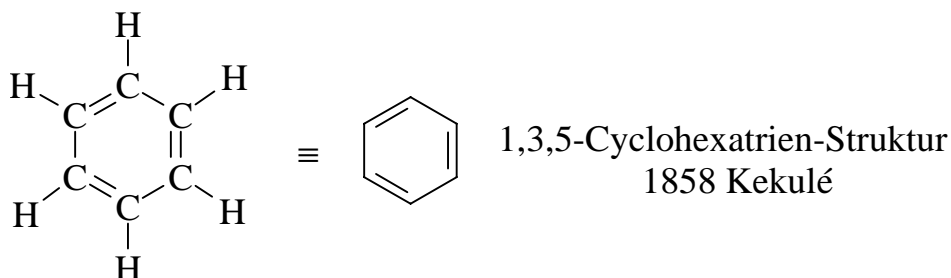


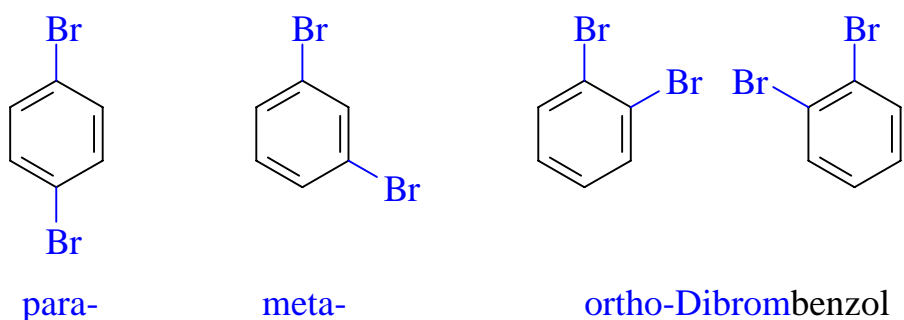
Aromatische Kohlenwasserstoffe

Benzol: C₆H₆ (Faraday 1825)

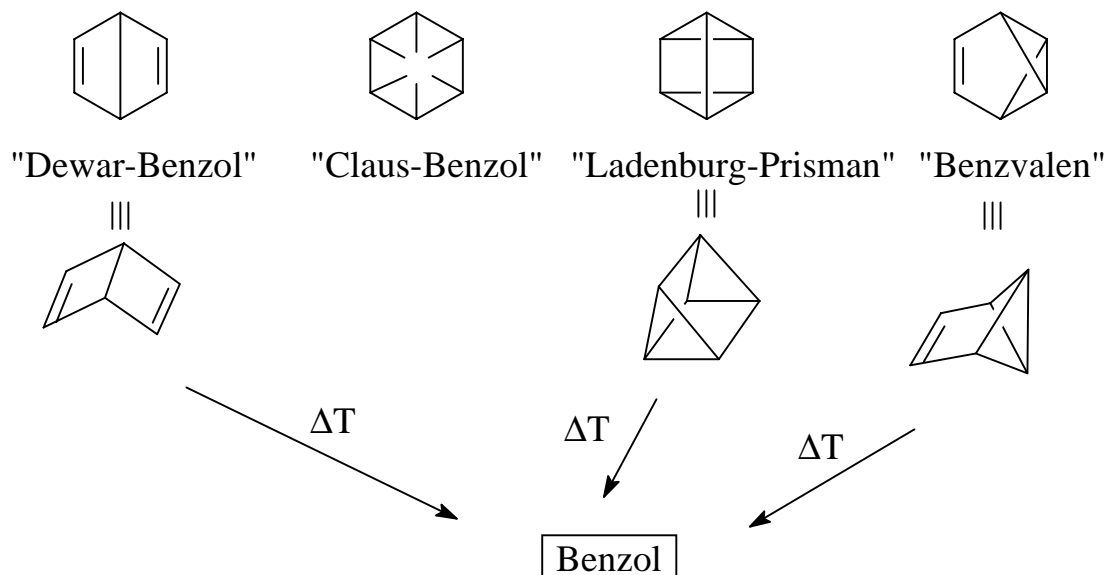
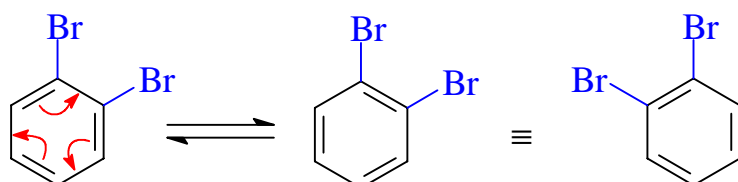
Vorgeschlagene Konstitutionen von Benzol



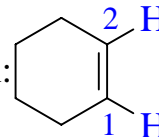
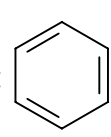
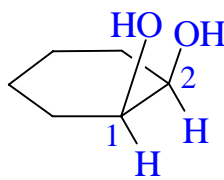
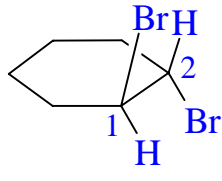
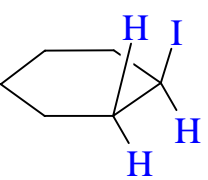
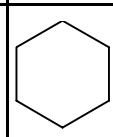
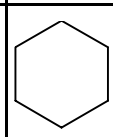
Erklärt nicht, warum es nur drei regioisomere disubstituierte Benzolderivate gibt.

