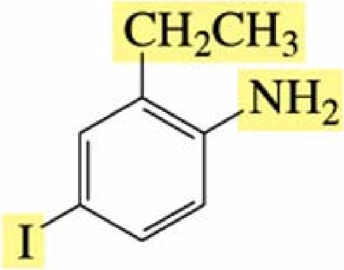
Se si usa un nome comune, il sostituente del composto monofunzionale di cui si usa il nome diventa il sostituente principale.



5-bromo-2-nitrotoluene

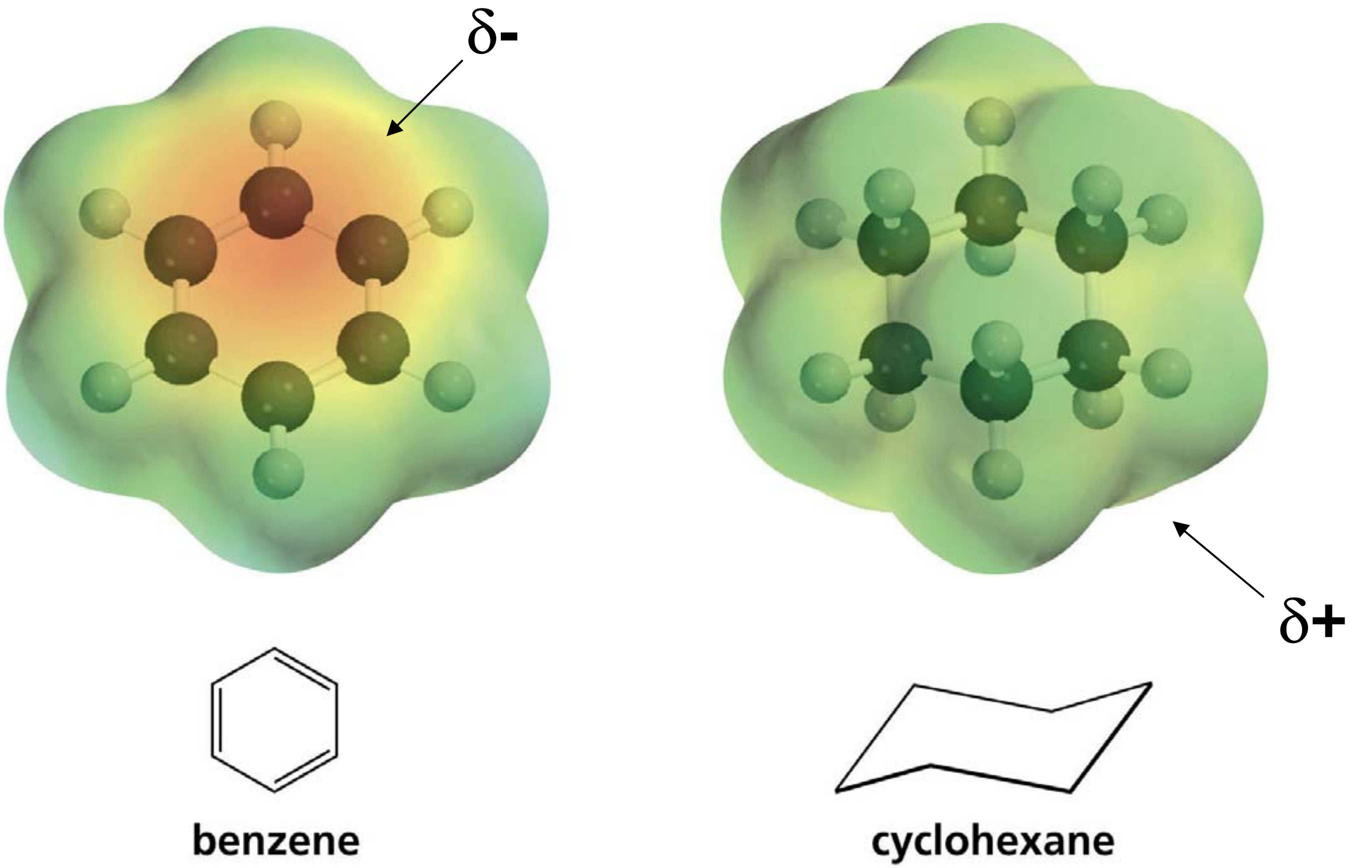


