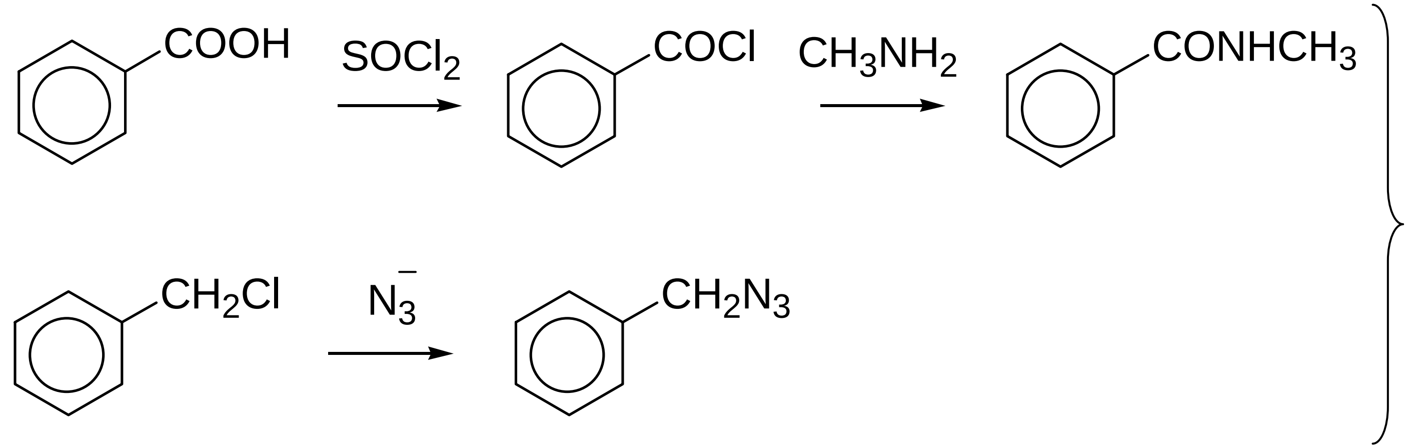
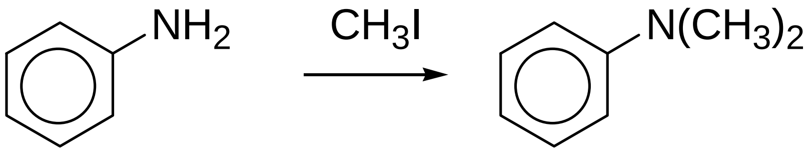
Altre reazioni dei composti aromatici

La reattività e le proprietà di gruppi funzionali vicini a sistemi aromatici può essere modificata anche sostanzialmente



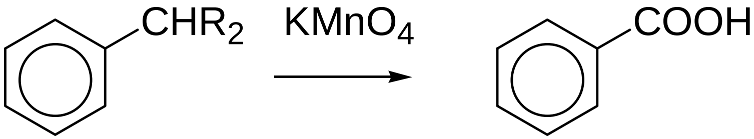
Nessuna modifica



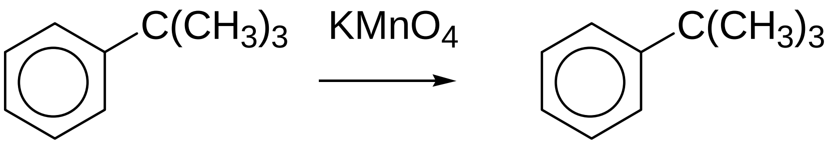
Più lenta che con ammine alifiatiche

Nessun prodotto

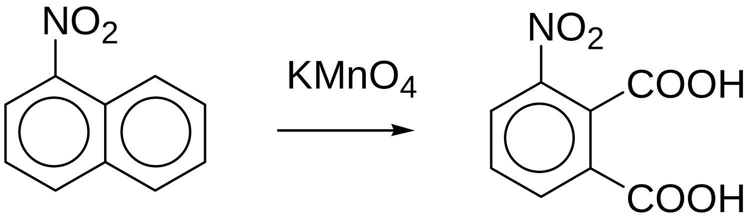
Altre reazioni dei sistemi aromatici: ossidazioni



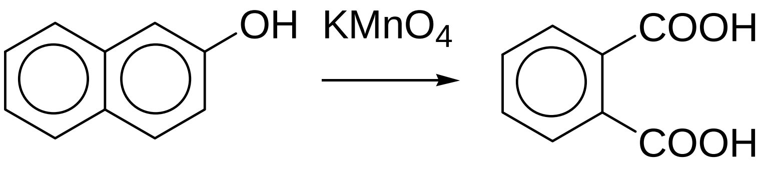
L’anello benzenico è resistente all’ossidazione mentre il gruppo metilico viene attivato dalla stabilità del radicale benzilico



Si può usare anche K_2CrO_4



L’ossidazione avviene all’anello più attivato



Alogenazione radicalica

$$\left.\begin{array}{l}
F_2 + 37\ \text{Kcal/mol} \xrightarrow{h\nu} 2\ F\cdot \\[2em]
Cl_2 + 58\ \text{Kcal/mol} \xrightarrow{h\nu} 2\ Cl\cdot \\[2em]
Br_2 + 46\ \text{Kcal/mol} \xrightarrow{h\nu} 2\ Br\cdot \\[2em]
I_2 + 36\ \text{Kcal/mol} \xrightarrow{h\nu} 2\ I\cdot
\end{array}\right\}$$

Reazioni endotermiche: è necessario un iniziatore (luce) e alta temperatura

Alogenazione radicalica

$$F\cdot + CH_4 \longrightarrow HF + CH_3\cdot + 33\ \text{Kcal/mol}$$

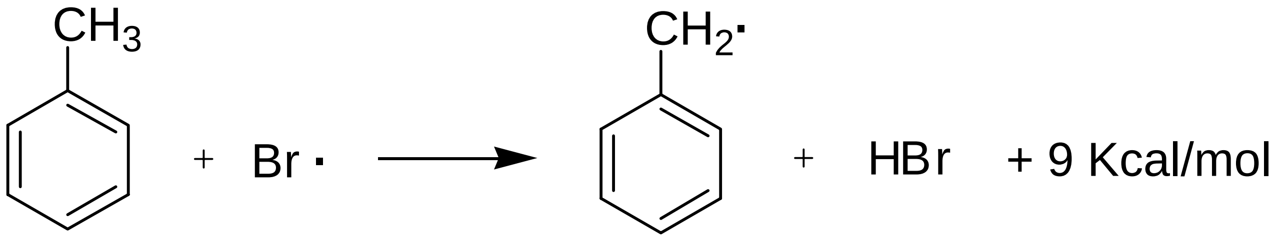
$$Cl\cdot + CH_4 \longrightarrow HCl + CH_3\cdot + 1\ \text{Kcal/mol}$$

$$Br\cdot + CH_4 + 15\ \text{Kcal/mol} \longrightarrow HBr + CH_3\cdot \quad \Big\}$$

