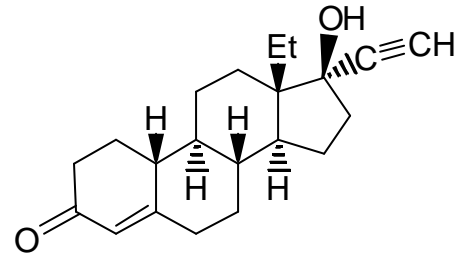
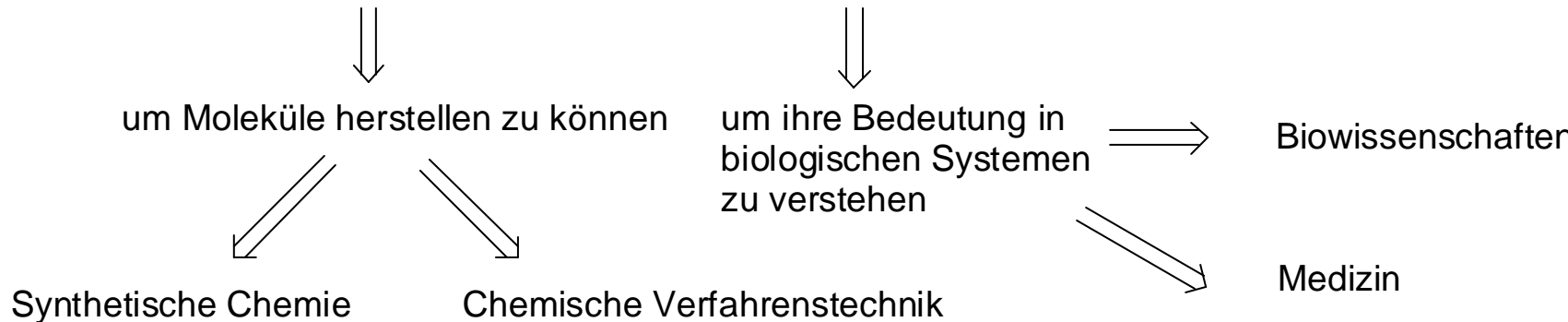


Colchicin

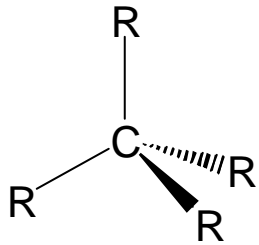


Norgestrel

- Ziele:
- 1) Die Struktur Organischer Moleküle kennen und verstehen lernen.  
Nomenklatur, Strukturformeln, 3D-Darstellung  
strukturelle Dynamik
  - 2) Die Reaktivität Organischer Moleküle kennen und verstehen und voraussagen zu lernen.



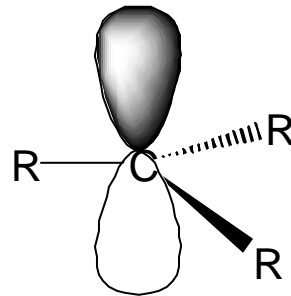
### 3 Typen von Hybridisierung am C-Atom



**$sp^3$**

4 äquivalente  
Atomhybridorbitale

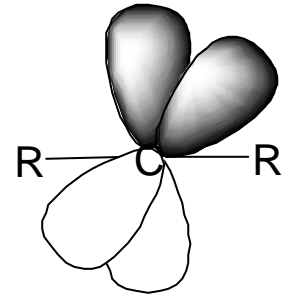
tetraedrisch angeordnete  
Reste R



**$sp^2$**

3 äquivalente  
Atomhybridorbitale

trigonal angeordnete  
Reste R  
+ 1 p Orbital



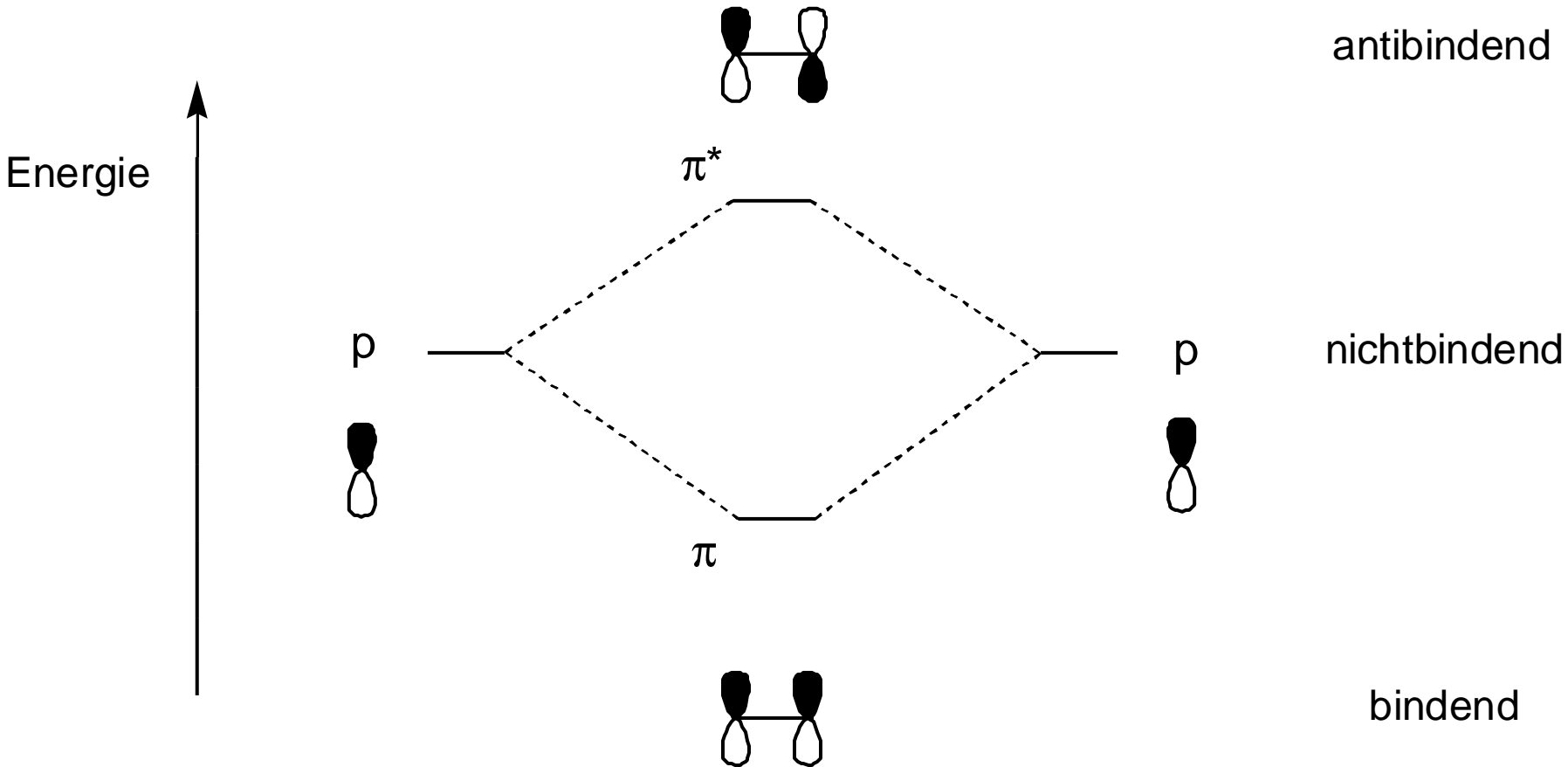
**$sp$**

2 äquivalente  
Atomhybridorbitale

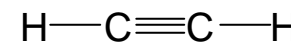
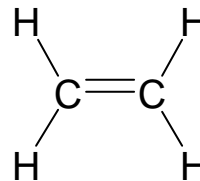
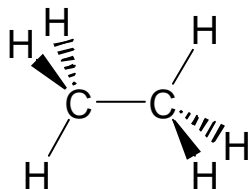
colinear angeordnete  
Reste R  
+ 2 p Orbitale

# Chemische Bindung: Durch Kombination von Atomorbitalen zu Molekülorbitalen

Beispiel:  $\pi$ -Bindung beim Ethylen



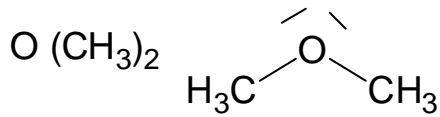
# Bildung von CC-Einfach-, CC-Doppel- und CC-Dreifachbindungen durch Verwendung verschiedener Typen von C-Hybridorbitalen



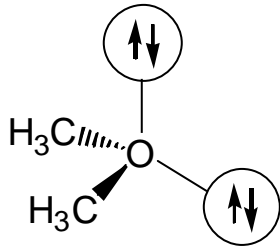
Bindungslänge[pm]	154	133	120
Bindungsstärke [kJ/mol]	368 (1)	636 (1.7)	837 (2.3)
Bindungs-Charakter	$C_{sp^3} - C_{sp^3}$	$C_{sp^2} = C_{sp^2}$	$C_{sp} \equiv C_{sp}$
Resultierende Geometrie	tetradrisch $109^\circ$	trigonal $120^\circ$	linear $180^\circ$

# Hybridisierung bei Heteroatomen

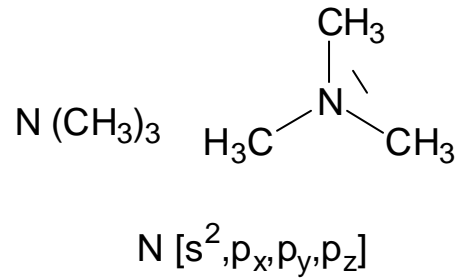
## Sauerstoff



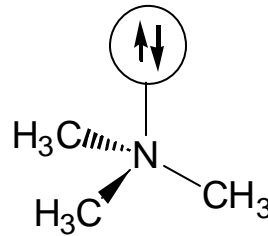
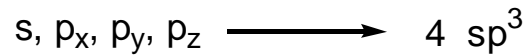
$sp^3$ -Hybridisierung



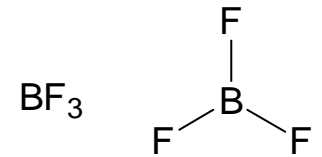
## Stickstoff



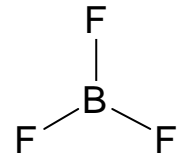
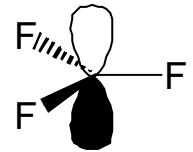
Hybridisierung