3-bromo-1-chlorophenol

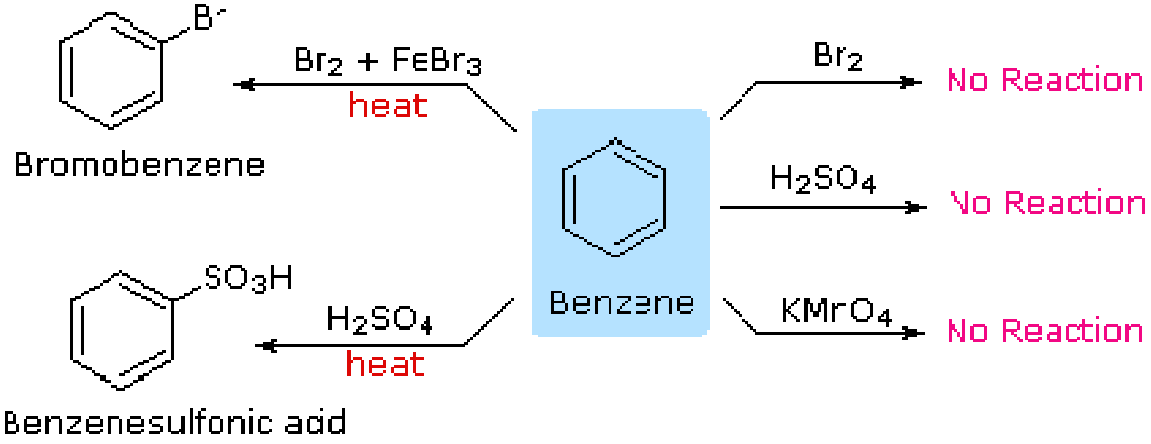


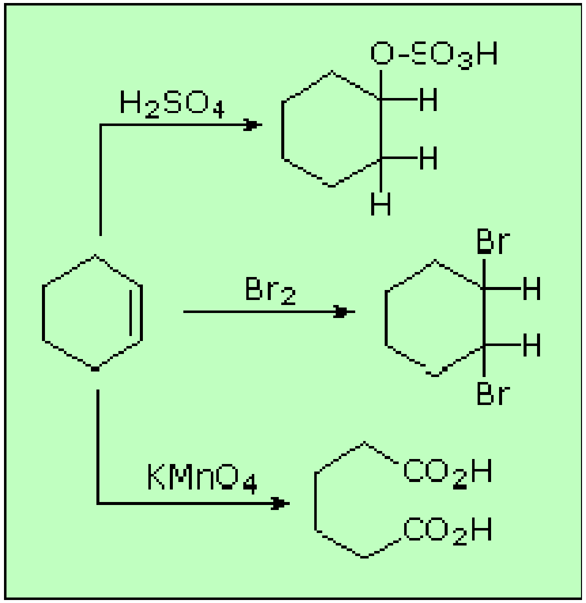
2-ethyl-4-iodoaniline

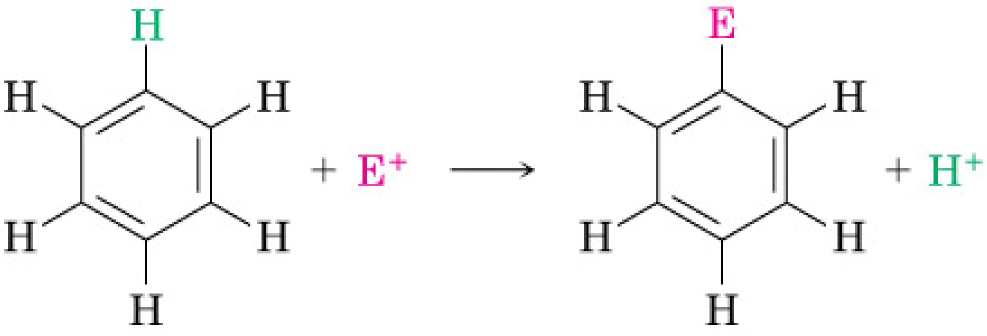
Reattività del benzene



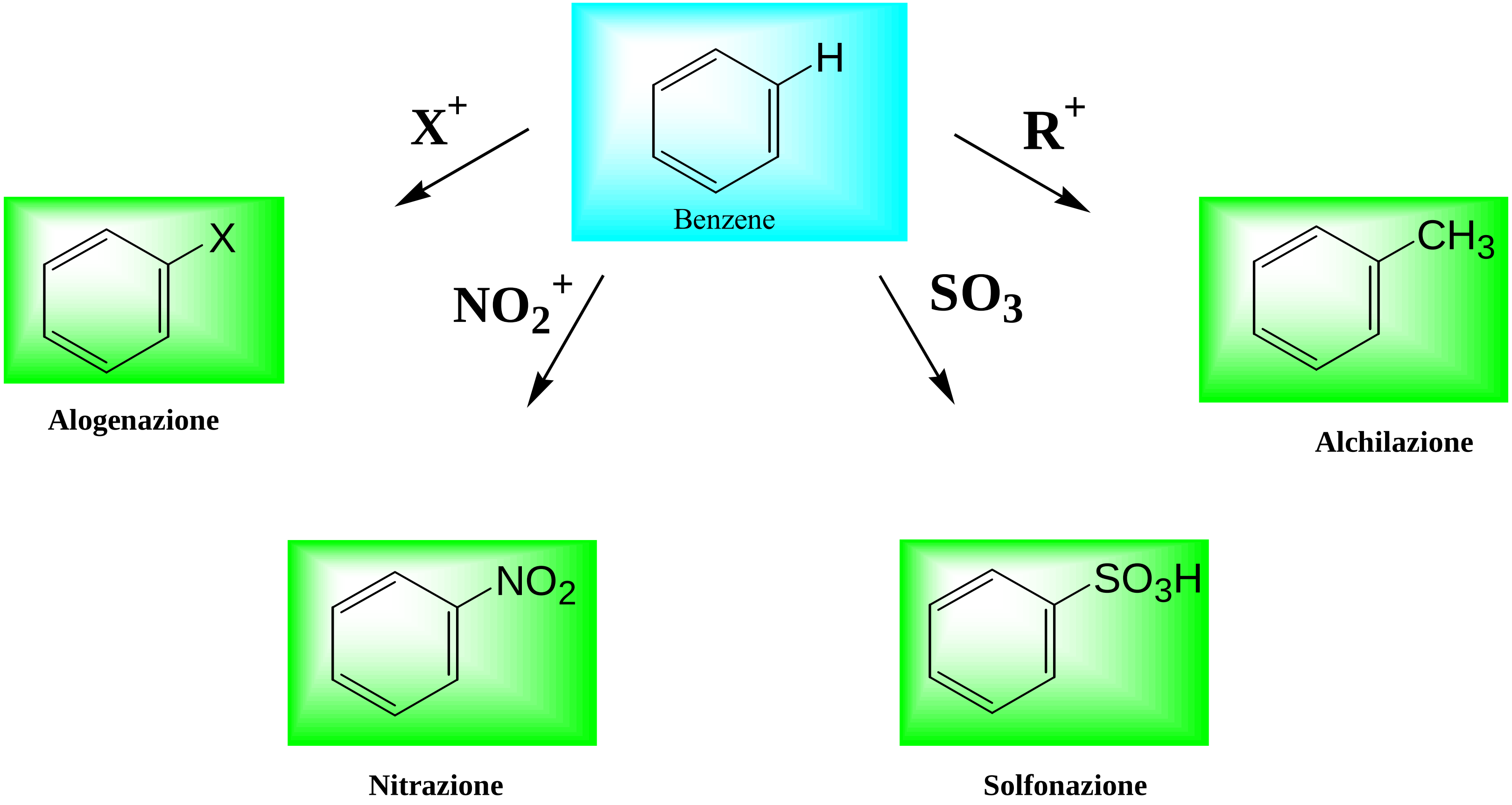
