Diene

Konstitutionsisomere

KUMULIERTE DIENE
1,2-Diene

1,2-Pentadien

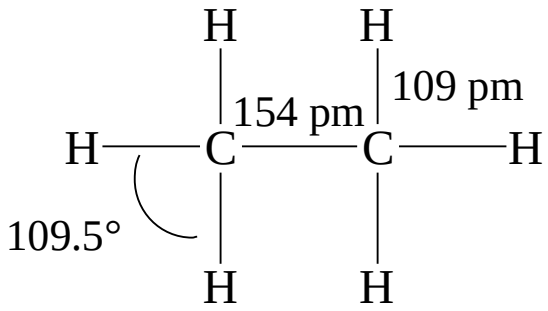
KONJUGIERTE DIENE
1,3-Diene

1,3-Pentadien

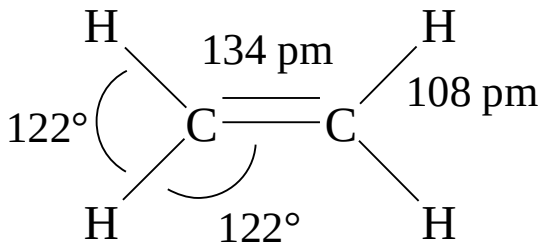
ISOLIERTE DIENE
1,4.Diene

1,4-Pentadien

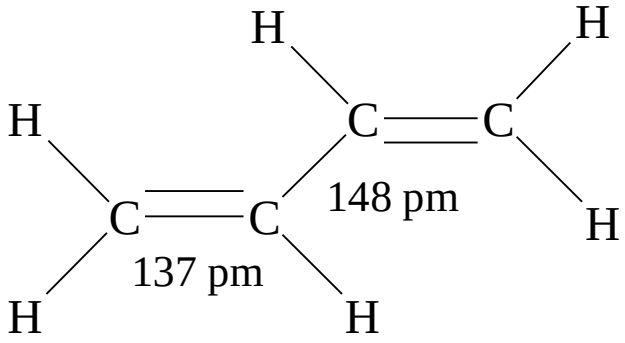
Struktur



CC-Einfachbindung



CC-Doppelbindung

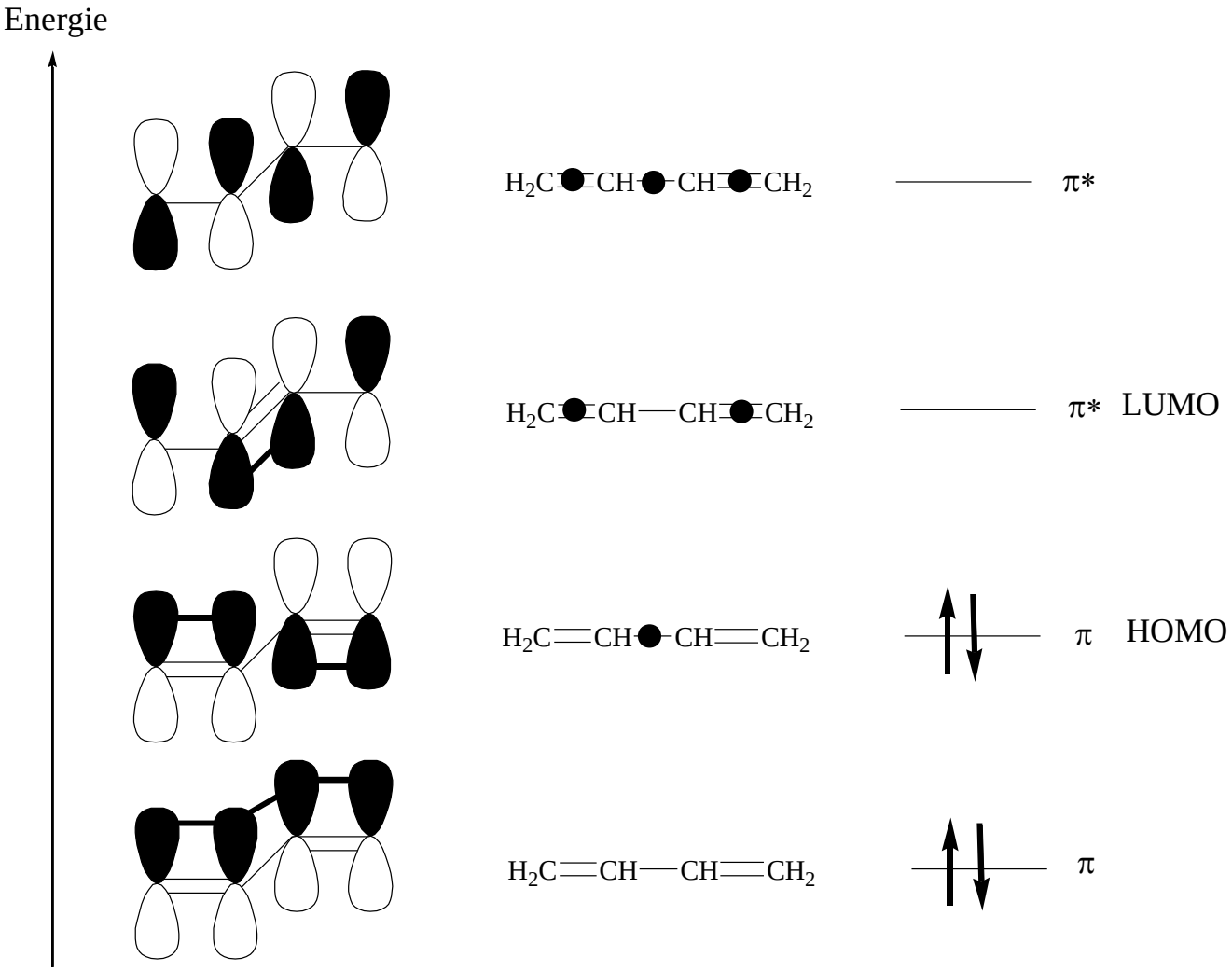


1,2-Dien

Molekülorbitale

HOMO = highest occupied molecular Orbital **LUMO** = lowest unoccupied molecular orbital

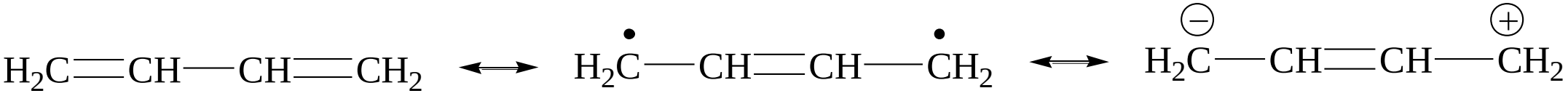
RESONANZ-, MESOMERIE-STABILISIERUNG



Mesomerie

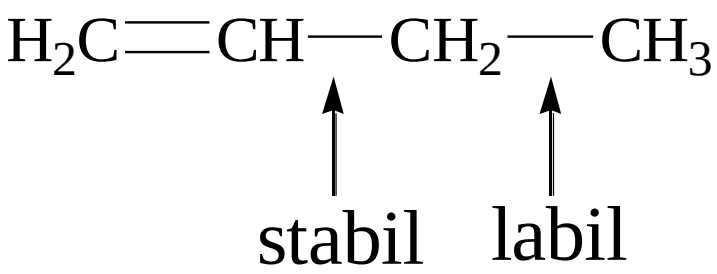
Die π-Elektronen sind über das gesamte Molekül „verteilt“.
Es können mehrere **MESOMERE GRENZFORMELN** gezeichnet werden.

Merke: Bei mesomeren Grenzformeln werden nur Elektronen „verschoben“;
die Atome bleiben auf ihrem Platz, und die Abfolge ihrer Bindung bleibt unverändert.

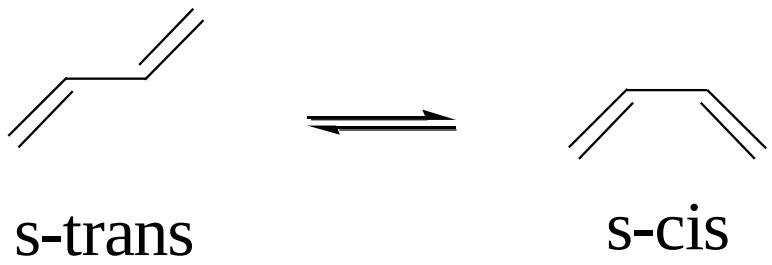


Die **RESONANZSTABILISIERUNG** des Butadiens beträgt ca. 15 kJ/mol

SCHMIDT-STAUDINGER REGEL:
σ-Bindungen neben π-Bindungen sind
durch σ-π-Kopplung stabilisiert.