## Bor



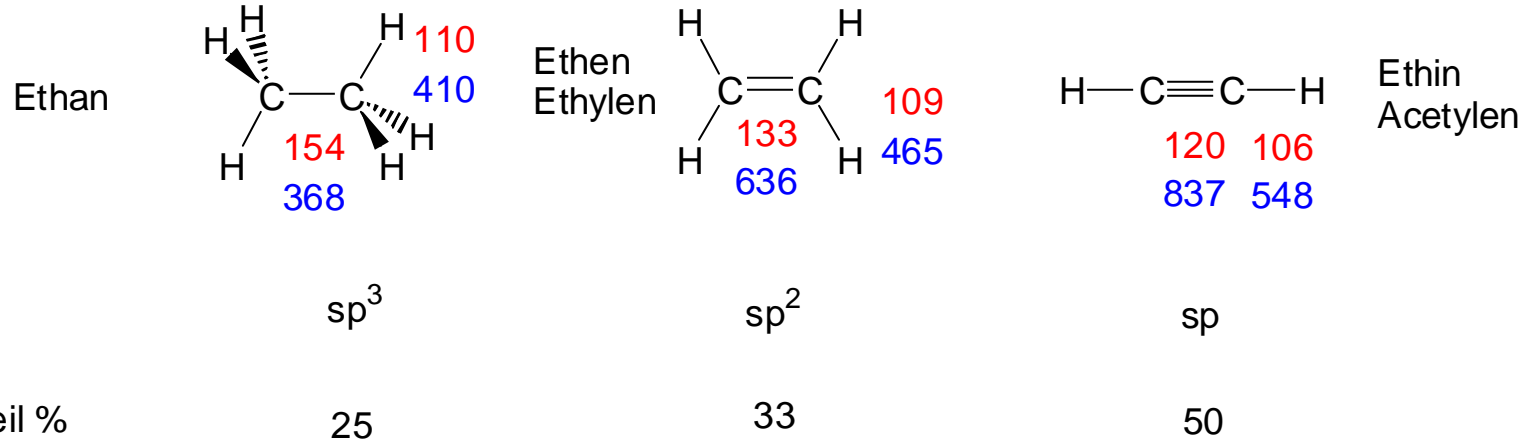
$sp^2$ -Hybridisierung



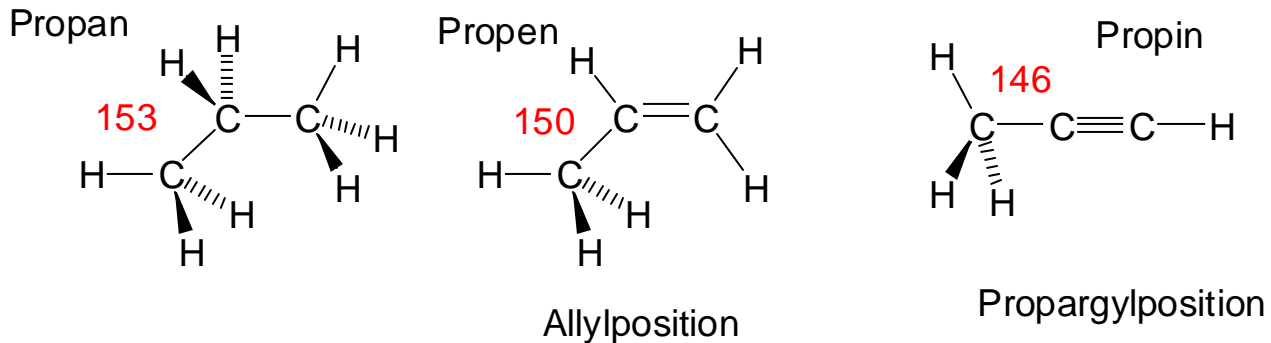
Bindungslänge[pm]

Bindungsstärke[kJ/mol]

Dissoziationsenthalpie für die homolytische Bindungsspaltung



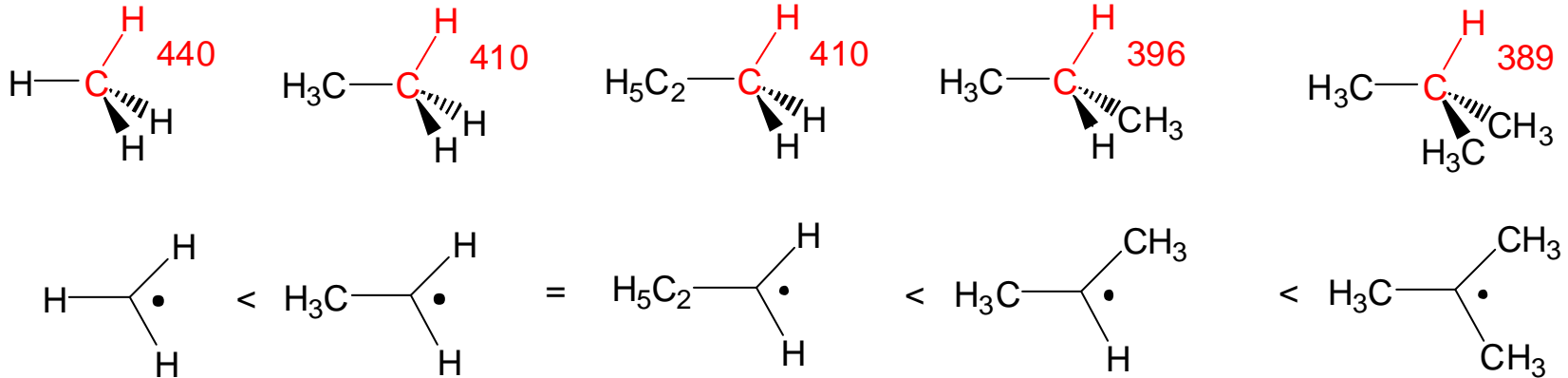
je höher der s-Anteil, desto kürzer die Bindung  
(desto höher die Elektronegativität, desto höher die Acidität)



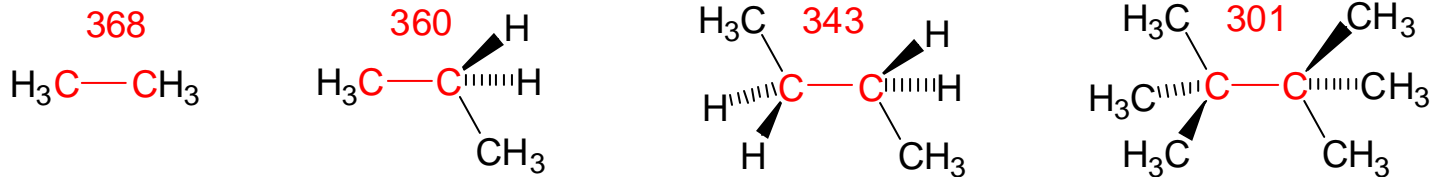
## Bindungsstärke[kJ/mol]

Dissoziationsenthalpien für die homolytische Bindungsspaltung

### C-H



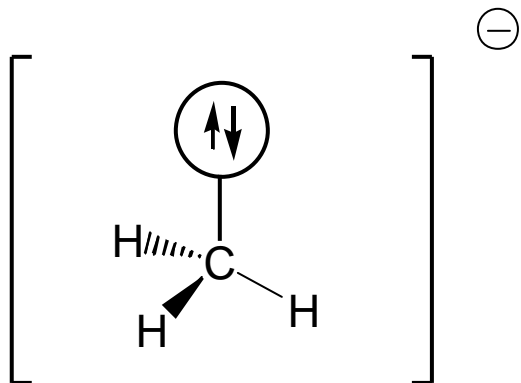
### C-C



höhere Alkylsubstitution -> höhere Stabilität des C-Radikals -> geringere Bindungsenergie der CH/CC-Bindung

## Carbanion

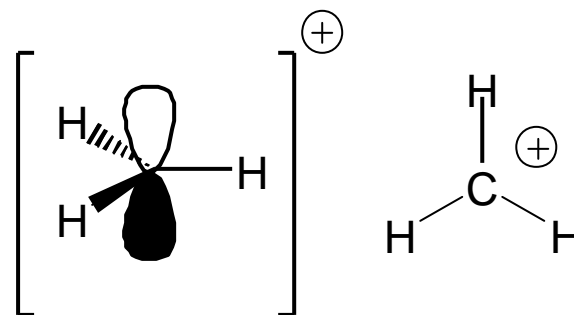
$\text{NH}_3$  isoelektronisch mit  $\text{CH}_3^-$



$\text{sp}^3$  tetredrisch

## Carbokation

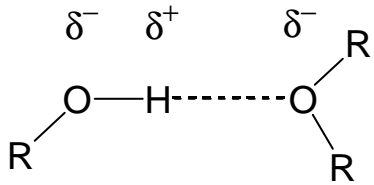
$\text{BF}_3$  isoelektronisch mit  $\text{CH}_3^+$



$\text{sp}^2$  planar



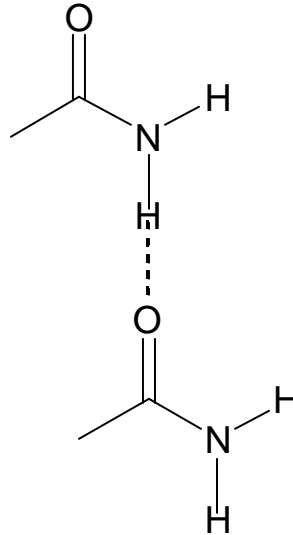
# Nicht-kovalente Wechselwirkungen: H-Brücken