Solo a T elevata

$$I\cdot + CH_4 + 31\ \text{Kcal/mol} \longrightarrow HF + CH_3\cdot \quad \Big\}$$

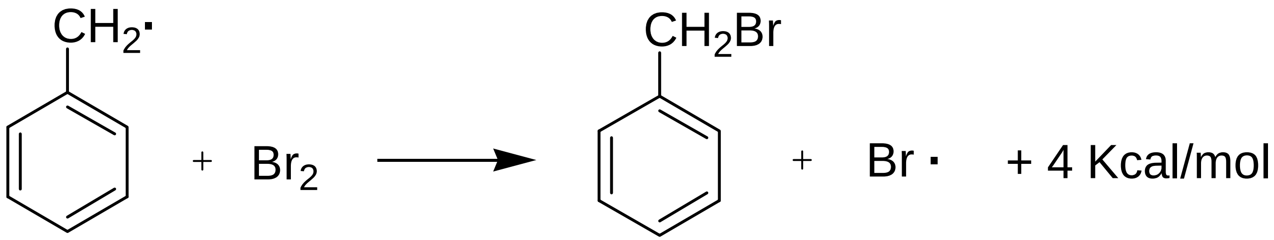
Non avviene



Alogenazione radicalica

$CH_3\cdot + F_2 \longrightarrow CH_3F + F\cdot + 60\ \text{Kcal/mol}$

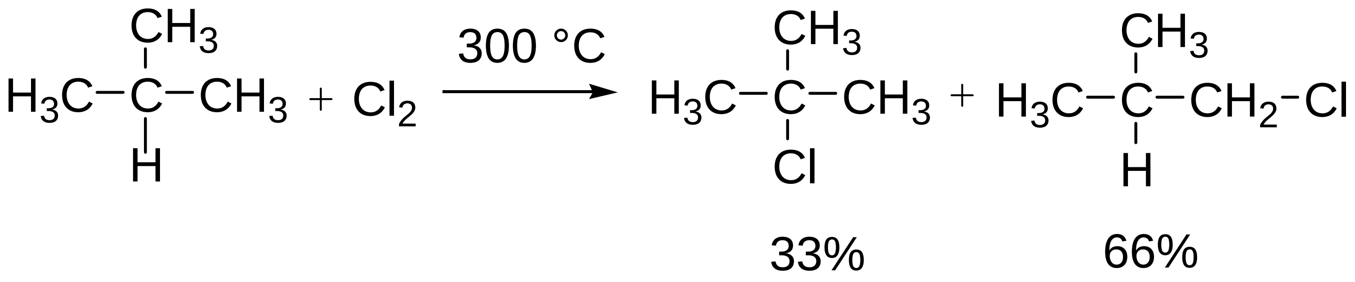
$CH_3\cdot + Cl_2 \longrightarrow CH_3Cl + Cl\cdot + 24\ \text{Kcal/mol}$



Alogenazione radicalica

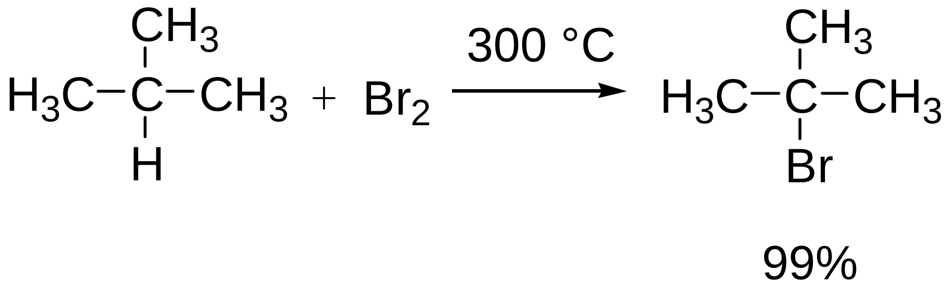
$$CH_4 + Cl_2 \longrightarrow CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$$

37% 24% 19% 8 %



$$H_3C-\overset{CH_3}{\underset{H}{C}}-CH_3 + Cl_2 \xrightarrow{300\ ^\circ C} H_3C-\overset{CH_3}{\underset{Cl}{C}}-CH_3 + H_3C-\overset{CH_3}{\underset{H}{C}}-CH_2-Cl$$

