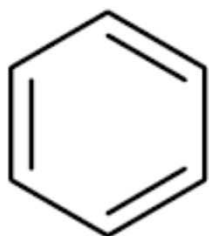


# Chimica Organica

## I composti aromatici

- struttura del benzene e concetto di aromaticità;
- nomenclatura;
- reazioni di sostituzione elettrofila aromatica e relativo meccanismo;
- effetto attivante/disattivante dei sostituenti nei benzeni sostituiti ed orientamento dei gruppi entranti.

# l'enigma del benzene



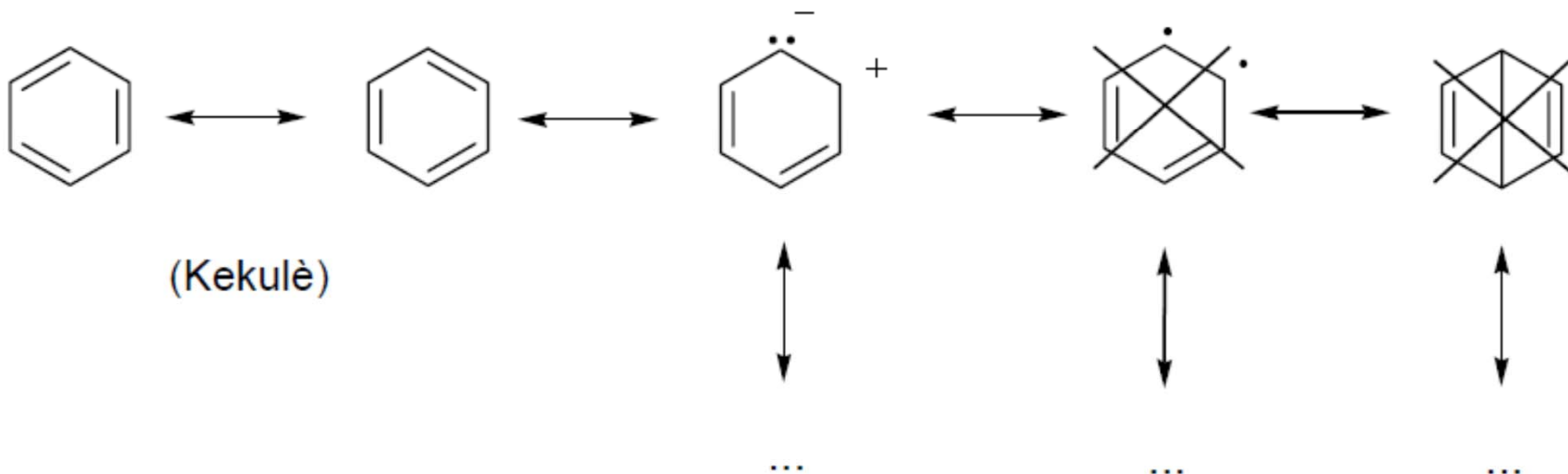
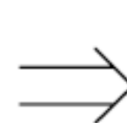
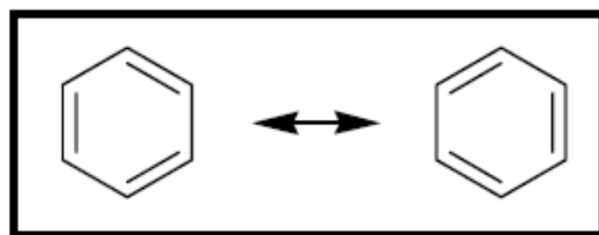
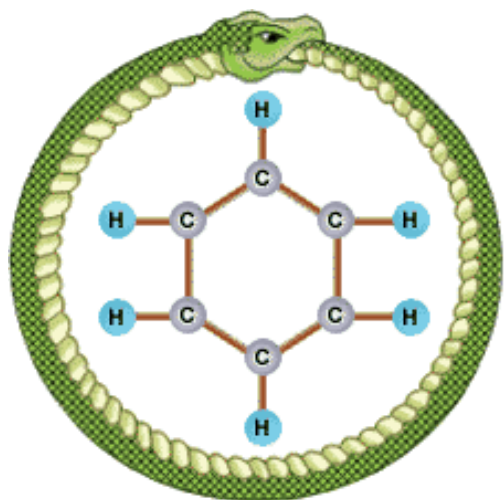
(1865)



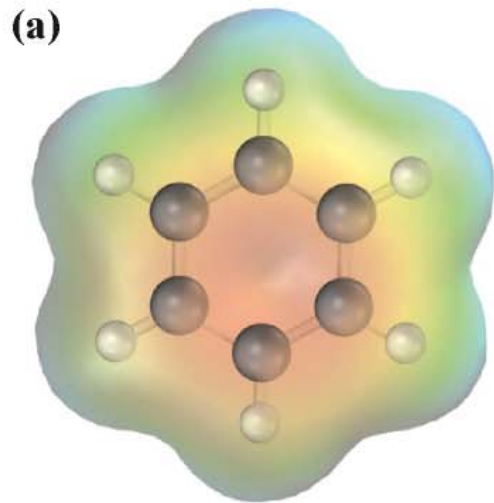
Friedrich August Kekulé

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

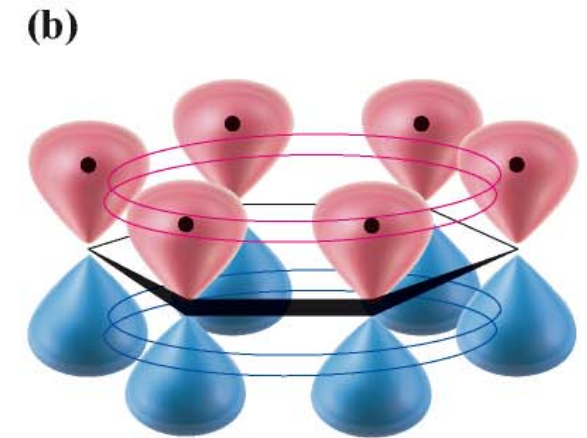
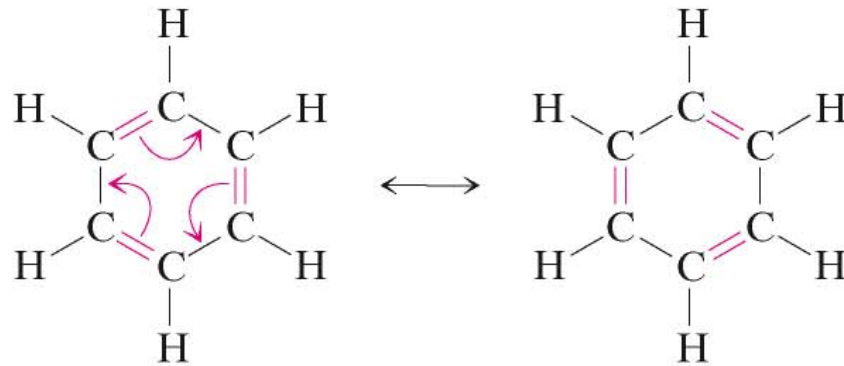
# la risonanza nei composti aromatici



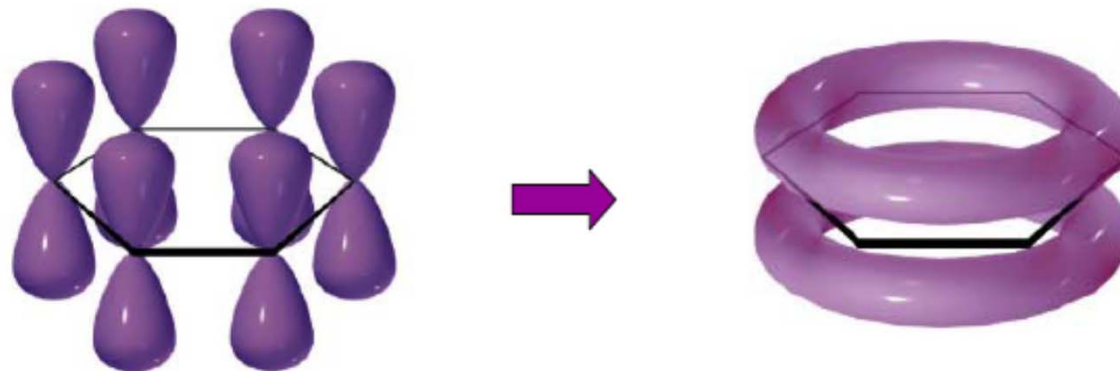
## benzene



mappa del  
potenziale  
elettrostatico

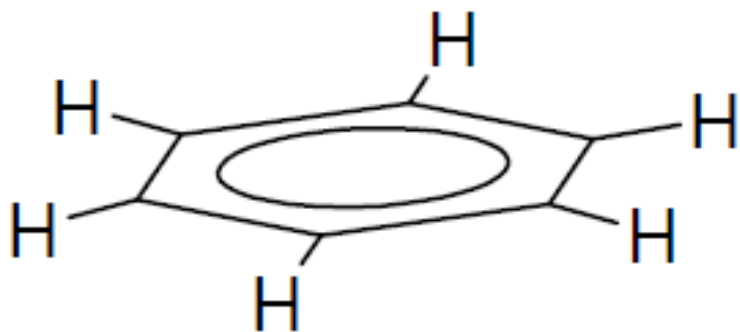


rappresentazione  
orbitale



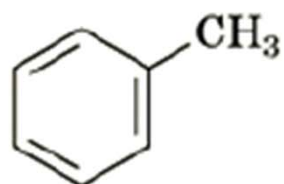
# i legami nel benzene

---

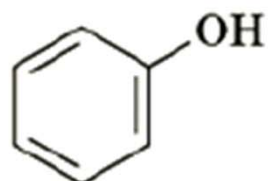


Distanza di legame C-C: 1.40 Å  
(C-C: 1.48 Å, C=C: 1.32 Å)