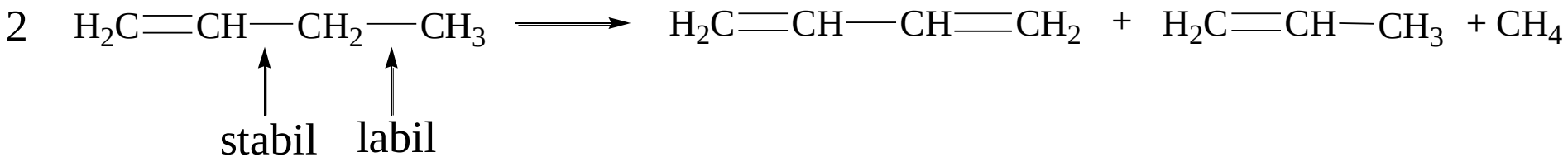


Konformation

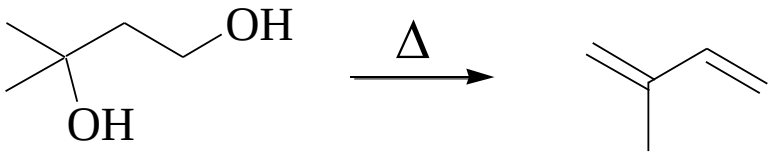


Synthese

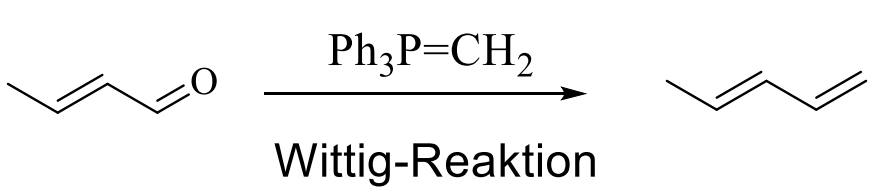
Dehydrierung von Alkanen

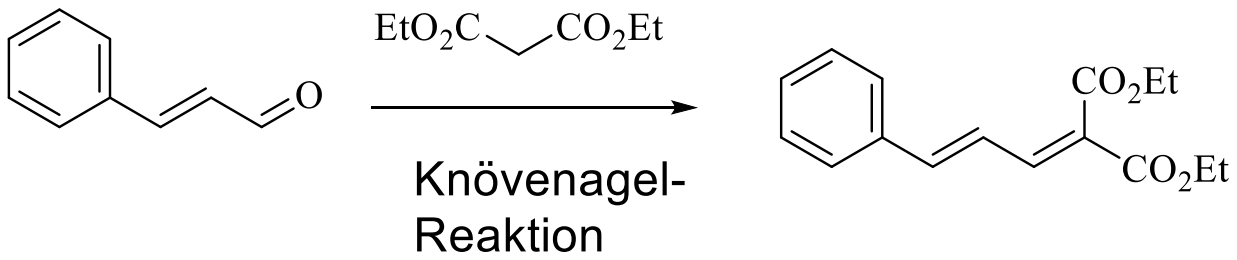


Dehydratisierung von Diolen



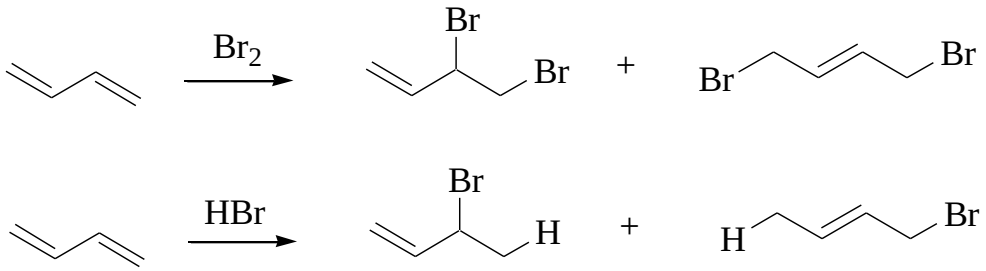
Andere Methoden zur Olefinierung



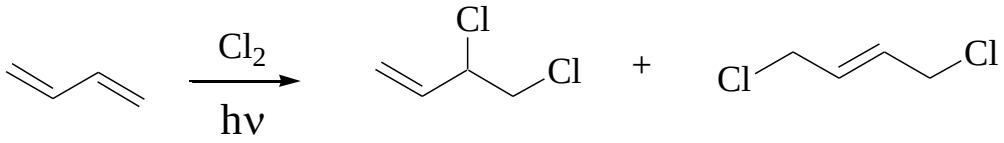


Reaktionen

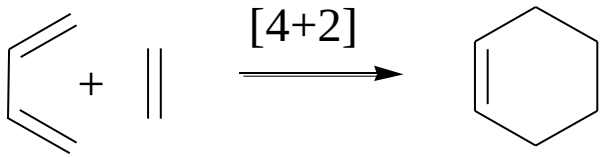
Elektrophile 1,2 und 1,4-Addition



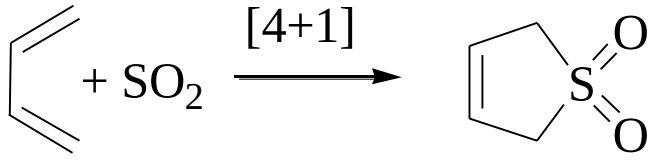
Radikalische Addition



Diels-Alder-Reaktion



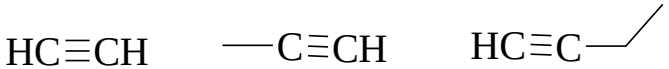
Chelotrope Reaktion



Alkine (Nomenklatur, Eigenschaften, Synthese, Reaktionen)

Nomenklatur

Name = [Position Dreifachbindung]-KW-Stamm + „in“



Ethin
Acetylen

Propin

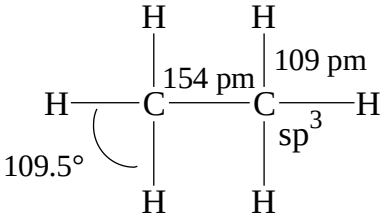
1-Butin

2-Butin

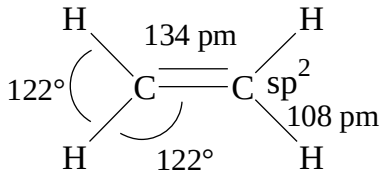
Ethinyl-

Propargyl-

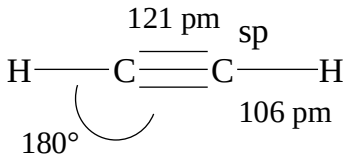
Allgemeines



CC-Einfachbindung
ΔH = 335 kJ/mol



CC-Doppelbindung
ΔH = 595 kJ/mol



CC-Doppelbindung
ΔH = 1257 kJ/mol

Acidität

sp^3

$H_3C^-CH_2^-\mathbf{H}$

$pK_a = 51$

niederer s-Anteil

sp^2

$H_2C{=}CH{-}\mathbf{H}$

$pK_a = 44$

sp

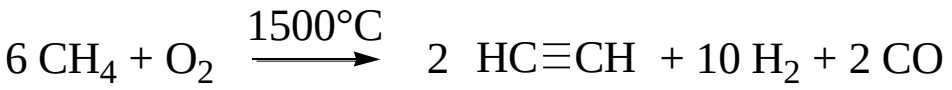
$HC{\equiv}C{-}\mathbf{H}$

$pK_a = 25$

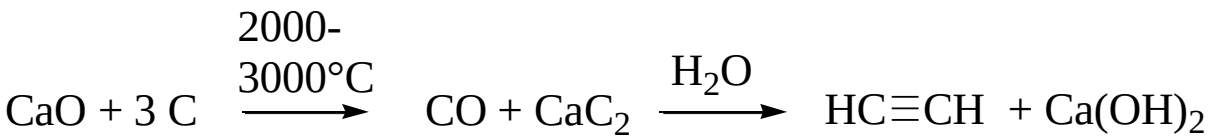
hoher s-Anteil

Darstellung

Technisch



$$6\,CH_4 + O_2 \xrightarrow{1500°C} 2\;HC{\equiv}CH + 10\,H_2 + 2\,CO$$

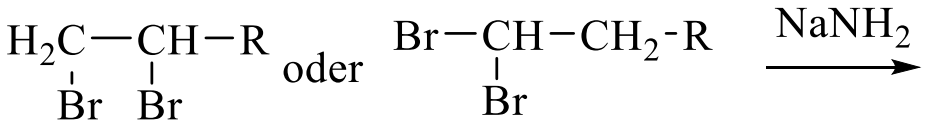


$$CaO + 3\,C \xrightarrow{2000\text{-}3000°C} CO + CaC_2 \xrightarrow{H_2O} HC{\equiv}CH + Ca(OH)_2$$

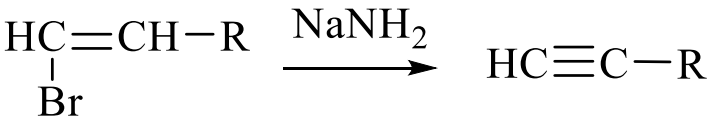
Calciumcarbid

Chemiepark Knapsack (NRW)

