

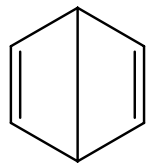
# Arene (Aromaten)

Benzen: Faraday erhielt 1825 durch Pyrolyse von komprimiertem Leuchtgas eine farblose Flüssigkeit.

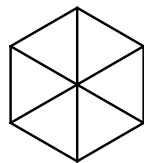
Empirische Formel:  $\text{CH}$ , Kp.:  $80.1^\circ\text{C}$ , Fp.:  $5.5^\circ\text{C}$ , reaktionsträge

Molekularformel:  $\text{C}_6\text{H}_6$

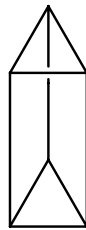
Historische Strukturvorschläge:



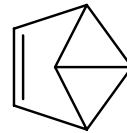
Dewar



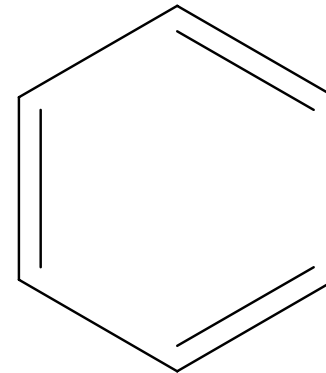
Claus



Ladenburg  
(Prisman)

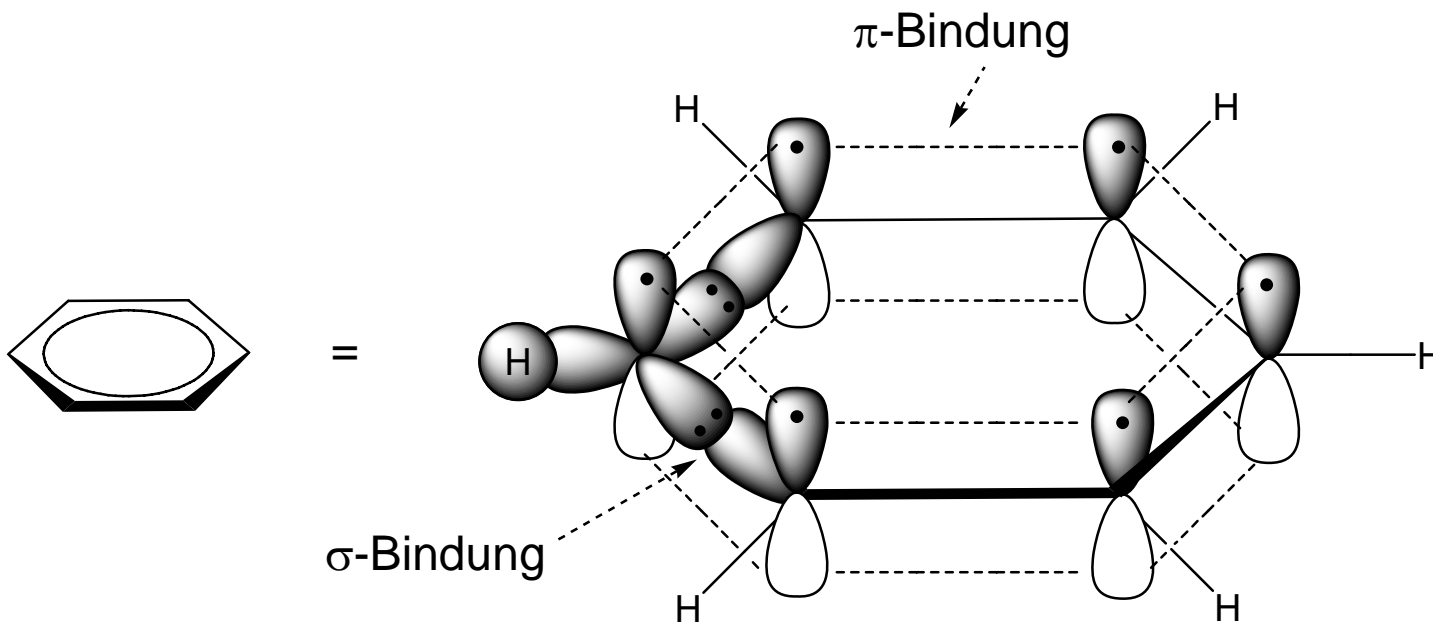
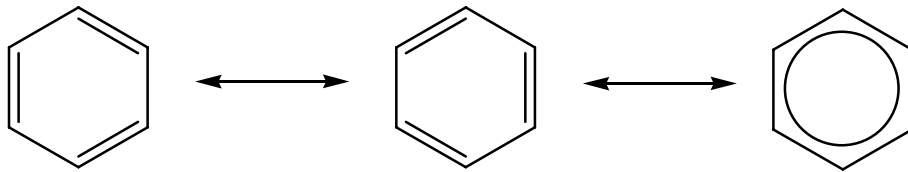


Benzvalen



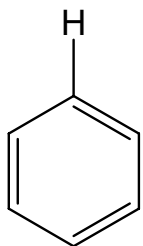
Kekulé  
(1865)

# Mesomere Grenzstrukturen des Benzens

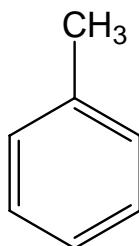


# Nomenklatur

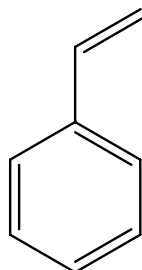
Trivialnamen:



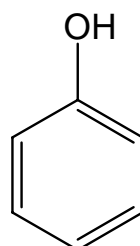
Benzen



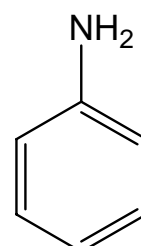
Toluen



Styren

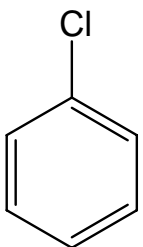


Phenol

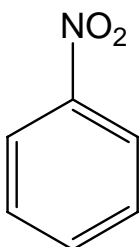


Anilin

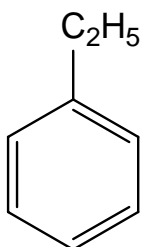
Systematische Namen:



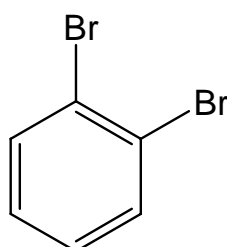
Chlorbenzen



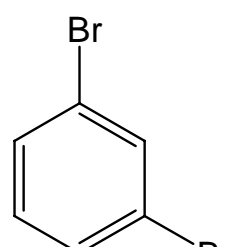
Nitrobenzen



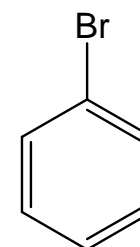
Ethylbenzen



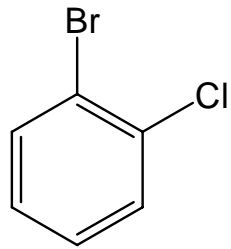
ortho-  
1,2-



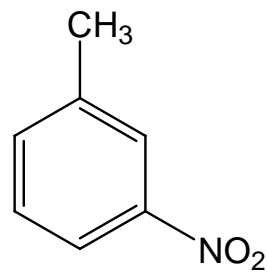
meta-  
1,3-



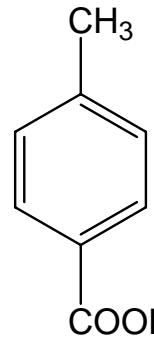
para-  
1,4-Dibrombenzen



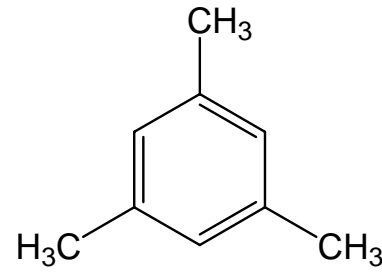
1-Brom-  
2-chlorbenzen



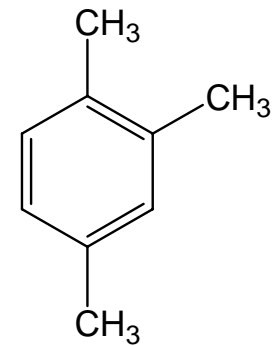
1-Methyl-  
3-nitrobenzen  
m-Nitrotoluen



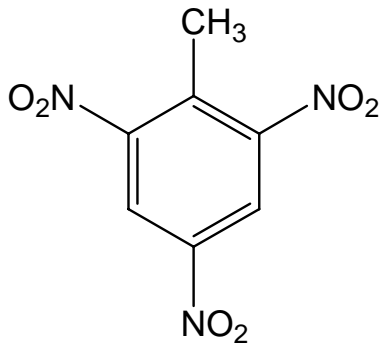
p-Methylbenzen-  
carbonsäure



1,3,5-Trimethylbenzen

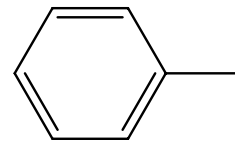


1,2,4-Trimethylbenzen

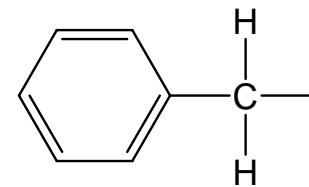


1-Methyl-2,4,6-trinitrobenzen

2,4,6-Trinitrotoluen (TNT)