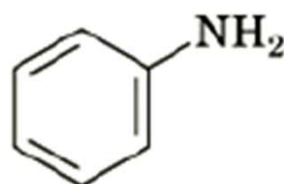
# derivati del benzene: nomi comuni



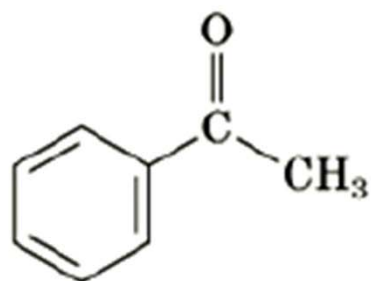
Toluene  
(p.e. 111°C)



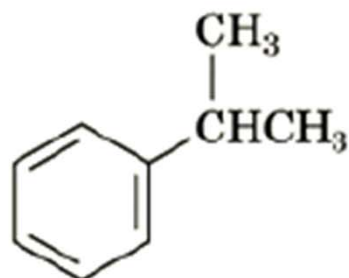
Fenolo  
(p.f. 43°C)



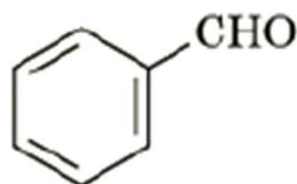
Anilina  
(p.e. 184°C)



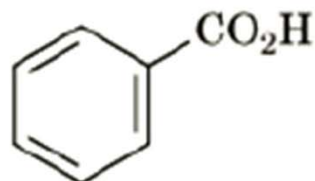
Acetofenone  
(p.f. 21°C)



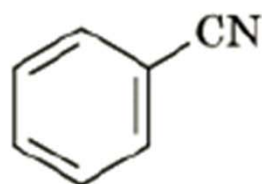
Cumene  
(p.e. 152°C)



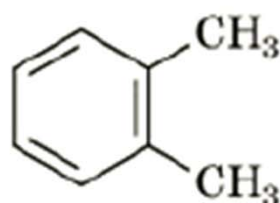
Benzaldeide  
(p.e. 178°C)



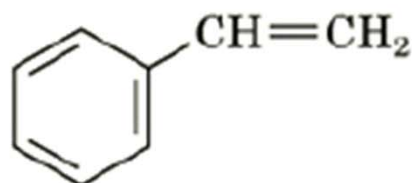
Acido benzoico  
(p.f. 122°C)



Benzonitrile  
(p.e. 191°C)



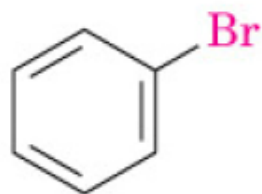
*orto*-Xilene  
(p.e. 144°C)



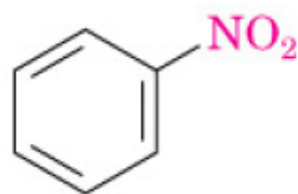
Stirene  
(p.e. 145°C)

# derivati del benzene: nomi IUPAC

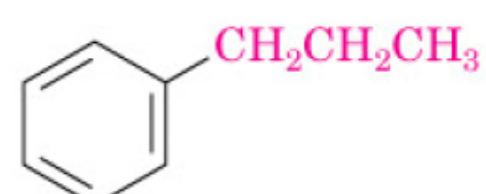
## Derivati monosostituiti



**Bromobenzene**



**Nitrobenzene**

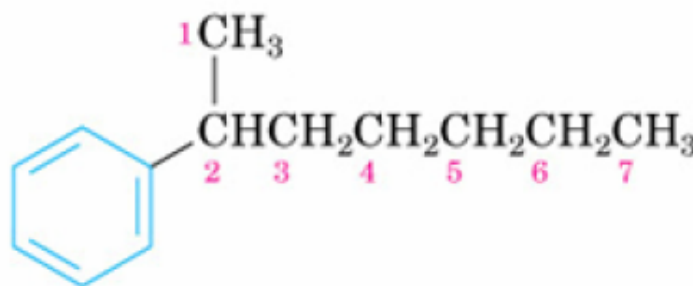


**Propilbenzene**

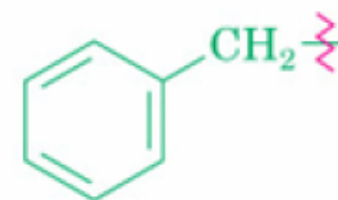
## Sostituenti:



**Gruppo fenilico**



**2-Fenileptano**

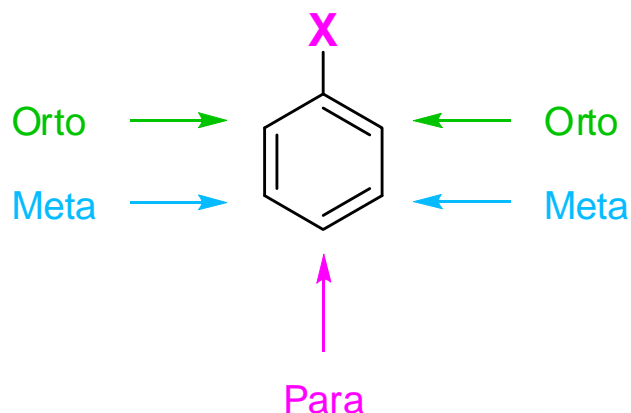


**Gruppo benzilico**

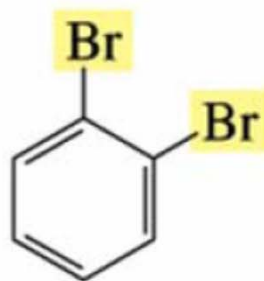


# derivati polisostituiti: nomenclatura IUPAC

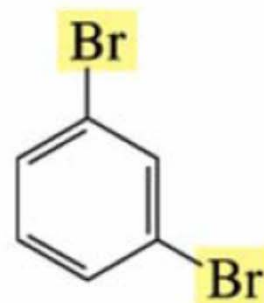
## Derivati polisostituiti



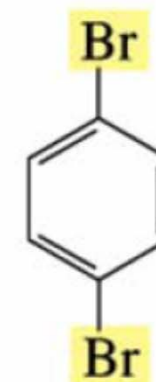
Si numera l'anello in modo che i sostituenti abbiano i numeri più bassi possibili.



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



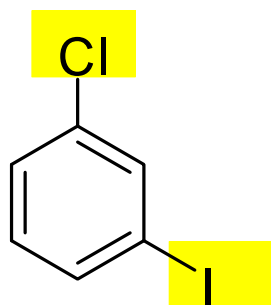
**1,3-dibromobenzene**  
***meta*-dibromobenzene**  
***m*-dibromobenzene**



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

# sostituenti diversi

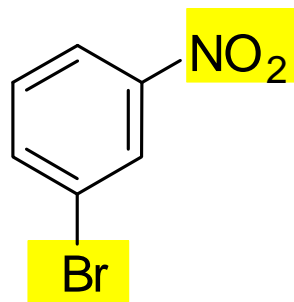
Se ci sono due sostituenti diversi, si usa l'ordine alfabetico



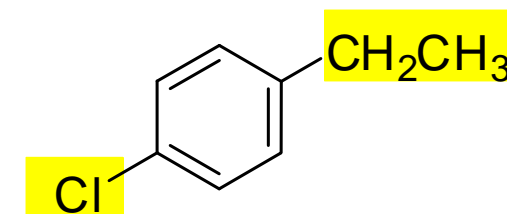
**1-cloro-3-iodobenzene**  
*meta*-cloriodiobenzene

**NON**

1-iodio-3-clorobenzene  
*meta*-iodioclorobenzene

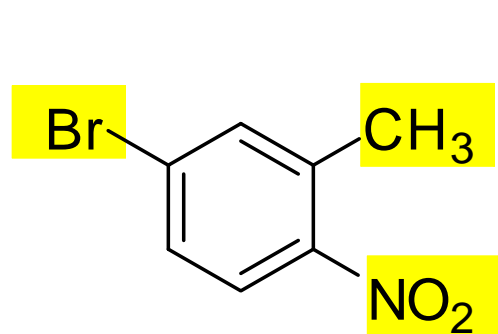


**1-bromo-3-nitrobenzene**  
*meta*-bromonitrobenzene

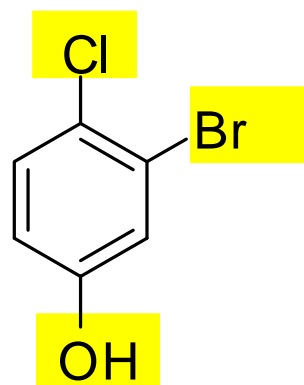


**1-cloro-4-etilbenzene**  
*meta*-cloroetilbenzene

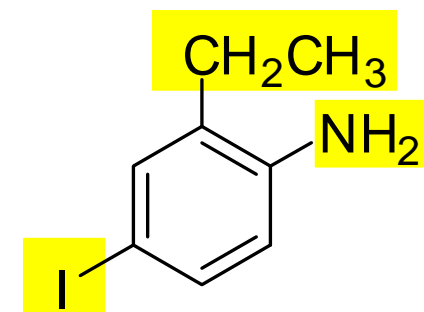
Se si usa un nome comune, il sostituente del composto monofunzionale di cui si usa il nome diventa il sostituente principale