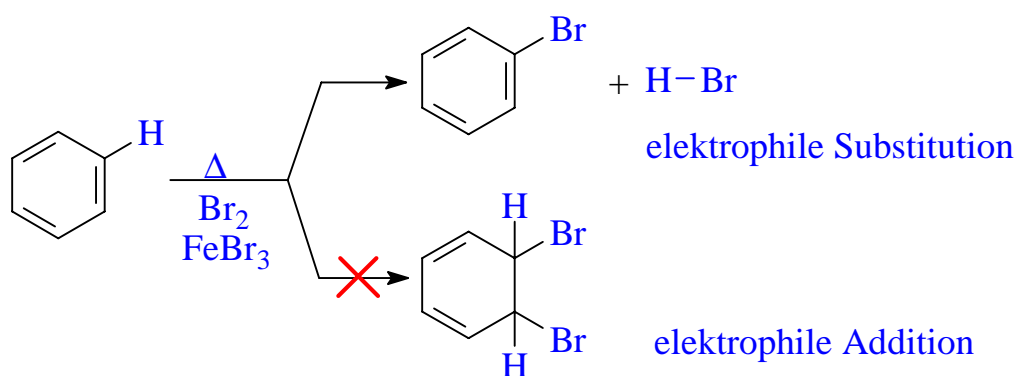


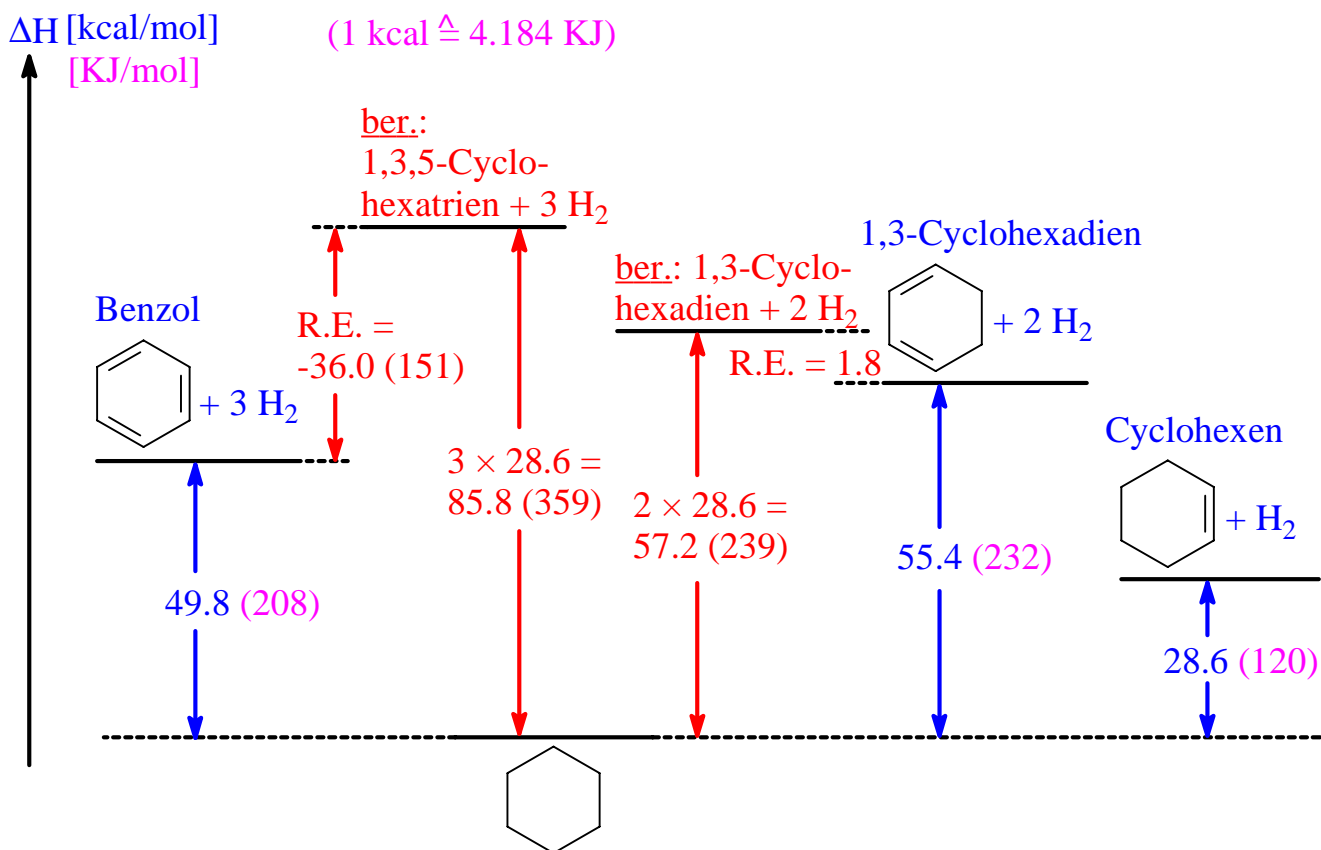
Erklärung von Kekulé: oszillierende Doppelbindungen



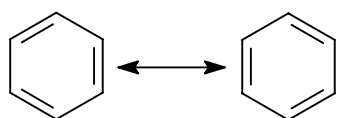
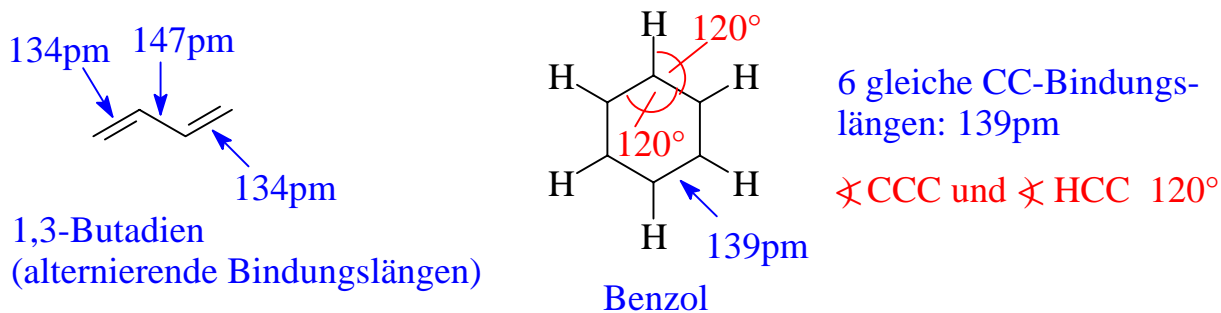
Vergleich der reaktiven Eigenschaften von Cyclohexen und Benzol

| | | |
|--|---|--|
| Reagenz | Cyclohexen:  | Benzol:  |
| KMnO ₄ Oxidation |  <i>cis</i> -1,2-Cyclohexandiol | keine Reaktion |
| Br ₂ / CCl ₄ |  <i>trans</i> -1,2-Dibromocyclohexan | keine Reaktion |
| H—I elektrophile Addition |  Iodocyclohexan | keine Reaktion |
| H ₂ / Ni katalytische Hydrierung |  Cyclohexan rasch bei 25°C, 1atm. H ₂ -Druck |  Cyclohexan langsam bei 100-200°C, 100 atm. H ₂ -Druck |

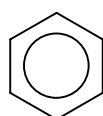




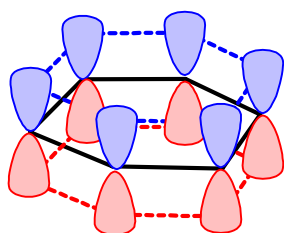
Resonanzenergie: R.E. = $\Delta H_{exp.} - \Delta H_{ber.} = 49.8 - 85.8 = -36$ kcal/mol