Reattività del benzene: sostituzione





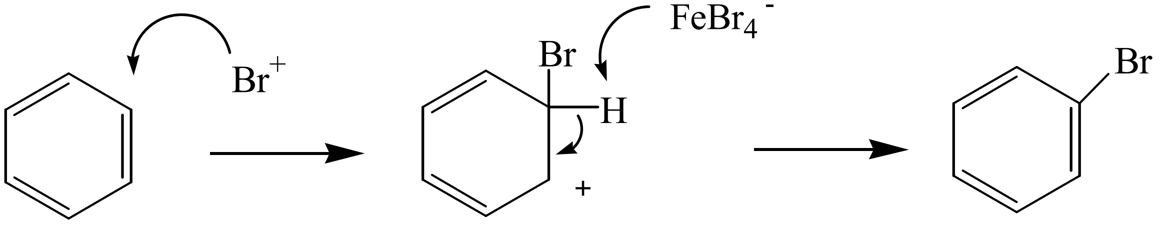


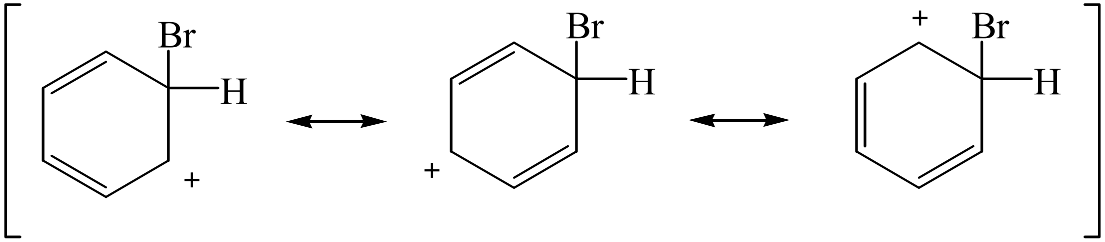
Reattività del benzene: sostituzione



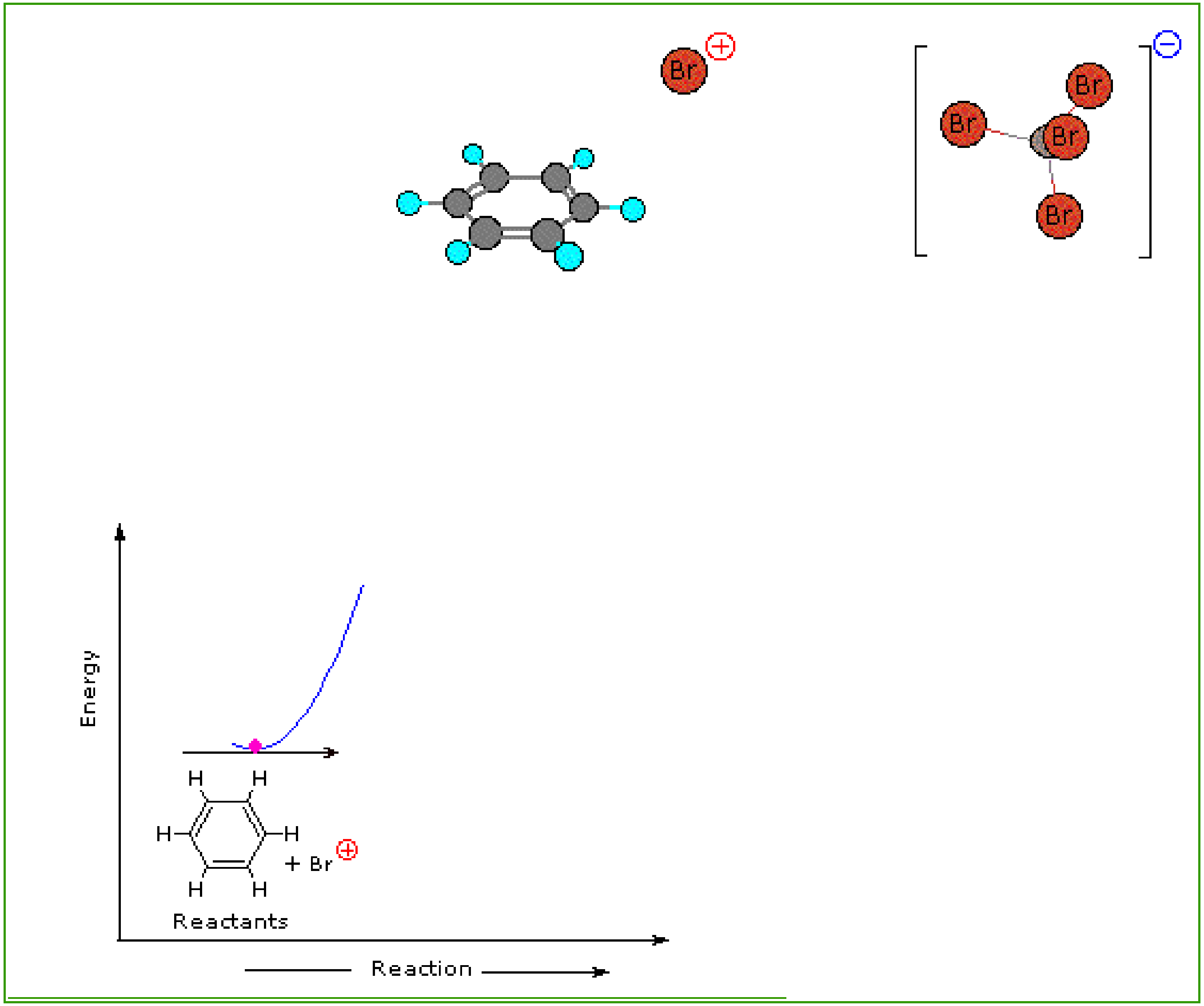
Reattività del benzene