**5-bromo-2-nitrotoluene**

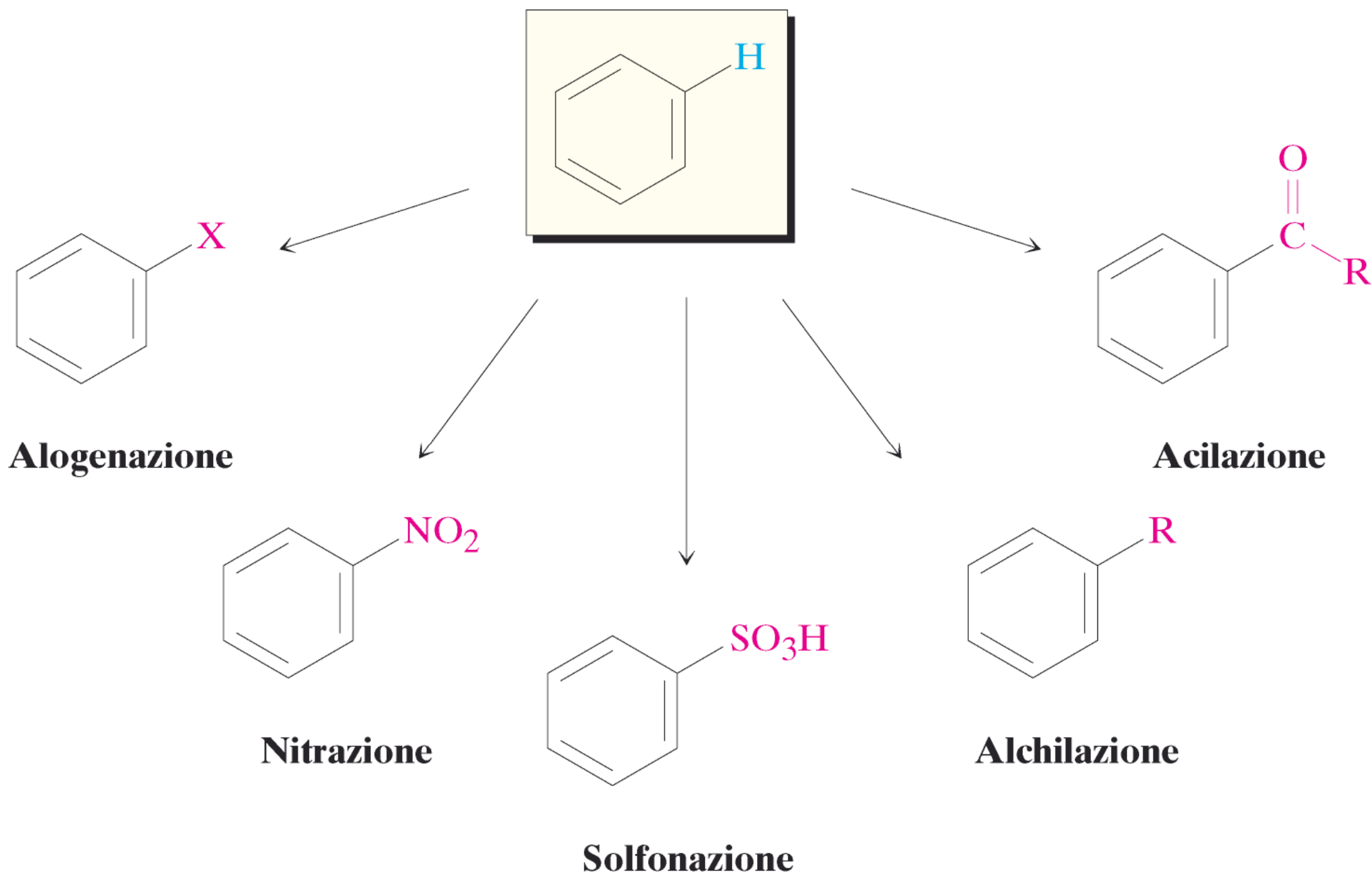


**3-bromo-4-clorofenolo**

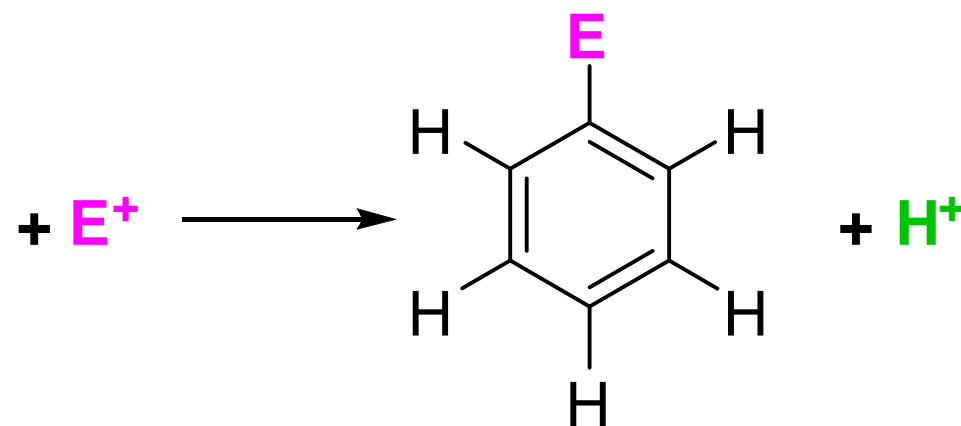
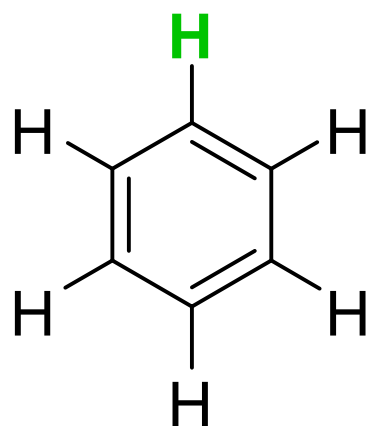
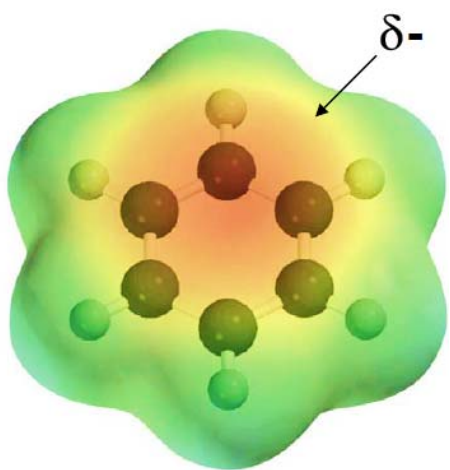
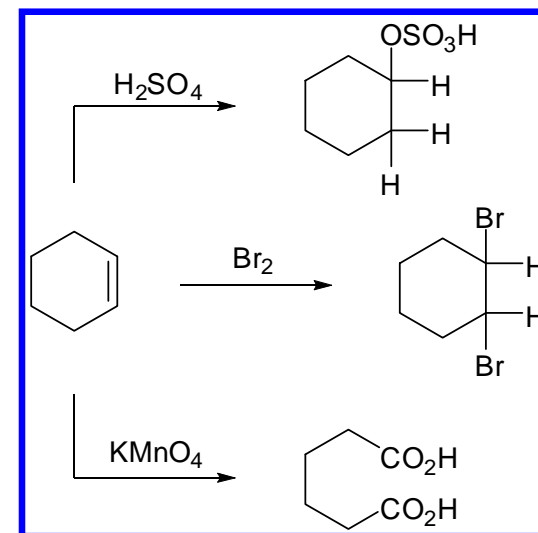
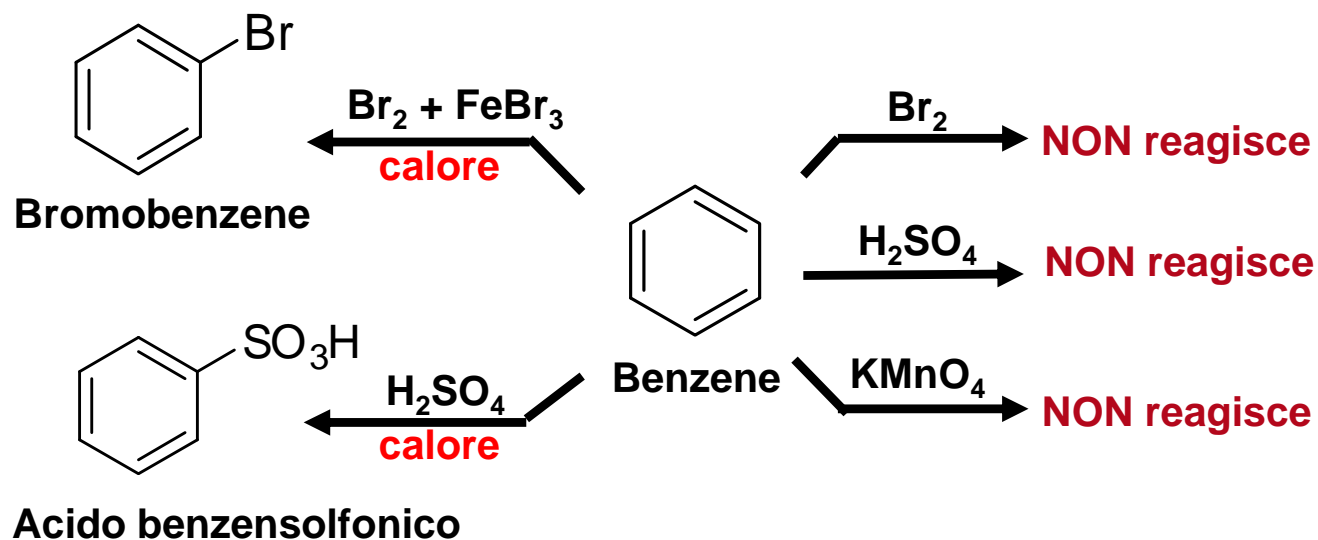