Resonanzstrukturen



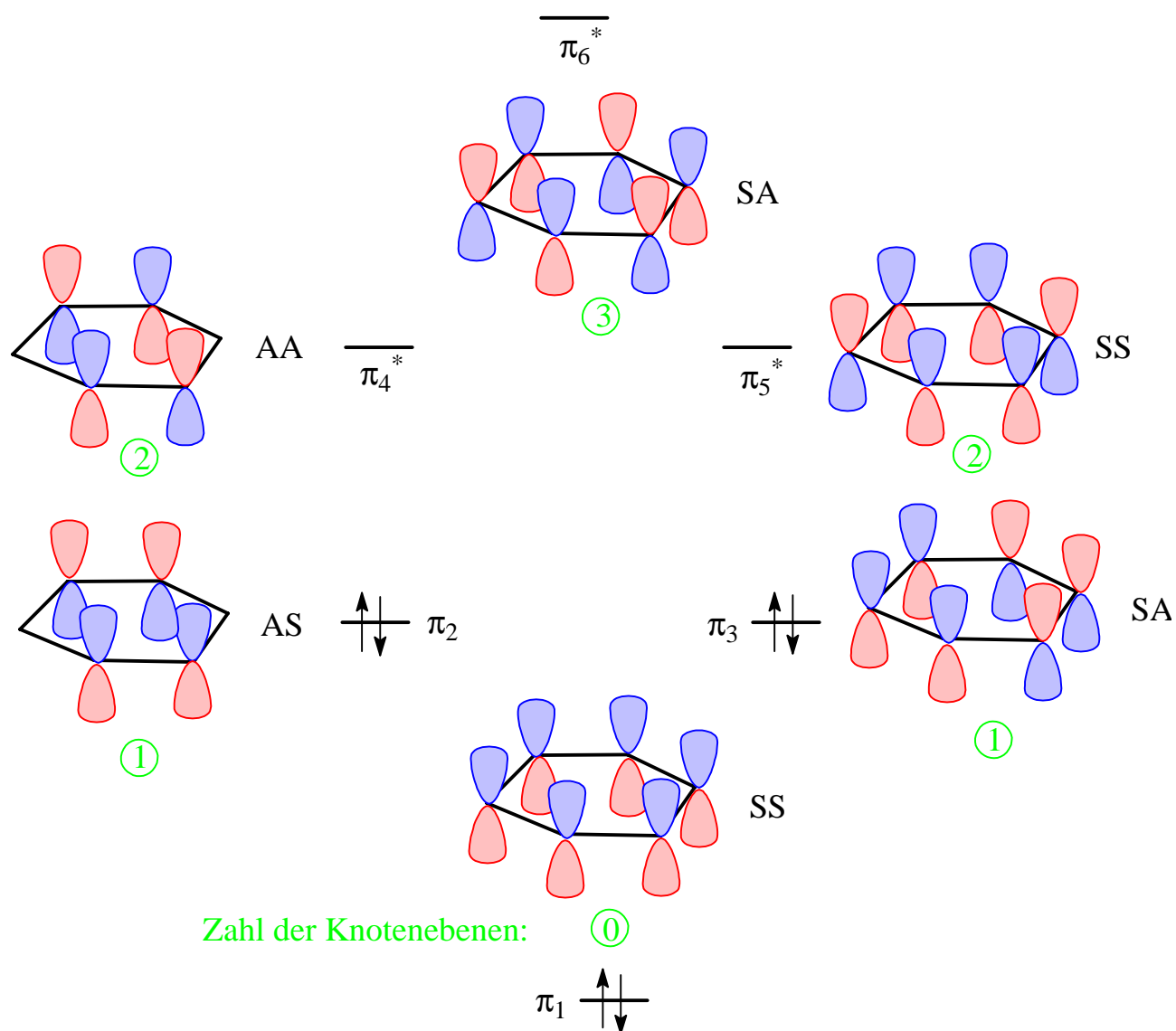
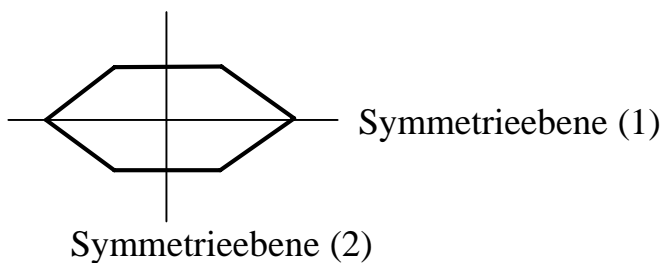
Kreis symbolisiert das delokalisierte π -Elektronensystem



energetisch niedrigste, bindende π -MO des Benzols
(ohne Knotenebene)

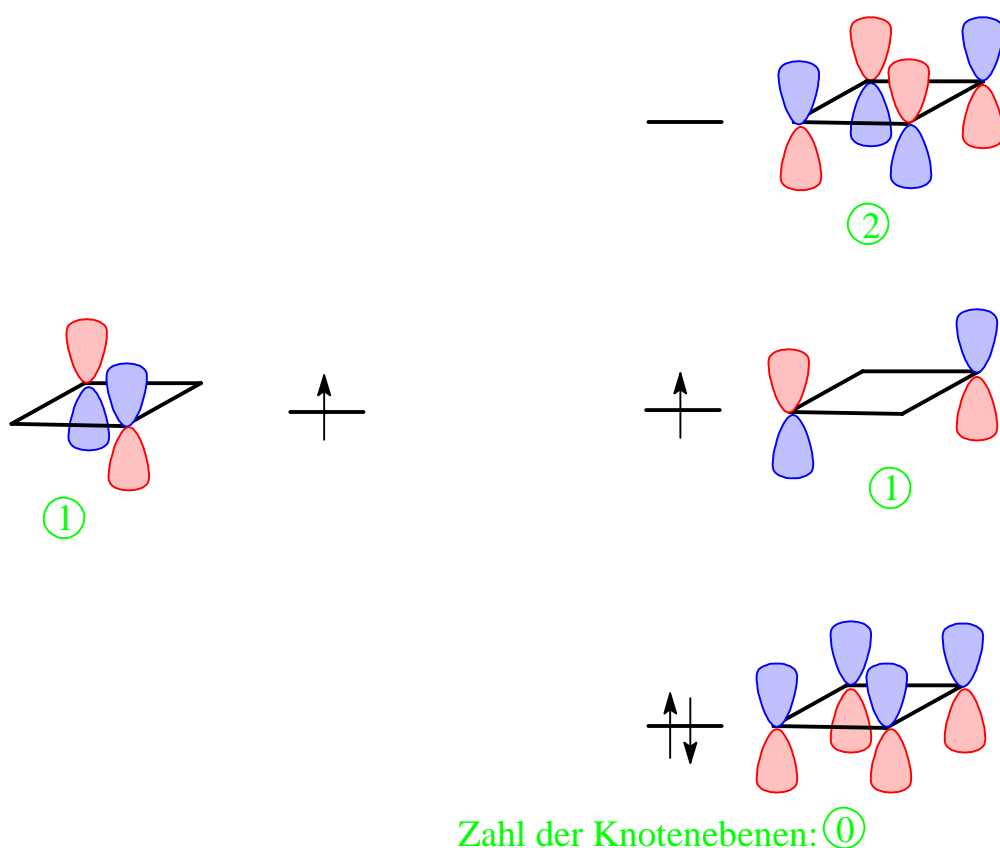
π -MO-Schema von Benzol

S - Symmetrisch
A - Antisymmetrisch



Der Grundzustand besitzt eine abgeschlossene Elektronenschale (Singulett-Grundzustand).