$$FeBr_3 + Br_2 \longrightarrow FeBr_4^- + Br^+$$

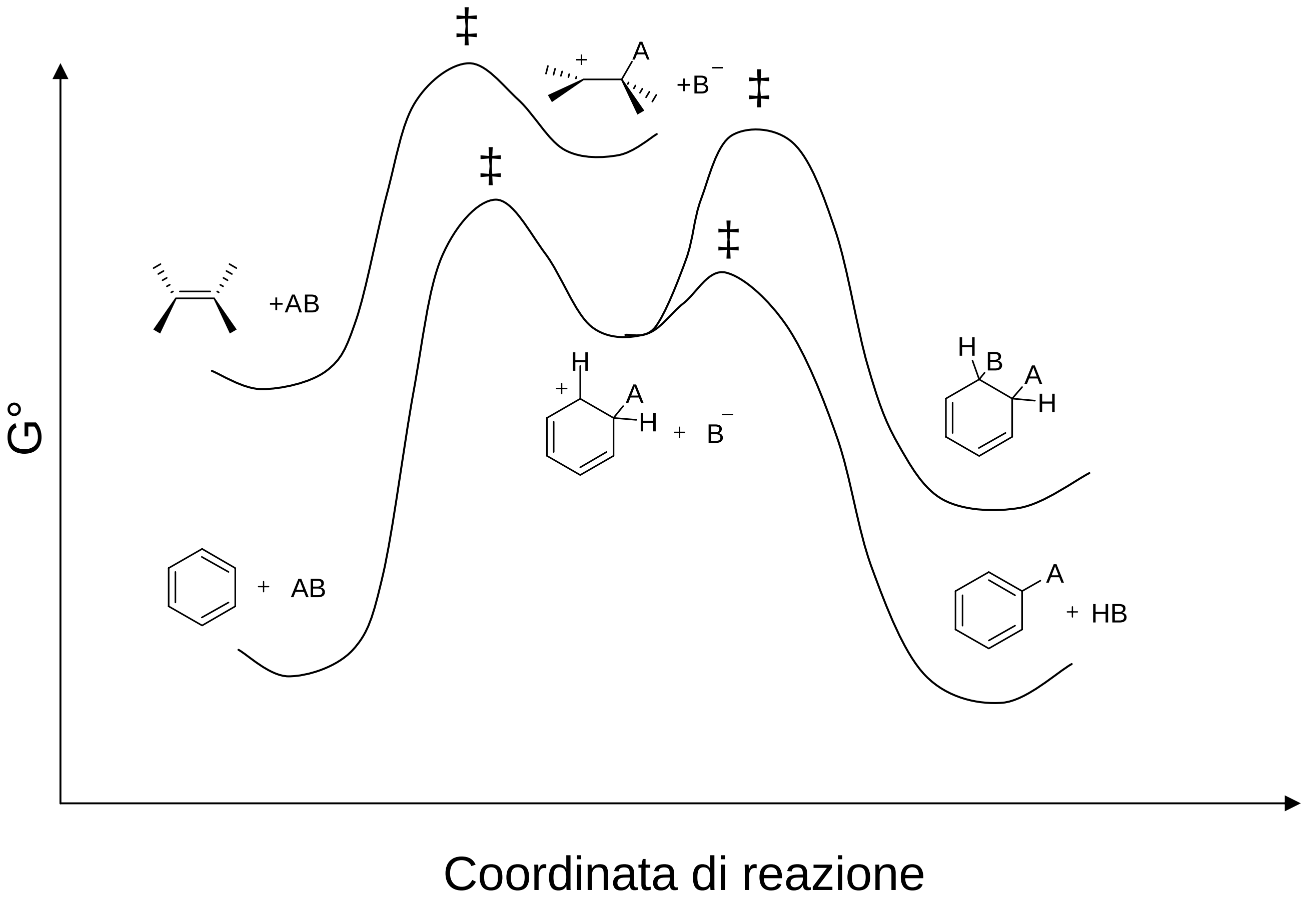




Sostituzione elettrofila aromatica



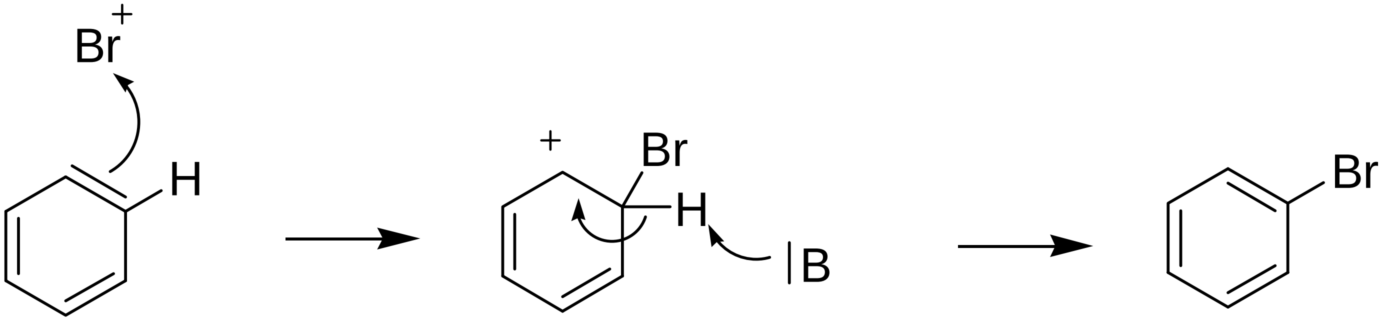
Sostituzione elettrofila vs addizione elettrofila