**2-etil-4-iodoanilina**

# reattività del benzene



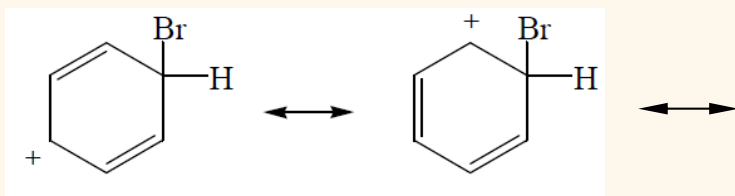
# sostituzione elettrofila aromatica



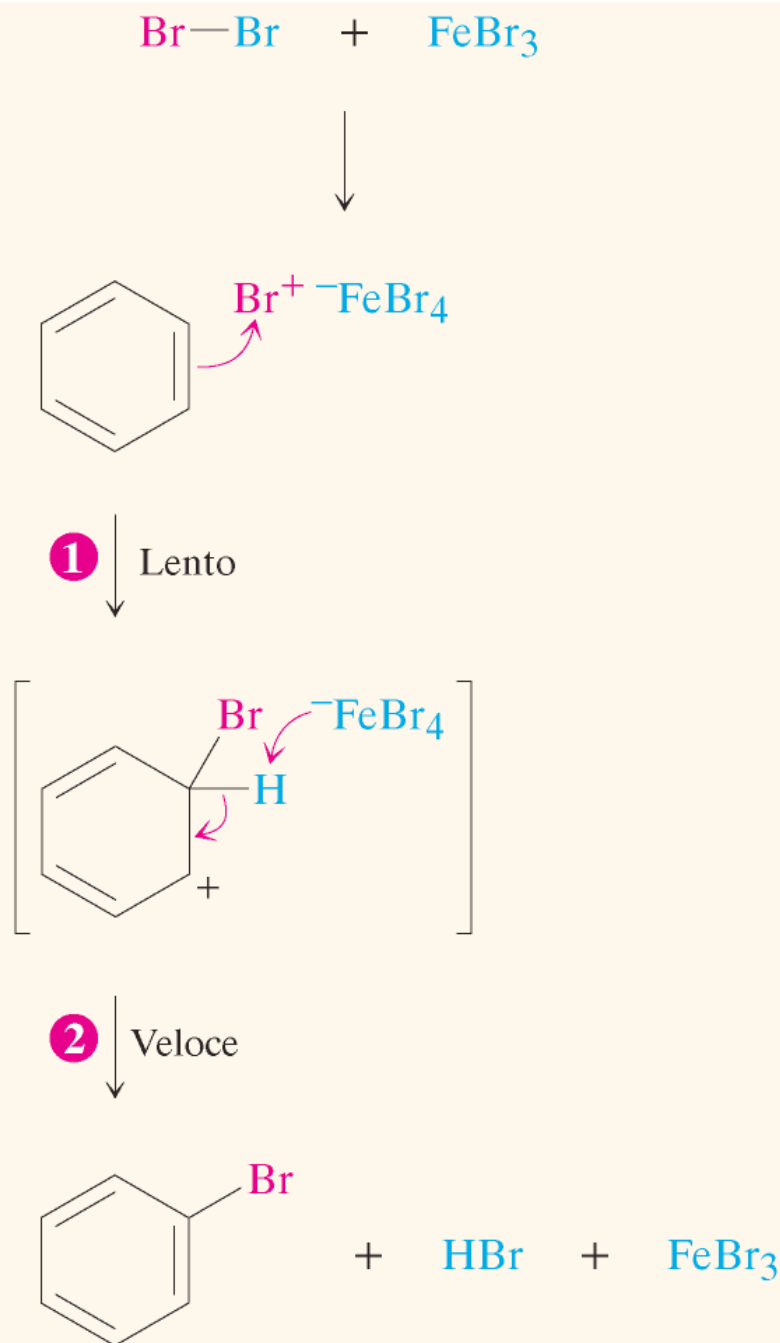
# meccanismo della bromurazione elettrofila

due stadi  
attraverso un carbocatione  
intermedio stabilizzato per  
risonanza

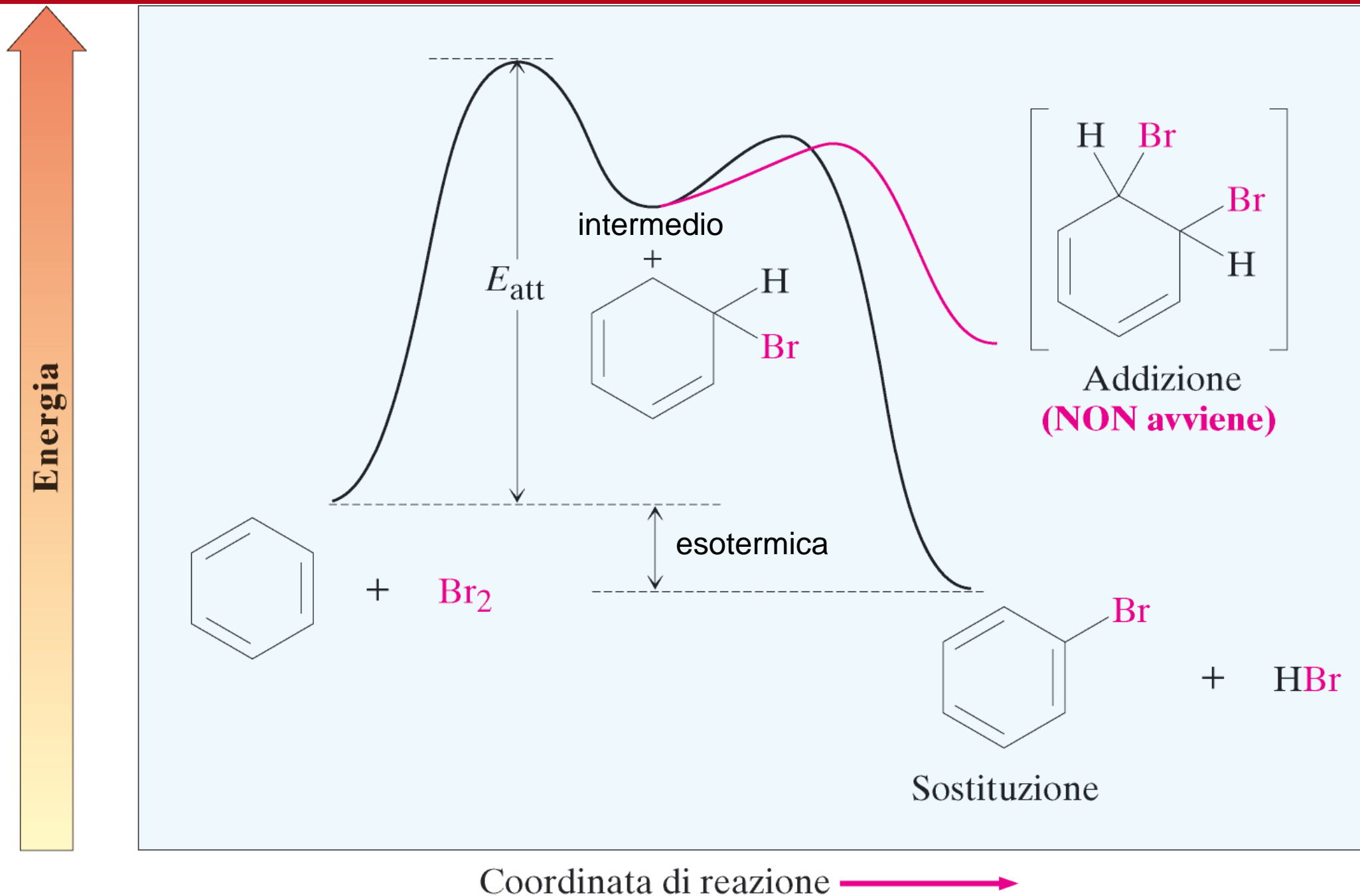
- 1** Una coppia di elettroni dell'anello benzenico attacca il bromo polarizzato positivamente, formando un nuovo legame C-Br e quindi un carbocatione intermedio non aromatico.