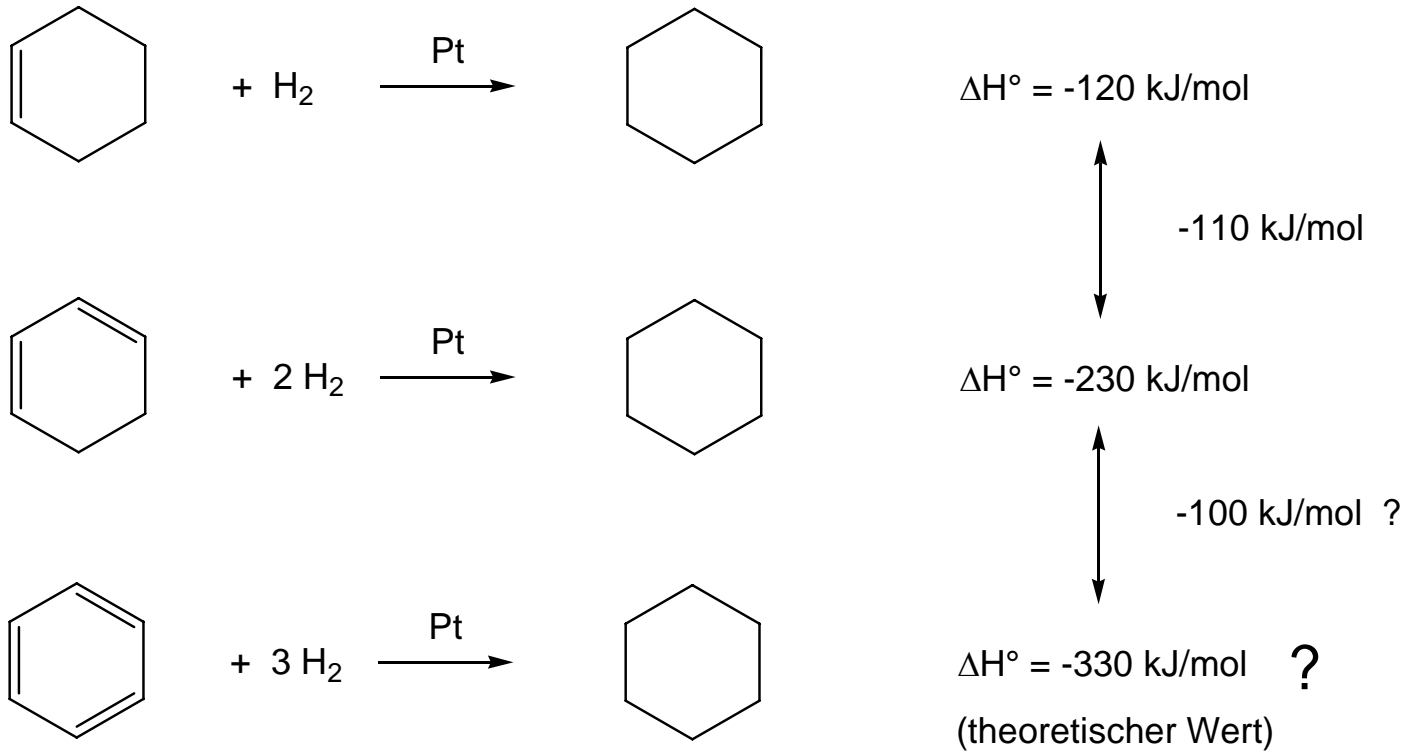


Phenylgruppe

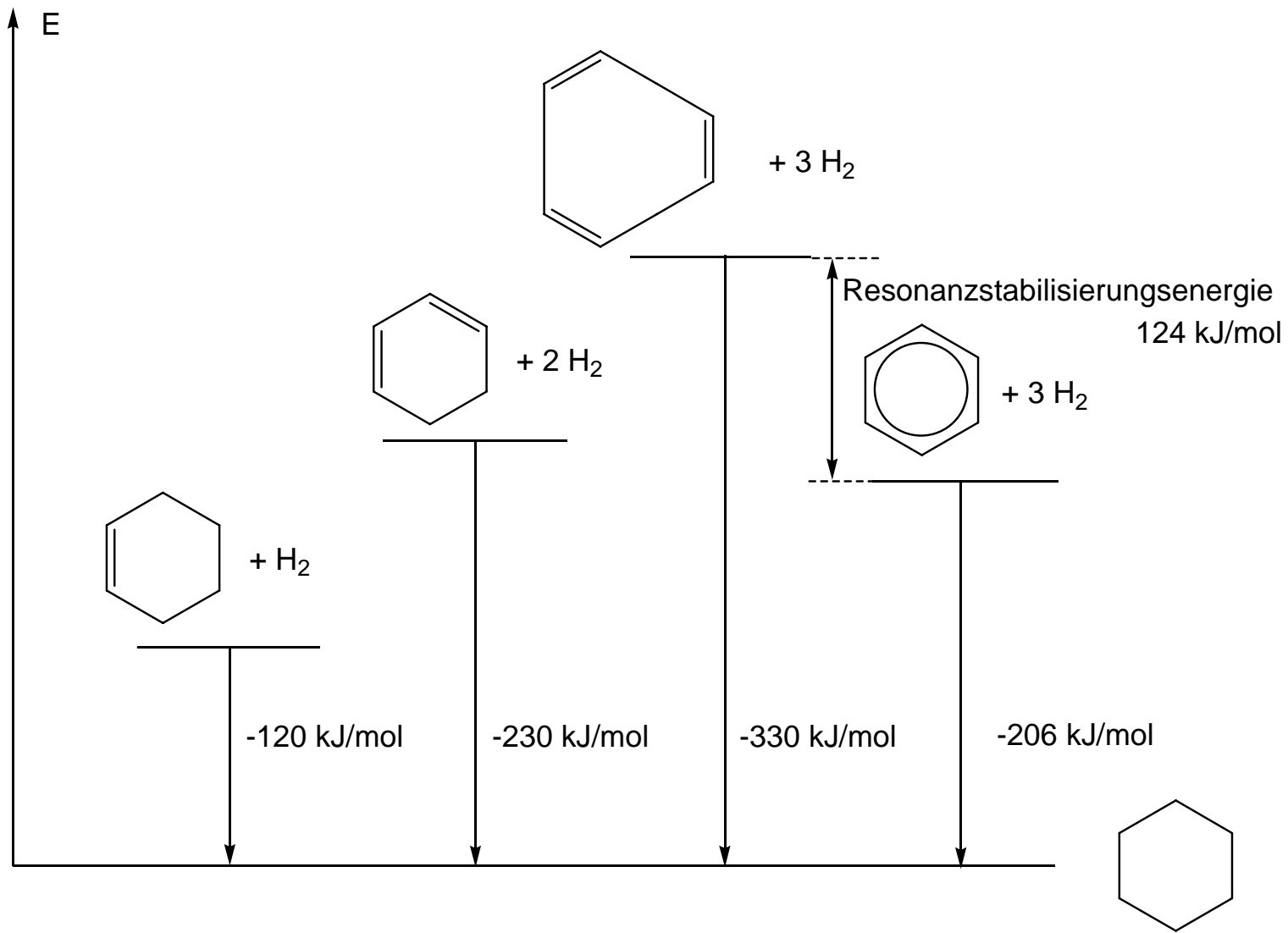


Benzylgruppe

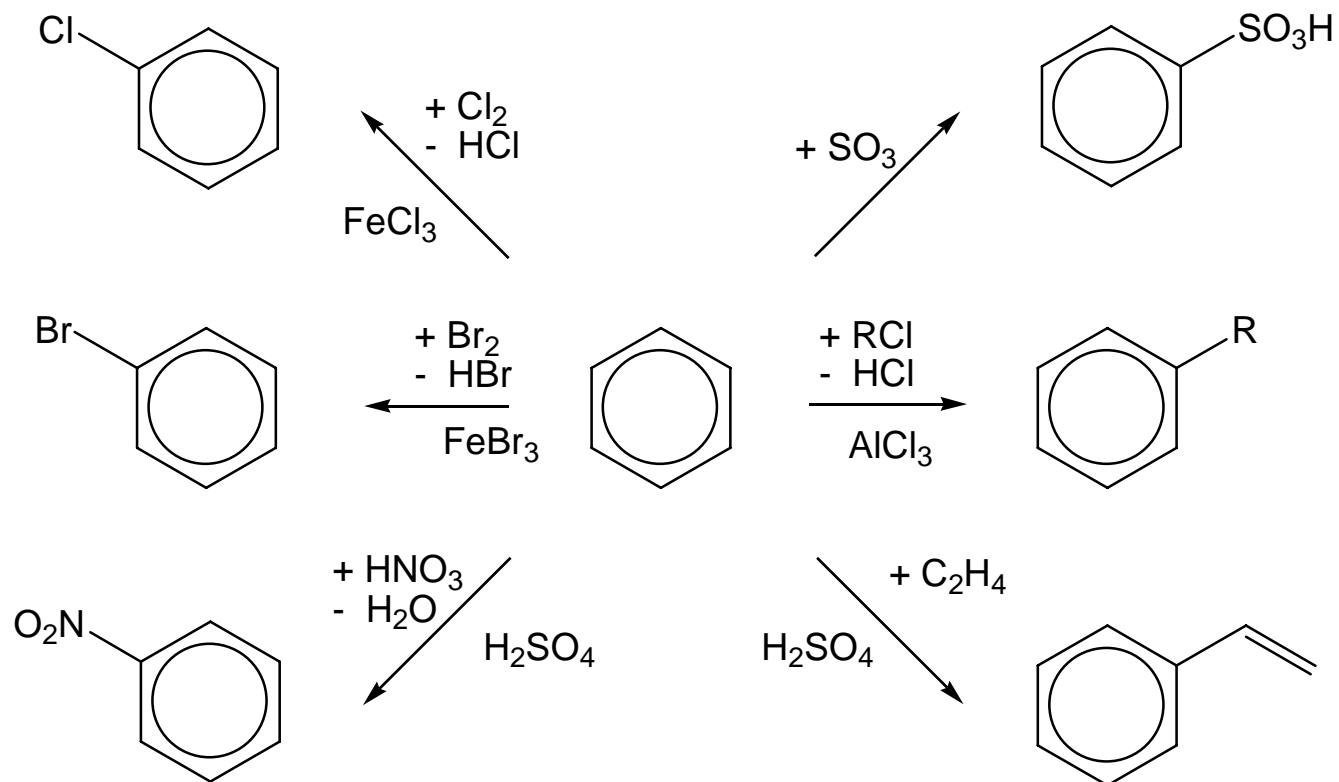
# Hydrierungswärmen zyklischer Alkene



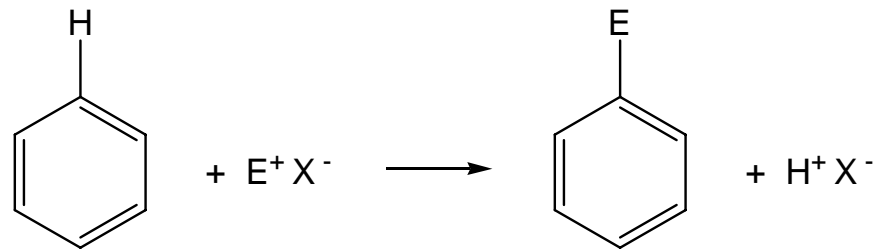
**Experimenteller Wert:  $\Delta H^\circ = -206 \text{ kJ/mol !}$**