Dehydrohalogenierung

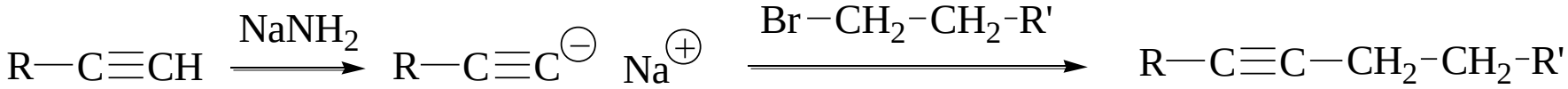


$$H_2C(Br)-CH(Br)-R \quad \text{oder} \quad Br-CH-CH_2\text{-}R \xrightarrow{NaNH_2}$$



$$HC(Br)=CH-R \xrightarrow{NaNH_2} HC{\equiv}C-R$$

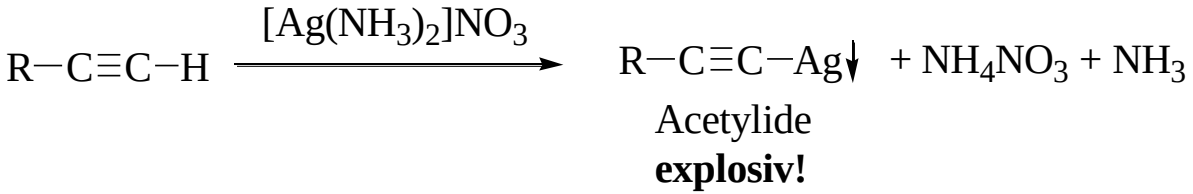
Alkinylierung



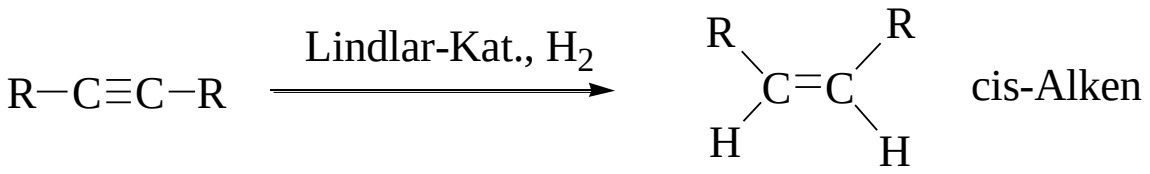
$$R-C{\equiv}CH \xrightarrow{NaNH_2} R-C{\equiv}C^{\ominus}\;Na^{\oplus} \xrightarrow{Br-CH_2-CH_2-R'} R-C{\equiv}C-CH_2-CH_2-R'$$

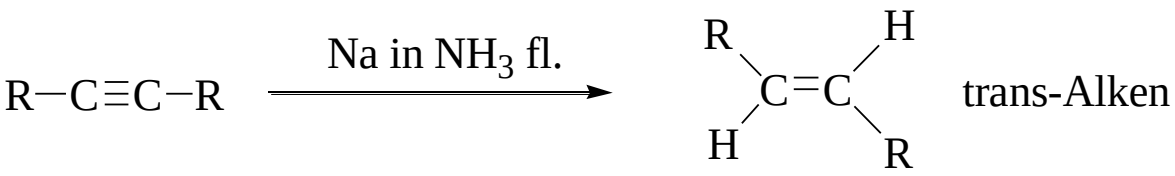
Reaktionen

Salzbildung

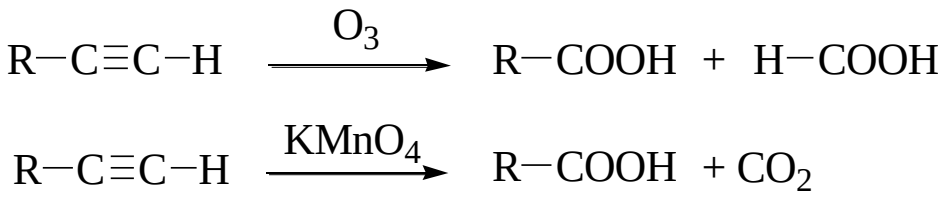


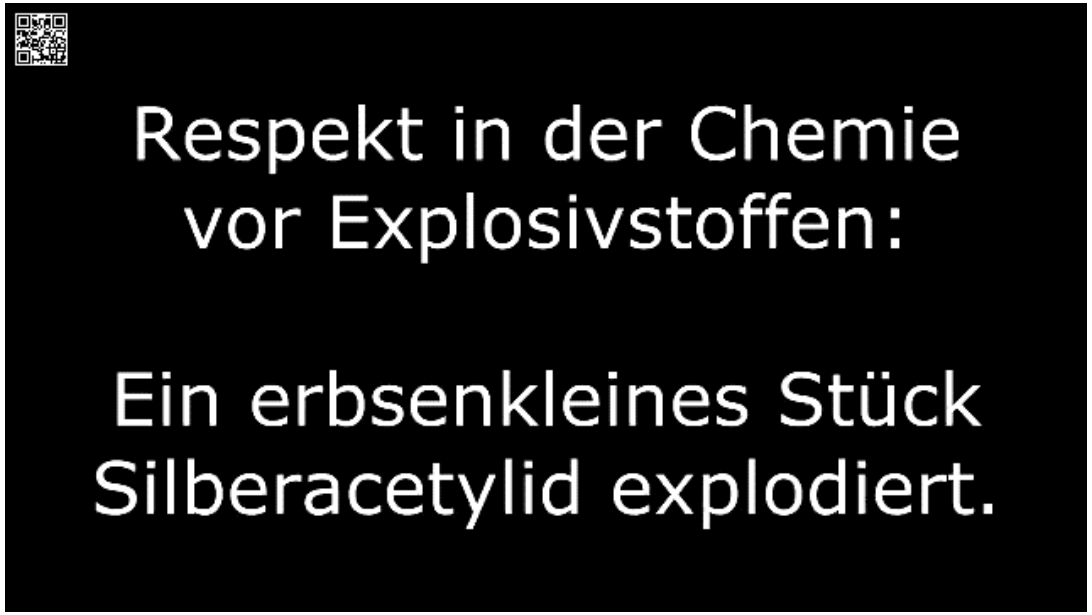
Reduktion



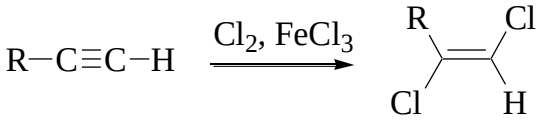


Oxidation

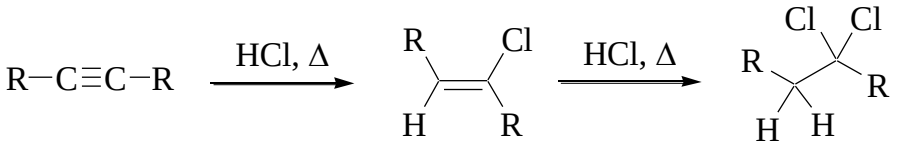




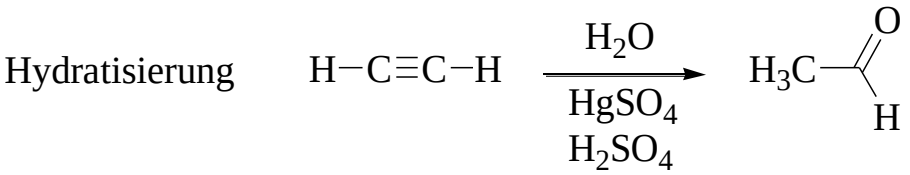
Elektrophile Addition

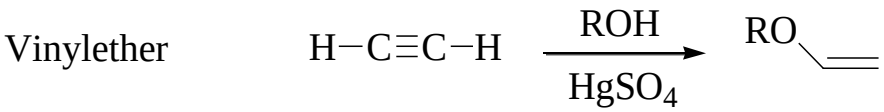


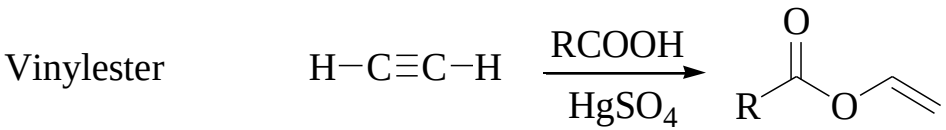
keine Reaktion ohne Lewissäure!