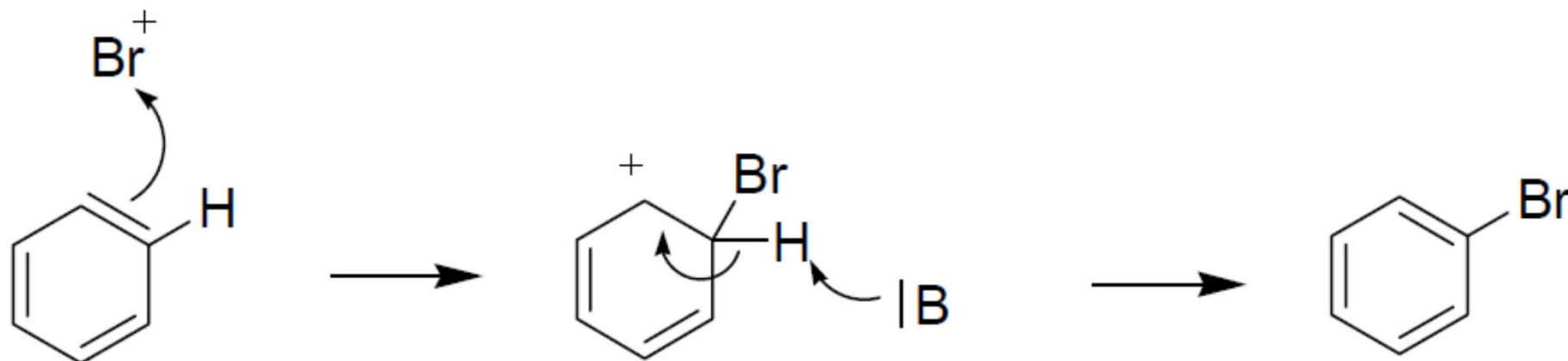
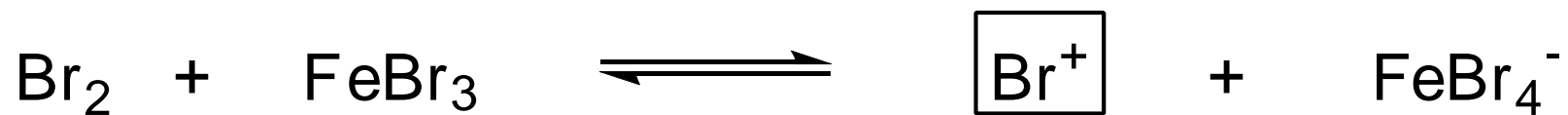
- 2** Una base strappa  $H^+$  dal carbocatione intermedio e si forma il prodotto di sostituzione neutro quando i due elettroni del legame C-H si muovono per rigenerare l'anello aromatico.



# diagramma dell'energia per la bromurazione



# sostituzioni elettrofile: alogenazione

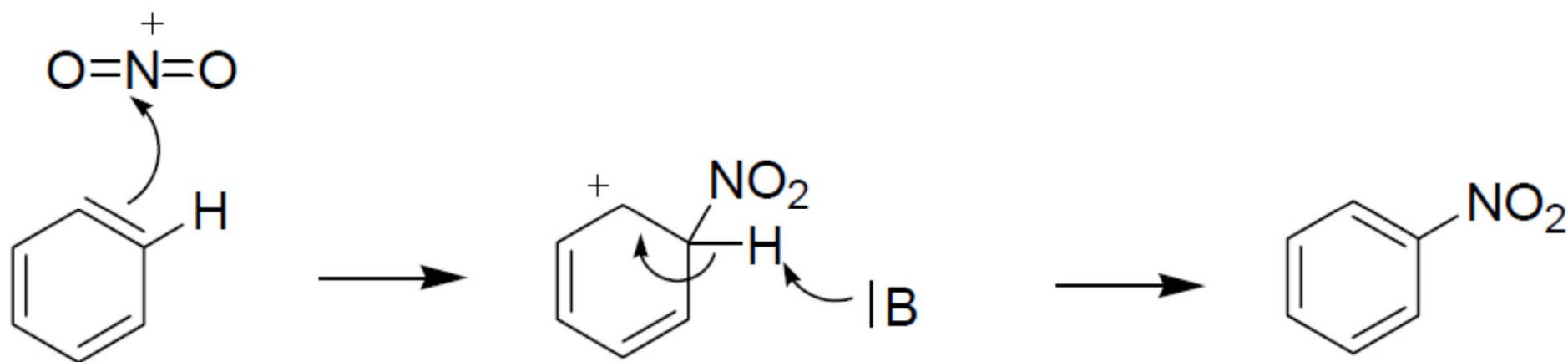


**X = Cl, Br, I**

# sostituzioni elettrofile: nitratura

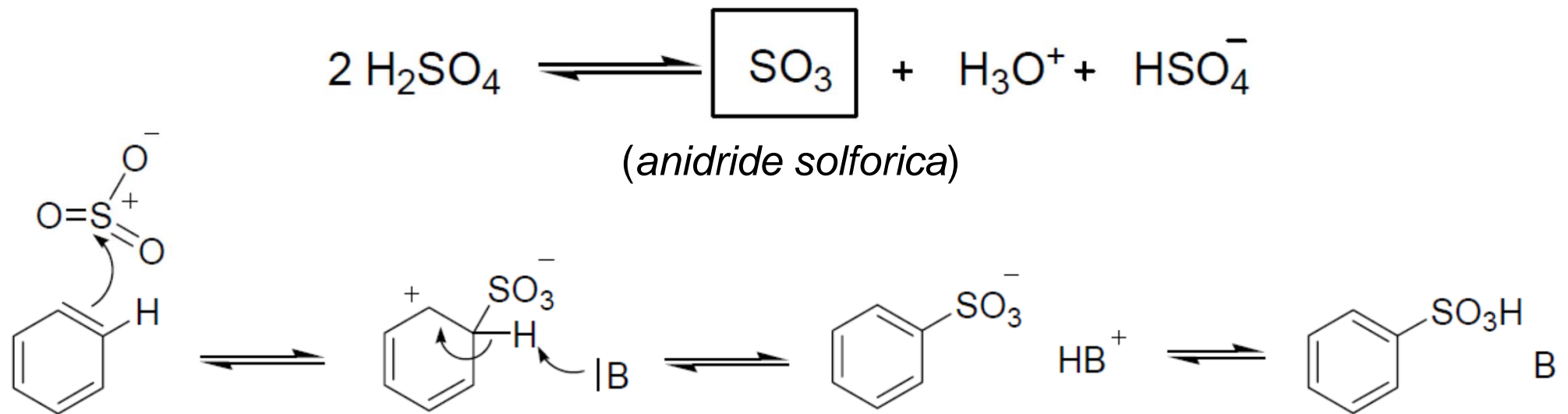


ione nitronio





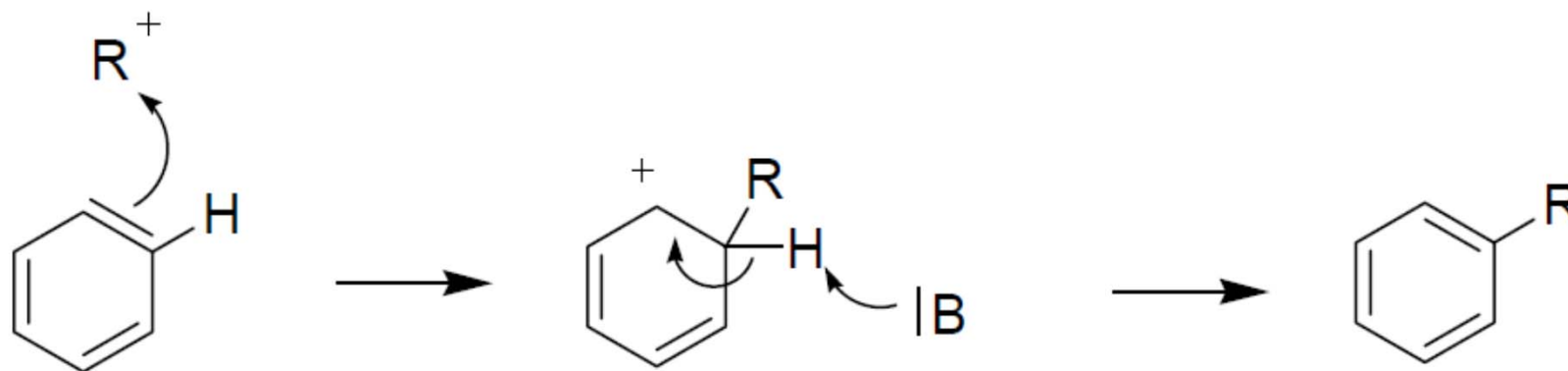
# sostituzioni elettrofile: solfonazione



**Reazione reversibile!**

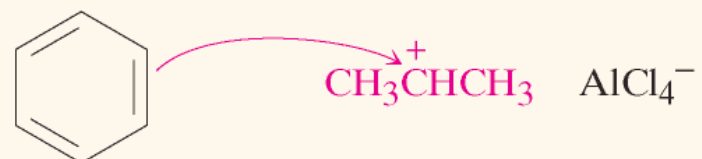
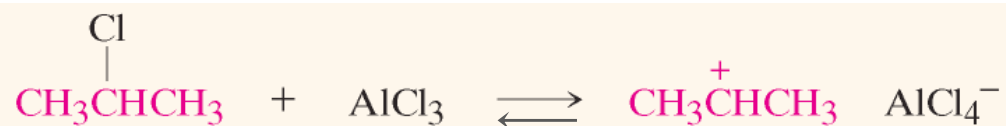
# sostituzioni elettrofile: alchilazione/acilazione