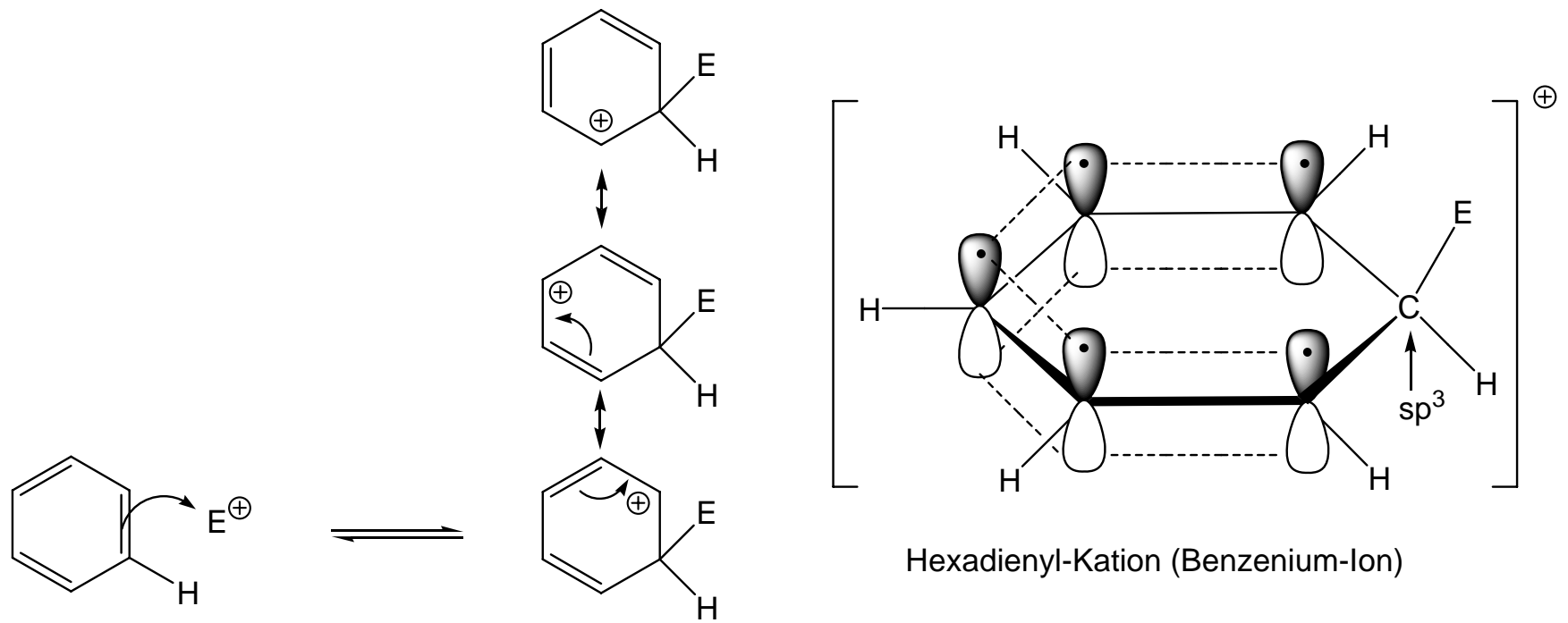
# Elektrophile aromatische Substitution



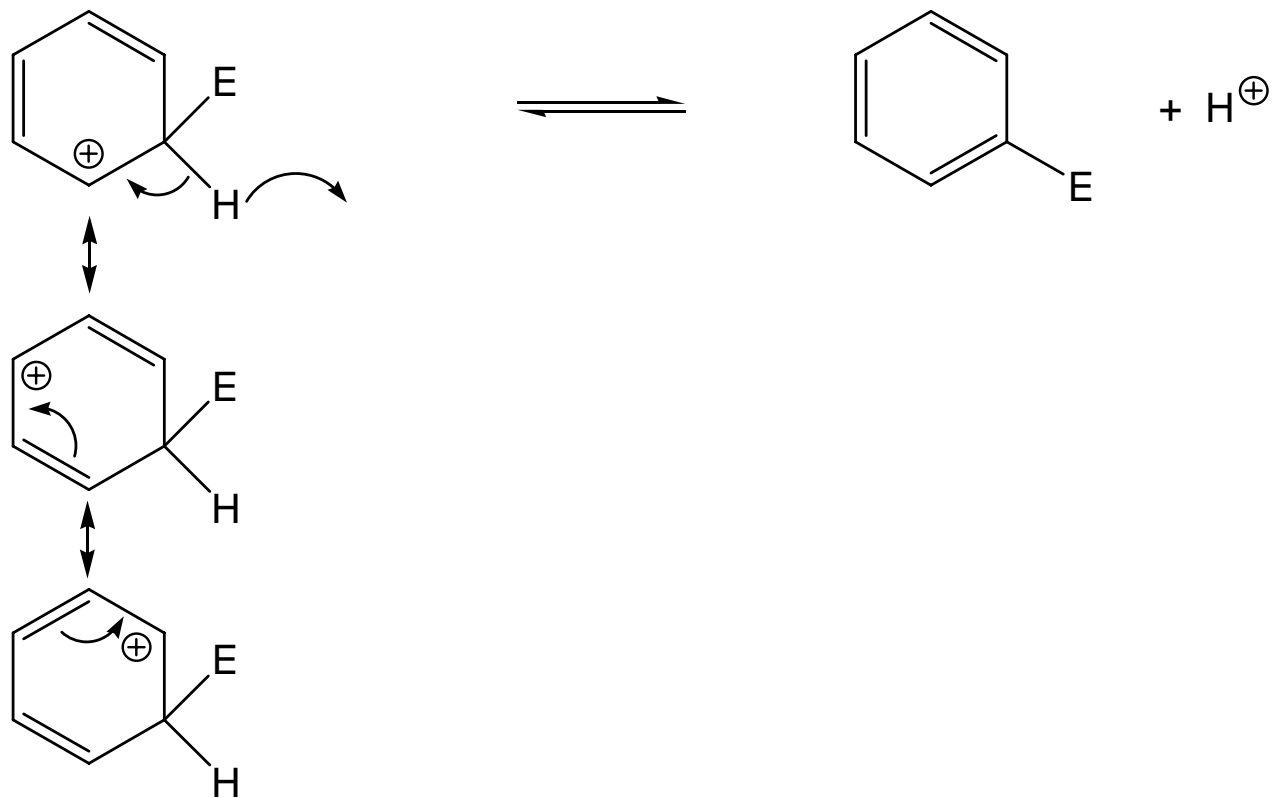
Mechanismus:



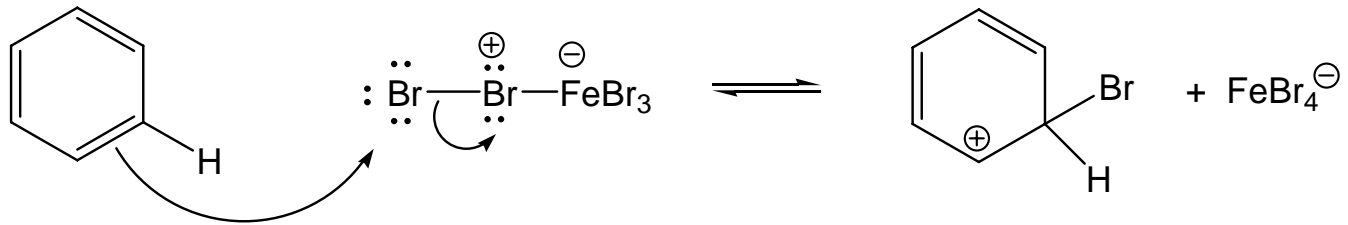
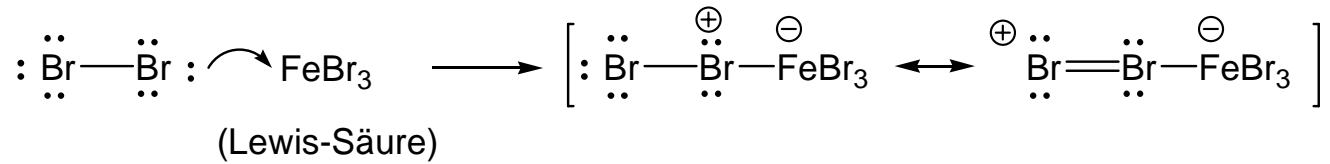
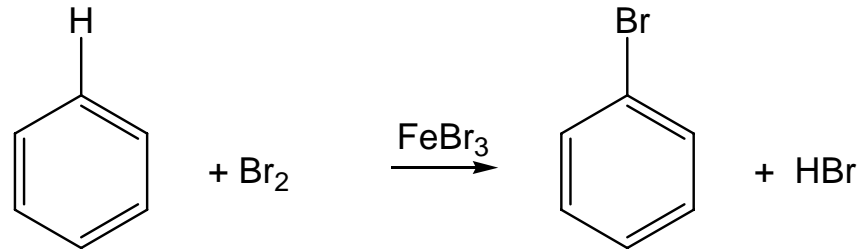
Schritt 1: Angriff des Elektrophils