96 pm      174 pm  
 435 kJ/mol    21 kJ/mol

Geometrie: möglichst linear

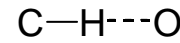
Bindungslänge O-H-O 270 pm



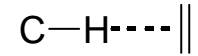
normale: 20-25 kJ/mol

starke: > 40 kJ/mol

schwache: 3 - 10 kJ/mol



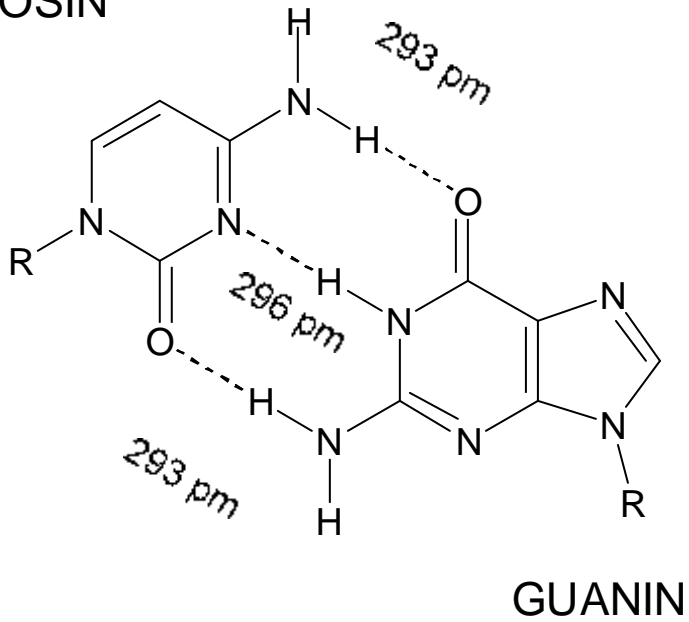
CHO-Brücke



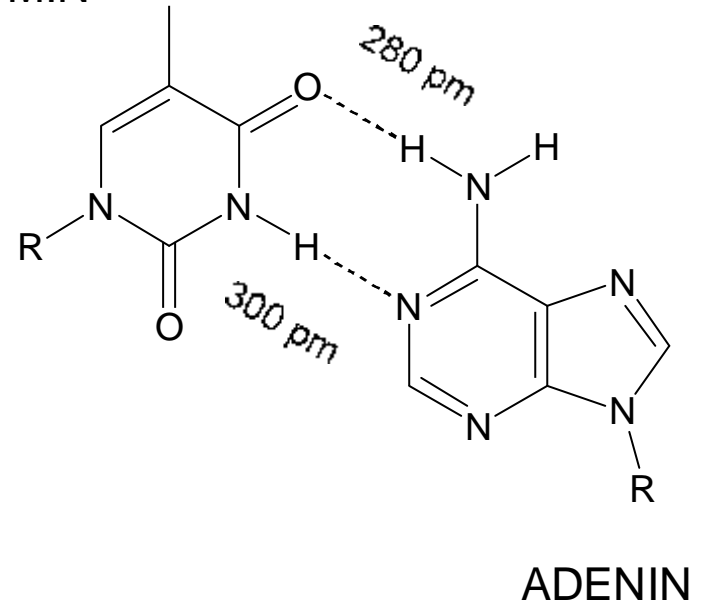
H-Brücke mit pi-System

# Nicht-kovalente Wechselwirkungen: H-Brücken

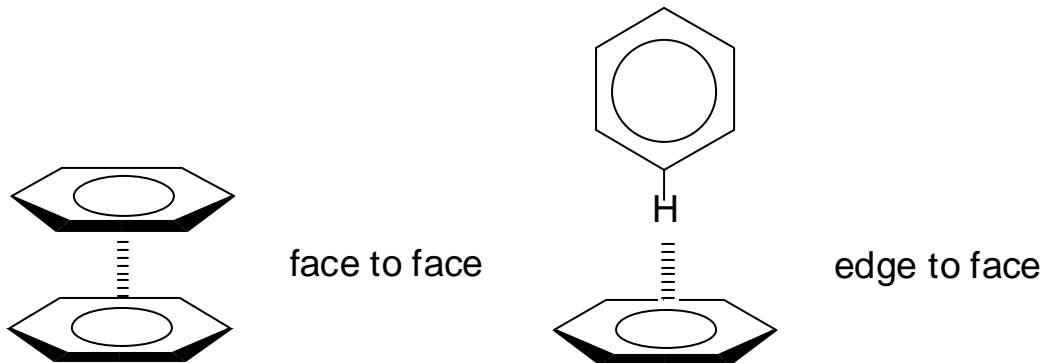
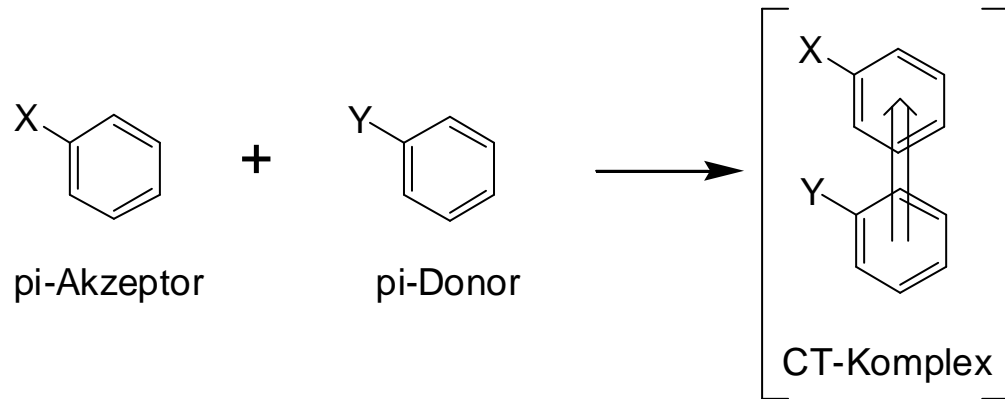
CYTOSIN



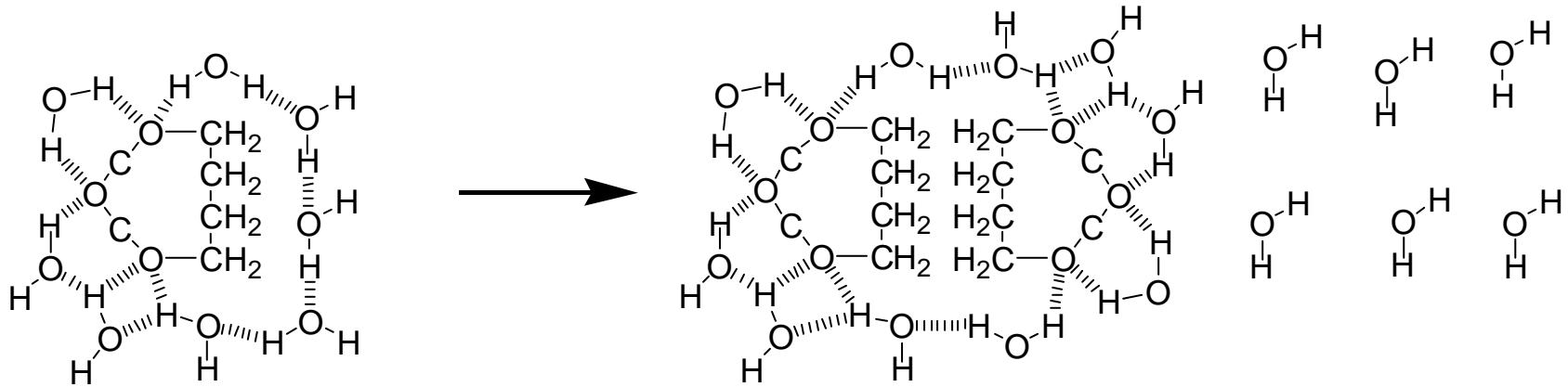
THYMIN



# Nicht-kovalente Wechselwirkungen: Charge-Transfer/ $\pi$ -stacking



# Nicht-kovalente Wechselwirkungen: Hydrophobe Wechselwirkungen



keine Ausbildung von H-Brücken an der hydrophoben Molekül-Oberfläche möglich.

Freisetzung von Lösungsmittel-Molekülen aus der Solvathülle:

⇨ entropisch begünstigt

Wasser-Moleküle müssen unter hohen Entropieverlusten die hydrophobe Molekül-Oberfläche überbrücken

Energiebeitrag:

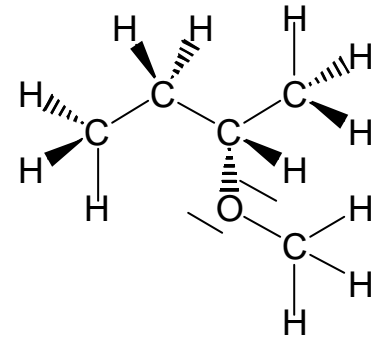
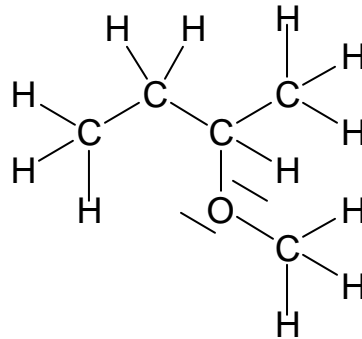
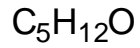
0,2 kJ/mol pro  $(100 \text{ pm})^2$  hydrophobe Fläche

2,5 kJ/mol pro CH Teilstruktur

$\text{CH}_3 = 3 \times \text{CH} = 7,5 \text{ kJ/mol}$  (1.8 kcal/mol)

# Strukturformeln

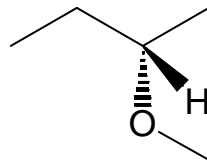
Isobutylmethylether



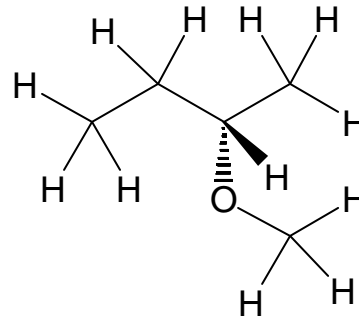
Summenformel

Kekule-Struktur

3D-Kekule Struktur



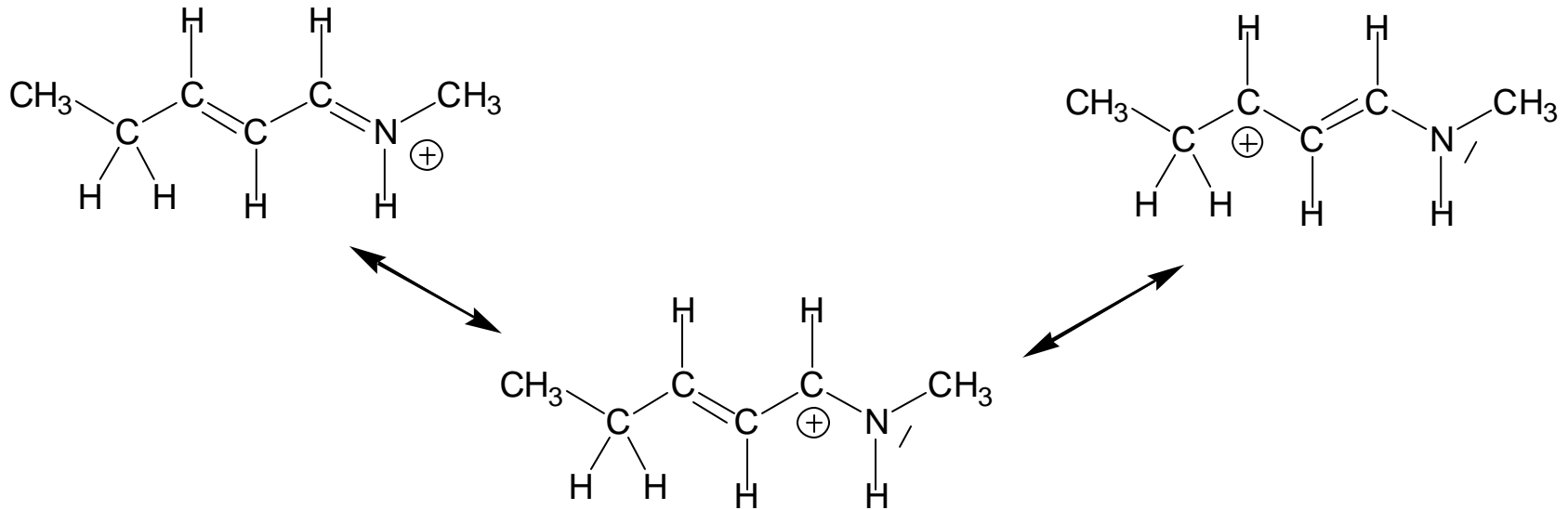
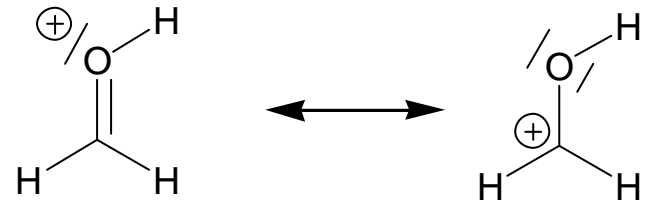
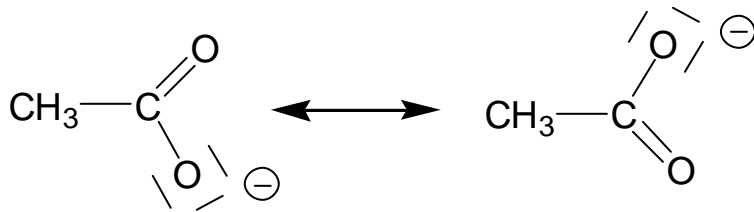
Gerüst-Struktur  
mit ausgewählten Hs



Gerüst-Struktur  
mit allen Hs

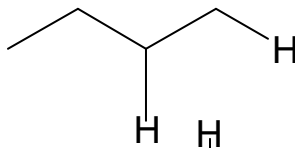
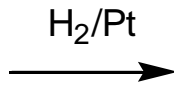
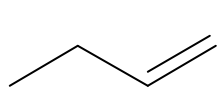
# Resonanz-Strukturen

In manchen Fällen ist es nicht möglich, die elektronische Struktur eines Moleküls mit einer einzigen Strukturformel korrekt wiederzugeben. In diesen Fällen benutzt man zwei oder mehrere idealisierte Grenzstrukturen (Resonanz-Strukturen). Jede Resonanzstruktur spiegelt eine Charakteristik des Moleküls wieder, ist jedoch keine exakte Abbildung aller Charakteristika.