## Alchilazione/Acilazione di Friedl-Craft

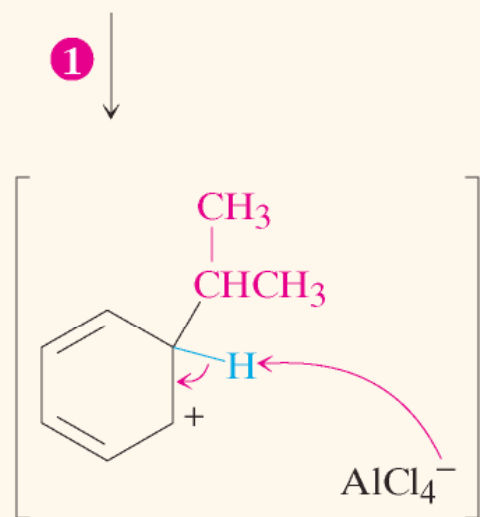


- La reazione non va in sistemi aromatici disattivati
- Solo alogenuri alchilici
- Polisostituzione nelle acilazioni

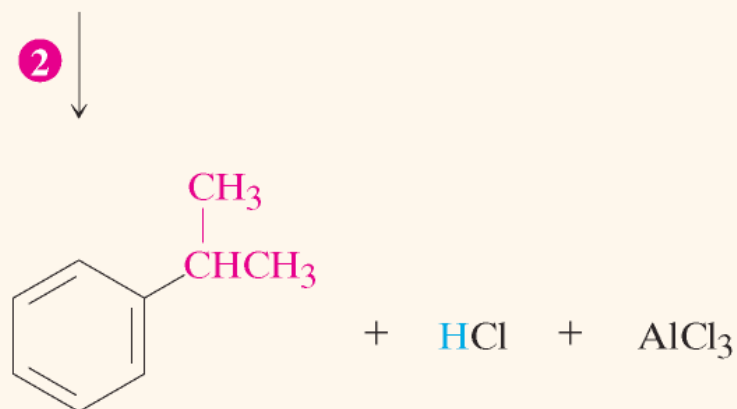
# meccanismo della alchilazione elettrofila



- 1** Una coppia di elettroni dell'anello aromatico attacca il carbocatione, formando un nuovo legame C-C e un nuovo carbocatione intermedio.



- 2** La perdita di un protone completa il processo con la formazione di un prodotto alchilato neutro.



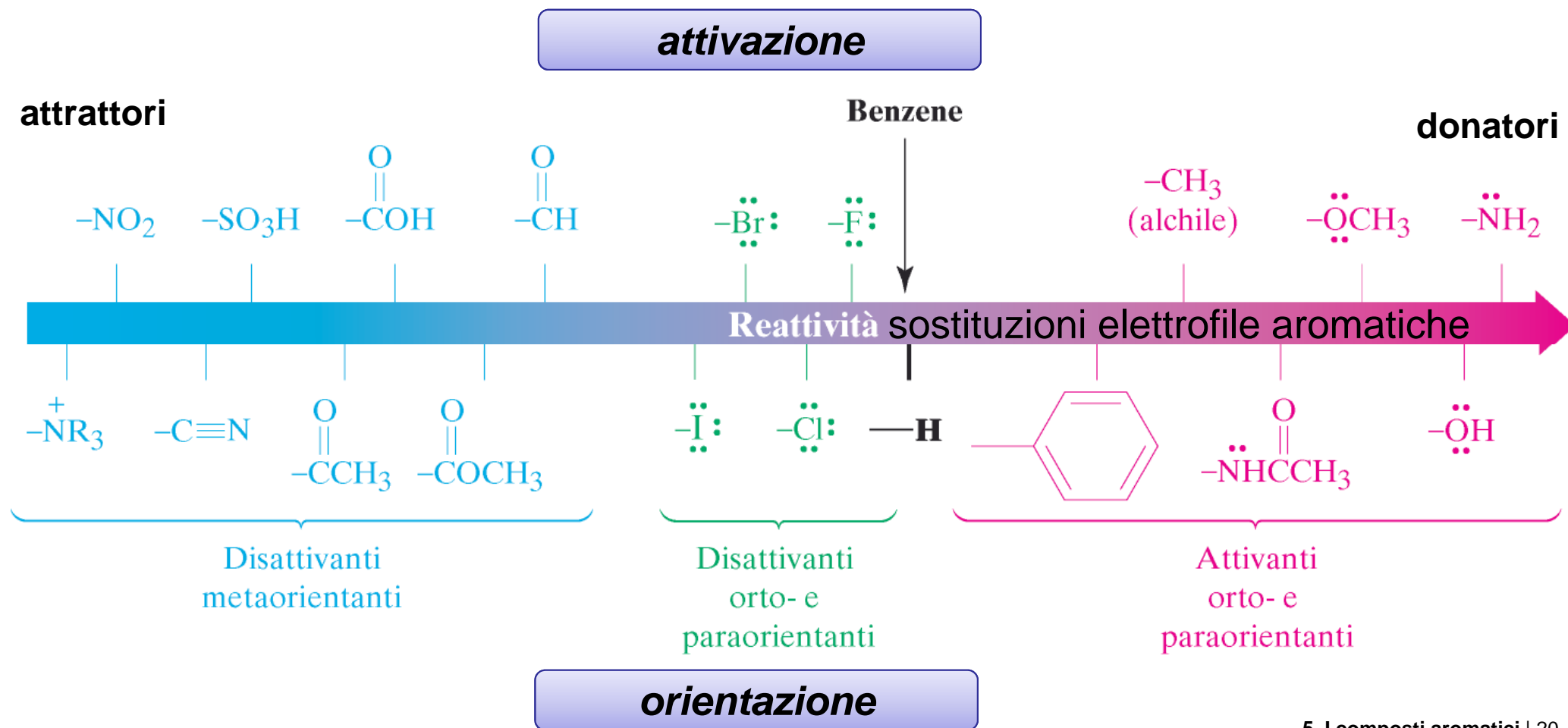
# effetti dei sostituenti

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

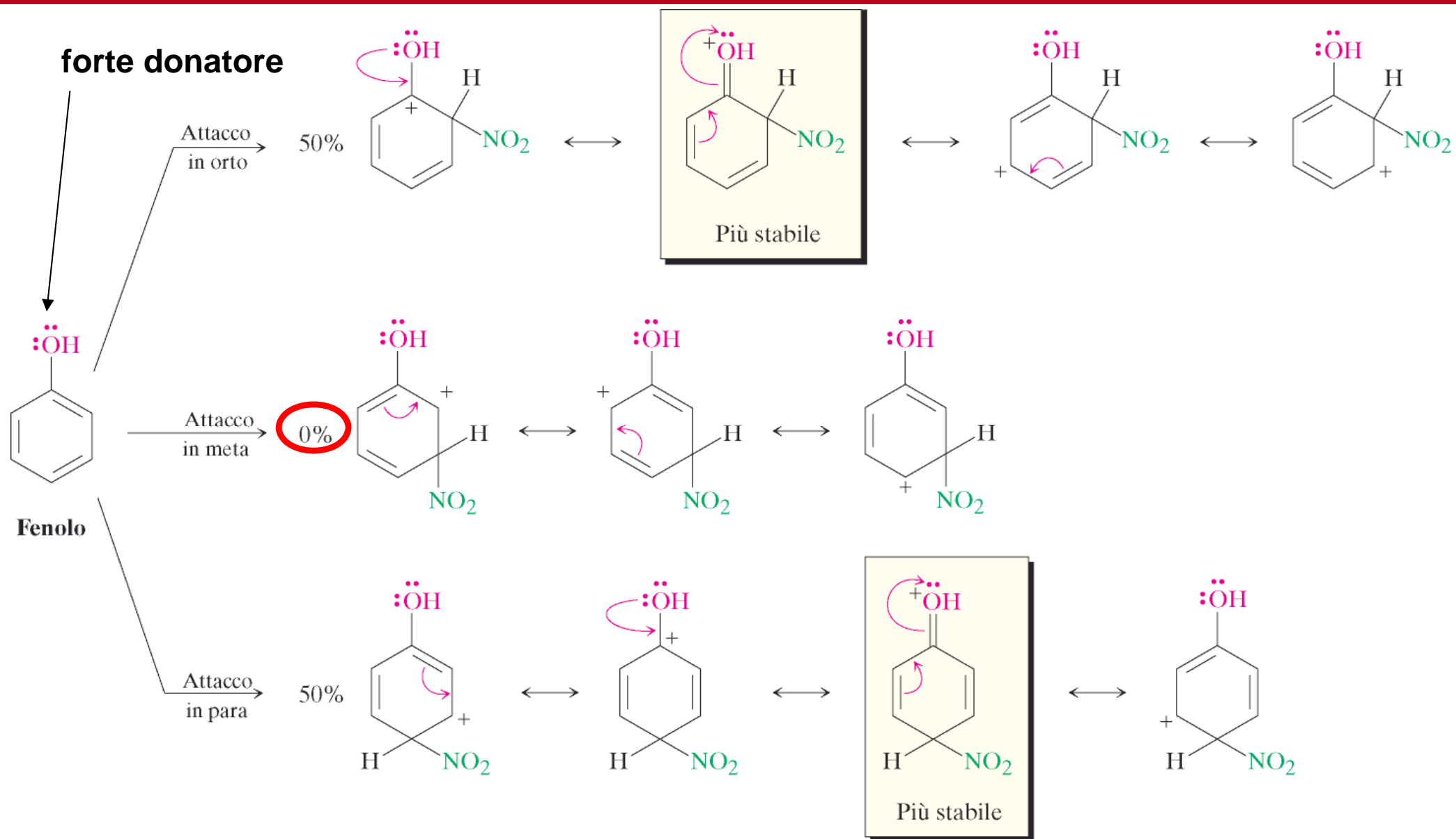
Un gruppo è un **disattivante** se sottrae elettroni all'anello

La donazione e l'attrazione degli elettroni possono essere dovuti a un effetto **induttivo** (elettronegatività)

o a un effetto di **risonanza** (sovrapposizione tra orbitali  $p$ ).