Sostituzione elettrofila aromatica: reazioni

1) Alogenazione

$$Br_2 + FeBr_3 \rightleftharpoons \boxed{Br^+} + FeBr_4$$

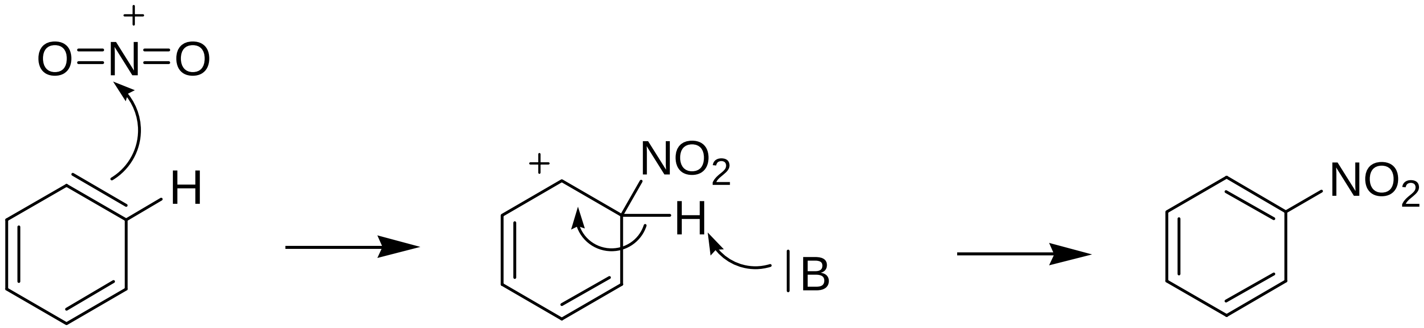


X = Cl, Br, I

Sostituzione elettrofila aromatica: reazioni

2) Nitrazione

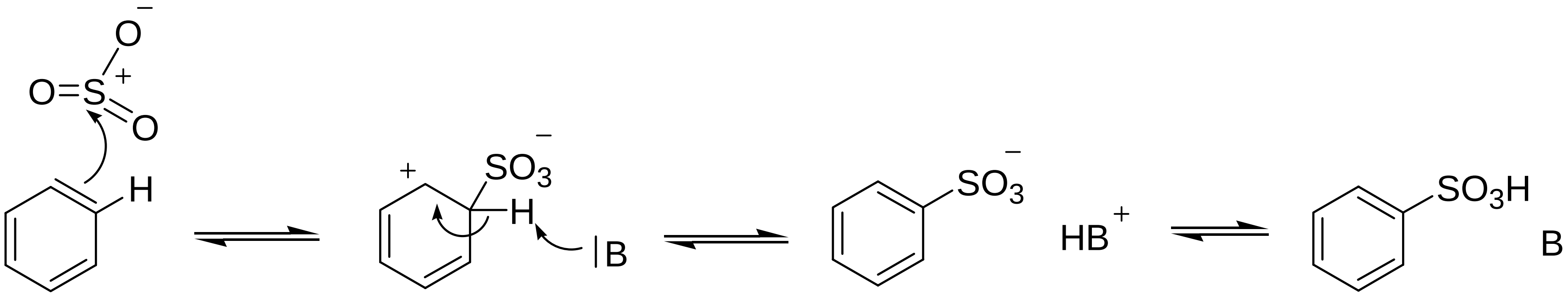
$$2\ HNO_3 \rightleftharpoons \boxed{NO_2^+} + H_2O + NO_3^-$$



Sostituzione elettrofila aromatica: reazioni

3) Solfonazione

$$2\ H_2SO_4 \rightleftharpoons \boxed{SO_3} + H_3O^+ + HSO_4^-$$

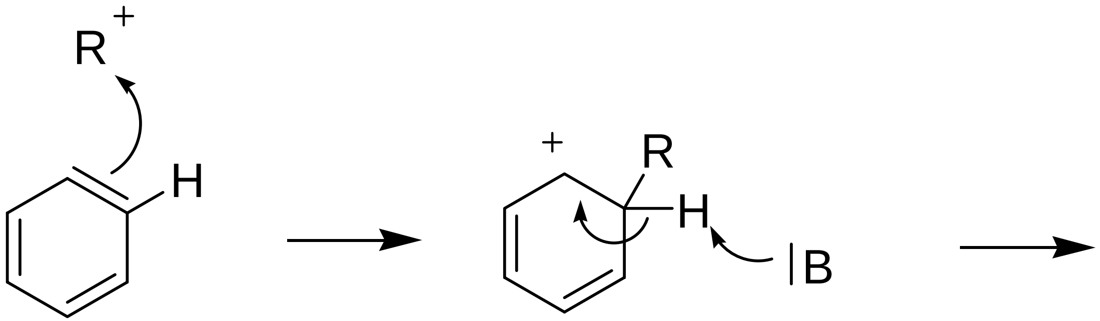


Reazione reversibile!

Sostituzione elettrofila aromatica: reazioni

4) Alchilazione/Acilazione di Friedl-Craft

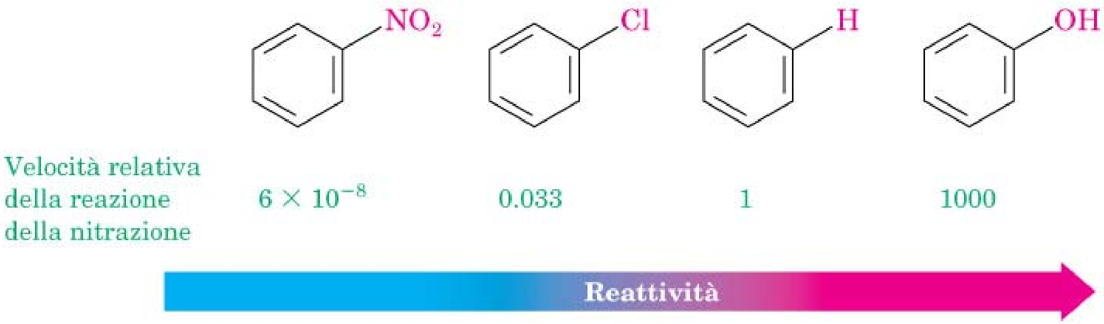
$$\mathrm{RCl,\ RCOCl} + \mathrm{AlCl_3} \rightleftharpoons \boxed{\mathrm{R^+,\ RCO^+}} + \mathrm{FeBr_4}$$



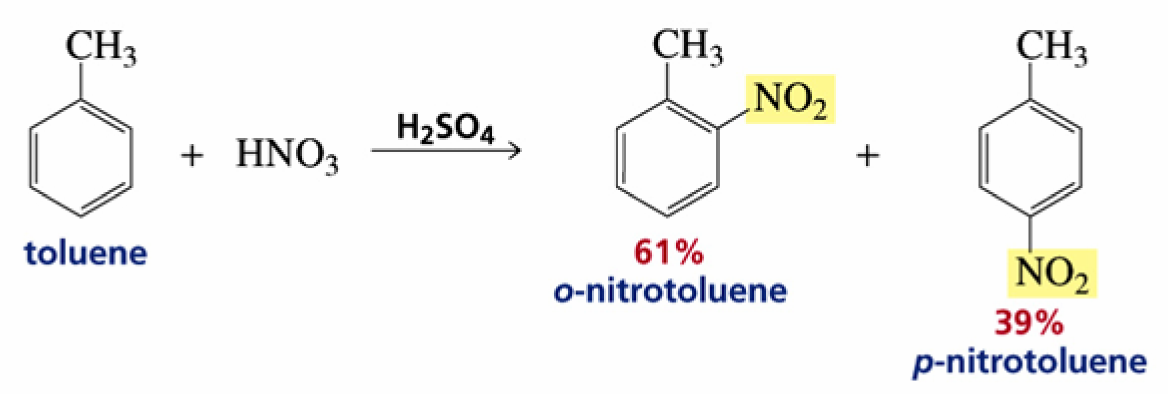
- La reazione non va in sistemi aromatici disattivati
- Solo alogenuri alchilici
- Polisostituzione nelle acilazioni