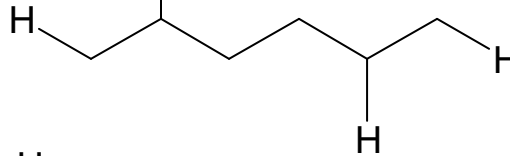
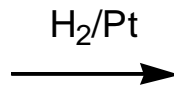
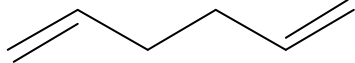


# Wechselwirkung zwischen $\pi$ -Systemen $\rightarrow$ Konjugation

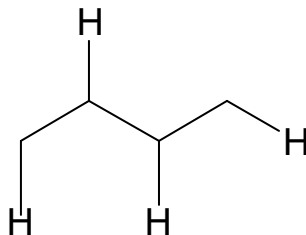
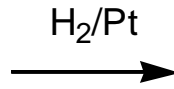
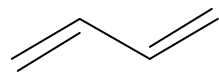
Hydrierwarmen als Ma fur die Stabilitat von  $\pi$ -Systemen



$$\Delta H^\circ = -127 \text{ kJ/mol}$$



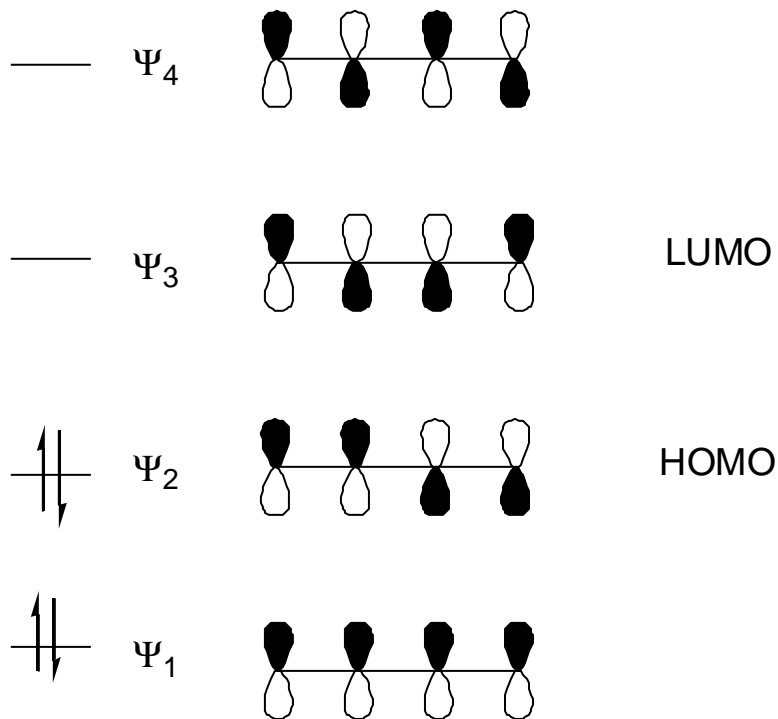
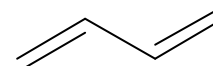
$$\Delta H^\circ = -253 \text{ kJ/mol}$$



$$\Delta H^\circ = -239 \text{ kJ/mol}$$

14 kJ/mol Stabilisierung durch Konjugation im 1,3-Butadien

# MOs von 1,3-Butadien



Grundzustand:

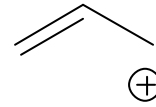
1. angeregter Zustand:  $\Psi_1^2, \Psi_2^1, \Psi_3^1$

$\Psi_1^2, \Psi_2^2$

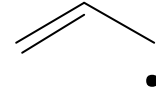


$\pi$ -Bindung + p-Orbital  $\rightarrow$  Allyl-System

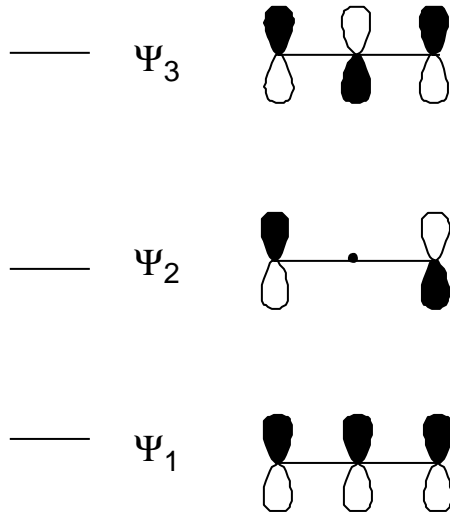
MOs des Allyl-Systems



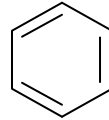
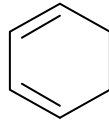
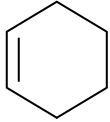
Allyl-Kation



Allyl-Radikal



"Extra"-Stabilität des aromatischen Systems (Planar!)



experimentell: 1 x 120 kJ/mol    230 kJ/mol    206 kJ/mol  
 Erwartungswert: ( 2 x 120 = 240)    ( 3 x 120 = 360)

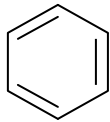
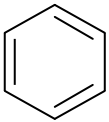
Hydrierwärmern [kJ/mol]  
 H<sub>2</sub> - > Cyclohexan

Die Zahl der beteiligten π-Elektronen ist wichtig:

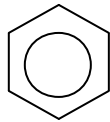
Hückel-Regel:  $4n + 2$

aromatische Systeme mit 2,6,10,14 .... π-Elektronen

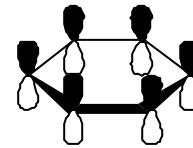
↓  
 154 kJ/mol Stabilisierung  
 beim aromatischen System  
 des Benzols



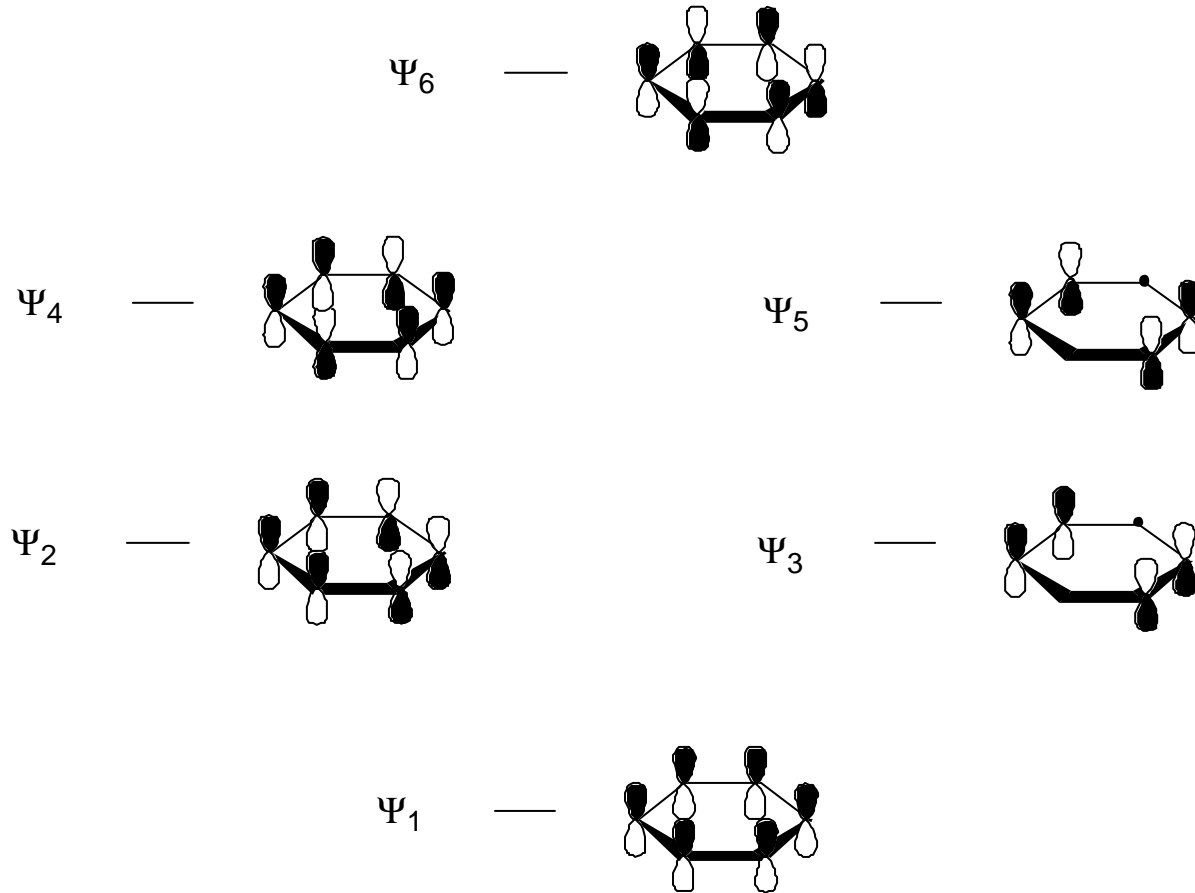
Mesomerie



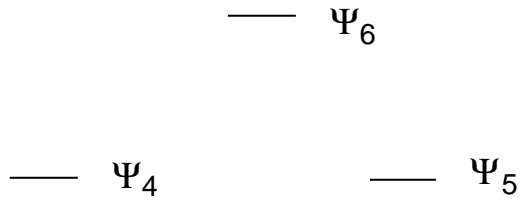
Benzol C-C = 139 pm  
 ges. C-C = 154 pm  
 C=C = 134 pm



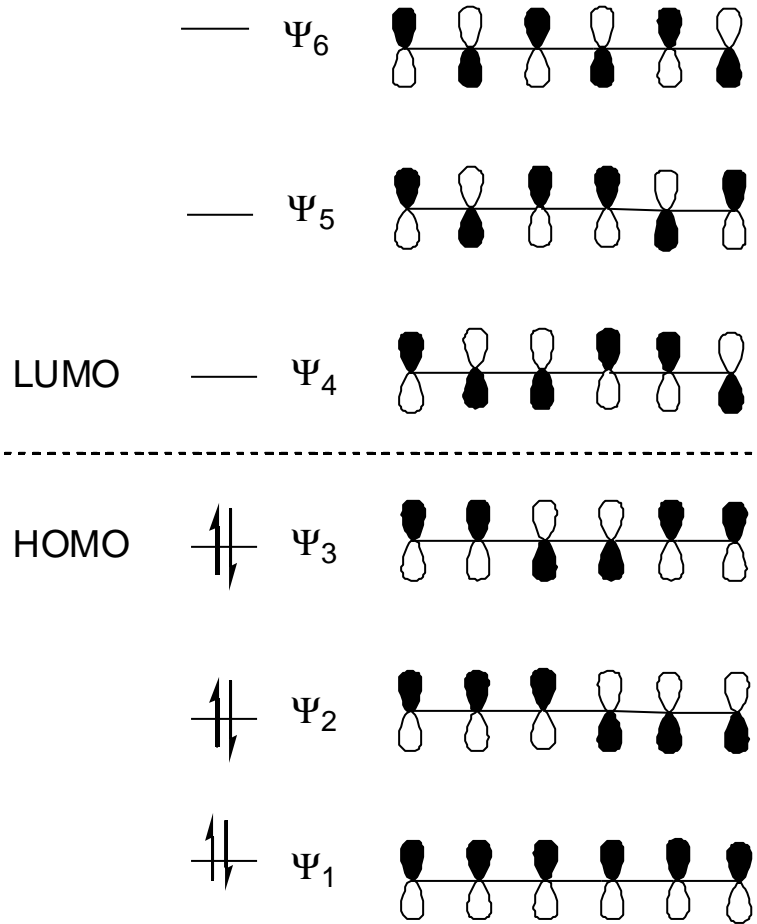
# Die 6 Molekülorbitale für das $\pi$ -System des Benzols