π -MO-Schema von 1,3-Cyclobutadien



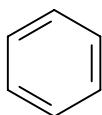
quadratisches Cyclobutadien: \square wird als Tripletts erwartet

jedoch $\square \rightleftharpoons \square$ rechteckig, \Rightarrow oszillierende Doppelbindungen

Hückel-Regel (E. Hückel 1933)

Eine Verbindung wird als aromatisch bezeichnet, wenn folgende Bedingungen erfüllt sind:

- 1.) Cyclisch konjugiertes π -System. (Die Konjugation darf nicht durch sp^3 -hybridisierte Kohlenstoffe unterbrochen sein.)
- 2.) Das System muß $[4n+2]$ π -Elektronen enthalten ($n = 0, 1, 2, 3, \dots$)
- 3.) Das Gebot der Planarität der Ringe, damit eine maximale Überlappung aller p-Atomorbitale erreicht wird.



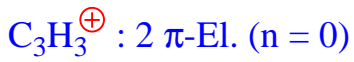
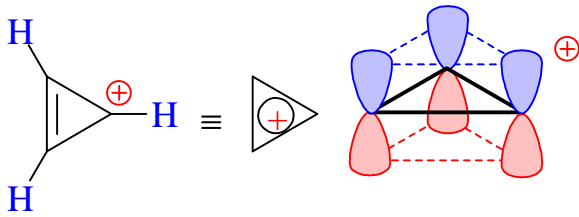
cyclisch konjugiert (+)
 $6\pi: [4n+2], n=1$ (+) \Rightarrow aromatisch
 planar (+)



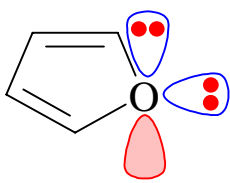
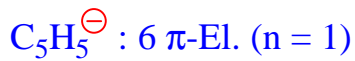
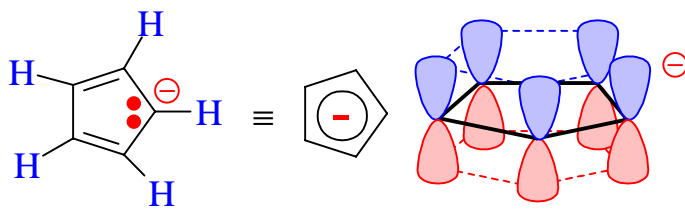
cyclisch konjugiert (+)
 $4\pi: \text{nicht } [4n+2]$ (-) \Rightarrow antiaromatisch
 planar (+)

Nicht-benzoide Aromaten (cyclisch konjugierte $[4n+2]$ π -Systeme)

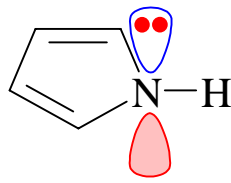
Cyclopropyl-Kation



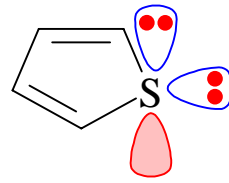
Cyclopentadienyl-Anion



Furan



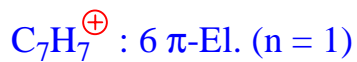
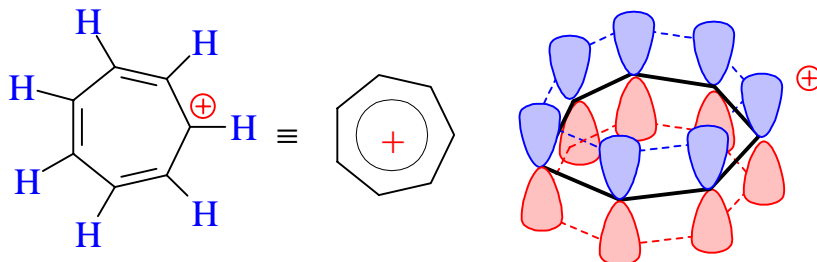
Pyrrol



Thiophen

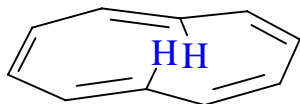
5-Ring-Heterocyclen (Heteroaromaten)

Cycloheptatrienyl-Kation Tropylium-Kation

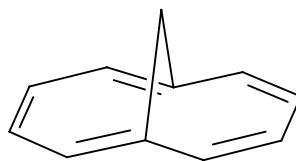


Nicht-benzoide Aromaten (Cyclisch konjugierte $[4n+2]$ π -Systeme)

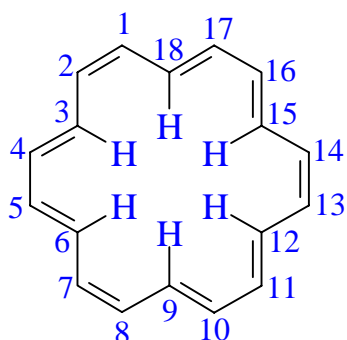
$n = 2$: 10 π -Elektronen



[10] Annulene
nicht planar und nicht stabil



1,6-Methano[10]annulene
planar, stabil, aromatisch

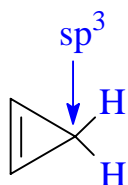


Cyclooctadecanonaen

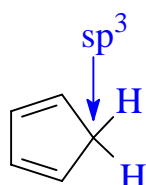
[18] Annulene

$C_{18}H_{18}$: 18 π -El. ($n = 4$)

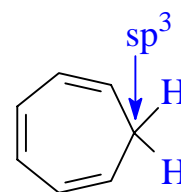
Cycloalkene (die cyclische Konjugation ist durch sp^3 -Zentren unterbrochen)



C_3H_4 : Cyclopropen

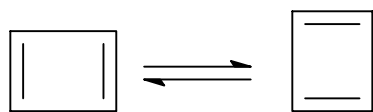


C_5H_6 : 1,3-Cyclopentadien



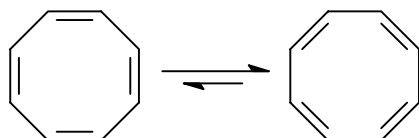
C_7H_8 : 1,3,5-Cycloheptatrien

Antiaromatische Verbindungen (cyclische $4n$ π -Systeme)

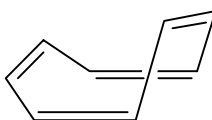


1,3-Cyclobutadien

4π -Elektronen ($n = 1$), oszillierende Doppelbindungen,
antiaromatisch, hochreaktiv