33% 66%

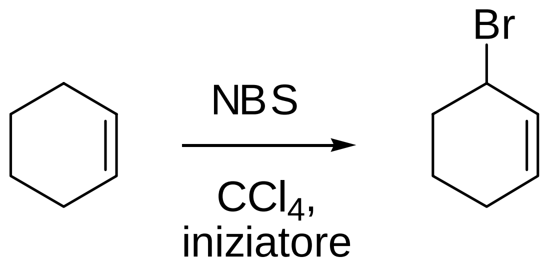


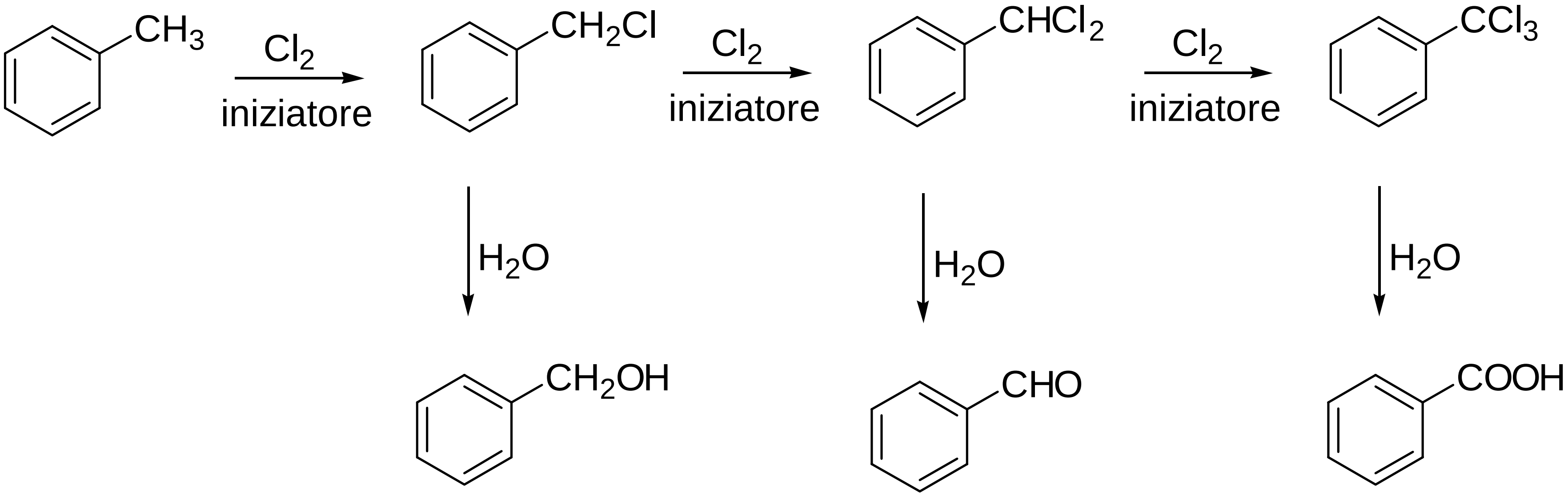
$$H_3C-\overset{CH_3}{\underset{H}{C}}-CH_3 + Br_2 \xrightarrow{300\ ^\circ C} H_3C-\overset{CH_3}{\underset{Br}{C}}-CH_3$$

99%

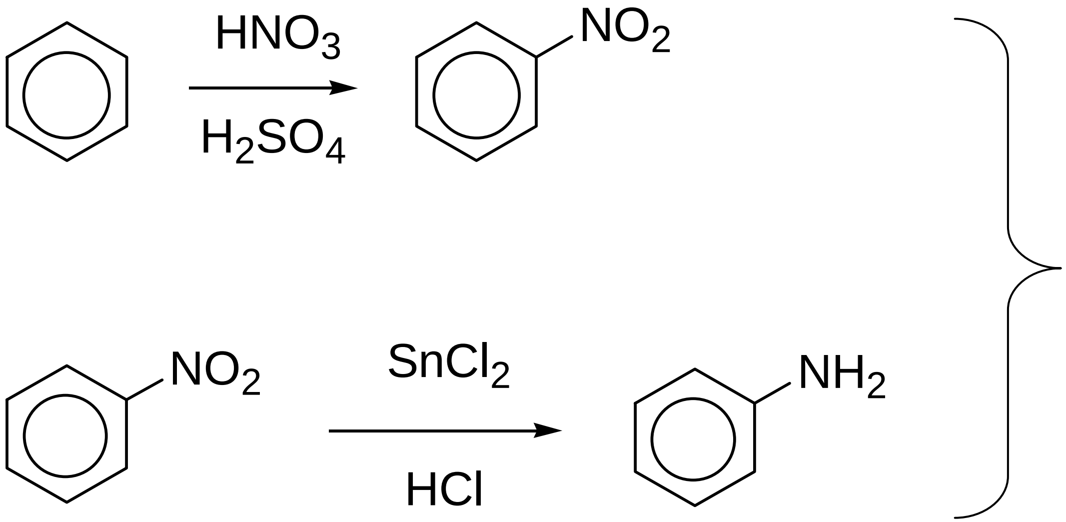
Principio di **reattività-selettività** il reagente meno reattivo è più selettivo

Alogenazione radicalica



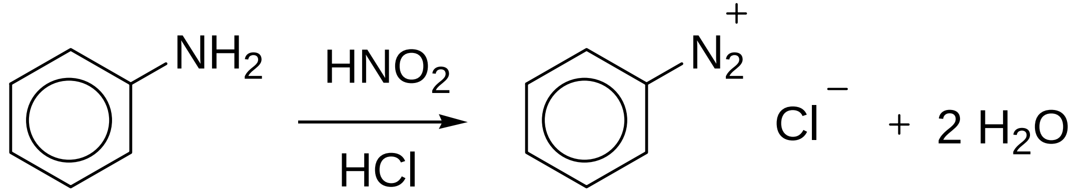


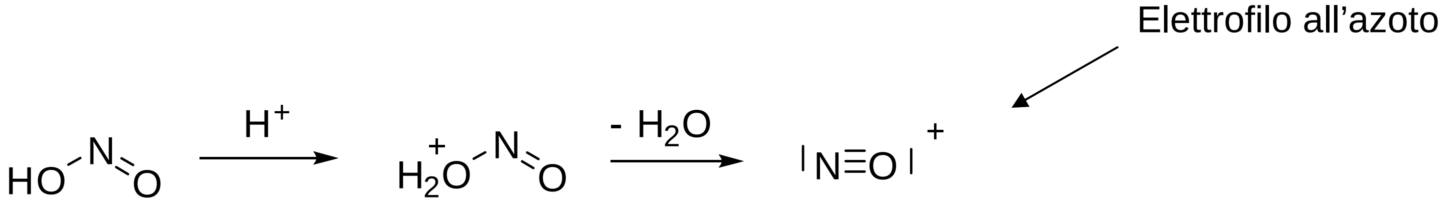
Riduzione del gruppo nitro

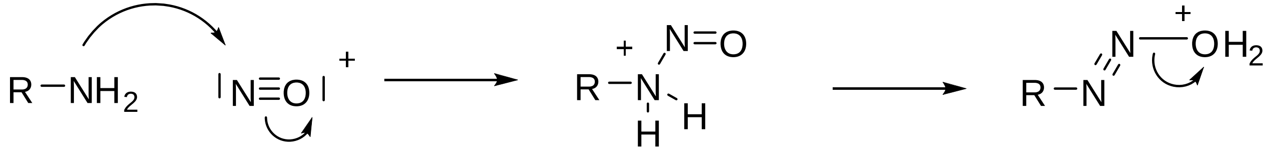


Introduzione del gruppo amminico sull'anello aromatico

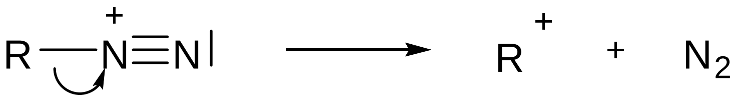
Sali di diazonio aromatici: SN1 aromatica