Effetto dei sostituenti

Velocità della reazione



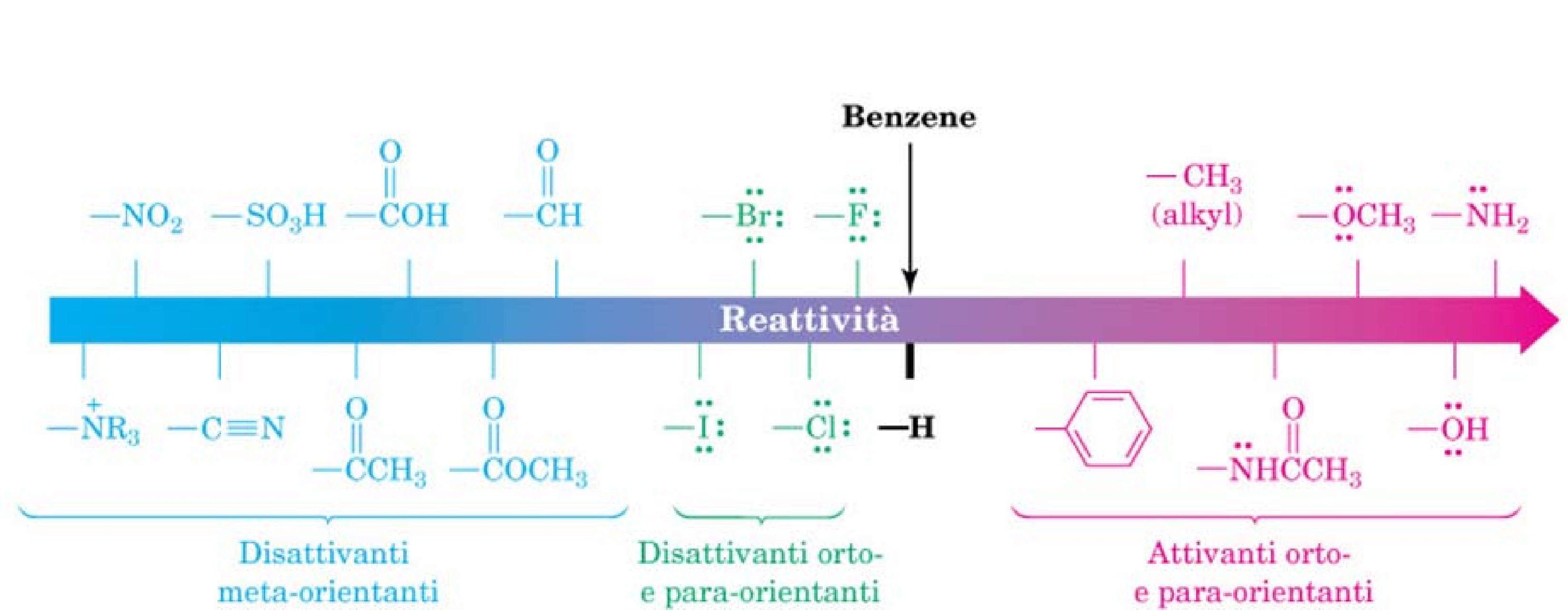
Orientazione



Sostituzione elettrofila aromatica: attivazione e orientazione

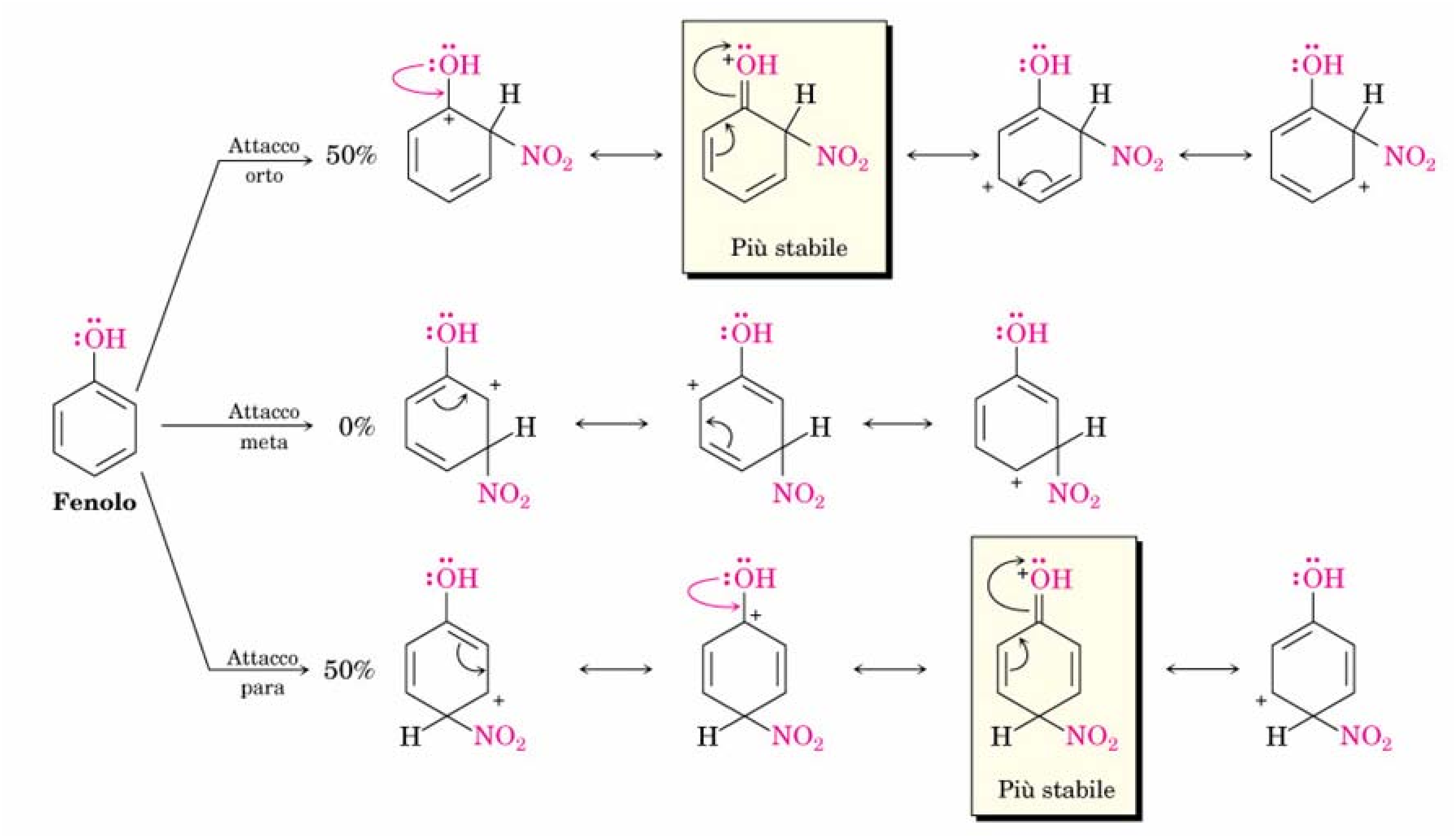
Un gruppo è un **attivante** se è capace di donare elettroni all'anello