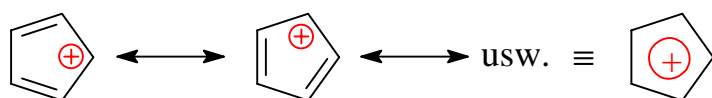


1,3,5,7-Cyclooctatetraen



Wannenkonformation

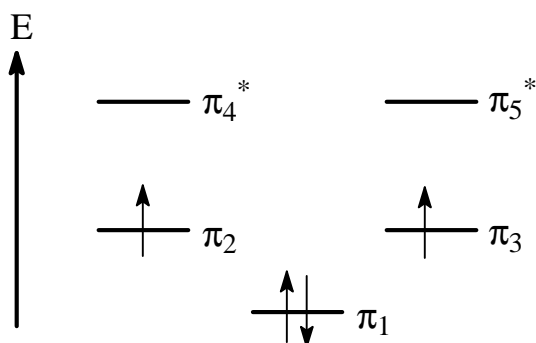
8π -Elektronen ($n = 2$), oszillierende Doppelbindungen,
nicht planar, nicht aromatisch
 \Rightarrow Polyolefin



2,4-Cyclopentadienyl-Kation

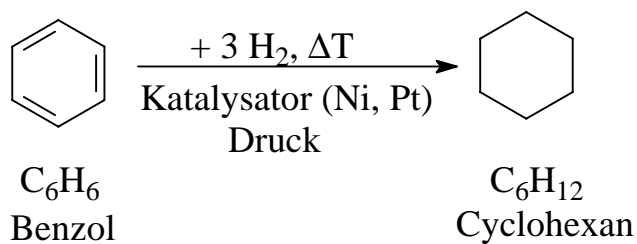
4π -Elektronen ($n = 1$), delokalisiertes System,
planar, antiaromatisch,
Triplett-Grundzustand (zwei ungepaarte Elektronen)

π -MO-Schema von Cyclopentadienyl-Kation

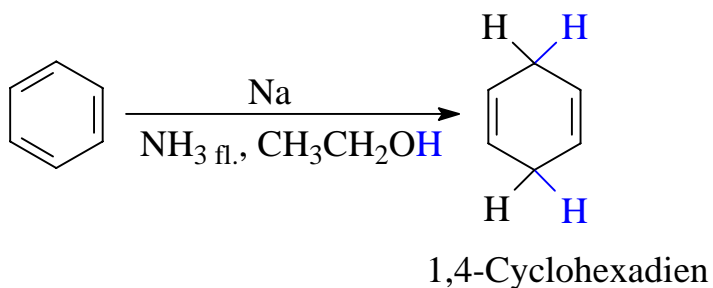


Reaktionen von Benzol

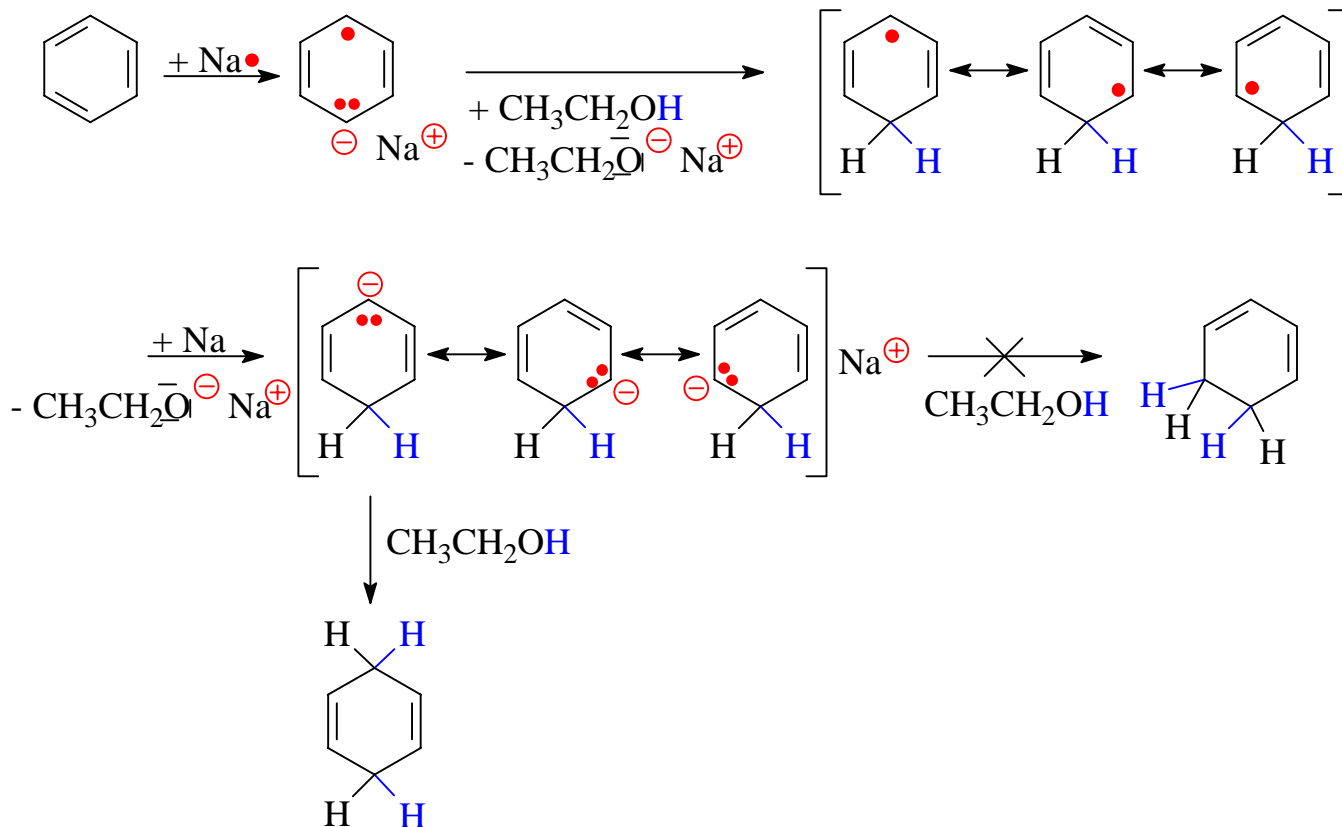
1) Katalytische Hydrierung



2) Reduktion mit Natrium in flüssigem Ammoniak

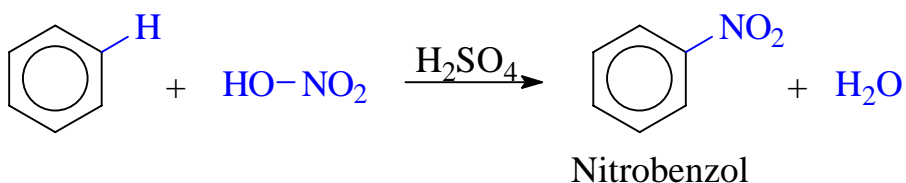


Mechanismus:

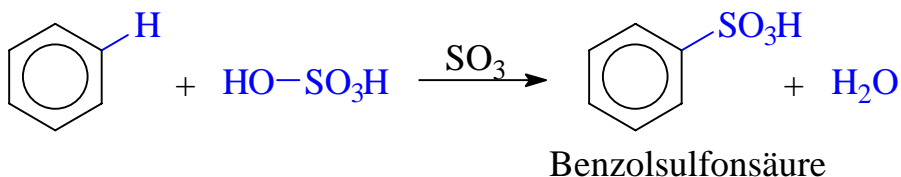


3) Elektrophile aromatische Substitution

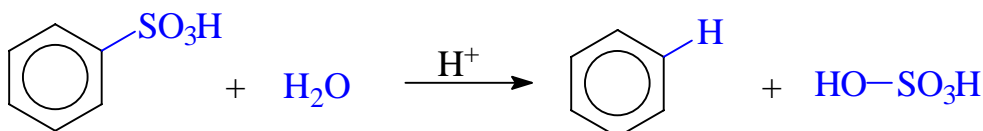
Nitrierung mit Salpetersäure/Schwefelsäure



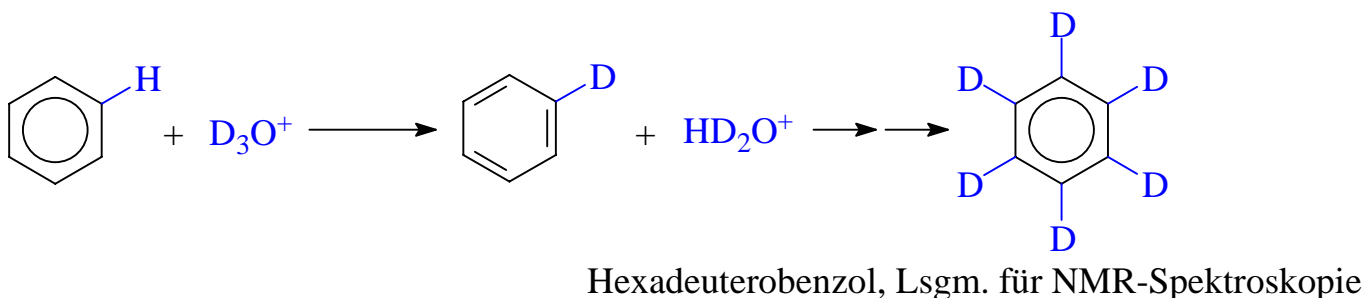
Sulfonierung mit konzentrierter Schwefelsäure



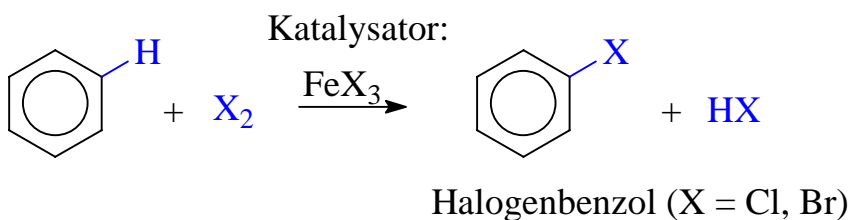
Protonierung (Umkehrung der Sulfonierung)



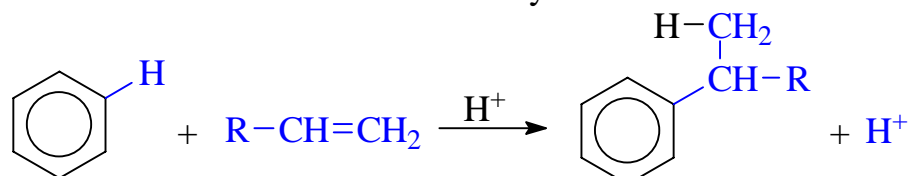
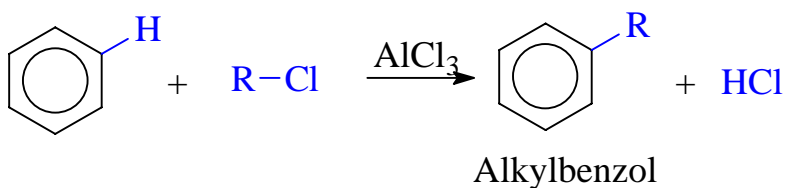
Deuterierung



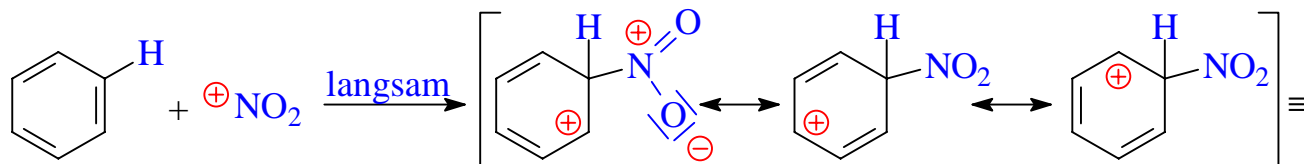
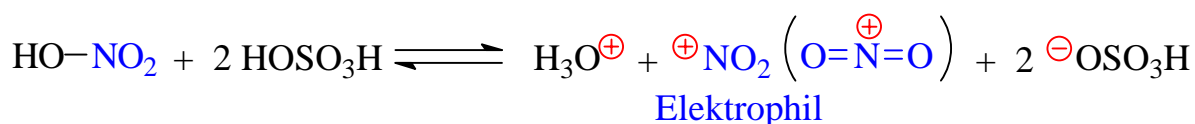
Halogenierung