MOs von Benzol



MOs von 1,3,5-Hexatrien

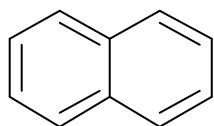


Grundzustand:  $\Psi_1^2, \Psi_2^2, \Psi_3^2$

Die Zahl der beteiligten  $\pi$ -Elektronen  
ist wichtig:

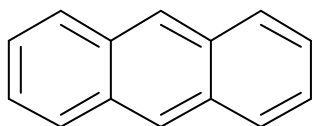
Hückel-Regel:  $4n + 2$

Naphthalin



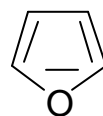
10  $\pi$ -Elektronen

Anthracen



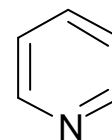
14  $\pi$ -Elektronen

Furan



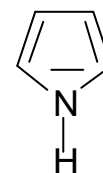
6  $\pi$ -Elektronen

Pyridin

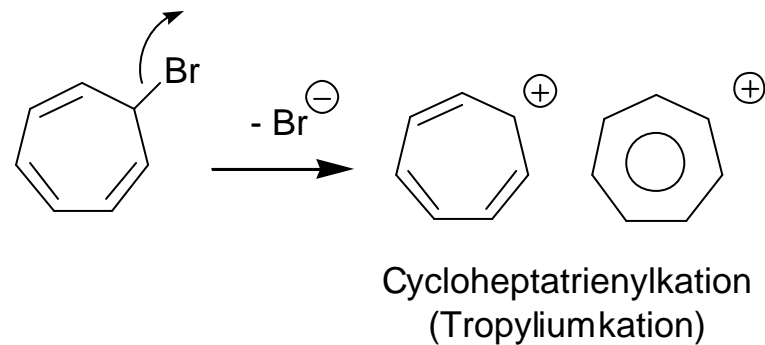
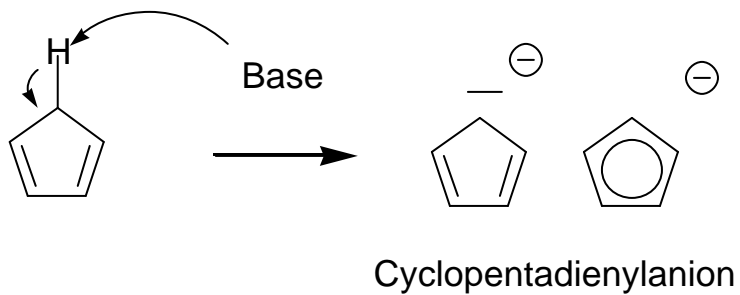


6  $\pi$ -Elektronen

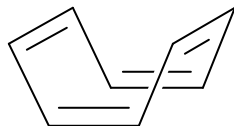
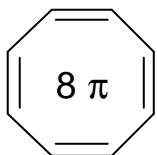
Pyrrol



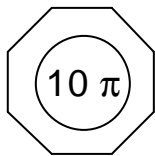
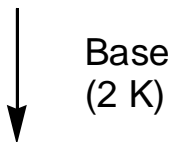
6  $\pi$ -Elektronen



Ein System mit  $4n$  p-Elektronen würde bei einer erzwungenen Planarität antiaromatisch.



Cyclooctatetraen ist gewinkelt



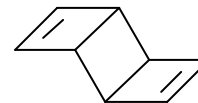
Das Dianion des COT ist mit seinen 10  $\pi$ -Elektronen wieder ein planarer Hückel-Aromat.



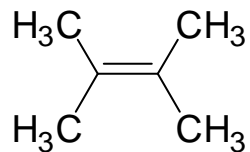
Cyclobutadien ist instabil



4 + 2 Cycloaddition

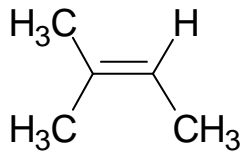


# Hyperkonjugation stabilisierende Wechselwirkung zwischen $\sigma$ und $\pi$ -Orbitalen



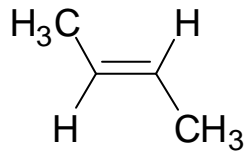
tetrasubstituiert

>



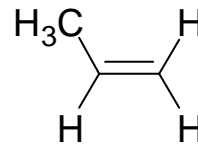
trisubstituiert

>



disubstituiert

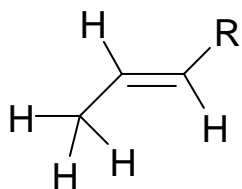
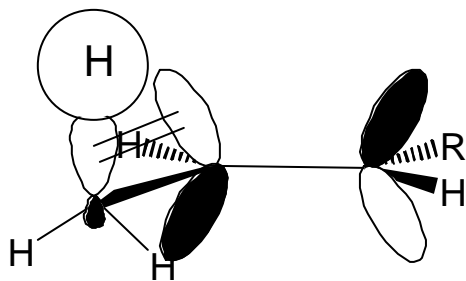
>



monosubstituiert

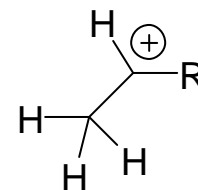
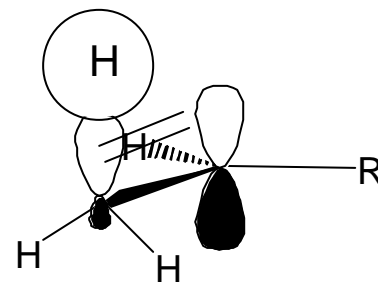
antibindendes  $\pi^*$