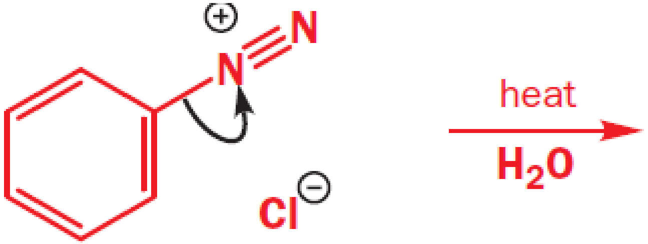

Elettrofilo all'azoto



Sali di diazonio aromatici

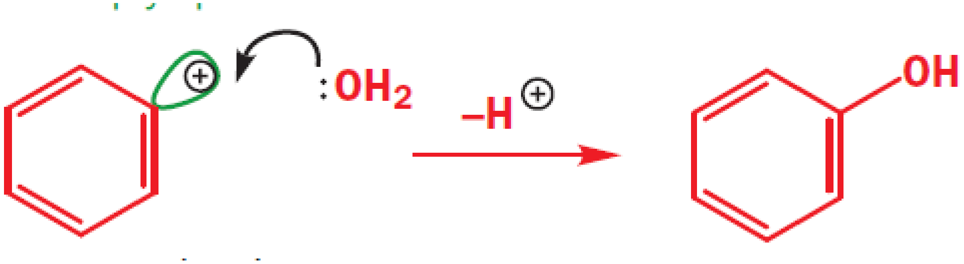


Se R è un gruppo alchilico la reazione è immediata, se R è un gruppo arilico la reazione è rallentata a basse temperature (0 °C).

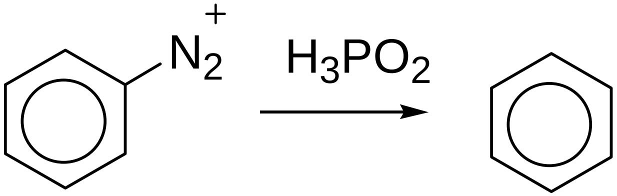


Carbocatione instabile

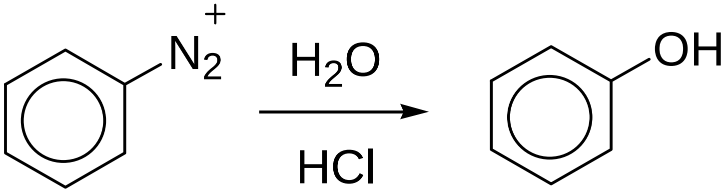
Il sale di diazonio è stabile ma generalmente non viene isolato (esplosivo allo stato solido). E’ un intermedio sintetico di grande utilità.



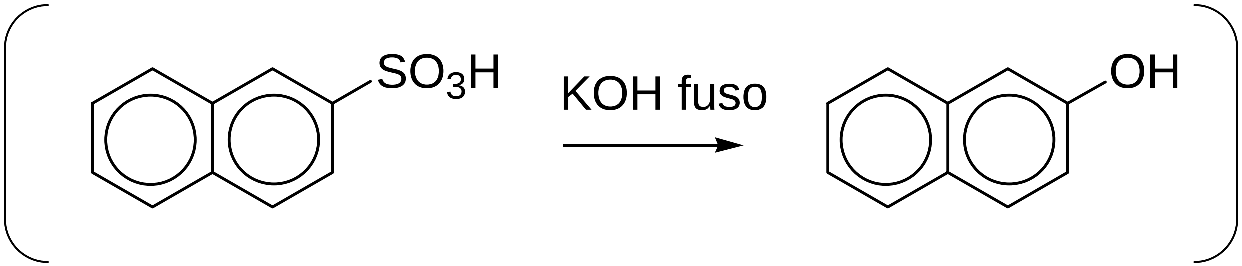
Sali di diazonio aromatici: trasformazioni