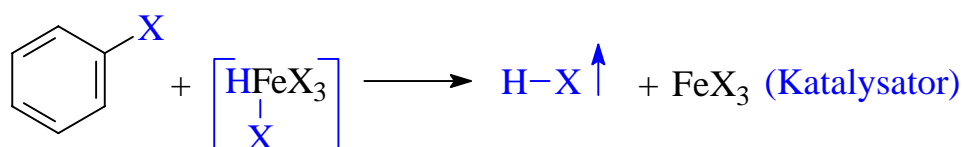
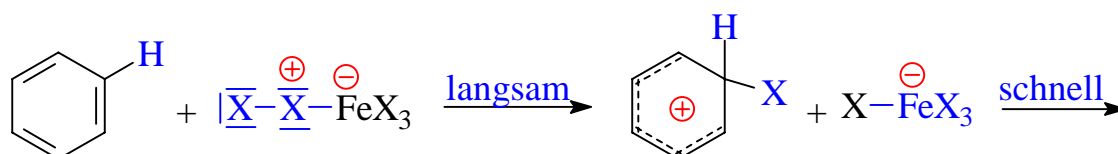
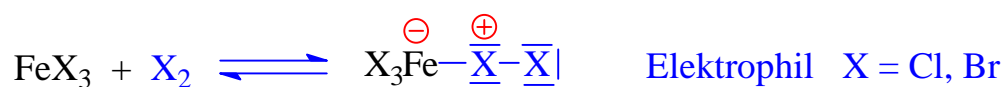
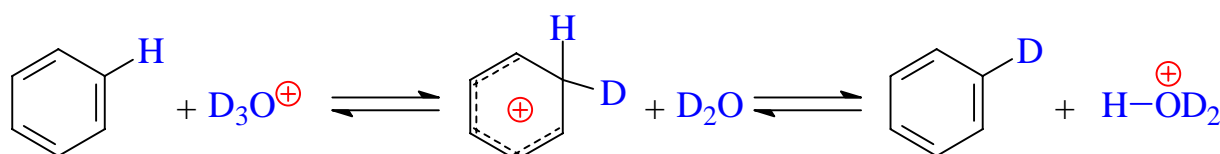
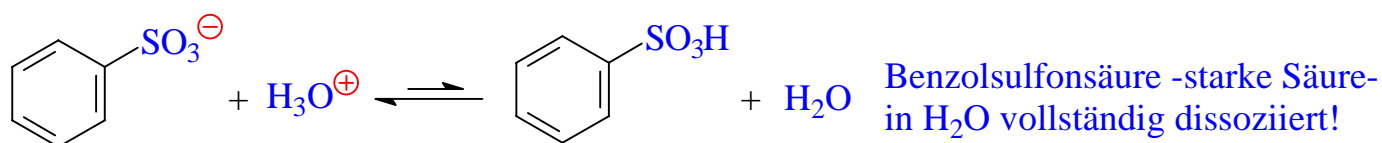
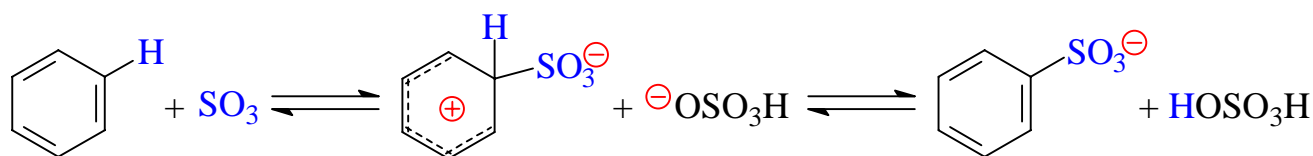
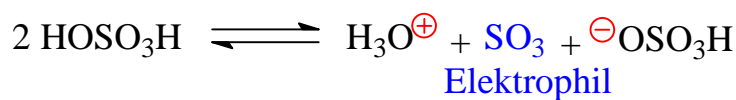
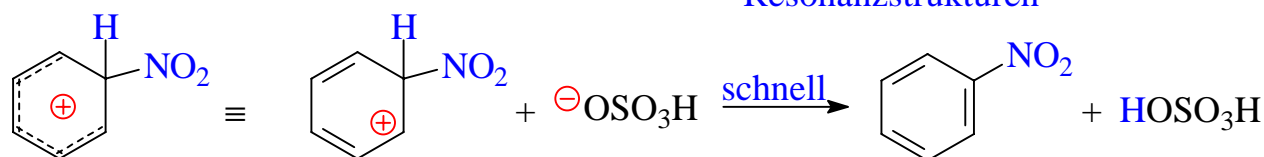
Friedel-Crafts-Alkylierung

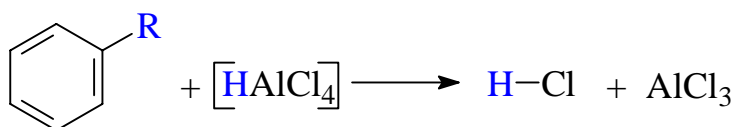
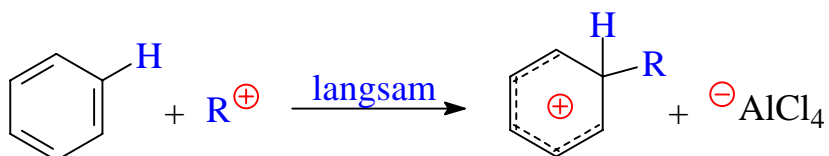
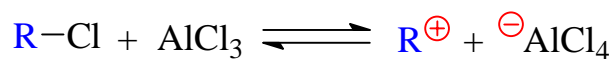


Mechanismus der elektrophilen aromatischen Substitution

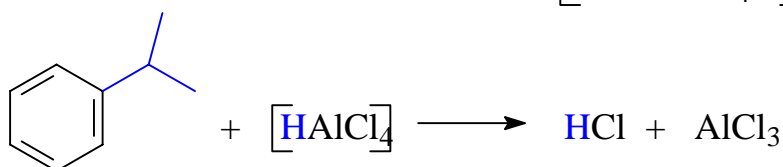
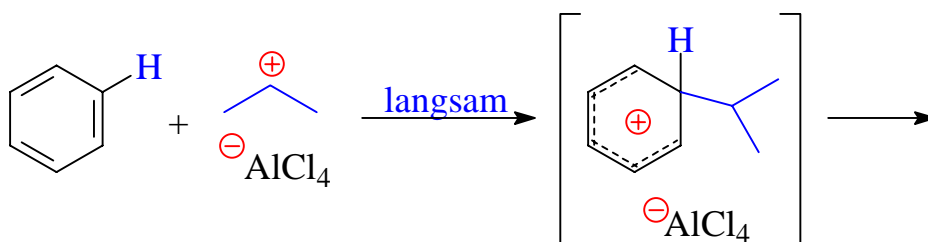
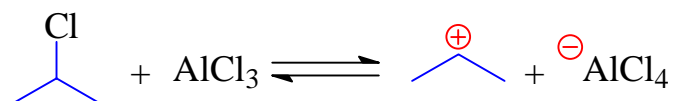


Resonanzstrukturen





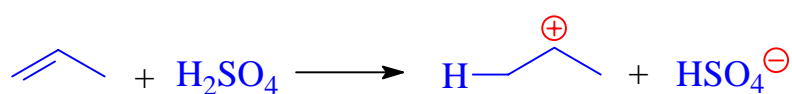
Cumol-Synthese



Isopropylbenzol
Cumol

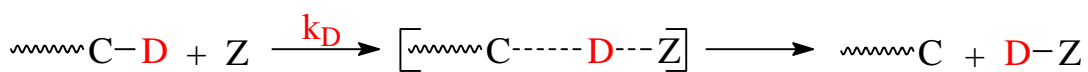
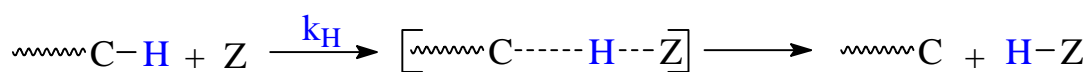
Rückgewinnung des
Katalysators

Generierung der Carbokationen aus dem entsprechenden Alken mittels Schwefelsäure (großtechnischer Prozess).