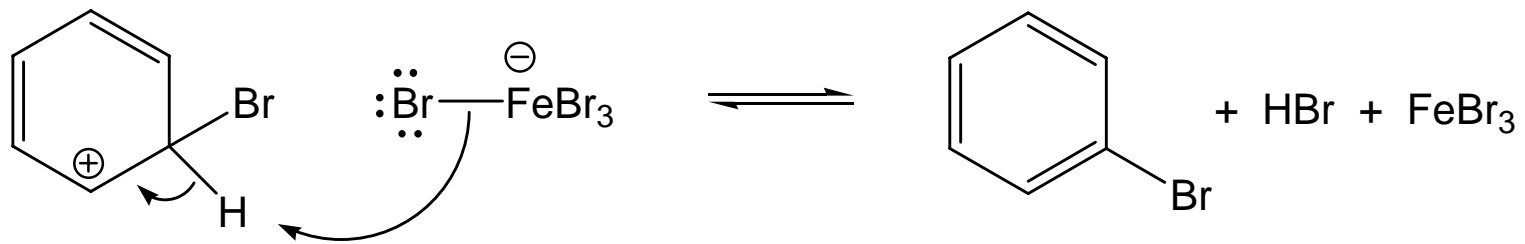


Schritt 2: Abspaltung des Protons

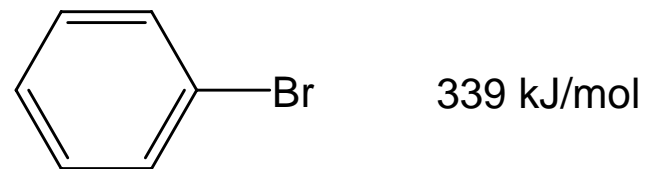
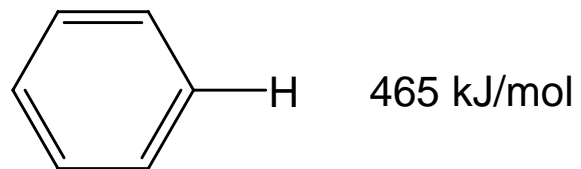


# Bromierung von Benzen





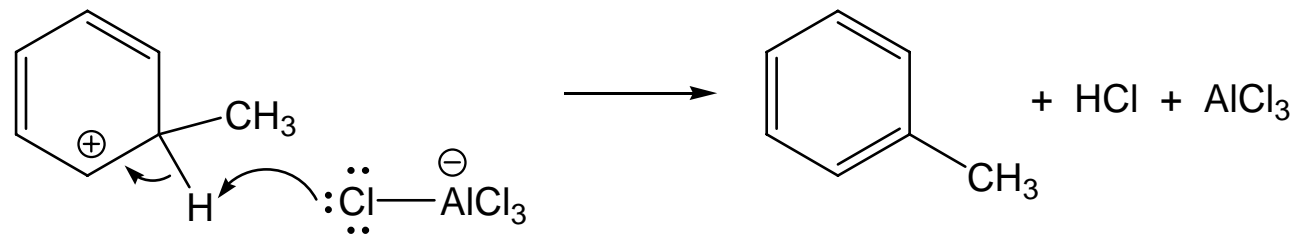
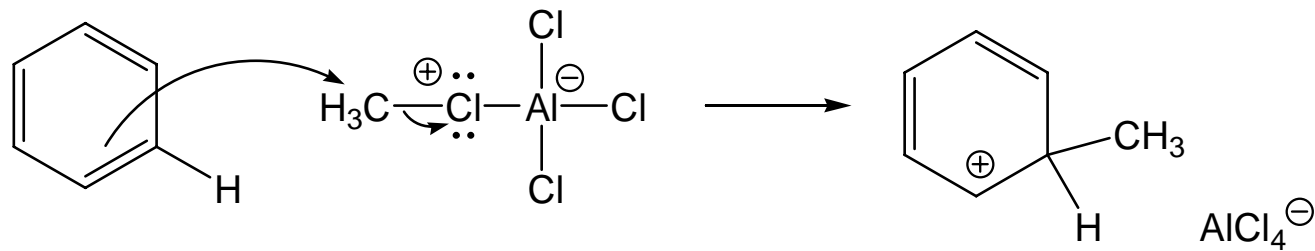
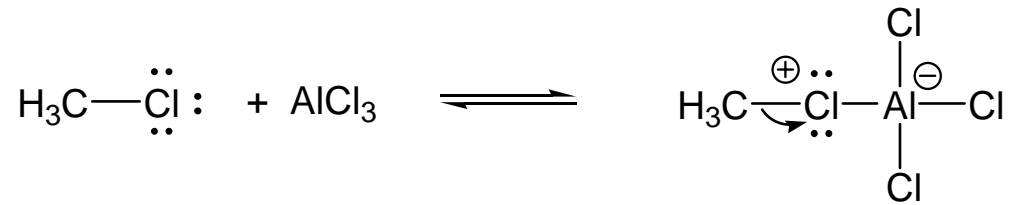
Bindungsenthalpien  $\Delta H^\circ$



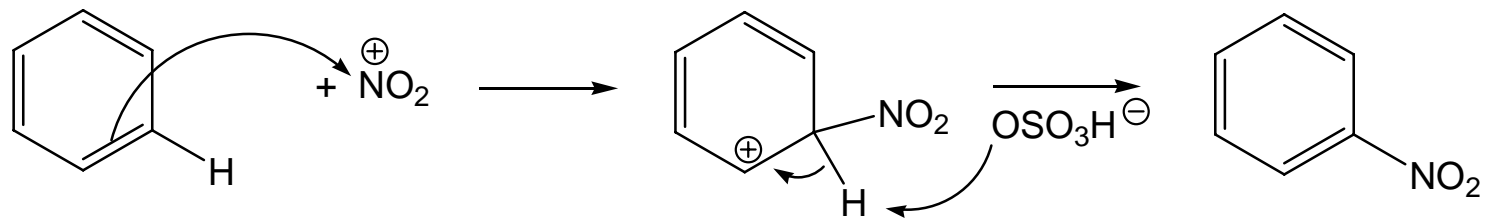
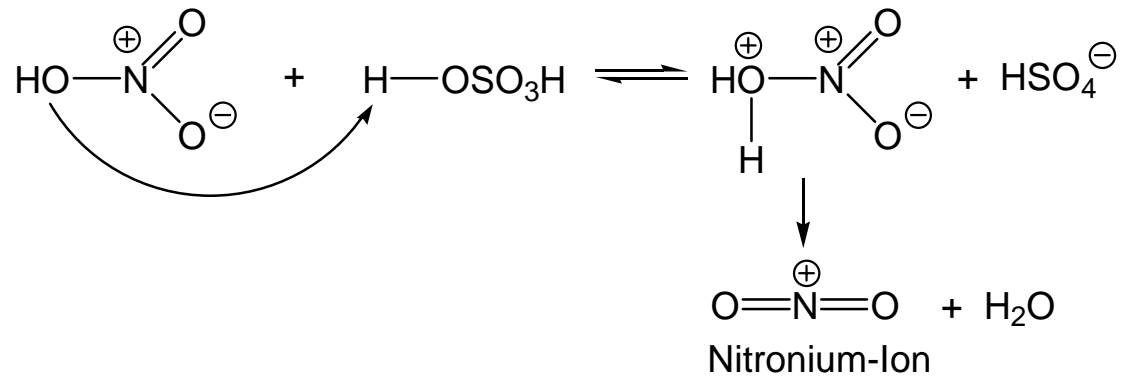
Abschätzung der Reaktionsenthalpie  $\Delta_r H^\circ$  für die Bromierung von Benzen:

$$\Delta_r H^\circ = (465 + 193 - 339 - 366) \text{ kJ/mol} = (658 - 705) \text{ kJ/mol} = -47 \text{ kJ/mol}$$

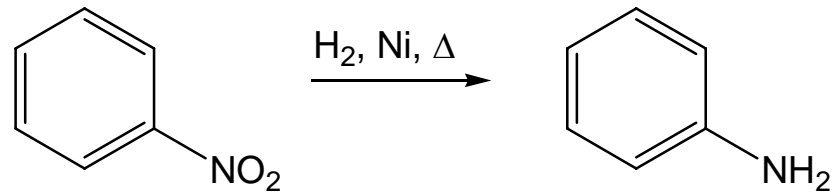
# Friedel-Crafts-Alkylierung von Aromaten



# Nitrierung von Aromaten

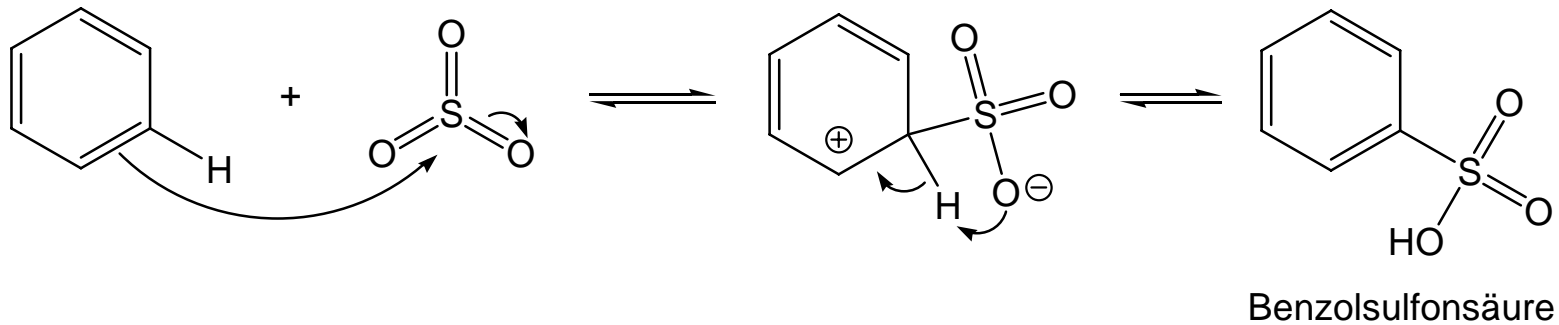
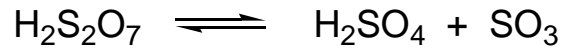