Un gruppo è un **disattivante** se sottrae elettroni all'anello

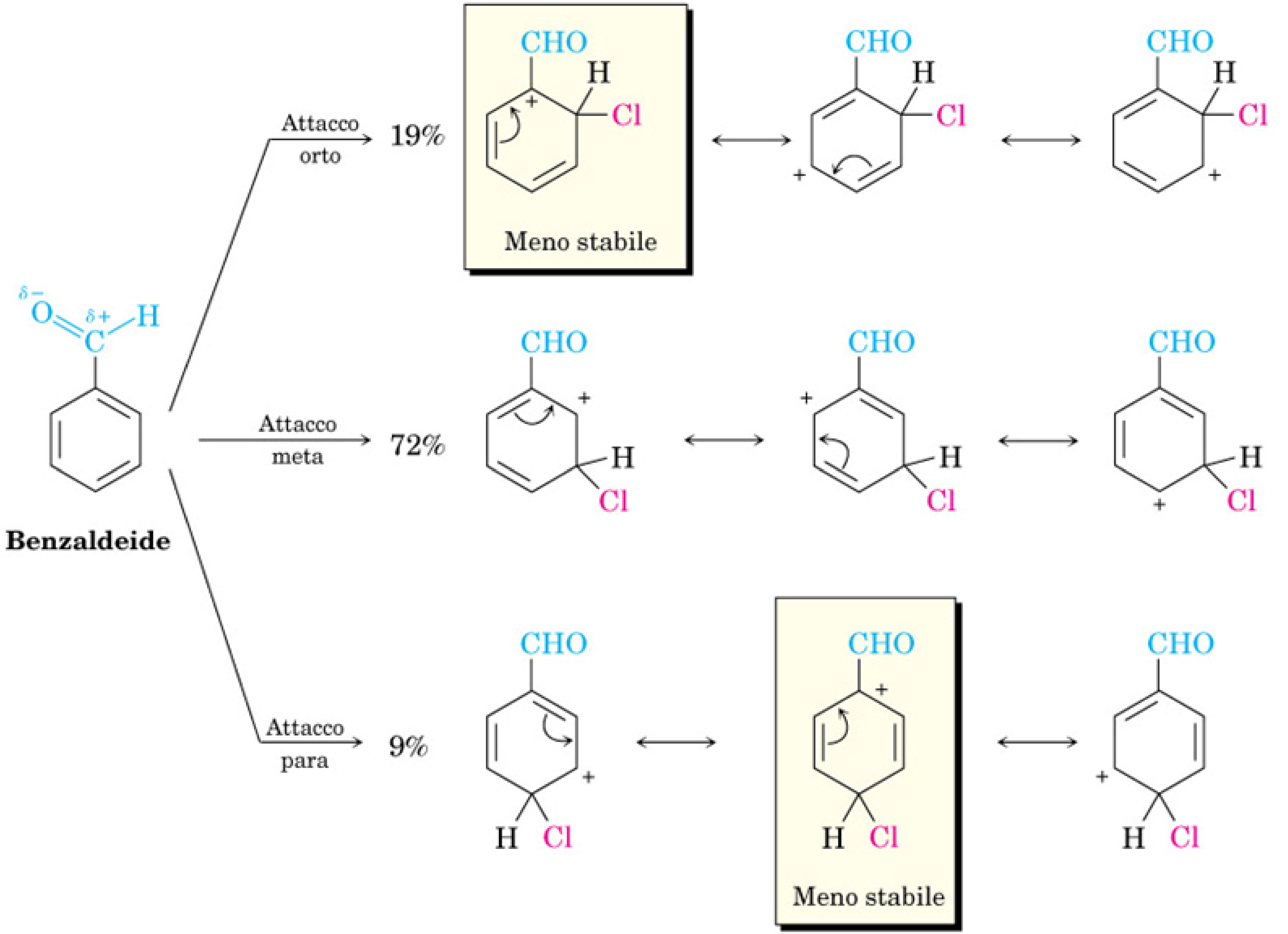


La donazione e l'attrazione degli elettroni possono essere dovuti a un effetto **induttivo** (elettronegatività) o a un effetto di **risonanza** (sovrapposizione tra orbitali *p*).

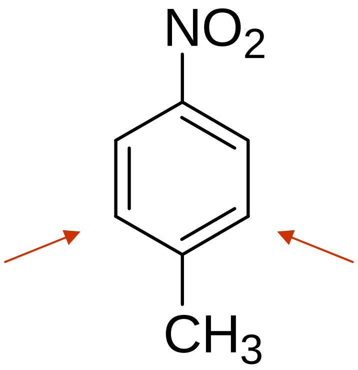
Effetto dei sostituenti: attivanti orto-para orientanti

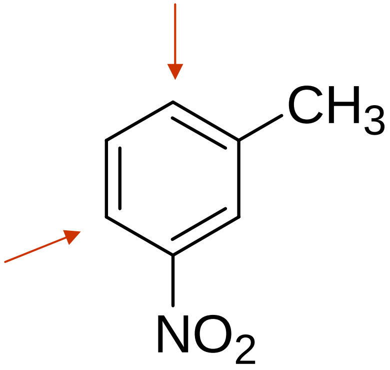


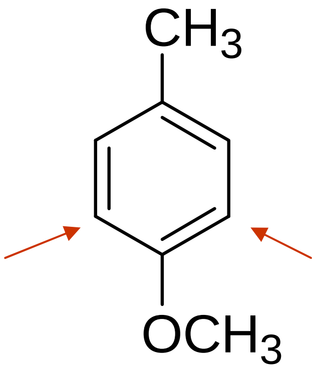
Effetto dei sostituenti: disattivanti meta-orientati