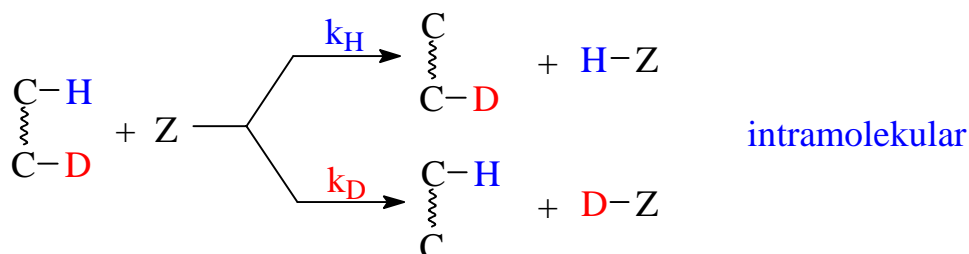


Propen

Kinetischer Isotopeneffekt

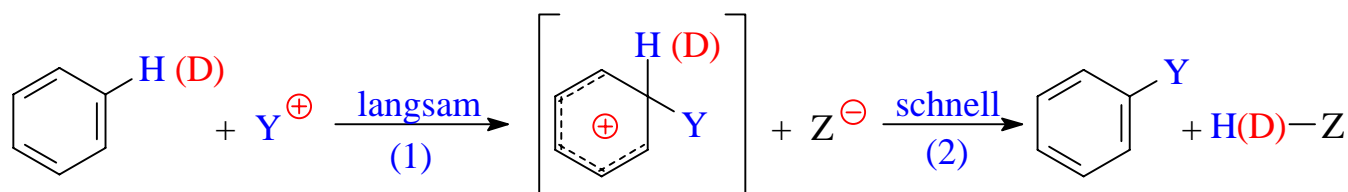


intermolekular



$$\frac{k_{\text{H}}}{k_{\text{D}}} \approx 5 - 8$$

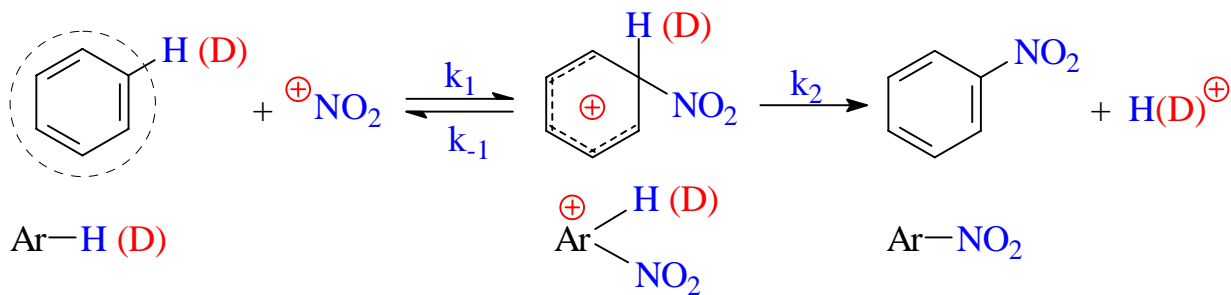
primärer Isotopeneffekt



In diesem Fall wird kein Isotopeneffekt erwartet, da Schritt (1) geschwindigkeitsbestimmend ist, in dem nicht die C—H bzw. C—D-Bindung gespalten wird.

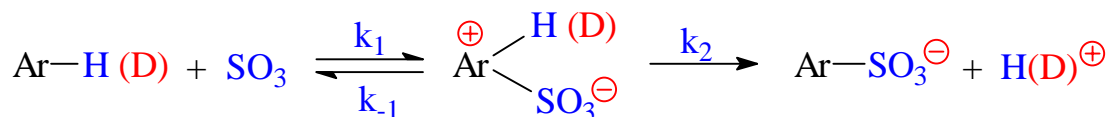
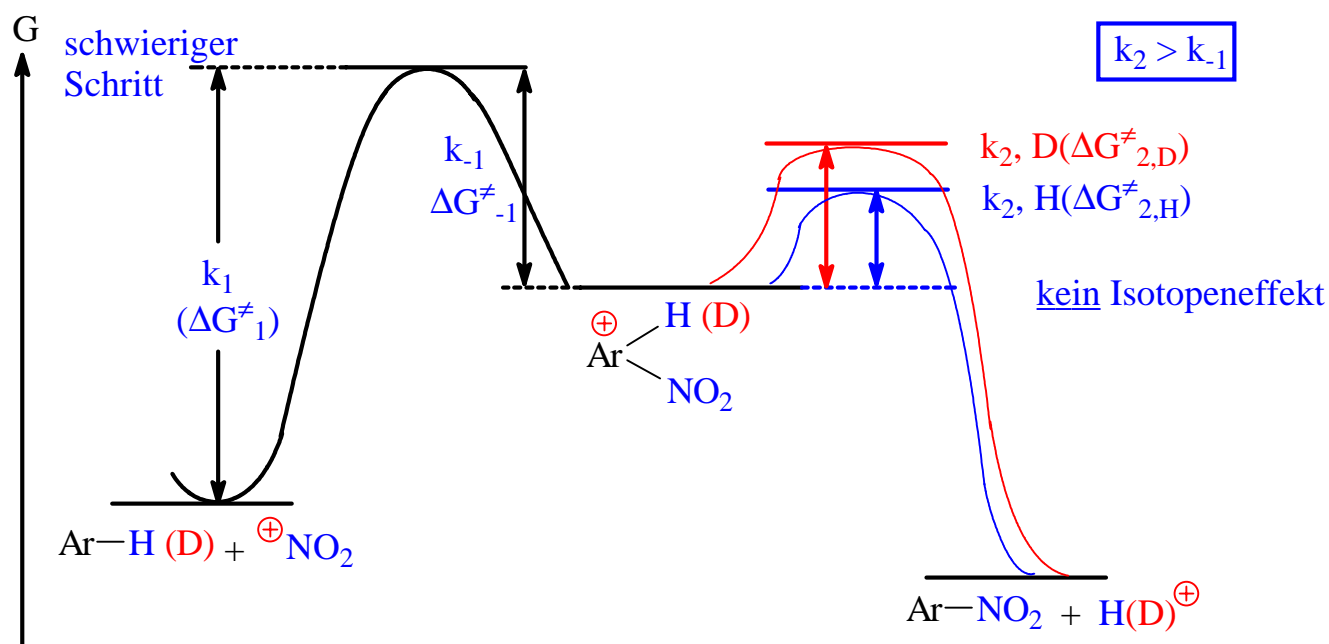
Kein Isotopeneffekt ($k_{\text{H}}/k_{\text{D}} \approx 1$) wurde bei der Nitrierung, Halogenierung und Friedel-Crafts-Alkylierung beobachtet.

Ein Isotopeneffekt ($k_{\text{H}}/k_{\text{D}} > 1$) wurde bei der Sulfonierung beobachtet.



Gibbs-Aktivierungsenthalpie: $\Delta G^\ddagger = -RT \ln \frac{h \cdot k}{k_B \cdot T}$

Gibbs-Enthalpie



$k_{2,\text{H}} \approx k_{-1}$

Isotopeneffekt: Ar-D reagiert langsamer als Ar-H