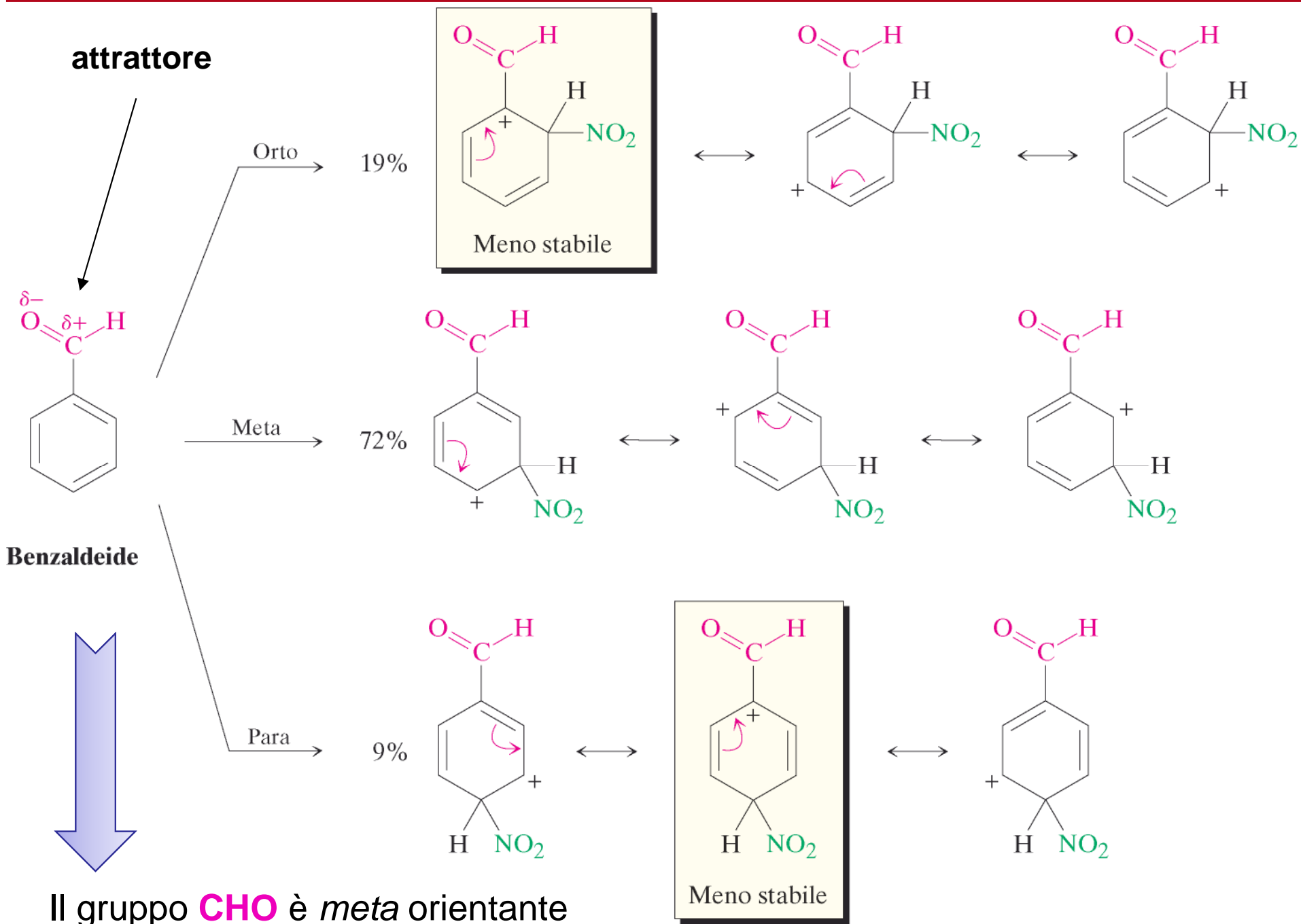


## nitrazione del fenolo

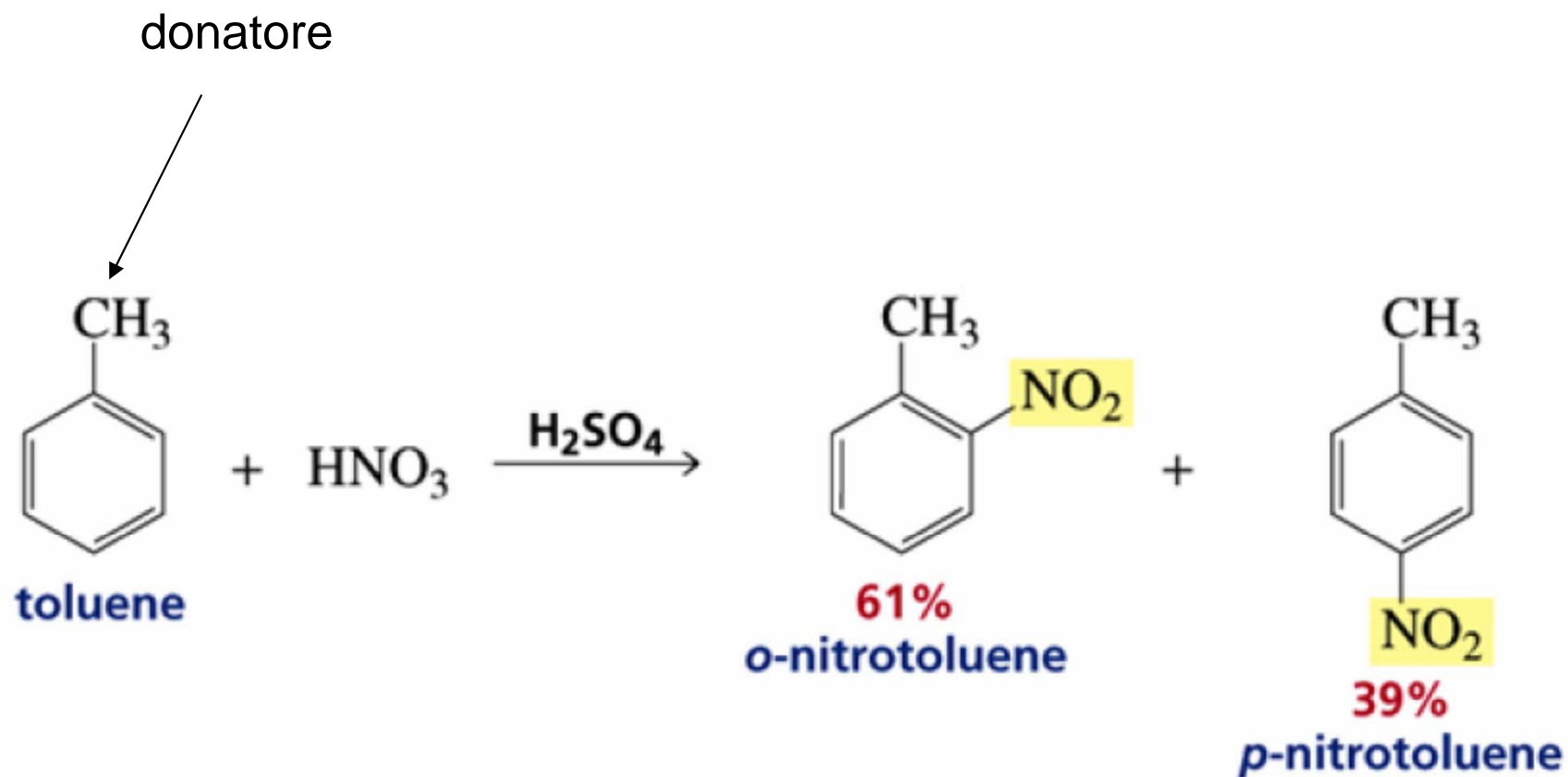


Il gruppo **OH** è orto-para orientante

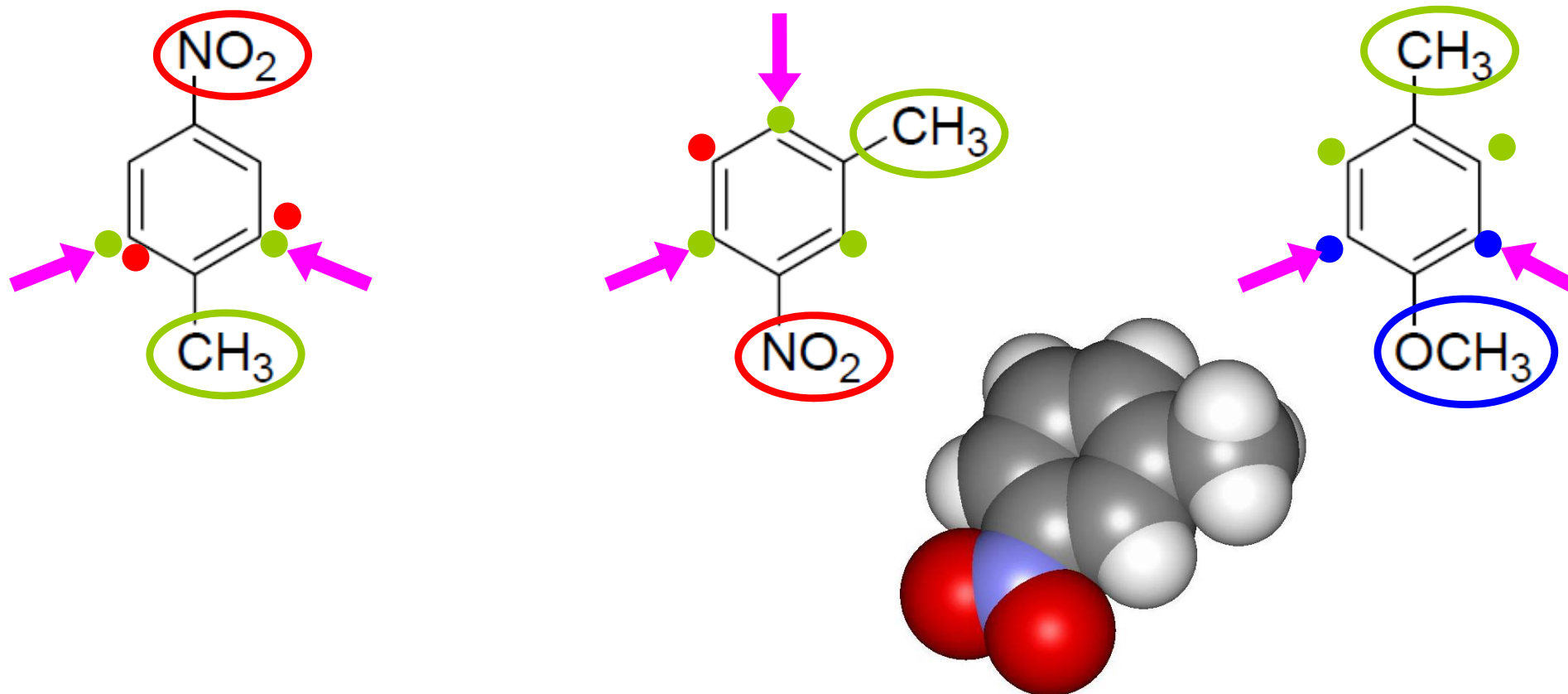
# nitrazione della benzaldeide



# nitrazione del toluene



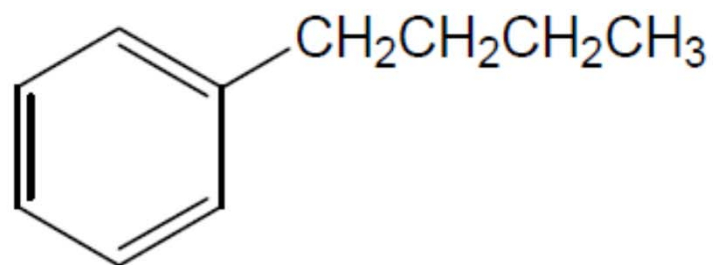
# effetto di più sostituenti



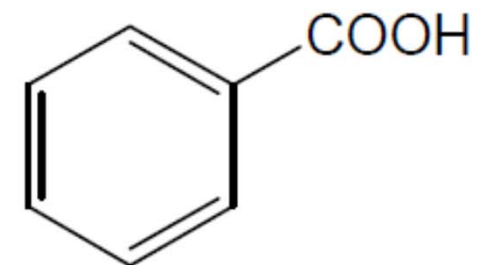
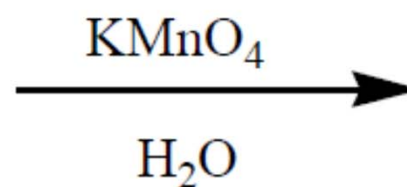
- Il gruppo **attivante** prevale sul **disattivante**.
- L'attivante **forte** prevale sull'attivante **debole**.
- Bisogna tener conto degli effetti sterici.



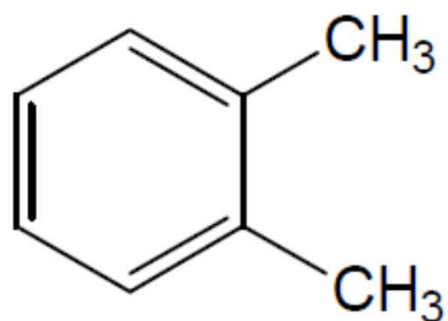
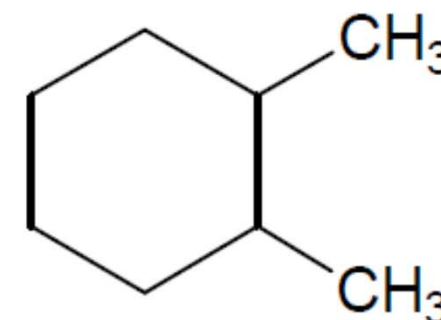
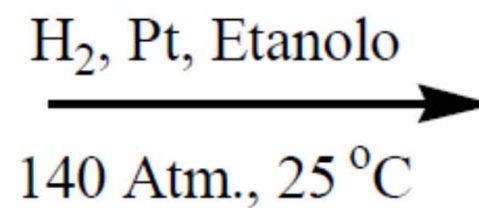
# ossidazioni e riduzioni



Butilbenzene

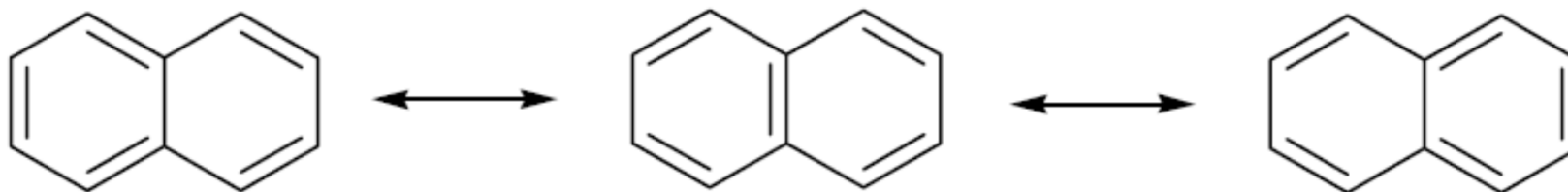