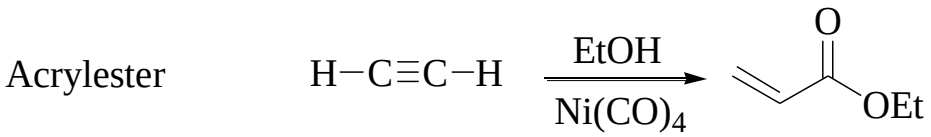


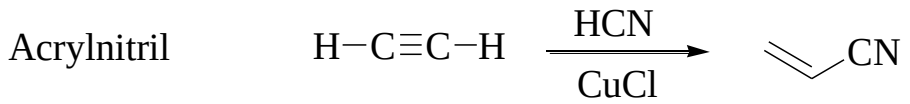
Reppe-Synthesen

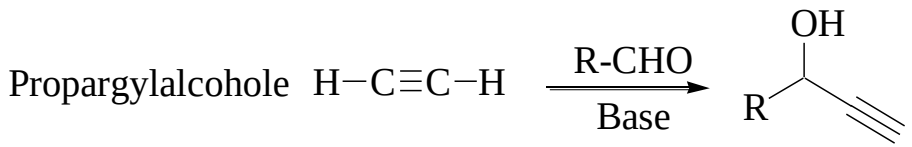




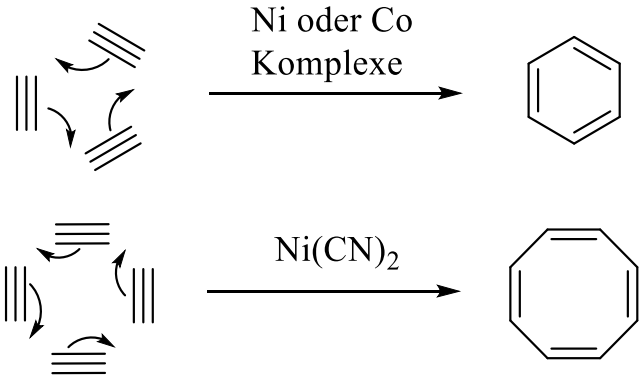




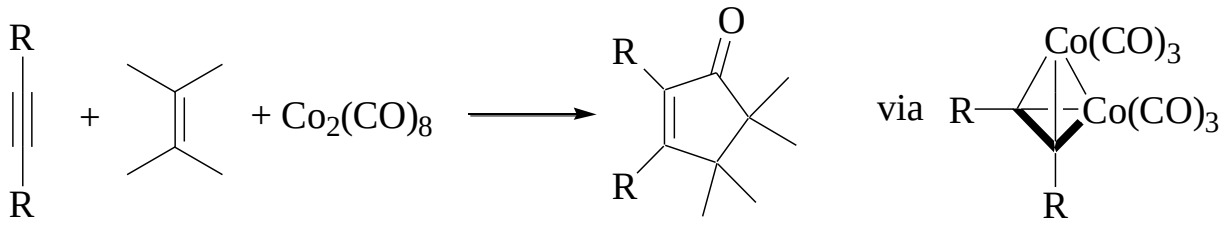




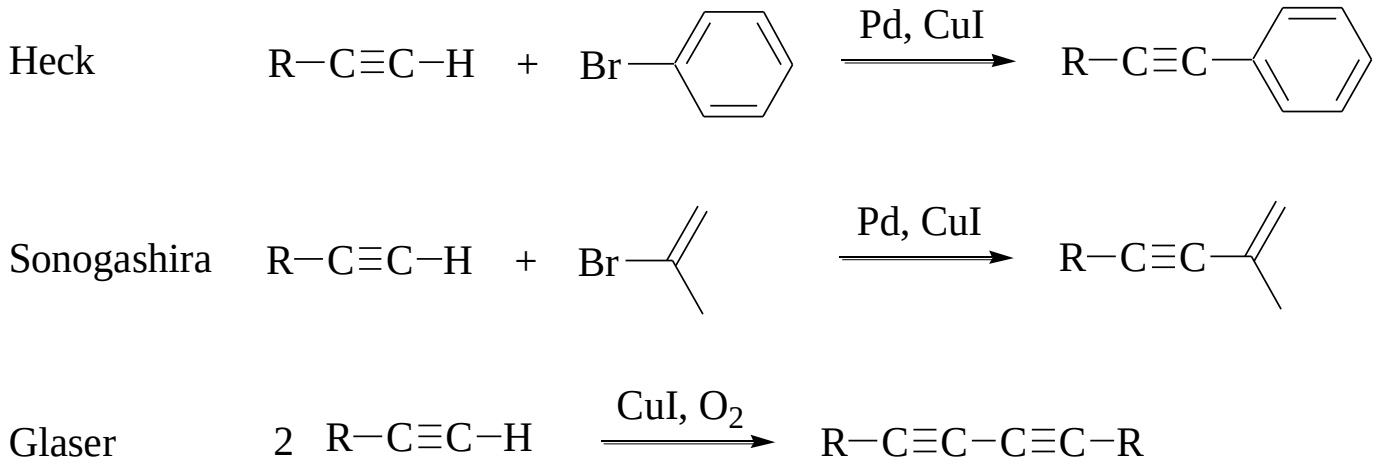
Cyclooligomerisierung



Pauson-Khand-Reaktion



Kupplungen



Benzol und andere aromatische Kohlenwasserstofe (Eigenschaften, Reaktionen)

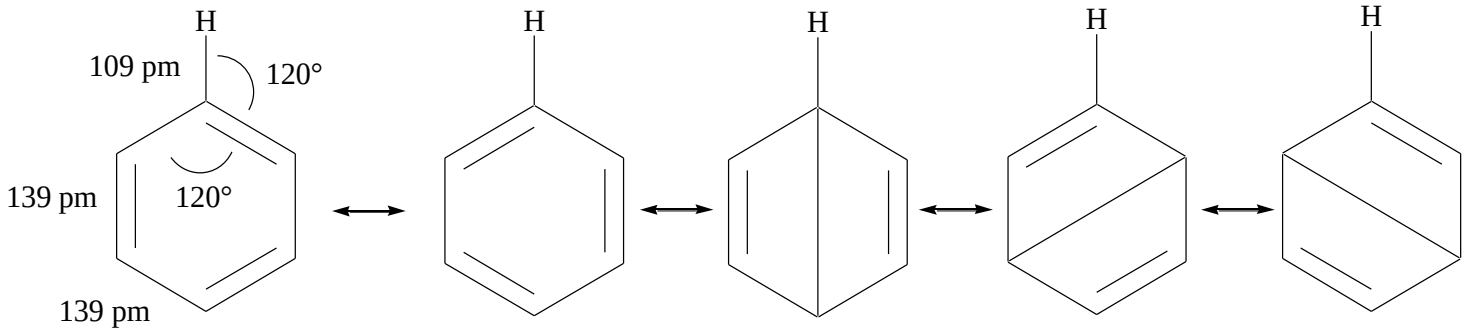
Aromatische Kohlenwasserstoffe wie das Benzol, sind Stoffe mit außergewöhnlichen Eigenschaften, die sich von denen der Alkene unterscheiden. Die Summe diese Eigenschaften wird **AROMATIZITÄT** genannt.

<u>Besondere Eigenschaften</u>

Ebene Molekülstruktur
Cyclisch konjugierte Doppelbindungen
Alle C sind sp^2 hybridisiert
Alle CC-Abstände sind im Benzol identisch
Wenig reaktiv (keine spontane Addition von Halogenen)
Kleinere Hydrierwärme als erwartet (**RESONANZSTABILISIERUNG** 151 kJ/mol)
Substitutionsreaktionen nach einem Additions-Eliminierungsmechanismus
Charakteristische Tieffeldverschiebung im Protonen-NMR