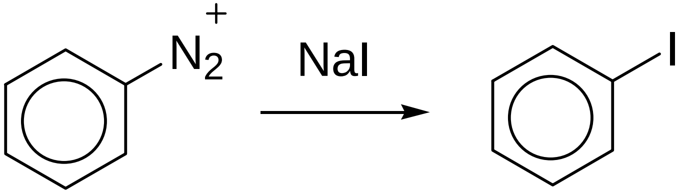
Sostituzione con H

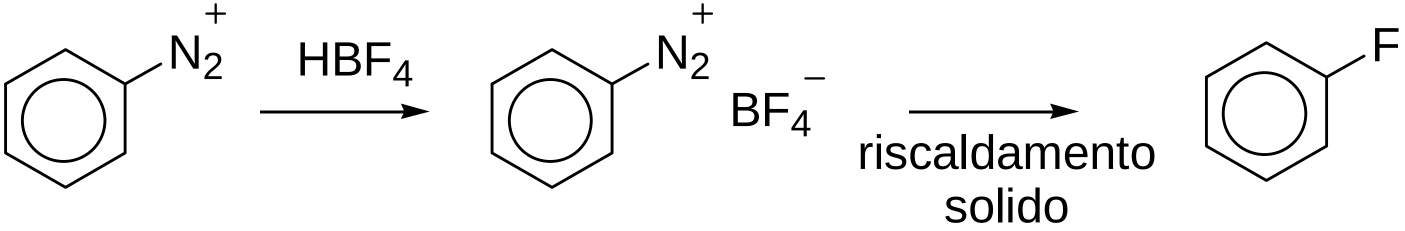


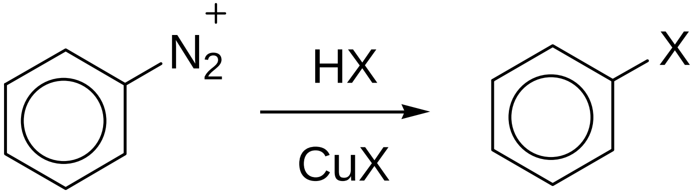
Sostituzione con OH



Sali di diazonio aromatici: sostituzione con alogeni

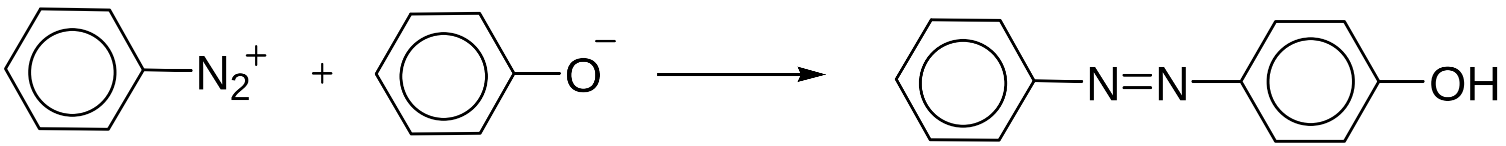


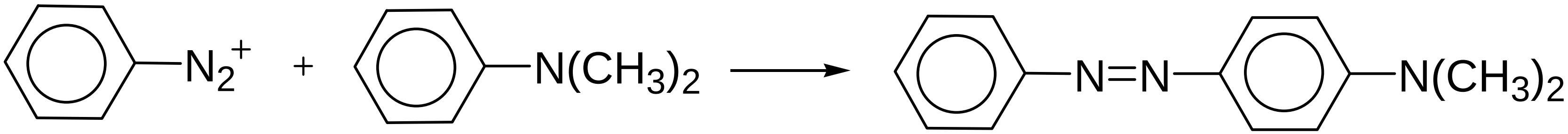




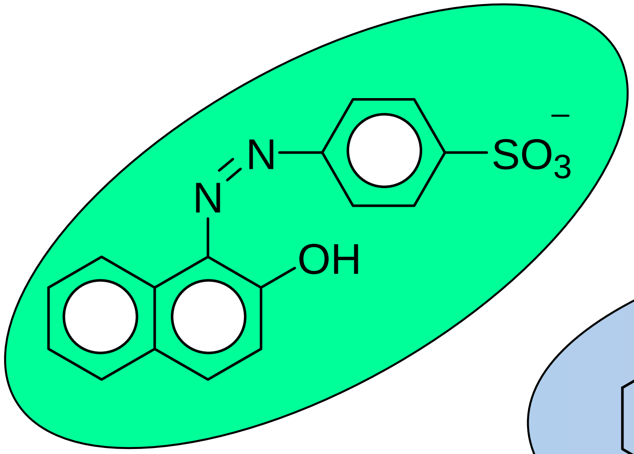
X = Cl, Br, CN

Sali di diazonio aromatici: trasformazioni

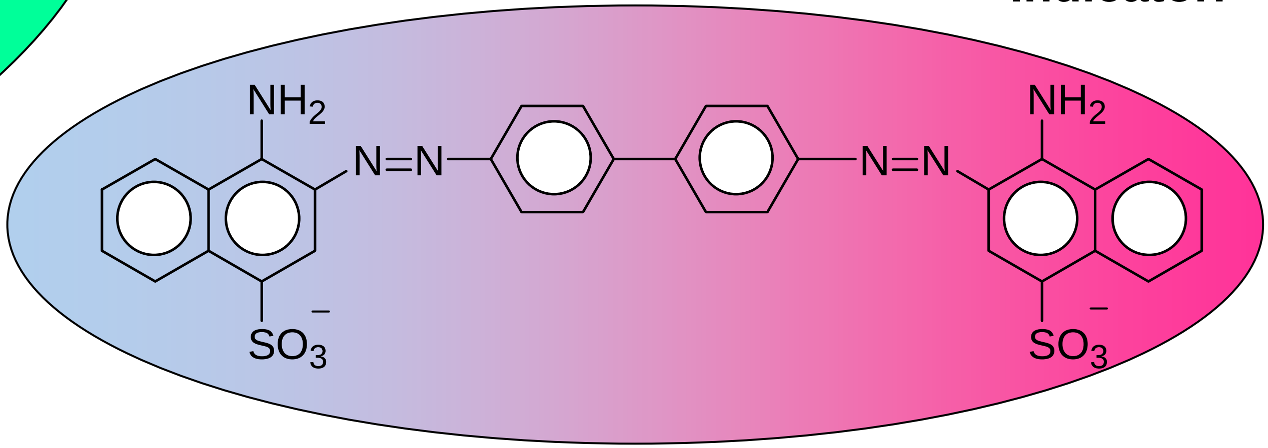




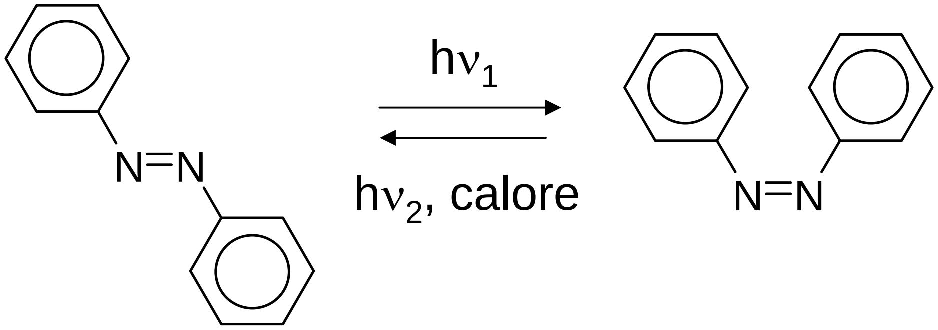