Sostituzione elettrofila aromatica: orientazione

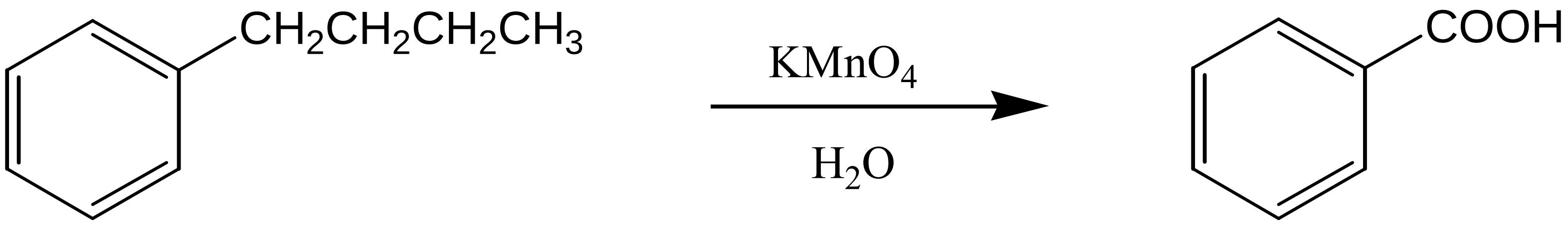






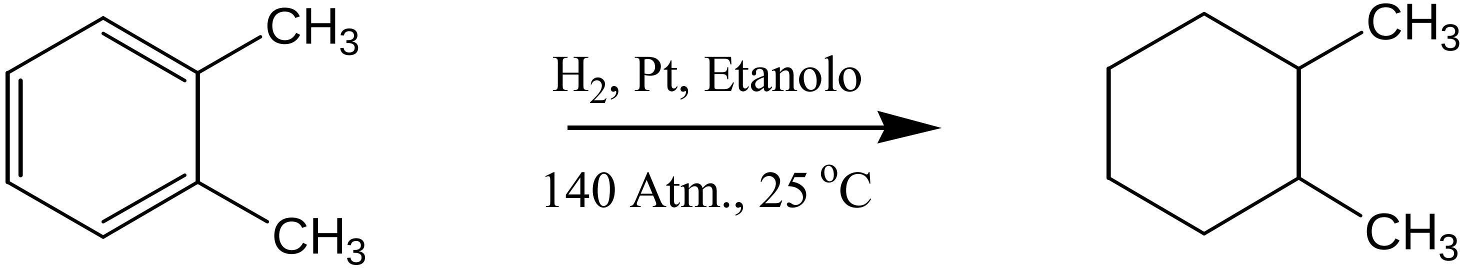
- ✓ Il gruppo attivante prevale sul disattivante.
- ✓ L’attivante forte prevale sull’attivante debole.
- ✓ Bisogna tener conto degli effetti sterici.

Ossidazione e riduzione dei composti aromatici



Butilbenzene

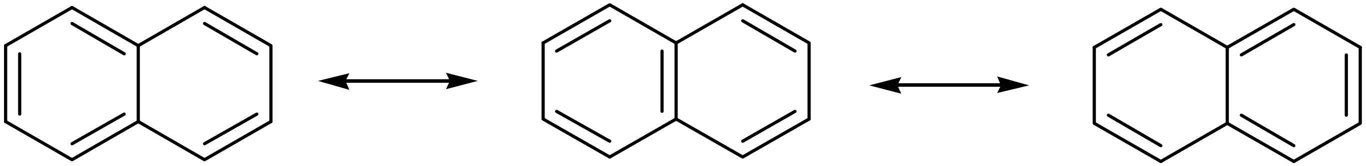
Acido Benzoico



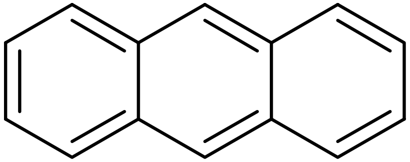
1,2-Dimetilbenzene
o-Xilene

1,2-Dimetilcicloesano

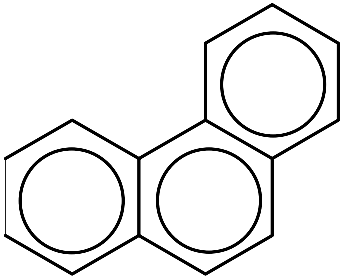
Altri composti aromatici



Naftalene

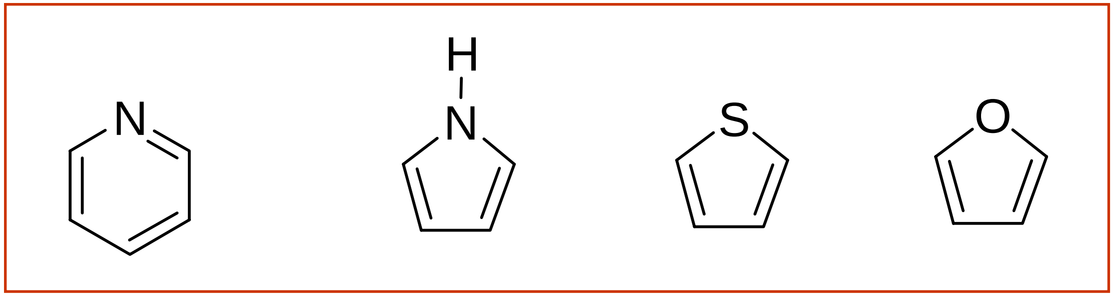


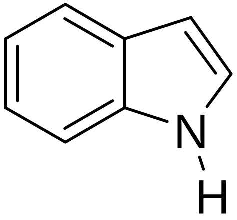
Antracene

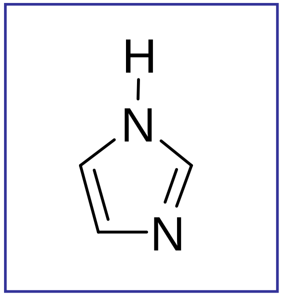


Fenantrene

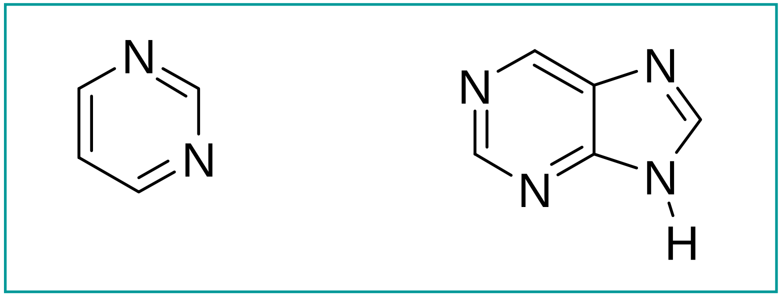
Composti eteroaromatici







Amminoacidi
(His)



Nucleobasi,
caffeina