bindende  $\sigma$



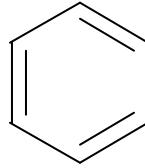
leeres p-Orbital

bindende  $\sigma$





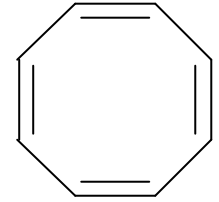
nicht-aromatisch



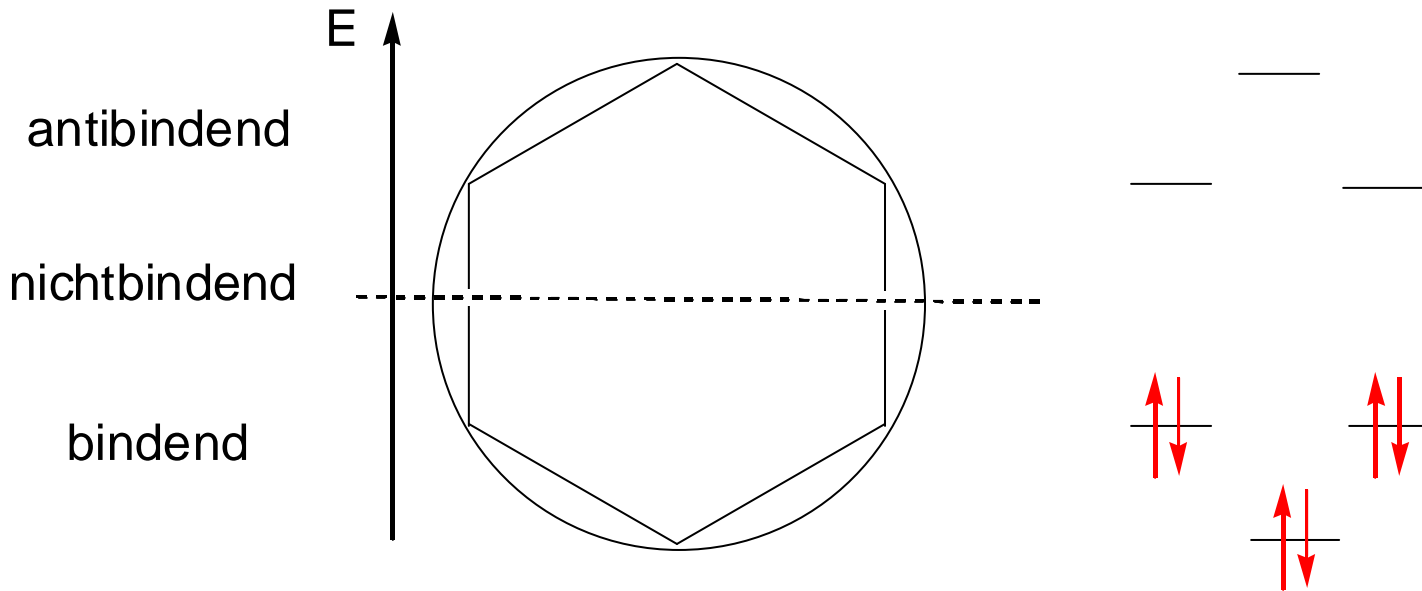
aromatisch

$6\pi$

Benzol



nicht-aromatisch

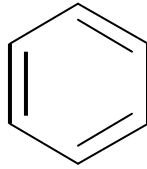




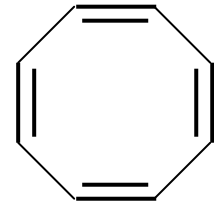


$4\pi$

nicht-aromatisch

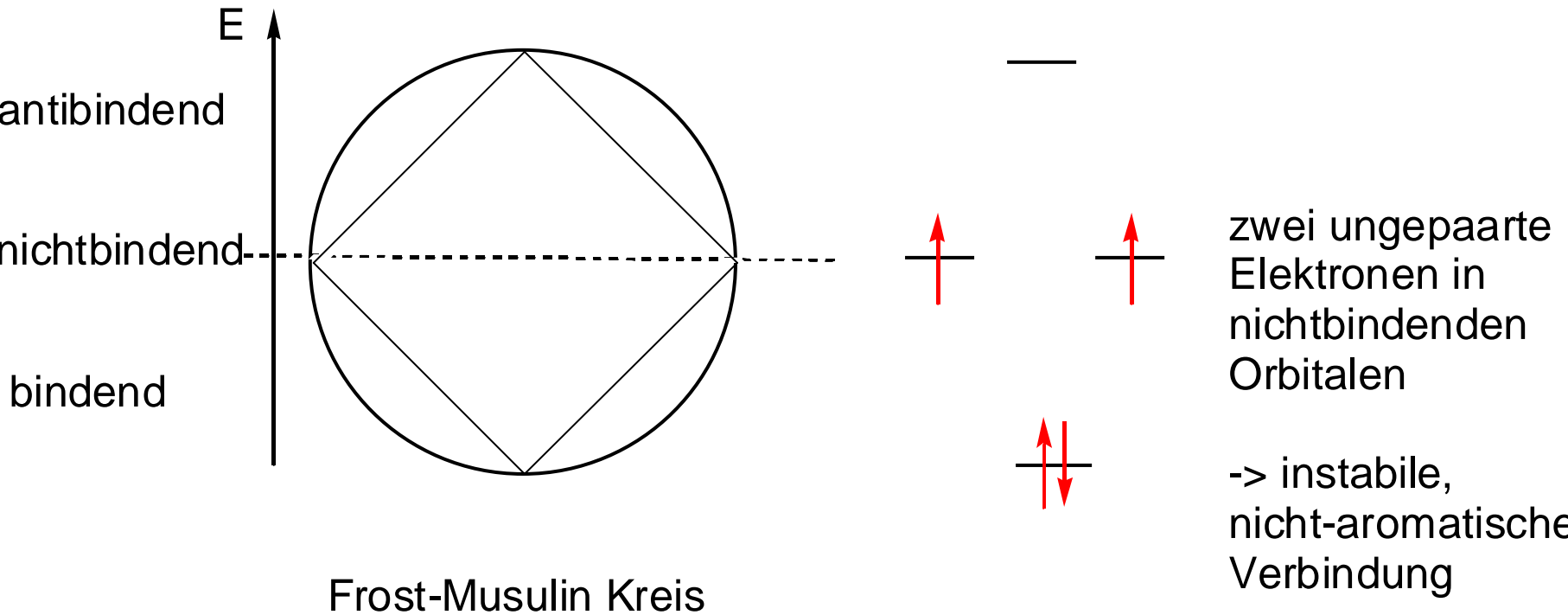


aromatisch



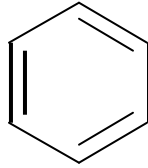
nicht-aromatisch

## Cyclobutadien

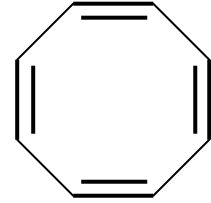




nicht-aromatisch



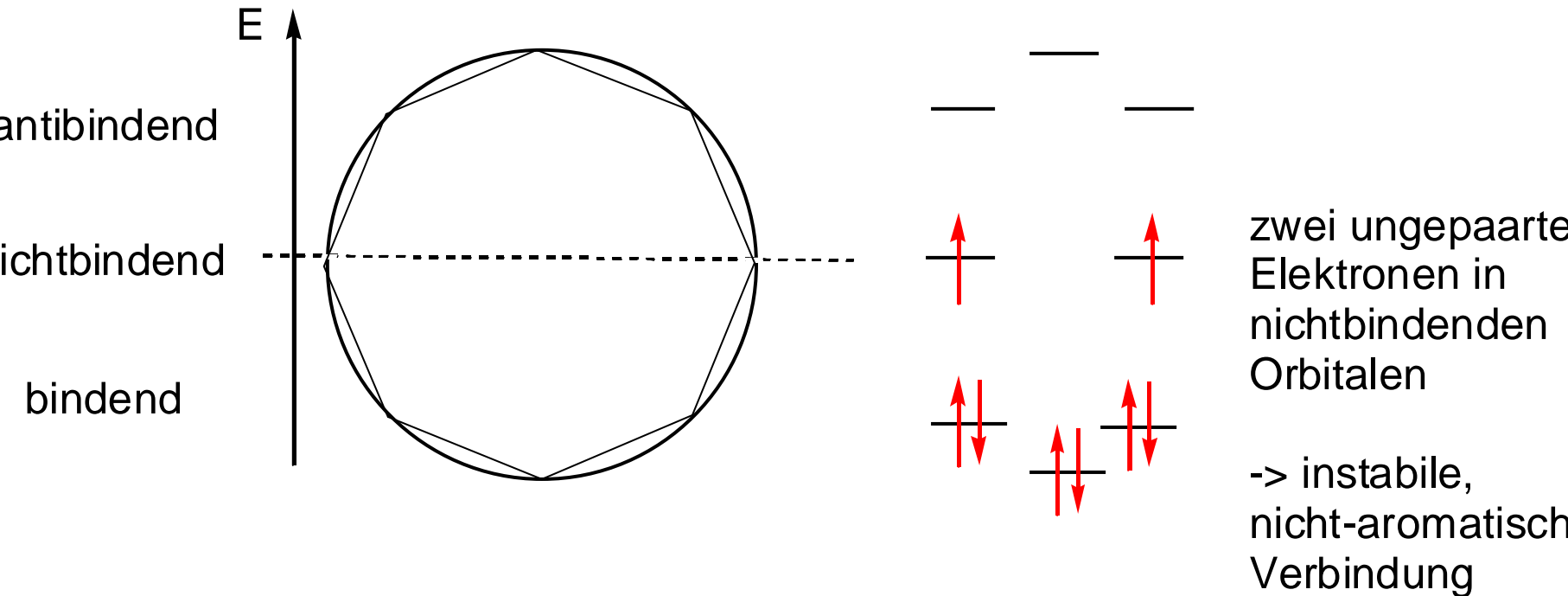
aromatisch



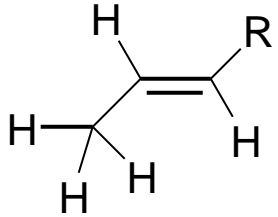
nicht-aromatisch

$8\pi$

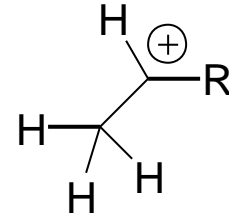
## Cyclooctatetraen



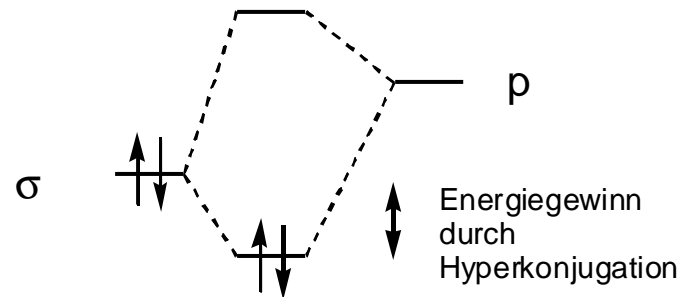
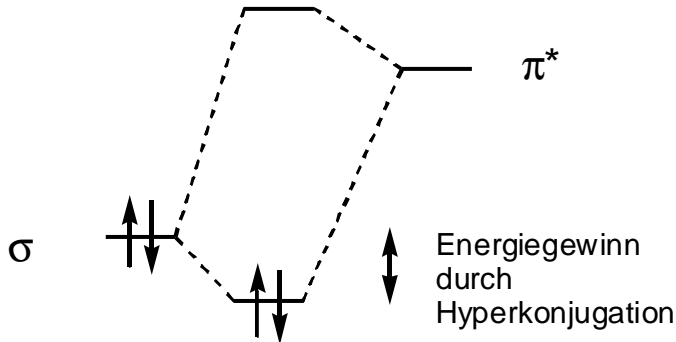
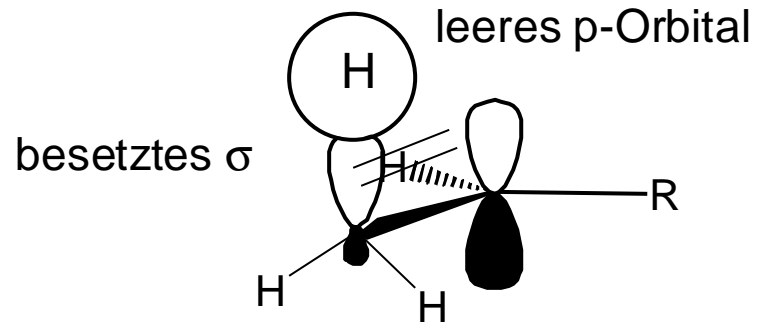
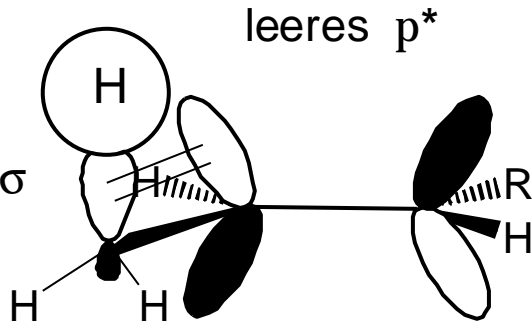
# s/p- Wechselwirkung: Hyperkonjugation



Eine zum  $\pi$  System einer Doppelbindung nicht-orthogonale CH-Bindung hat einen stabilisierenden Effekt.



Eine zum p-Orbital eines Carbokations nicht-orthogonale CH-Bindung hat einen stabilisierenden Effekt.



# Substrukturen: Funktionelle Gruppen

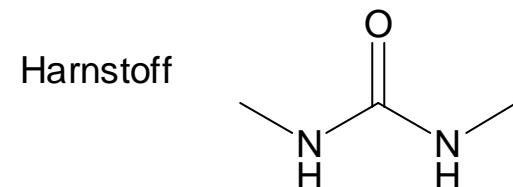
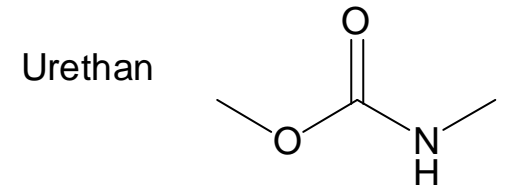
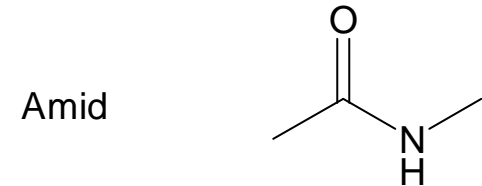
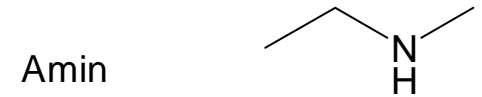
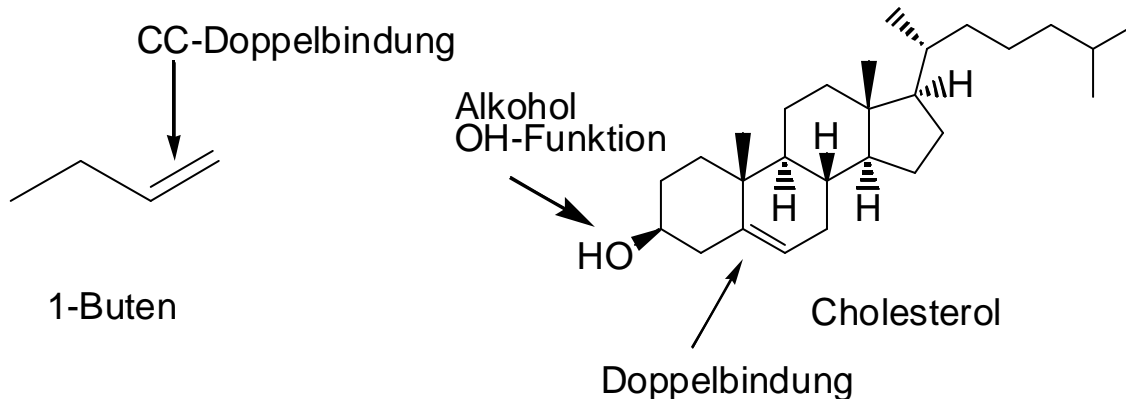
> 10.000.000 Organische Verbindungen

schwierig, alle auswendig zu lernen und mit umzugehen.

aber nur ca. 30 Familien von Verbindungen, jede mit einer charakteristischen funktionellen Gruppe.

Eine funktionelle Gruppe ist Teil eines größeren Moleküls. Sie wird aus Atomen oder einer Gruppe von Atomen mit einem charakteristischen, chemischen Verhalten gebildet.

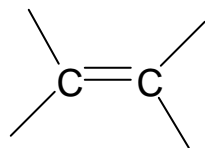
Jede funktionelle Gruppe hat eine charakteristische Reaktivität.