Coloranti



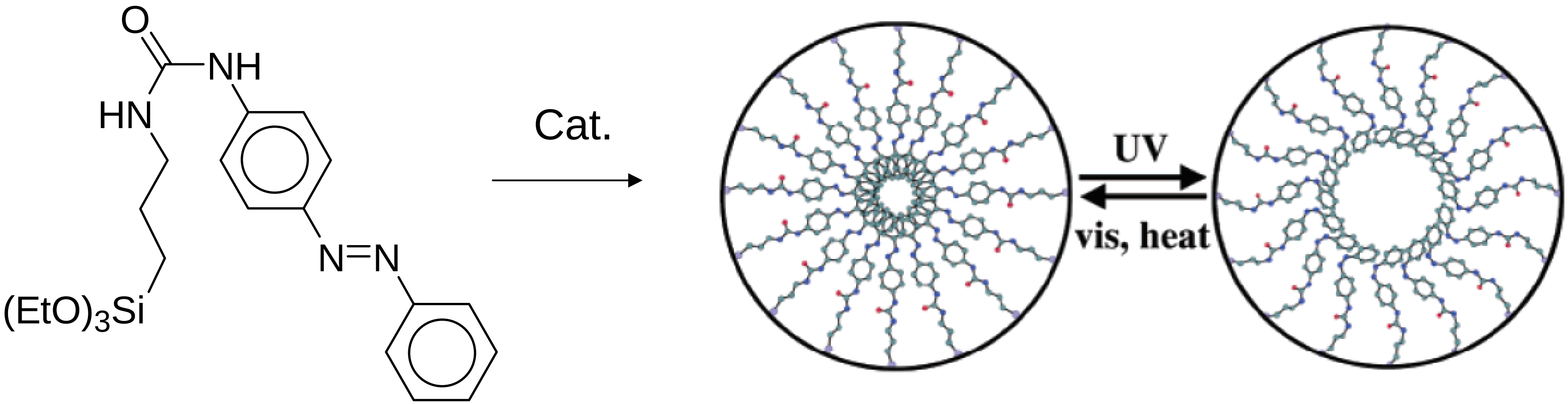
Indicatori



Azobenzeni: fotoisomerizzazioni

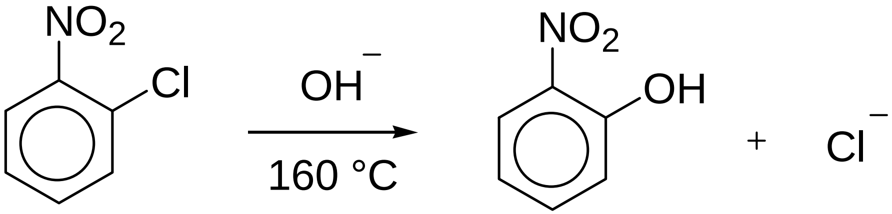


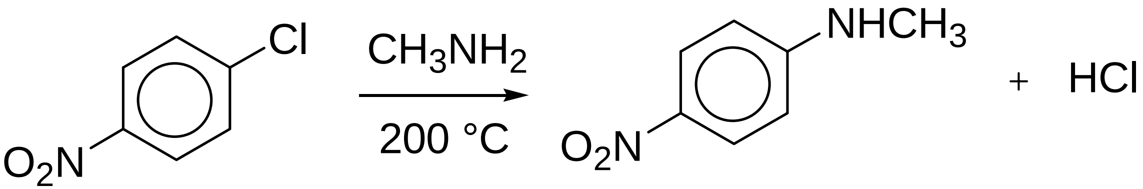
trans **cis**

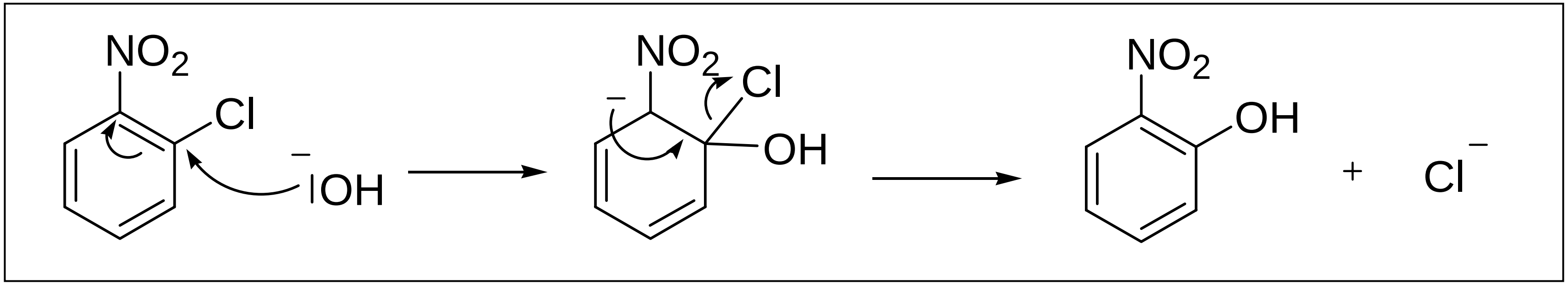


Nano Lett. **2004**, *4*, 551-554

Sostituzioni nucleofiliche aromatiche

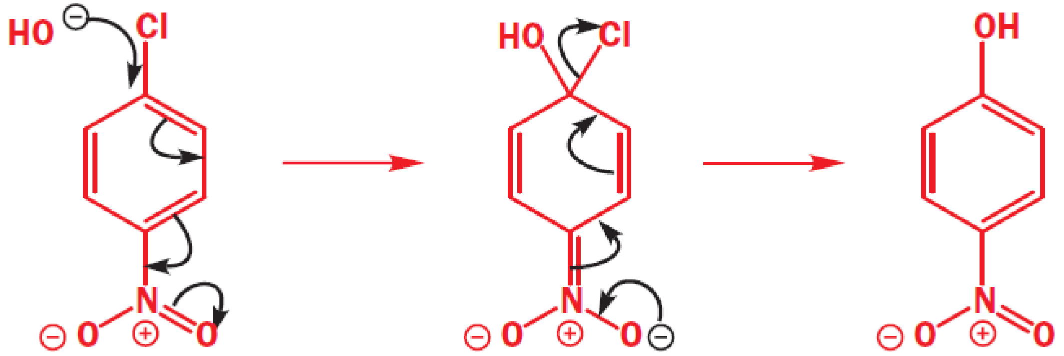


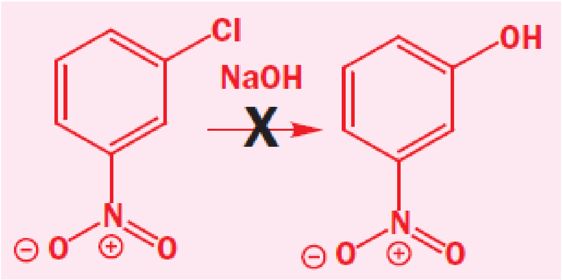




Gruppi elettron-attrattori stabilizzano il carbanione e facilitano l’attacco del nucleofilo