<u>Struktur / Molekülorbitale</u>

HÜCKEL-REGEL (4n+2) π-Elektronen in ebenem, cyclisch konjugierten System

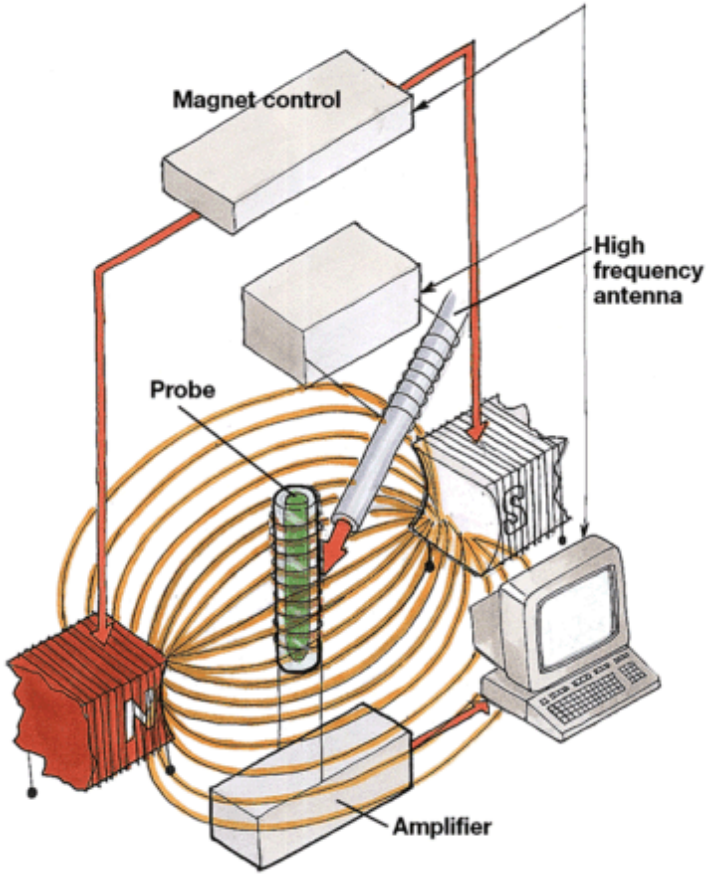


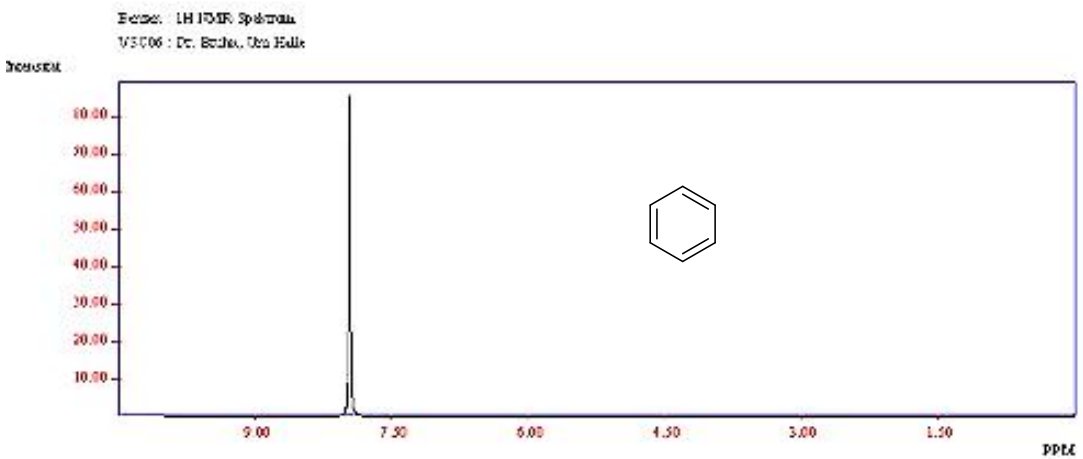
Kekule-Mesomerie-Strukturen

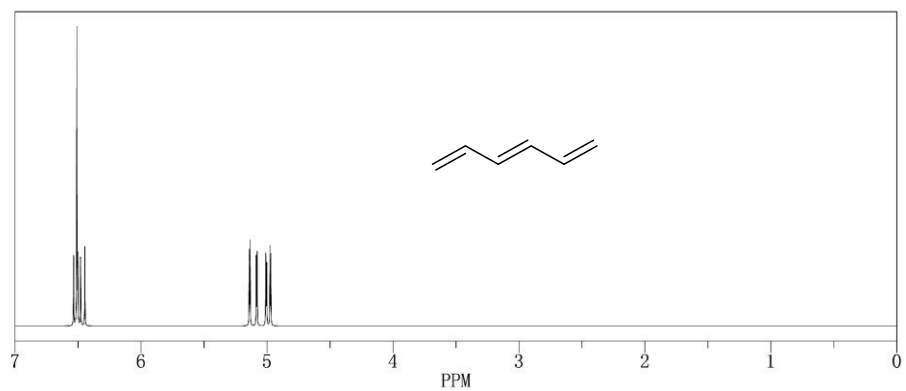
Dewar-Mesomerie-Strukturen

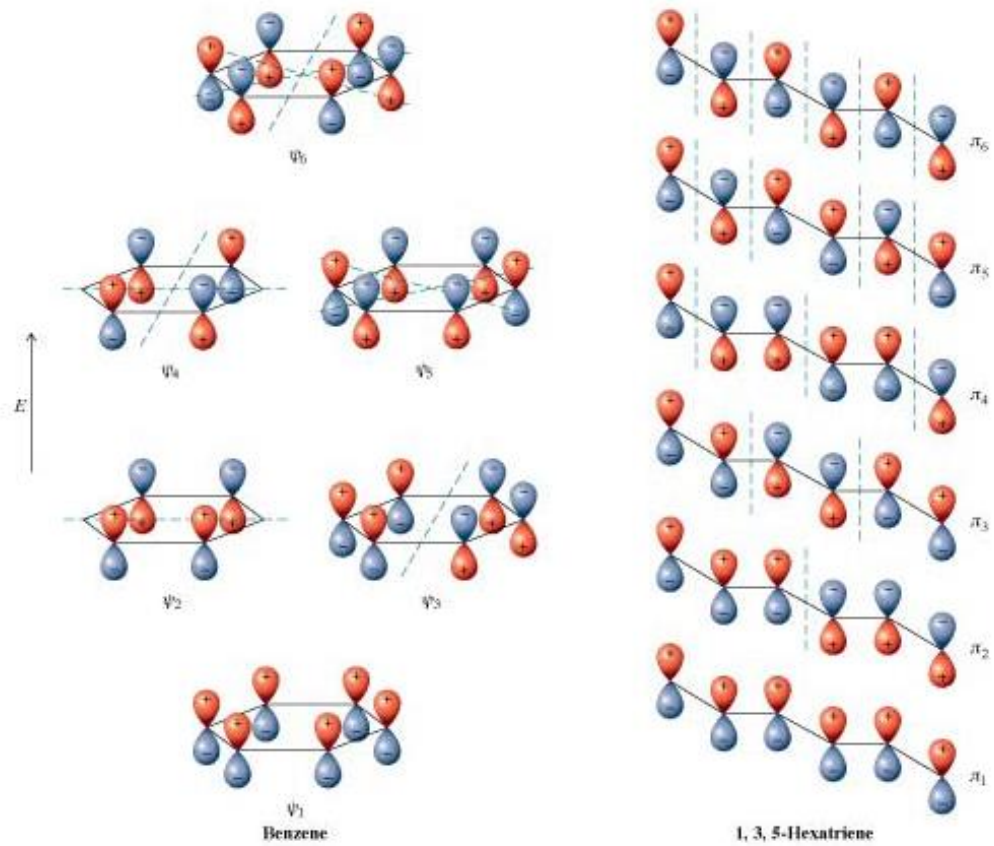
NMR-Spektrometer

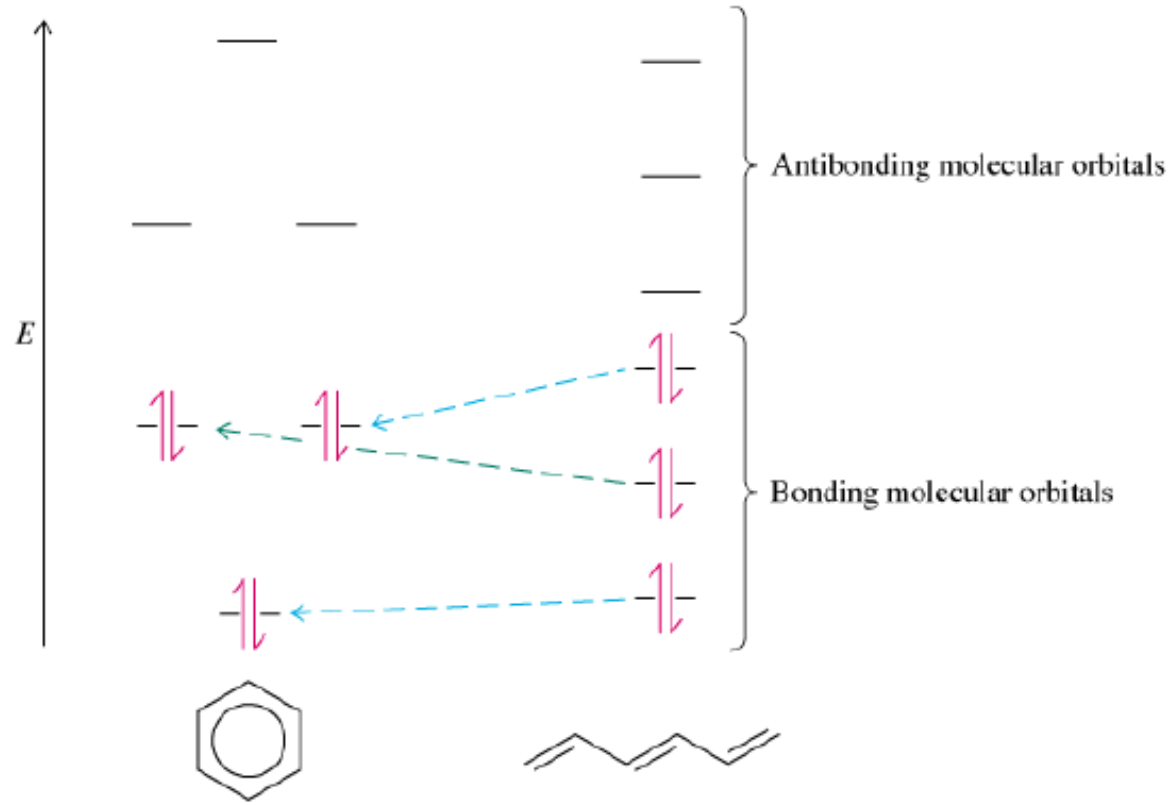
Bruker 600 MHz Spektrometer





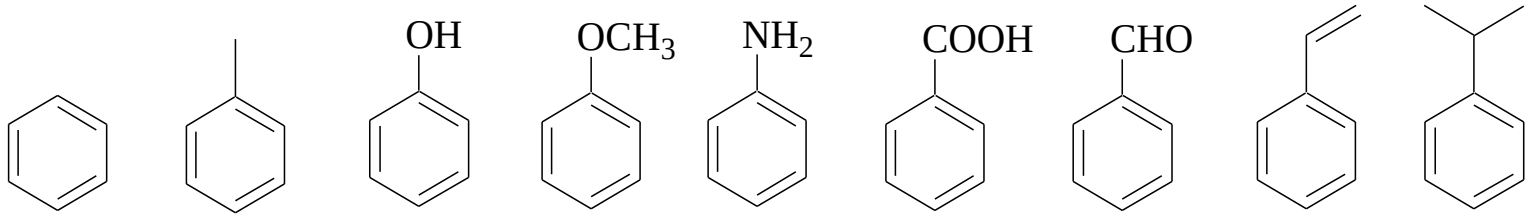



E
Benzene
1, 3, 5-Hexatriene

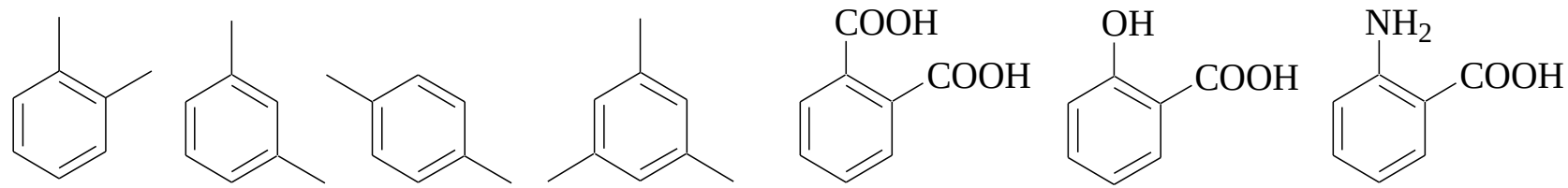

E
Antibonding molecular orbitals
Bonding molecular orbitals

Nomenklatur NAME = [Substituenten]-Stammname Stammname ist meist Trivialname

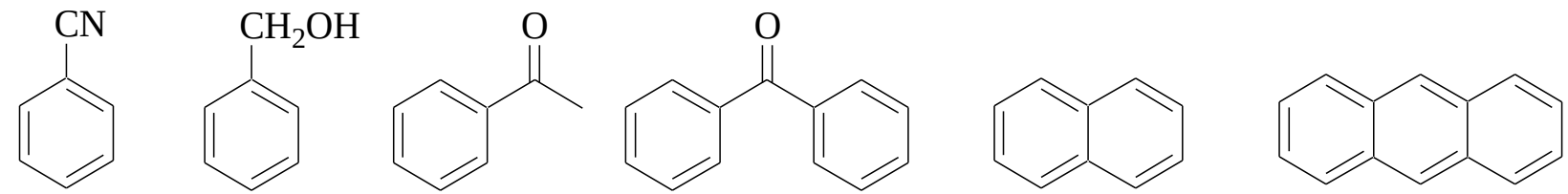
Als **SUBSTITUTENT**: Phenyl-; Benzo