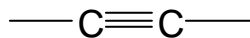
# Substrukturen: Funktionelle Gruppen

Keine funktionelle Gruppen, nur  $sp^3$  verknüpfte C-Atome: Alkane

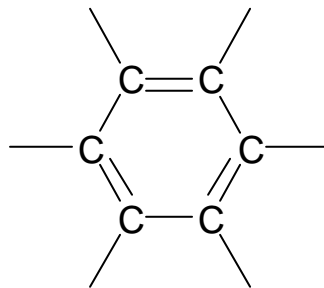
Funktionelle Gruppen mit C-C-Mehrfachbindungen:



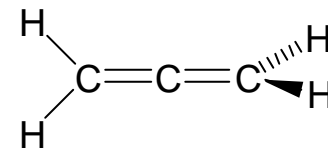
Alkene  
(Olefin)



Alkyne

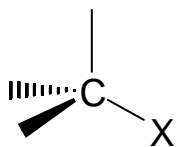


Arene  
(Aromatische Ringe)

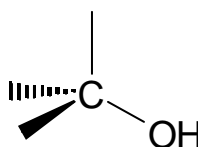


Allene  
(Cumulen)

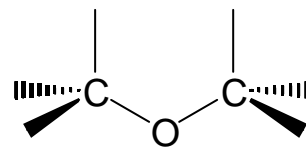
Funktionelle Gruppen mit C einfachgebunden zu einem elektronegeren Atom



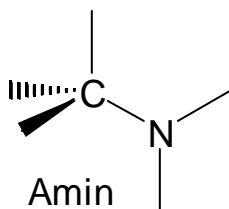
Alkylhalogenid  
Halogenalkan  
 $X = F, Cl, Br, I$



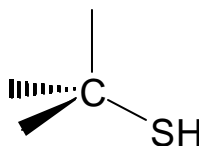
Alkohol



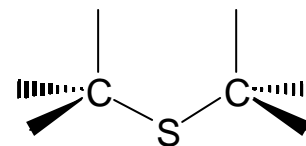
Ether



Amin



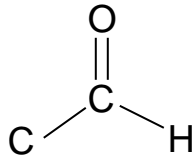
Thiol  
(Mercaptan)



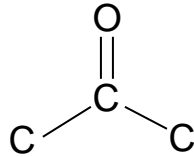
Thioether

# Substrukturen: Funktionelle Gruppen

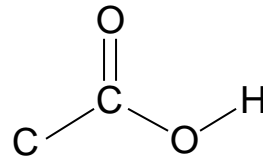
Funktionelle Gruppen mit einer C-O Doppelbindung (Carbonylgruppe)



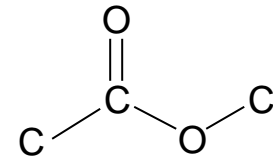
Aldehyd



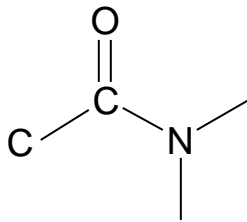
Keton



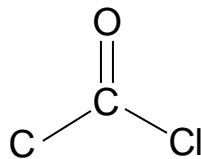
Carbonsäure



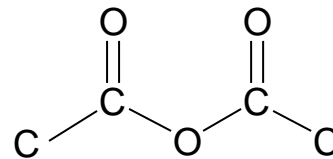
Ester  
(Carbonsäureester)



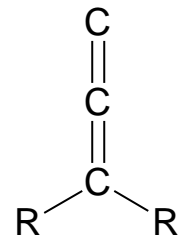
Amid  
(Carbonsäureamid)



Säurechlorid  
(Carbonsäurechlorid)



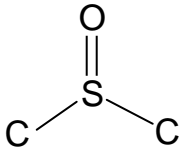
Anhydrid  
(Carbonsäureanhydrid)



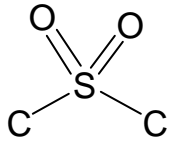
Keten

# Substrukturen: Funktionelle Gruppen

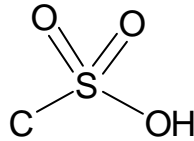
## Funktionelle Gruppen mit S und N



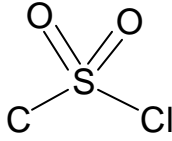
Sulfoxid



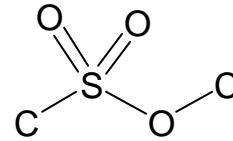
Sulfon



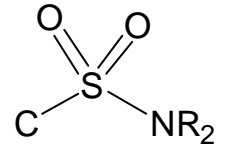
Sulfonsäure



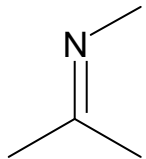
Sulfonsäurechlorid



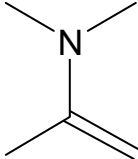
Sulfonsäureester



Sulfonsäureamid



Imin



Enamin



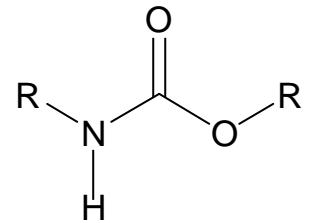
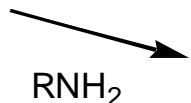
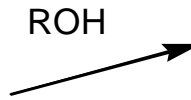
Nitril



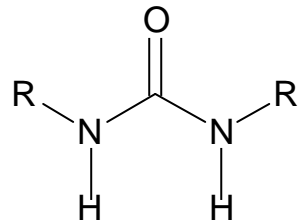
Isonitril



Isocyanat



Urethan



Hamstoff

# Struktur -> Molekulare Eigenschaften

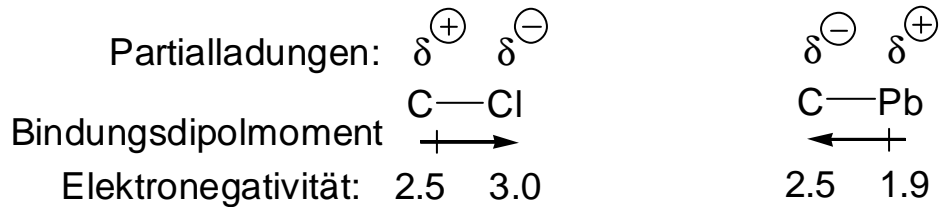
OC 3.1  
Koert

Ladungsverteilungen innerhalb des Moleküls

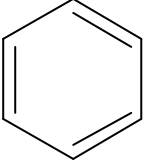
Polar kovalente Bindungen

Elektronegativität    Dipolmoment

1) Elektronegativitäts-Werte aus dem Perioden-System -> Bindungspolarität



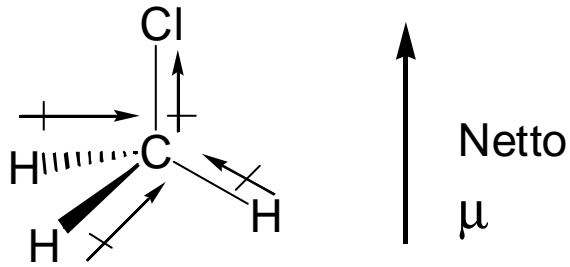
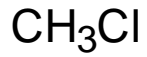
2) Vektorielle Summe der Bindungsdipolmomente ergibt das Molekül-Dipolmoment

Verbindung:	NaCl	$\text{H}_3\text{C} \text{---} \text{N}^{\oplus} \begin{matrix} \text{=O} \\ \diagdown \\ \text{O}^{\ominus} \end{matrix}$	CH <sub>3</sub> Cl	H <sub>2</sub> O	CH <sub>3</sub> OH	NH <sub>3</sub>	
Dipolmoment (D):	9.0	3,46	1,87	1,85	1,70	1,47	BF <sub>3</sub> CH <sub>4</sub> 0

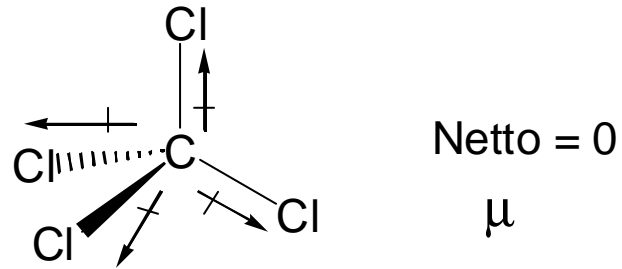


# Moleküldipolmoment

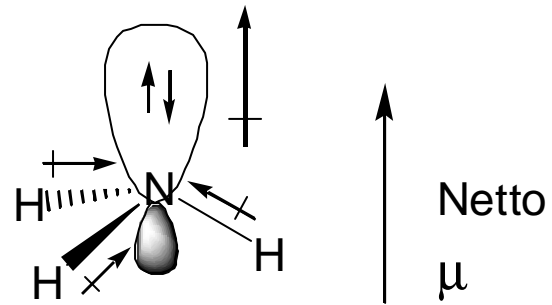
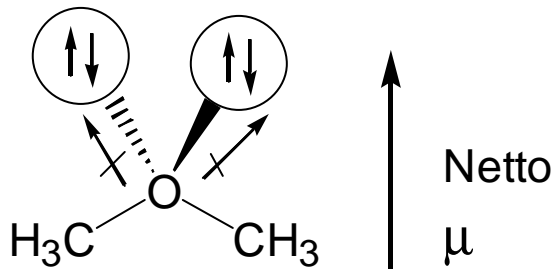
OC 3.2  
Koert



$\mu = 1.87 \text{ D}$  (Debye)



$\mu = 0 \text{ D}$  (Debye)



$\mu = 1.47 \text{ D}$  (Debye)

# Siedepunkt - Löslichkeit

OC 3.3  
Koert

Siedepunkt:

Einfluß von H-Brücken

und anderen nichtkovalenten

Wechselwirkungen

$\text{H}_3\text{COH}$  Sdp.  $65^\circ\text{C}$  H-Brücken!

$\text{H}_3\text{CCl}$  Sdp.  $-24^\circ\text{C}$

Löslichkeit: Similia similibus solvuntur

Charakterisierung von Lösungsmittel.

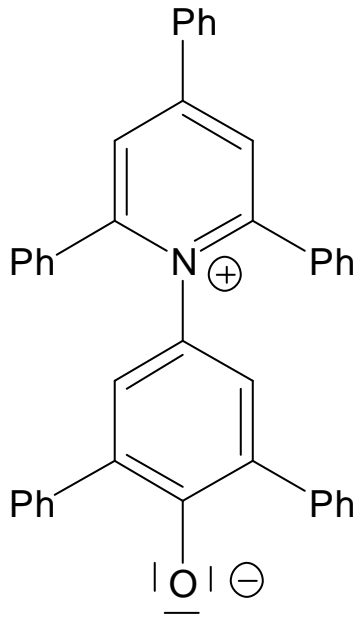
$\epsilon_T$  = Dielektrizitätskonstante