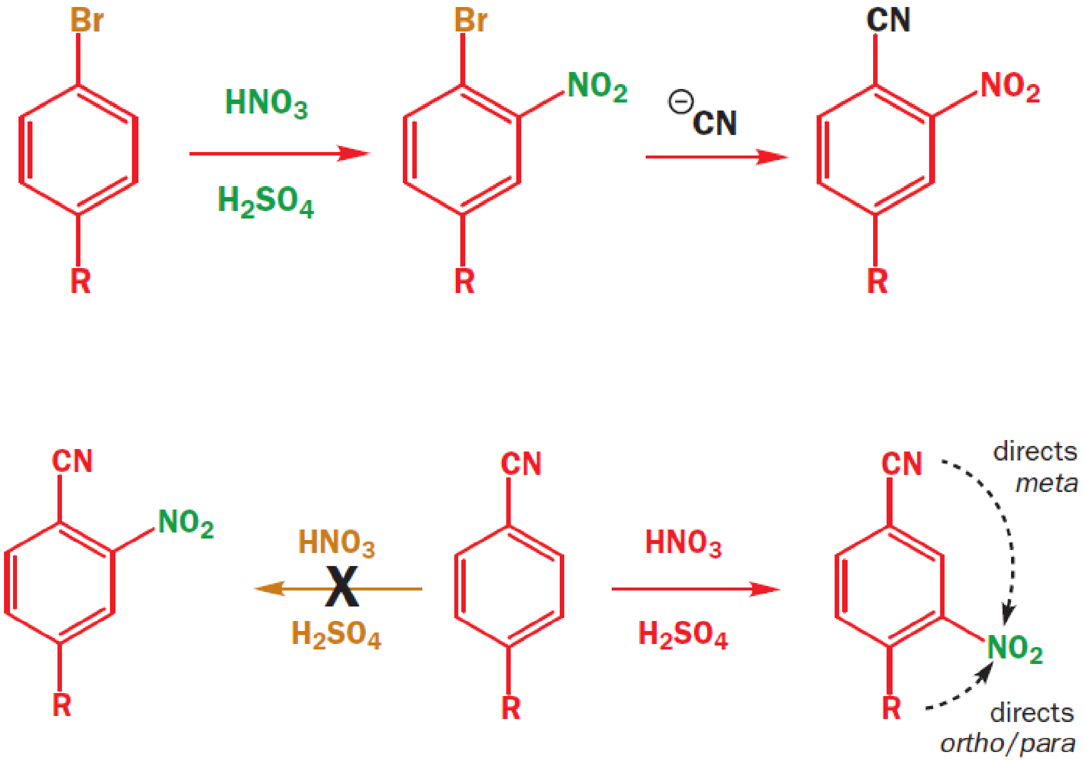
Sostituzioni nucleofiliche aromatiche





Gli effetti di attivazione e direzione sono inversi nelle sostituzione nucleofile rispetto alle sostituzioni elettrofile