Benzol Toluol Phenol Anisol Anilin Benzoesäure Benzaldehyd Styrol Cumol



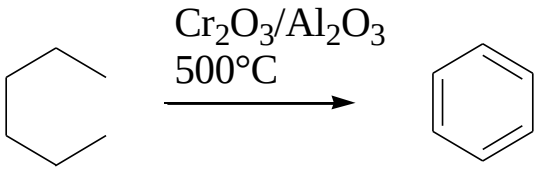
o-Xylol m-Xylol p-Xylol Mesitylen Phthalsäure Salicylsäure Anthranilsäure



Benzonitril Benzylalkohol Acetophenon Benzophenon Naphthalin Anthracen

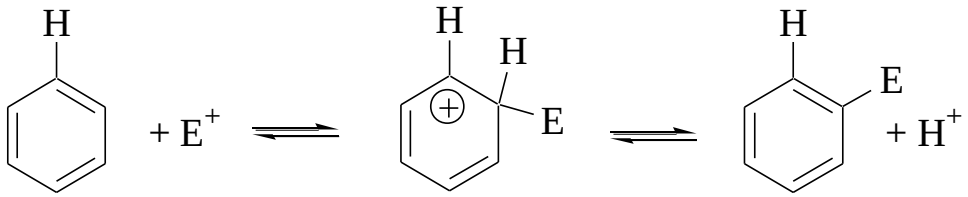
Gewinnung

Aus Steinkohleteer und Erdöl oder aus n-Hexan durch **PLATFORMING**



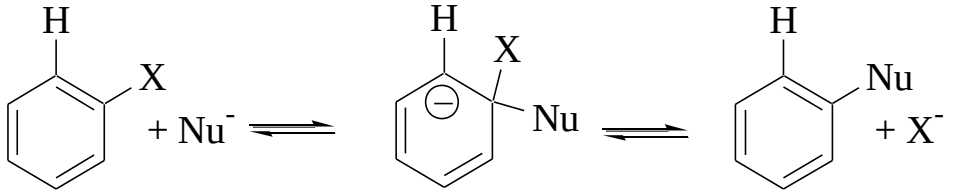
Reaktionen

Elektrophile Substitution



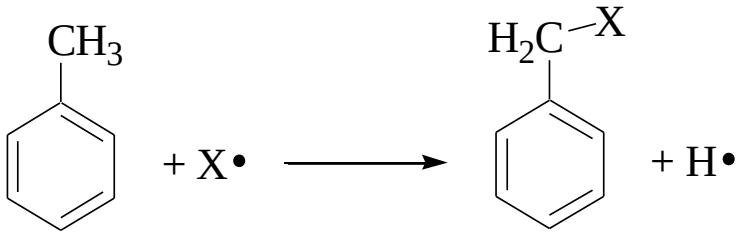
σ-Komplex

Nucleophile Substitution



Meisenheimer-Komplex

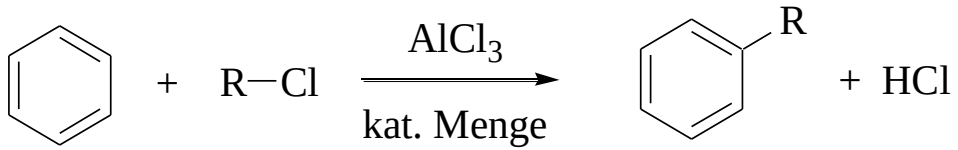
Radikalische Substitution (Seitenkette)



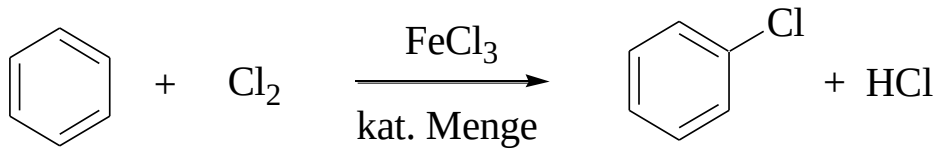
Merke: SSS = Sonne, Siedehitze, Seitenkette (radikalisch)
KKK= Kälte, Katalysator, Kern (electrophil)