Verwendung: Anilinsynthese



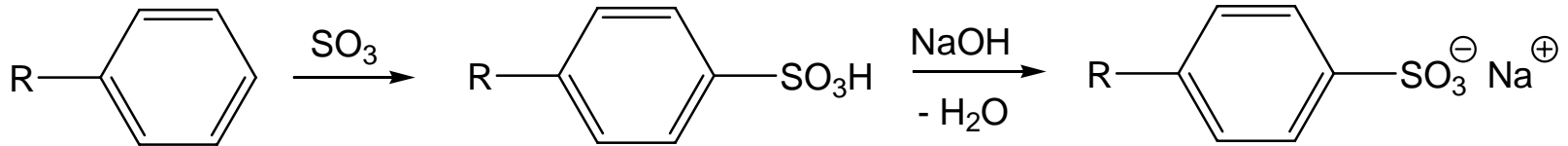
# Sulfonierung von Aromaten

"Rauchende Schwefelsäure":  $\text{H}_2\text{S}_2\text{O}_7$  (Oleum)

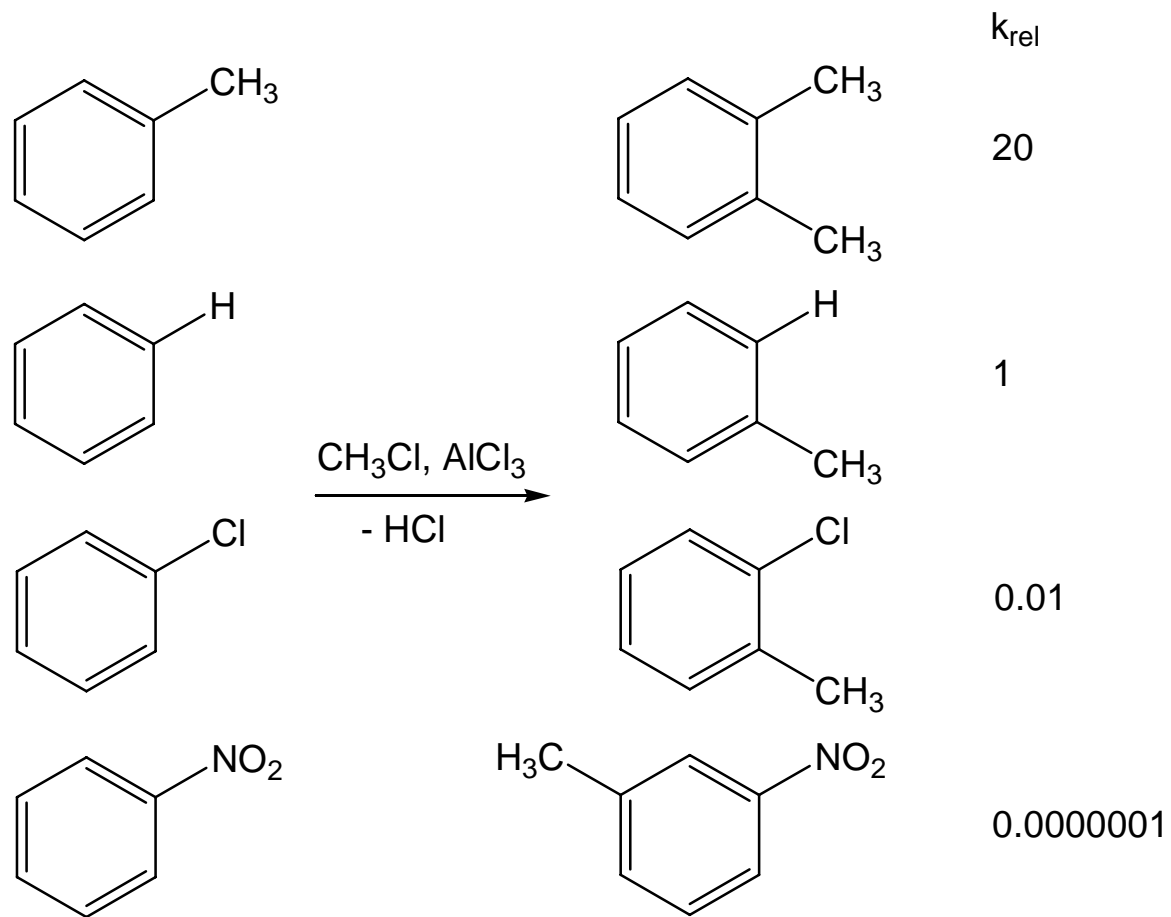


Herstellung aromatischer Detergentien (Waschmittel, Seifen)

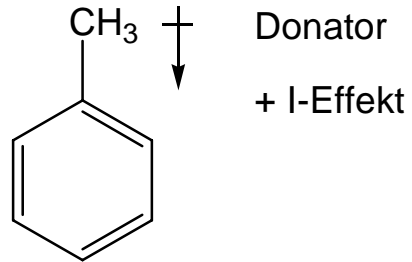
R = verzweigte Alkylgruppe



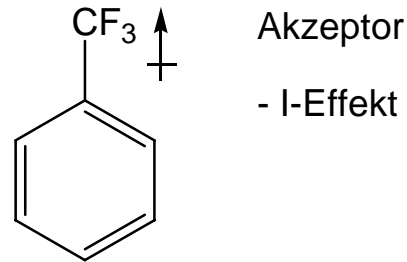
# Aktivierung und Desaktivierung des Benzenringes



## Induktive Aktivierung und Desaktivierung durch Alkylgruppen

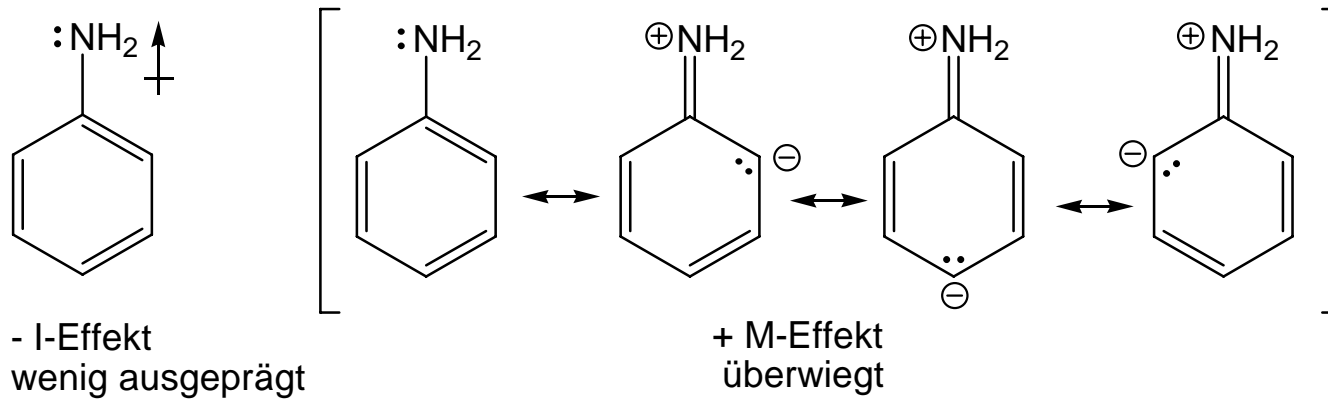


relativ elektronenreicher  
Ring (reaktiv)

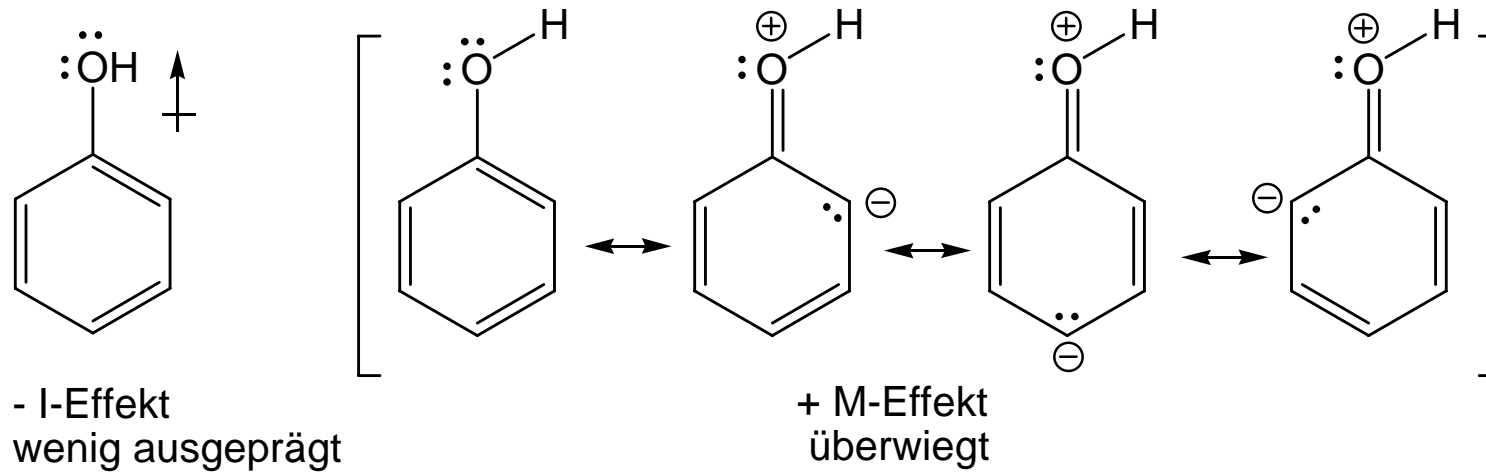


relativ elektronenarmer  
Ring (weniger reaktiv)