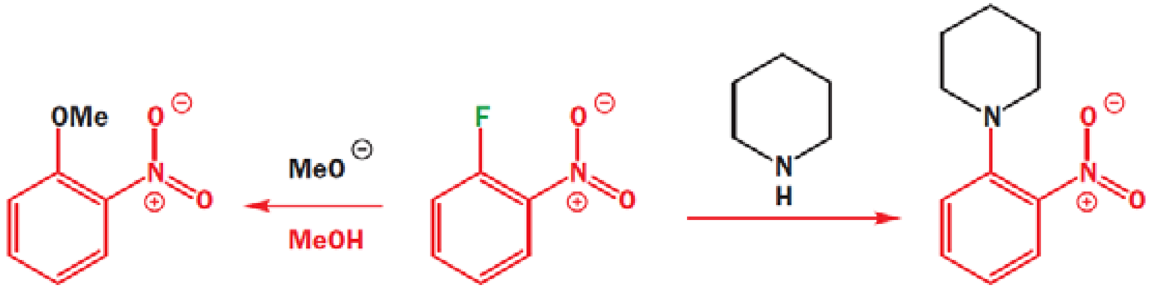
Sostituzioni nucleofiliche aromatiche

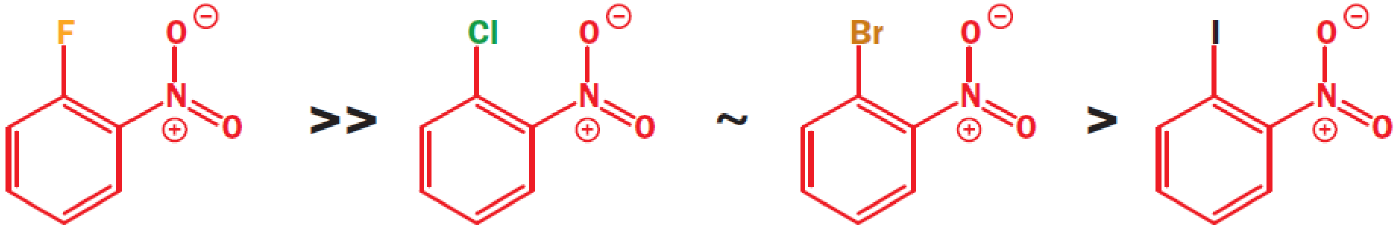


E’ possibile ottenere prodotti non preparabili con reazione SE Ar

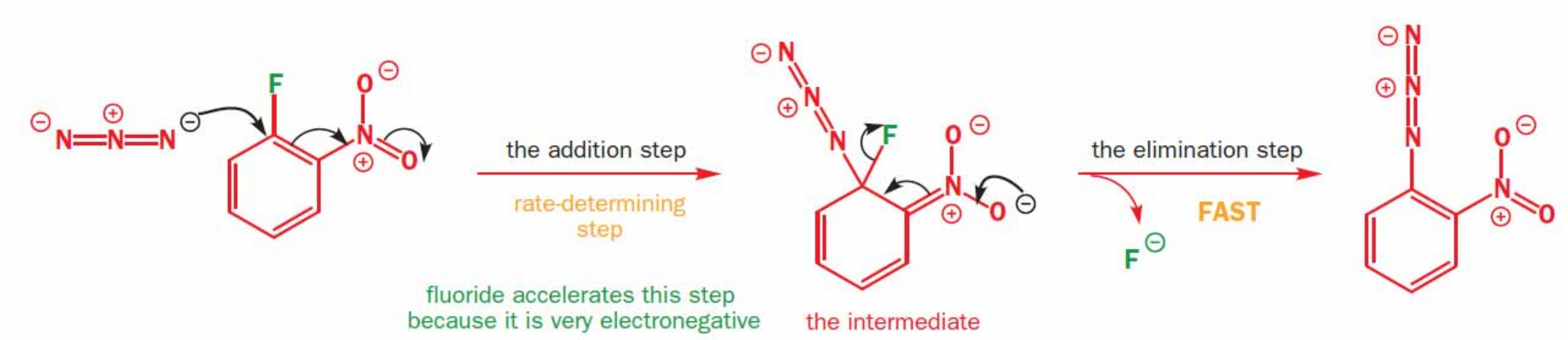
Sostituzioni nucleofiliche aromatiche

Effetto del gruppo uscente



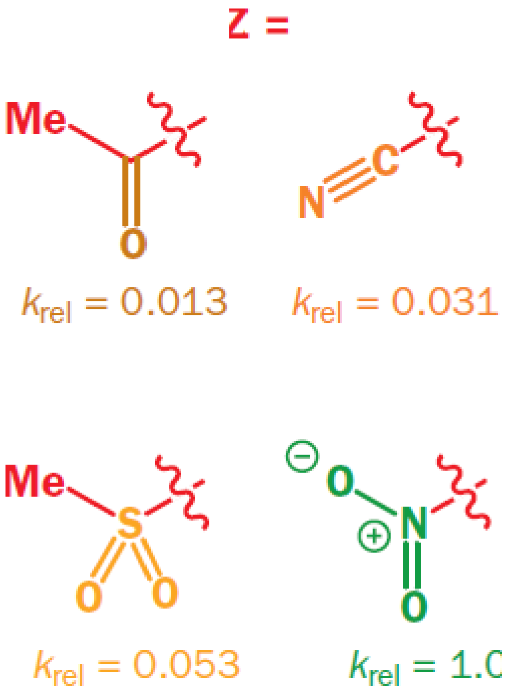


F è il peggior gruppo uscente

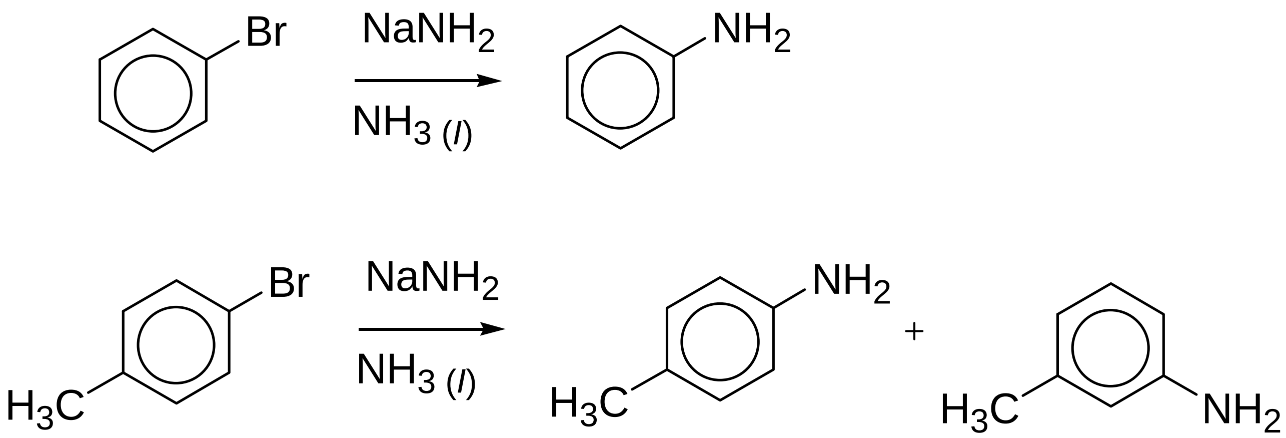


Sostituzioni nucleofiliche aromatiche

Effetto del sostituente attivante

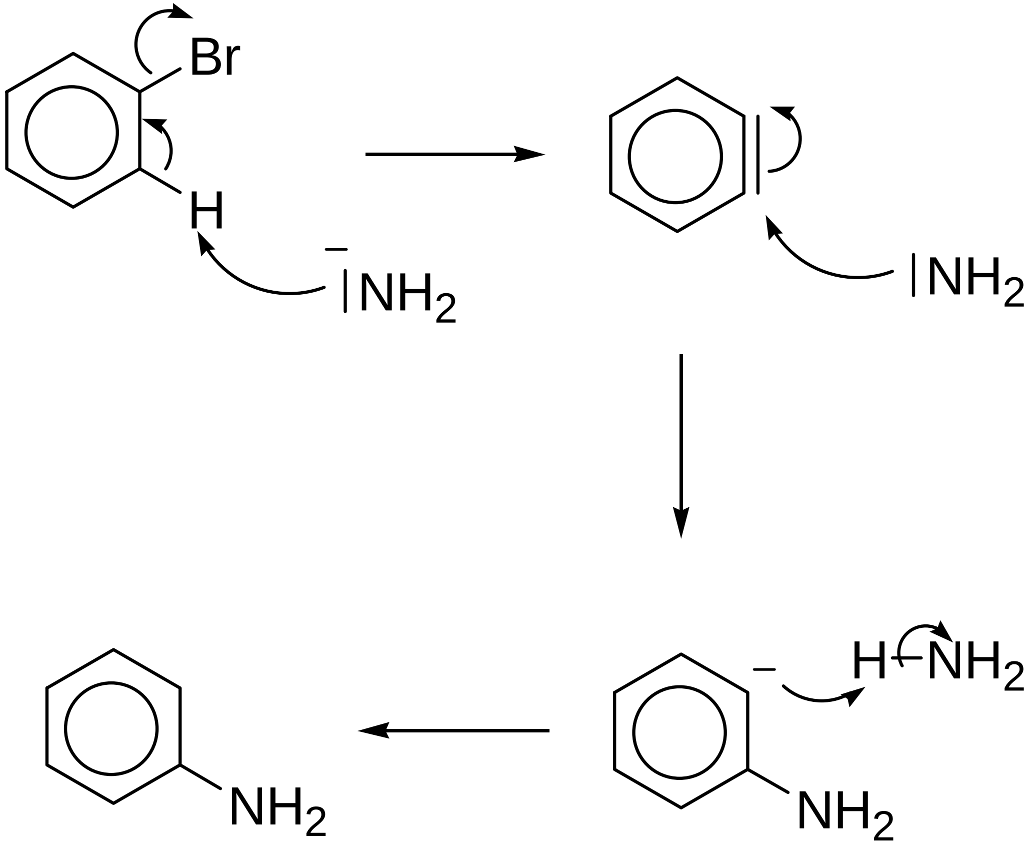


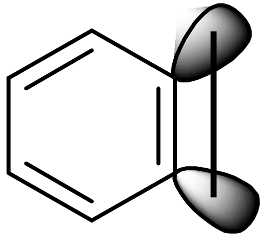
Sostituzioni con intermedio benzino



Non si tratta di una reazione di sostituzione nucleofila

Sostituzioni con intermedio benzino





benzino

In questa reazione lo ione ammide non agisce da nucleofilo bensì da base