Acido Benzoico

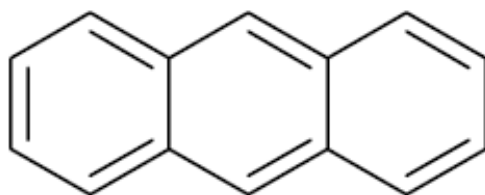
1,2-Dimetilbenzene  
(o-Xilene)

1,2-Dimetilcicloesano

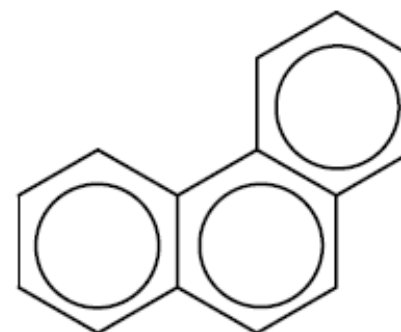
# altri composti aromatici



**Naftalene**



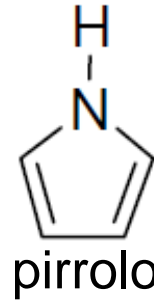
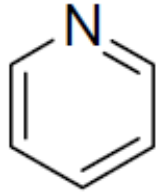
**Antracene**



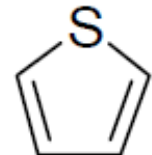
**Fenantrene**

# composti eteroaromatici

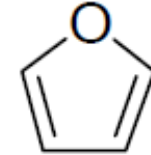
piridina



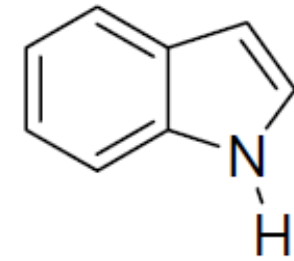
pirrolo



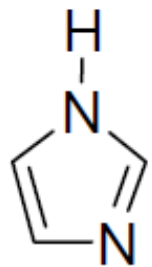
tiofene



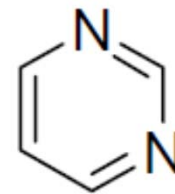
furano



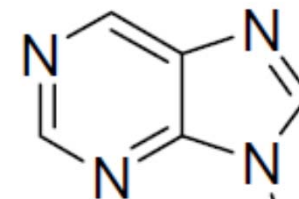
indolo



imidazolo

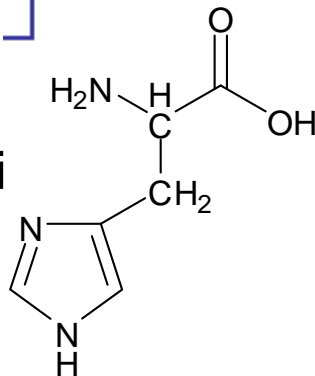


pirimidina



purina H

Amminoacidi  
(His)



Nucleobasi, caffeina