## Induktive und mesomere Effekte (Resonanzeffekte, Konjugationseffekte) im Anilin



## Induktive und mesomere Effekte im Phenol



Aminosubstituenten: + M-Effekt übertrifft - I-Effekt

Aktivierung des arom. Systems

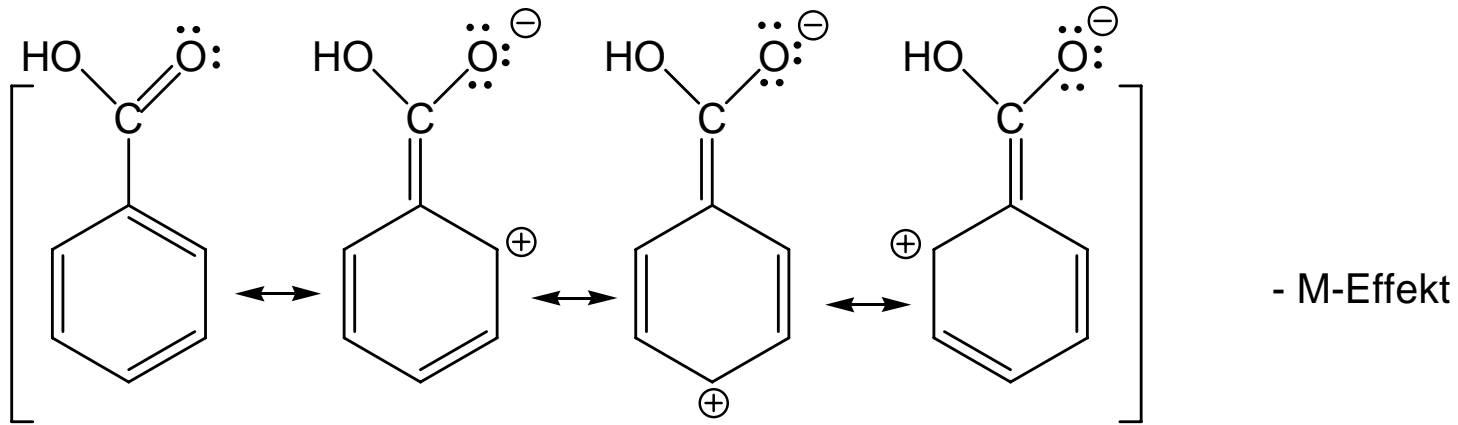
Hydroxysubstituenten: + M-Effekt übertrifft - I-Effekt

Aktivierung des arom. Systems

Halogensubstituenten: - I-Effekt übertrifft + M-Effekt

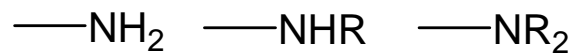
Desaktivierung des arom. Systems

## Desaktivierung durch Mesomerie (Resonanz)



Zusammenfassung:

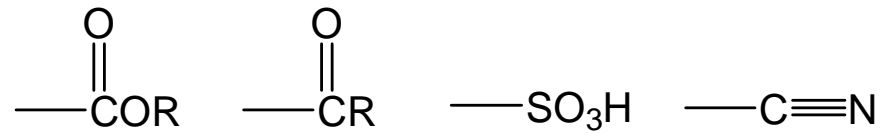
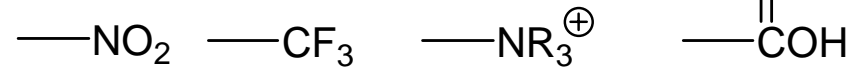
stark aktivierend



schwach aktivierend

Alkyl, Phenyl

stark desaktivierend

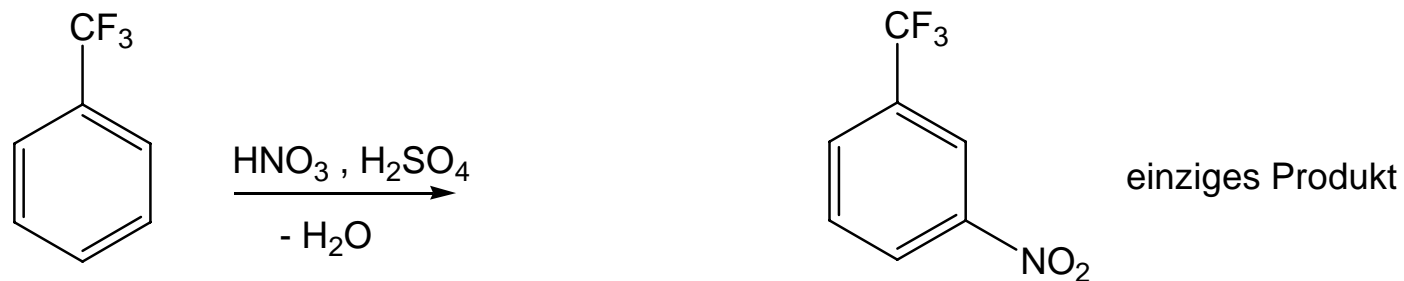
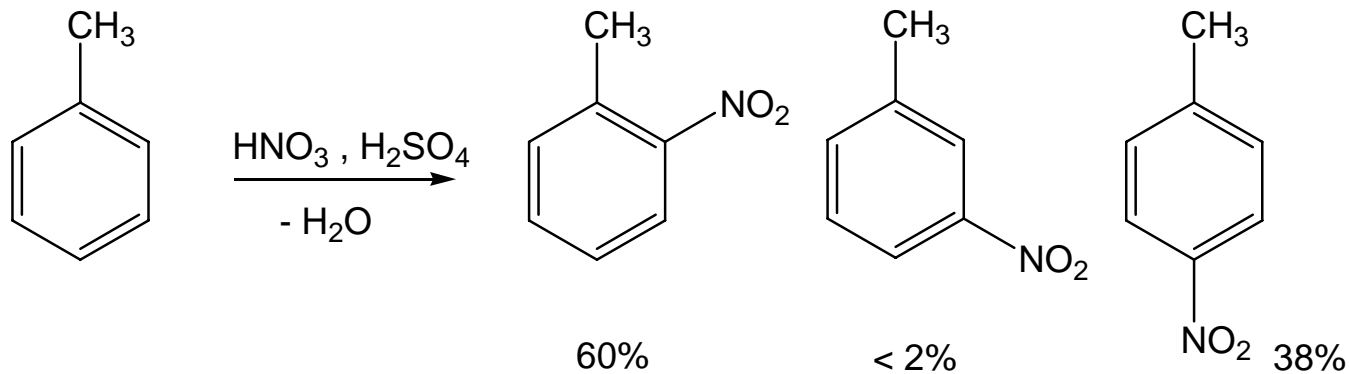


schwach desaktivierend



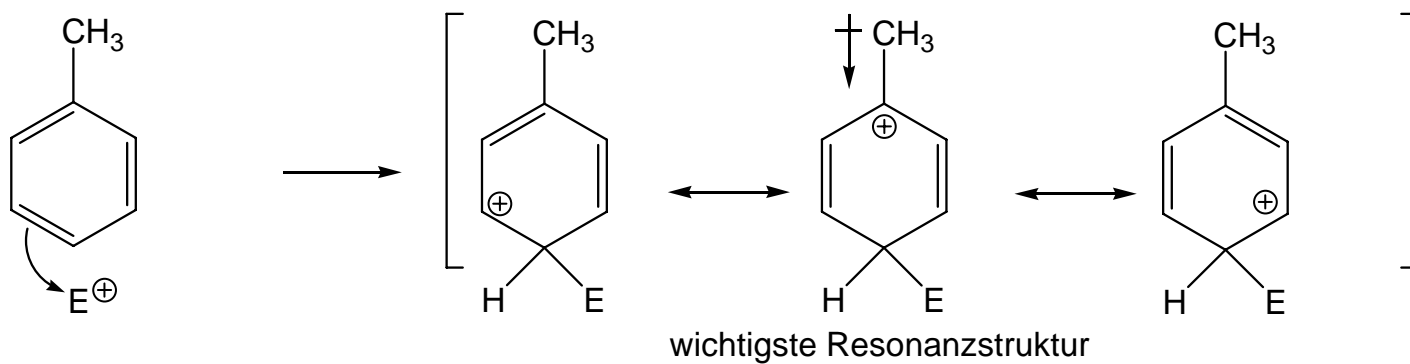
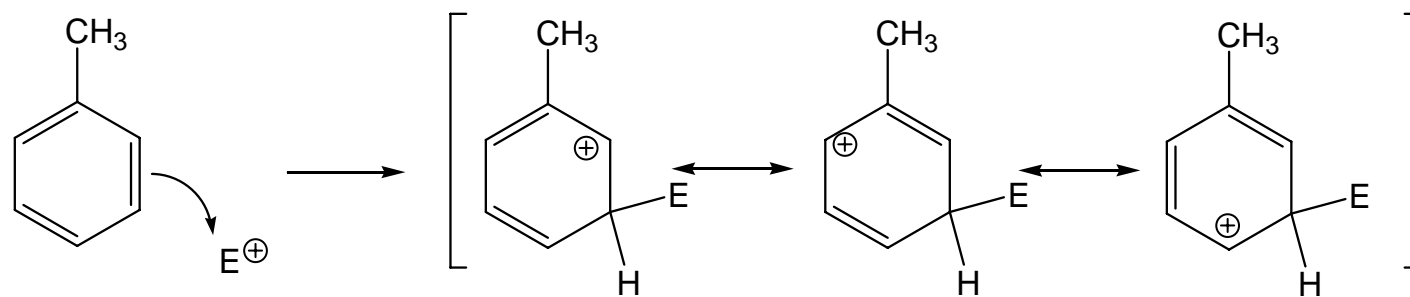
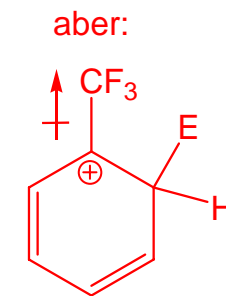
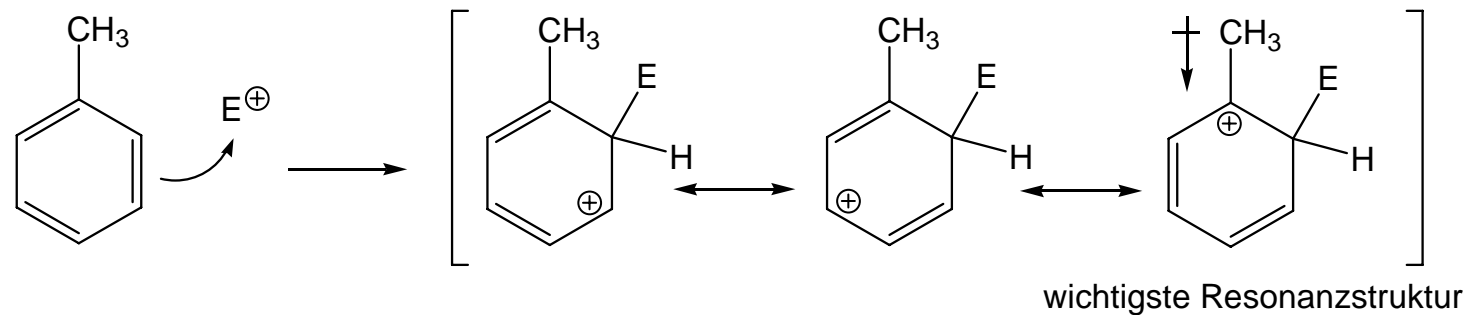
# Orientierung der Zweitsubstitution an Aromaten