Elektrophile Substitution

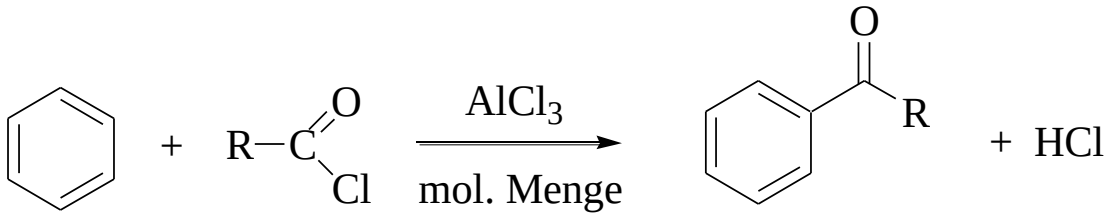
Friedel-Crafts-Alkylierung



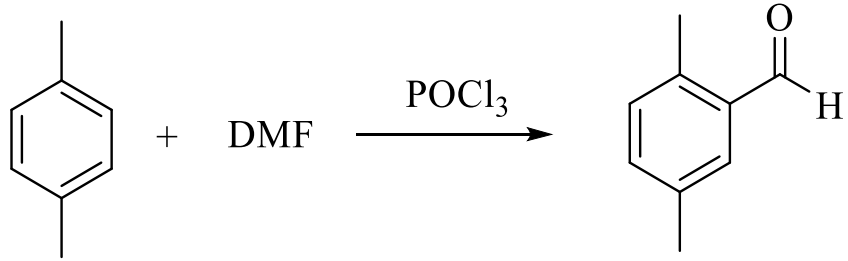
Halogenierung



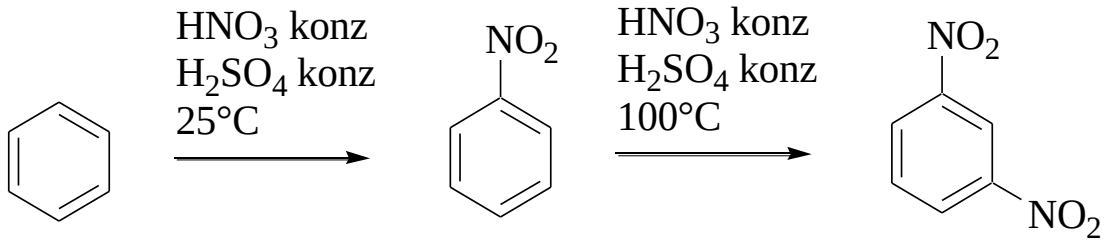
Friedel-Crafts-Acylierung



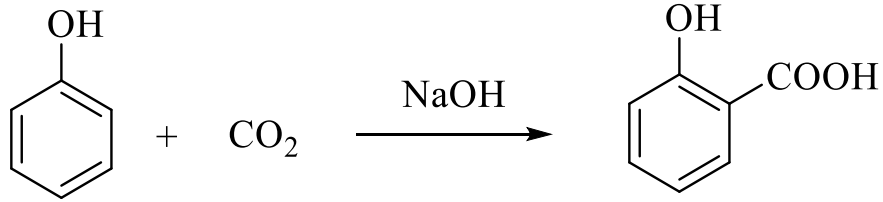
Vilsmeier-Formylierung



Nitrierung



Kolbe-Schmitt-Carboxylierung



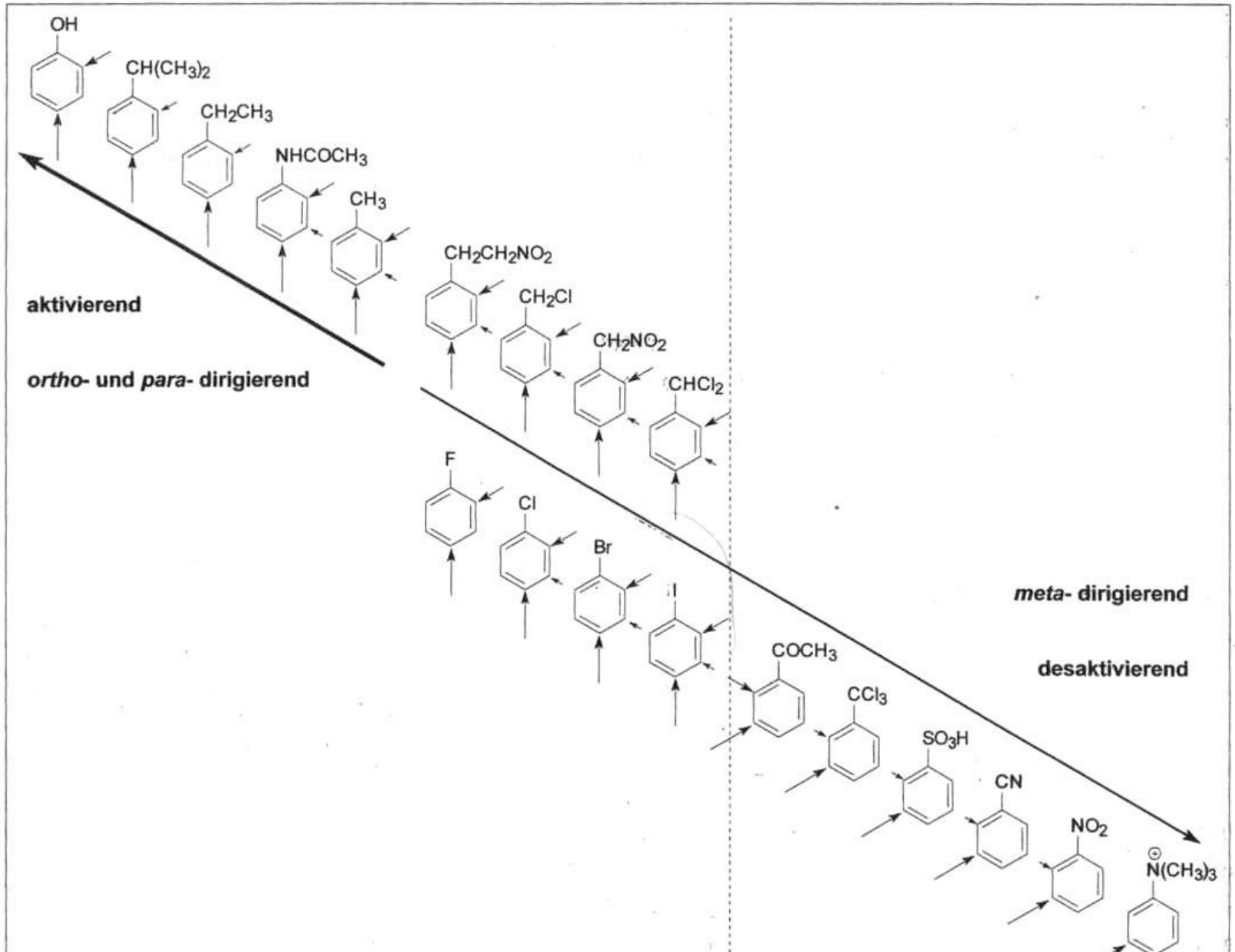
Substitutenteneinflüsse

Bereits am Benzol vorhandene Substituenten beeinflussen die Reaktivität und die **REGIOSELEKTIVITÄT** der Substitution. Man unterscheidet 3 Arten von Substitutenten:

SUBSTITUENTEN ERSTER ORDNUNG: -OH, -OMe, -NH_2, Alkyl
+M-Effekt +I-Effekt
Erhöhen die Reaktivität
Dirigieren S_E nach *ortho, para*

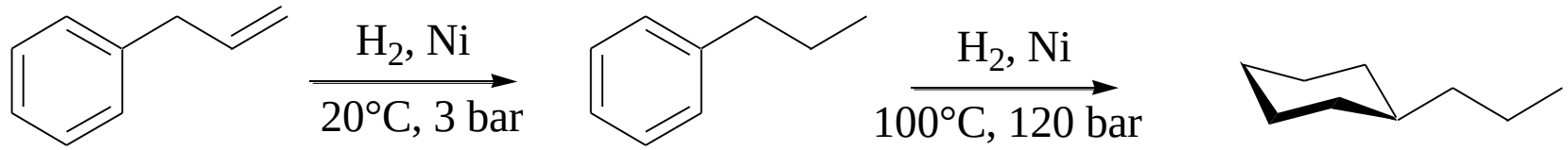
SUBSTITUTENTEN ZWEITER ORDNUNG: -NO_2, -CN, -CHO, -COOR, -CF_3
-M-Effekt -I-Effekt
Erniedrigen die Reaktivität
Dirigieren S_E nach *meta*

SUBSTITUTENTEN DRITTER ORDNUNG: Halogene
+M-Effekt und starker –I-Effekt
Erniedrigen leicht die Reaktivität
Dirigieren S_E nach *ortho, para*

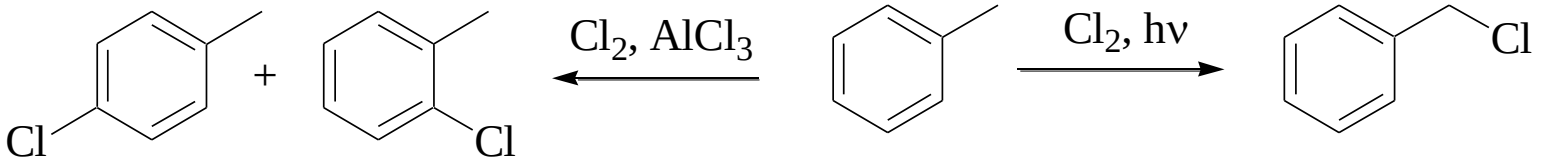

OH
CH(CH3)2
CH2CH3
NHCOCH3
CH3
aktivierend
ortho- und para- dirigierend
CH2CH2NO2
CH2Cl
CH2NO2
CHCl2
F
Cl
Br
I
COCH3
CCl3
SO3H
CN
NO2
N(CH3)3
meta- dirigierend
desaktivierend

Beispiele für Aromatenreaktionen

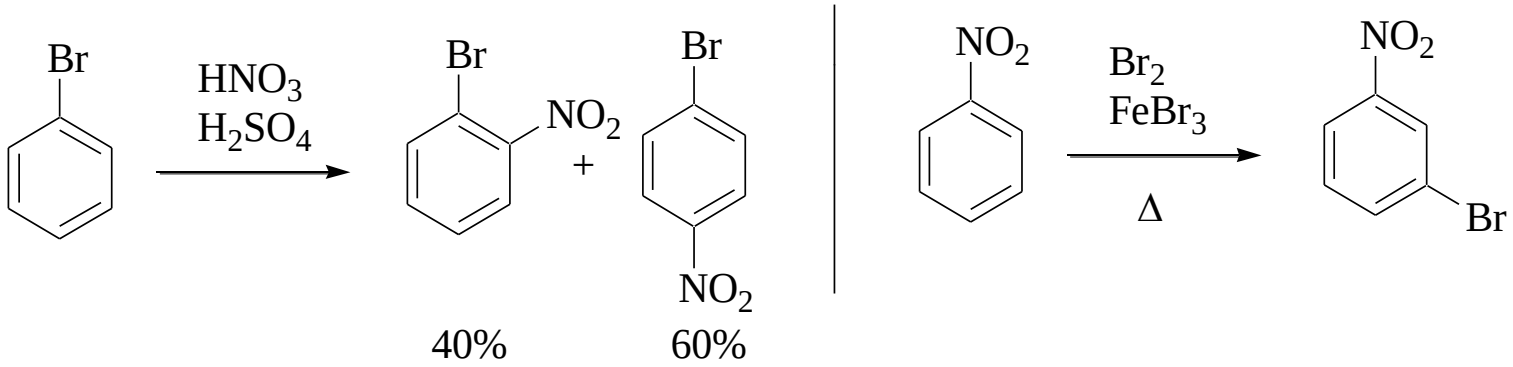
Reduktion



Seitenkettenhalogenierung (SSS), Kernhalogenierung (KKK)

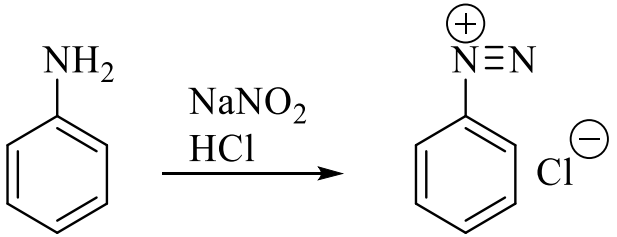


Bromierung/Nitrierung

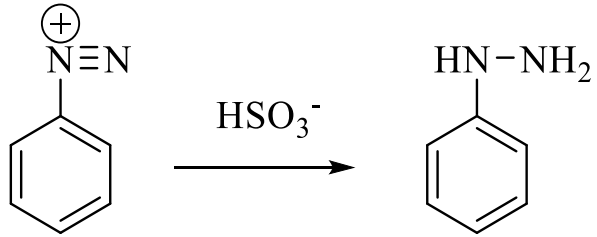


Diazoniumsalze

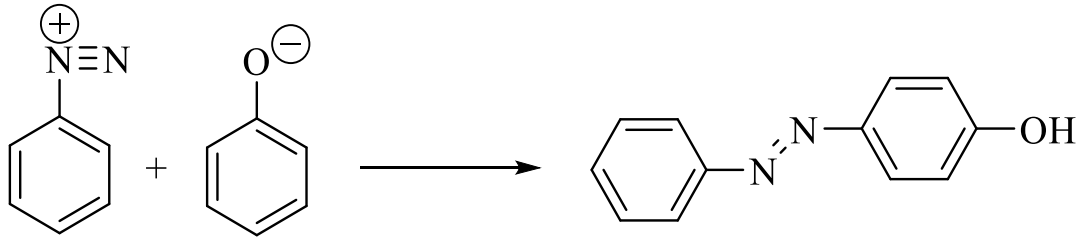
Darstellung:



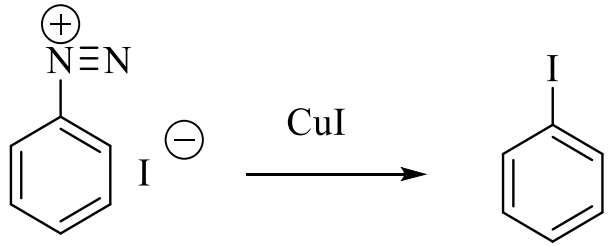
Reduktion:



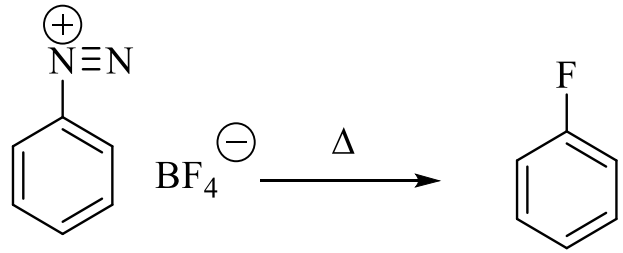
Azokupplung:

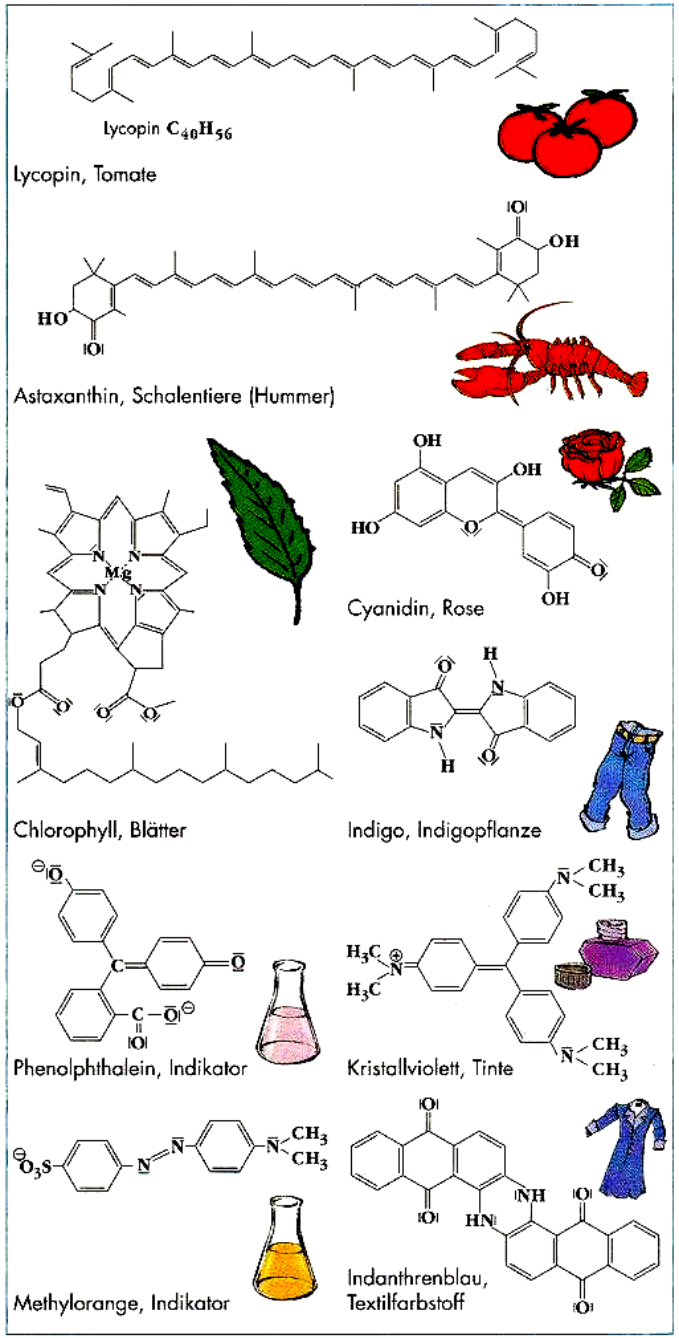


Sandmaier:

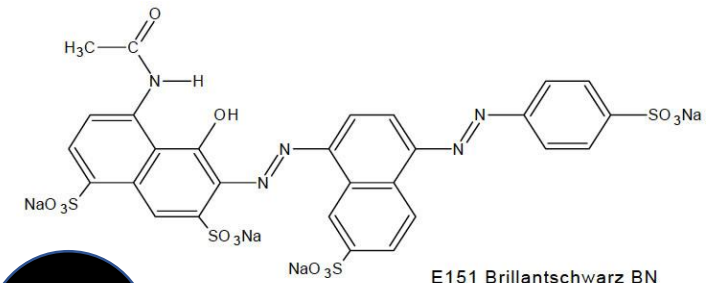


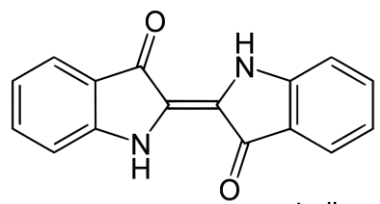
Balz-Schiemann:

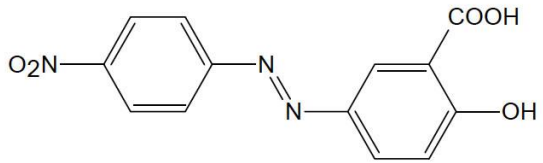


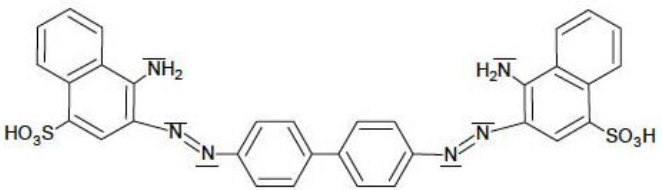


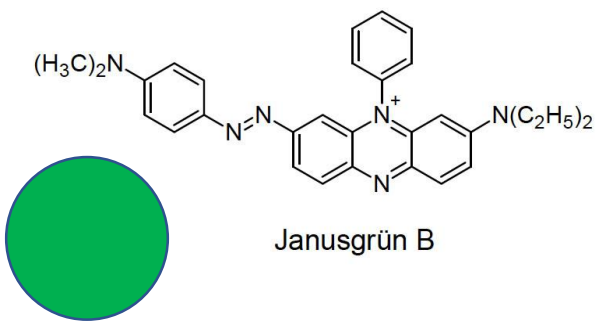
absorbiertes Licht	
Wellenlänge (in nm)	Farbe
730	purpur
640	rot
590	orange
550	gelb
530	gelbgrün
510	grün
490	blaugrün
450	blau
425	indigoblau
400	violett



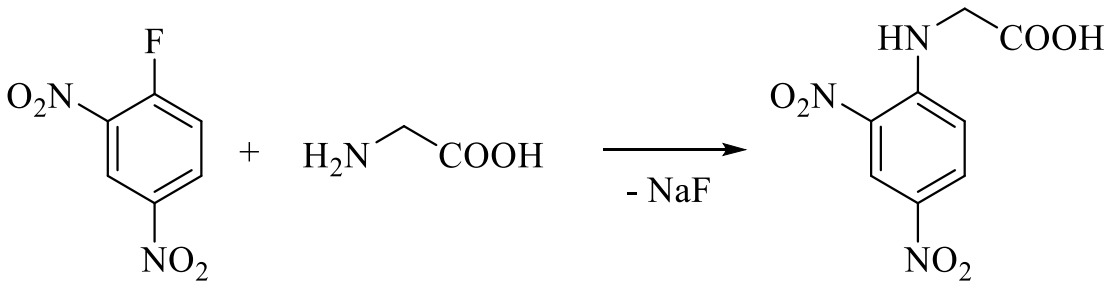






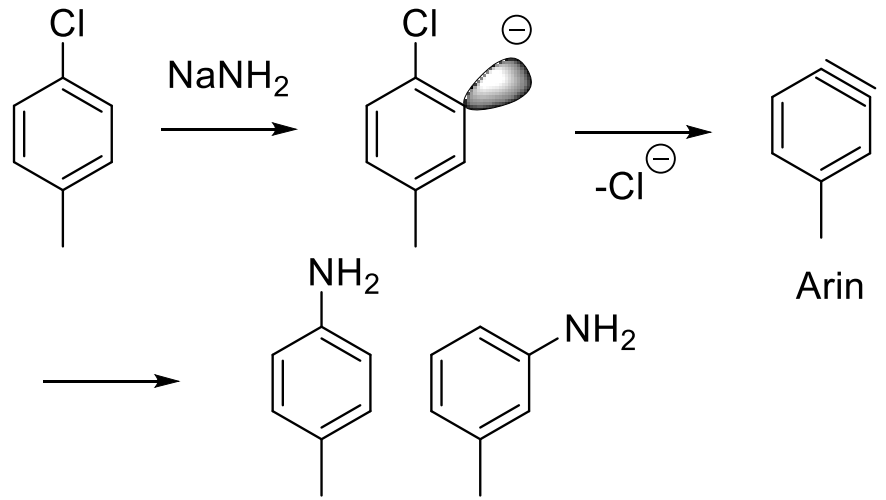


Nucleophile Reaktion



Sangers Reagenz

Arinmechanismus



Polycyclische Aromaten