Dirigierender induktiver Einfluss von Alkylsubstituenten

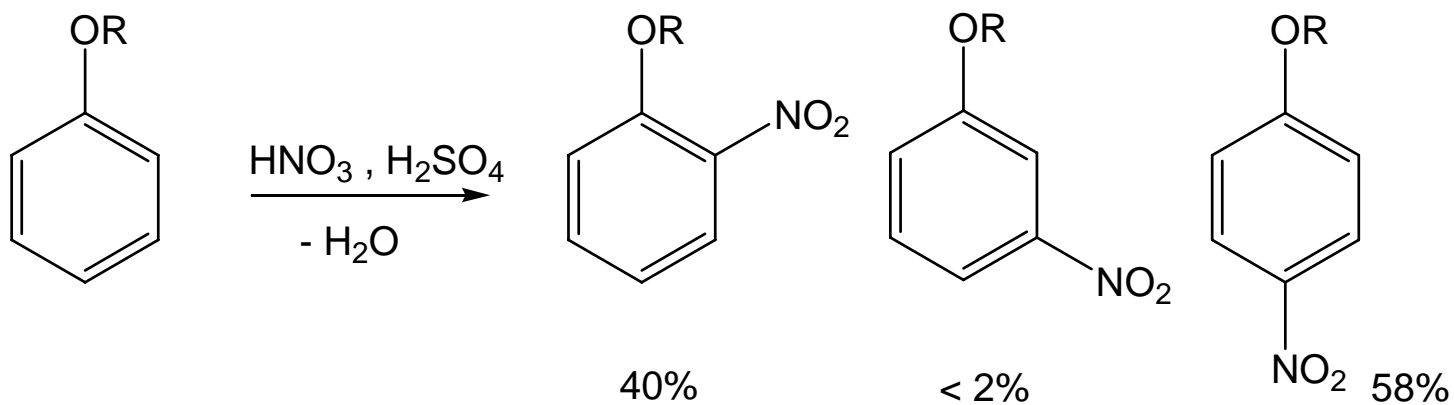


Alkylsubstituenten mit + I-Effekt dirigieren den Zweitsubstituenten in ortho/para-Position.  
Alkylsubstituenten mit - I-Effekt dirigieren den Zweitsubstituenten in meta-Position.

Resonanzstrukturen nach Angriff des Elektrophils auf Toluol in o-, m- und p-Position

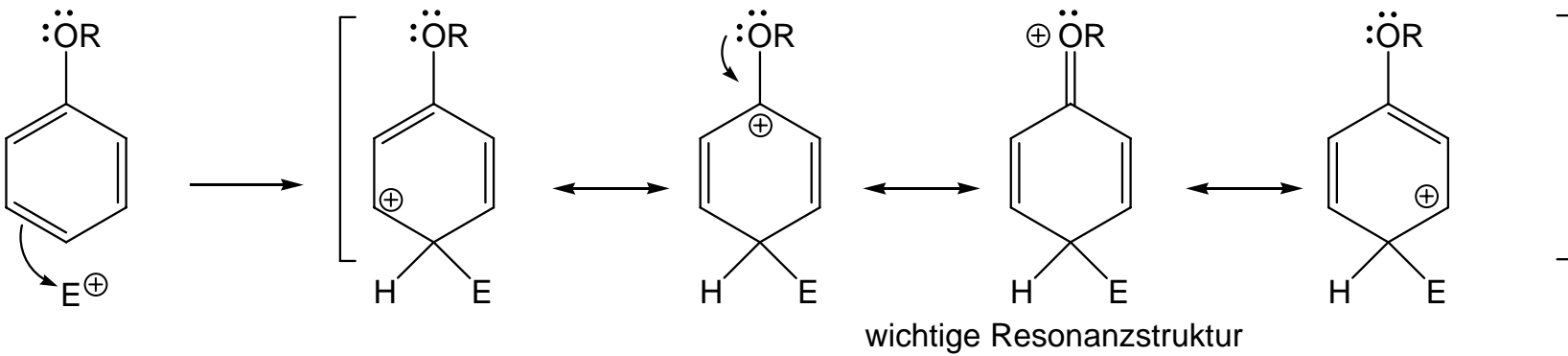
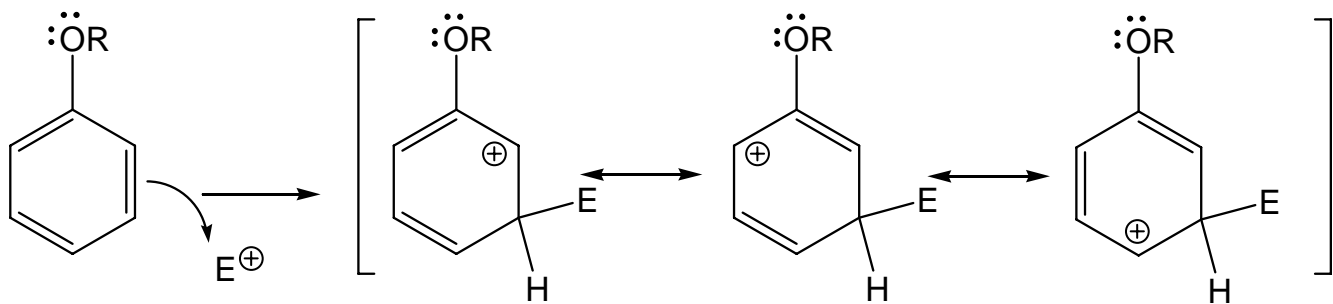
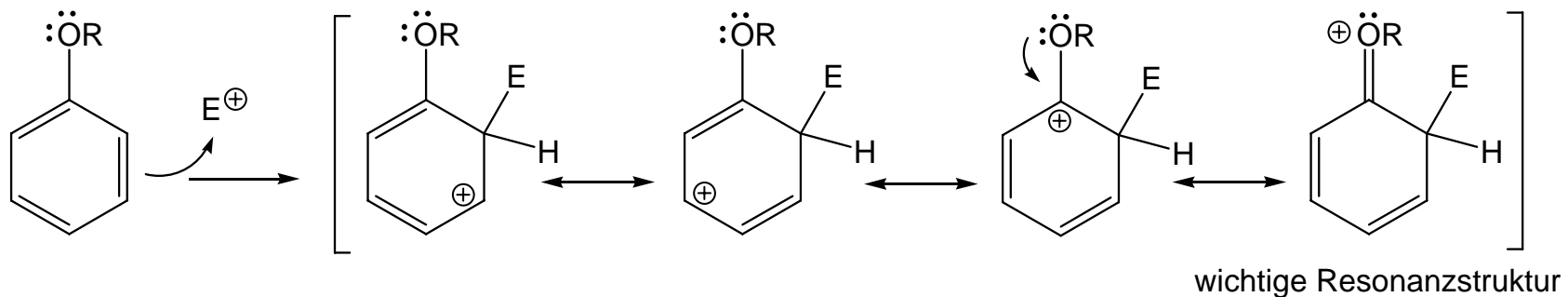


Dirigierender mesomerer Einfluss von Alkoxy- (+ M) bzw. Nitrosubstituenten (- M)

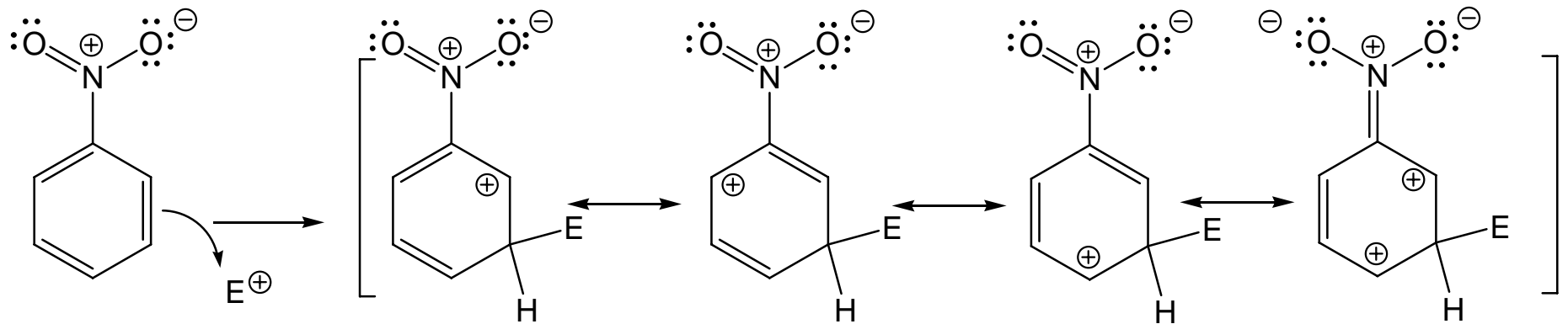
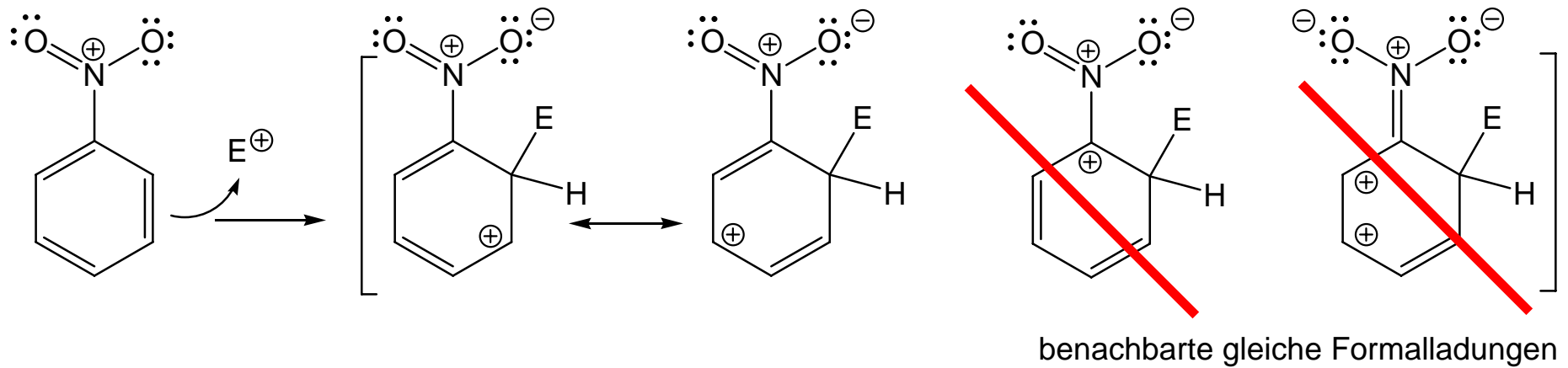


Alkoxy substituenten mit +M-Effekt dirigieren den Zweitsubstituenten in ortho/para-Position.  
Nitrosubstituenten mit -M-Effekt dirigieren den Zweitsubstituenten in meta-Position.

Resonanzstrukturen nach Angriff des Elektrophils auf Alkoxybenzen in o-, m- und p-Position



Resonanzstrukturen nach Angriff des Elektrophils auf Nitrobenzen in o- und m-Position



# Dirigierende Wirkung von Substituenten bei elektrophilen aromatischen Substitutionen

---

ortho / para - dirigierend

---

meta - dirigierend

---

stark aktivierend



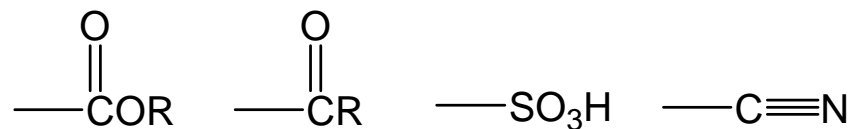
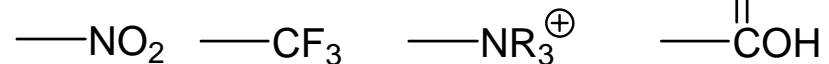
schwach aktivierend

Alkyl, Phenyl

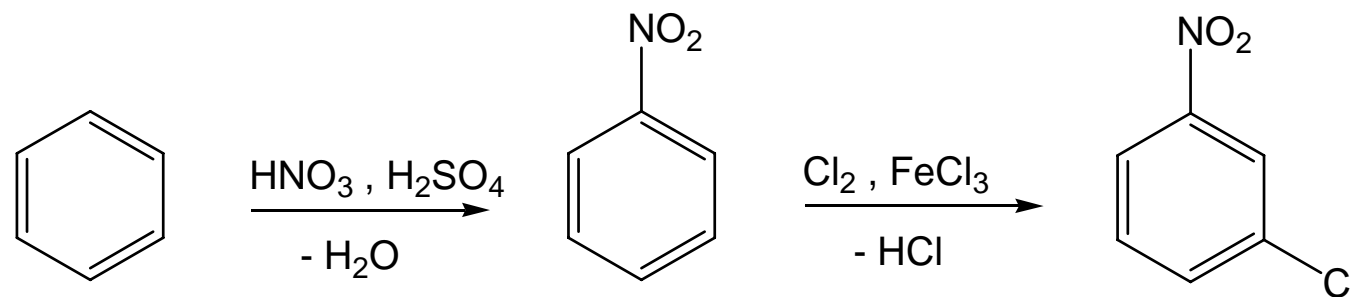
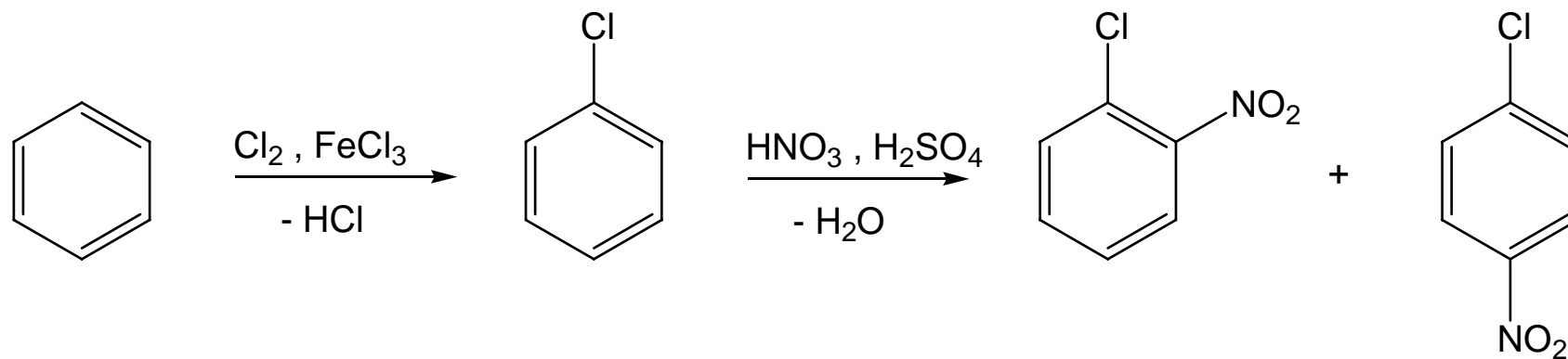
schwach desaktivierend



stark desaktivierend

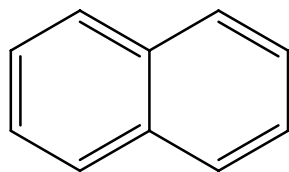


Darstellung von ortho / para - bzw. meta - Chlornitrobenzol

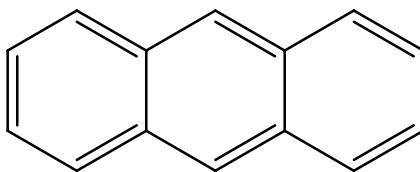


# Weitere aromatische Systeme

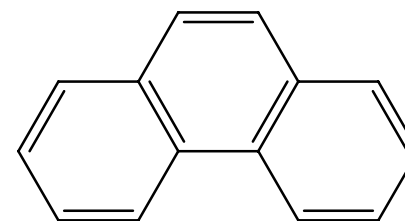
Kondensierte Ringsysteme mit  $(4n + 2) \pi$  - Elektronen



Naphthalin ( $10 \pi$  - Elektronen)

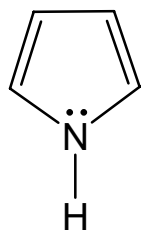


Anthracen ( $14 \pi$  - Elektronen)

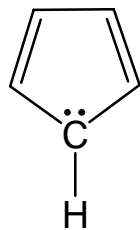


Phenanthren ( $14 \pi$  - Elektronen)

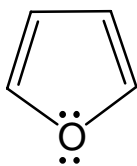
Heteroaromaten



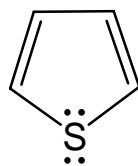
Pyrrol



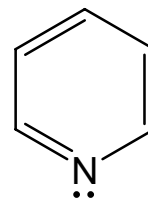
Cyclopentadienyl-Anion



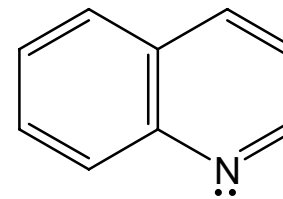
Furan



Thiophen



Pyridin



Chinolin

## Reaktivitätsunterschiede zwischen Fünfring- und Sechsringheterocyclen