$\mu$  = Dipolmoment

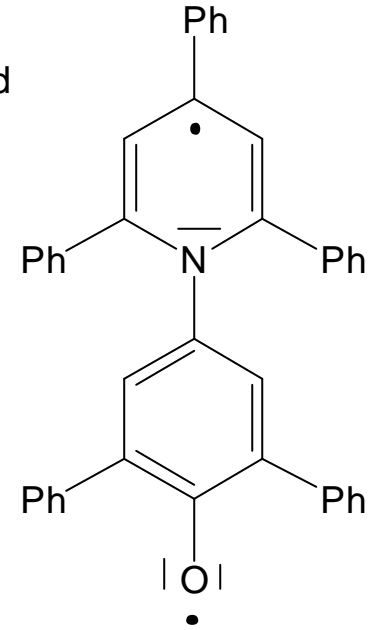
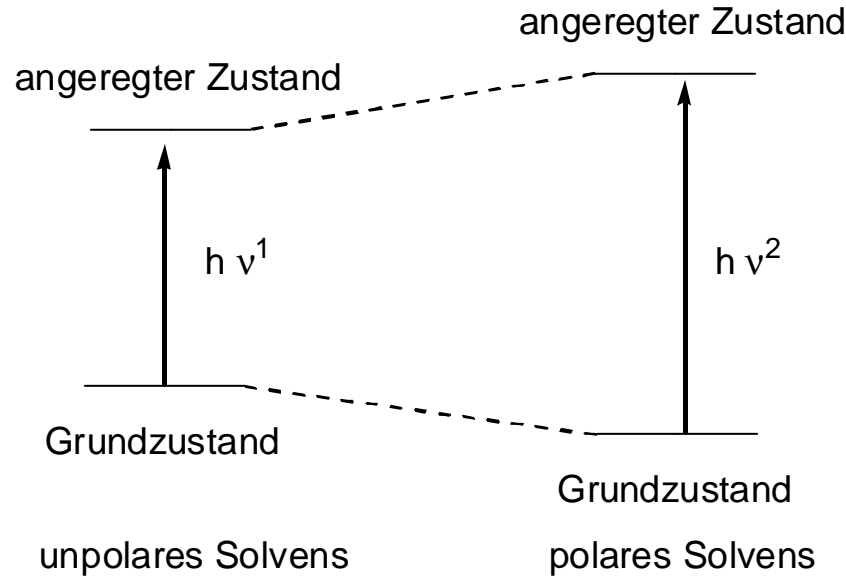
$E_T$  = empirischer Polaritätsparameter

# Polarität von Lösungsmitteln

Prof. Reichardts solvatochromer Farbstoff als Basis für den empirischen Polaritätsparameter  $E_T$ .



polarer Grundzustand



angeregter Zustand

größere Frequenz = kleinere Wellenlänge = energiereicheres Licht



MeOH (rot,  $\lambda_{\max}$  515 nm)

EtOH (violett,  $\lambda_{\max}$  550 nm)

MeOMe (grün,  $\lambda_{\max}$  677 nm)



zunehmende Lösungsmittelpolarität

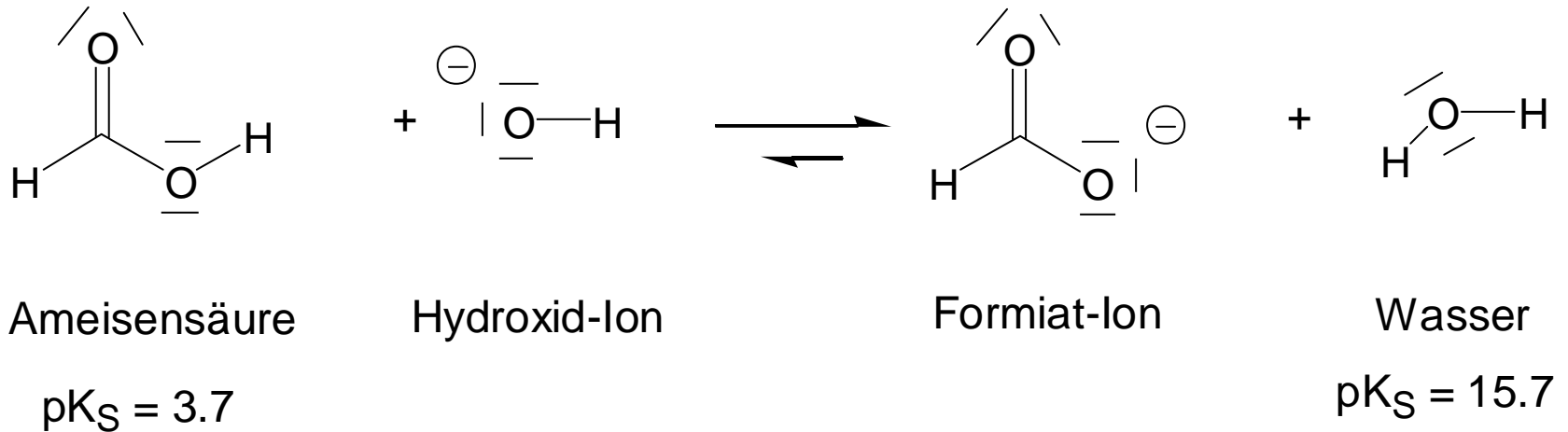
# Wichtige Lösungsmittel in der Organischen Chemie

	protisch polar			aprotisch polar			
	H <sub>2</sub> O	MeOH	EtOH	MeCN	DMSO	DMF	Aceton
E <sub>T</sub>	63.1	55.5	51.9	46.7	45	43.8	42,2
ε	78	32.7	24.5	38	47	37	21
	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>	AcOEt	THF	Et <sub>2</sub> O	Benzol	Hexan
E <sub>T</sub>	41.1	39.1	38.1	37.4	34.6	34.5	30.9
ε	8.9	4.8	6.0	7.6	4.3	2.3	1.0
	mäßig polar					unpolar	

# Säure-Base-Eigenschaften

OC 3.6  
Koert



Vorhersage von Protonen-Transfer:



Eine Säure wird Protonen an die konjugierte Base einer Säure mit höherem  $pK_S$ -Wert abgeben.

Im Gegensatz dazu wird eine konjugierte Base Protonen von einer Säure mit kleinerem  $pK_S$ -Wert aufnehmen.

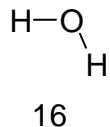
# Säure-Base-Eigenschaften

	Säure	Name	pK <sub>S</sub>	Base	Name	
<p><b>Schwächere Säure</b></p>  <p><b>Stärkere Säure</b></p>	CH <sub>3</sub> CH <sub>2</sub> OH	Ethanol	16.0	CH <sub>3</sub> CH <sub>2</sub> O <sup>⊖</sup>	Ethanolat-Ion	<p><b>Stärkere Base</b></p>  <p><b>Schwächere Base</b></p>
	H <sub>2</sub> O	Wasser	15.7	HO <sup>⊖</sup>	Hydroxid-Ion	
	HCN	Blausäure	9.2	CN <sup>⊖</sup>	Cyanid-Ion	
	CH <sub>3</sub> COOH	Essigsäure	4.7	CH <sub>3</sub> COO <sup>⊖</sup>	Acetat-Ion	
	HF	Fluorwasserstoff	3.2	F <sup>⊖</sup>	Fluorid-Ion	
	HNO <sub>3</sub>	Salpetersäure	-1,3	NO <sub>3</sub> <sup>⊖</sup>	Nitrat-Ion	
	HCl	Salzsäure	-7.0	Cl <sup>⊖</sup>	Chlorid-Ion	

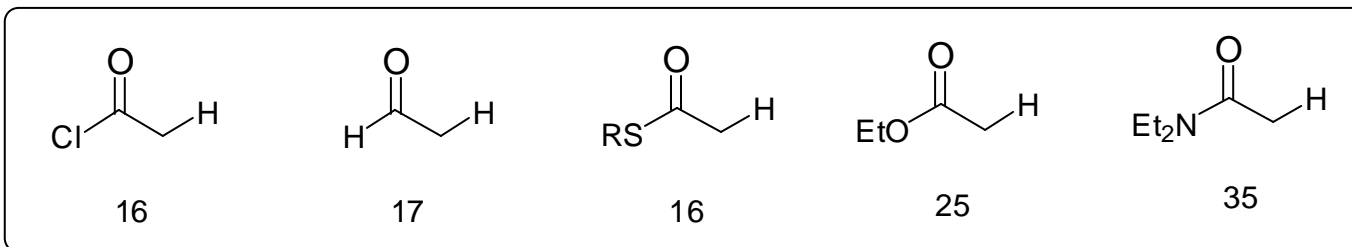
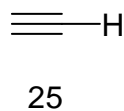
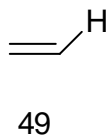
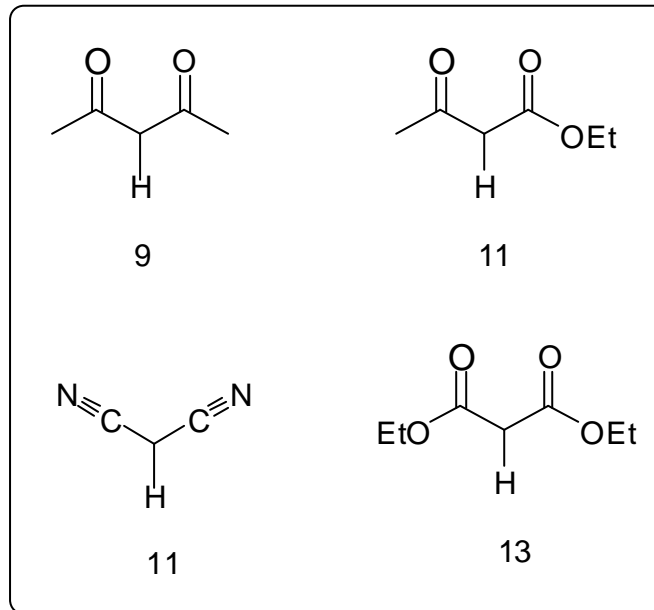
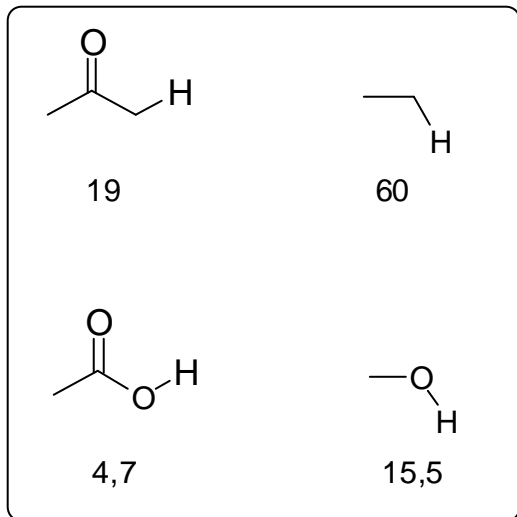
# Aciditäts-Konstanten

OC 3.8  
Koert

pK<sub>a</sub>



Stabilität der verbleibenden  
negativen Ladung  
ist entscheidend!

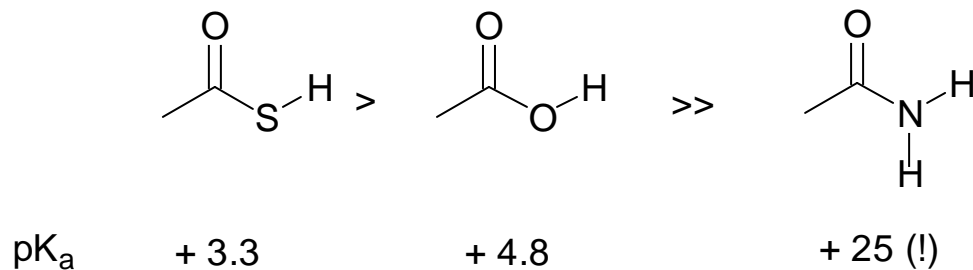
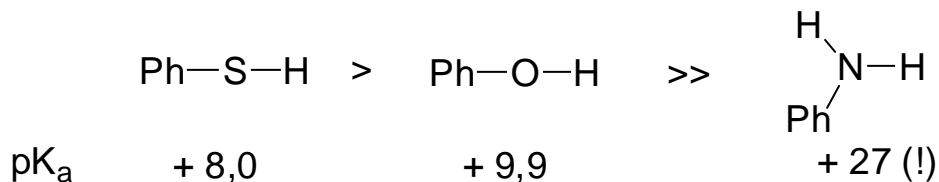
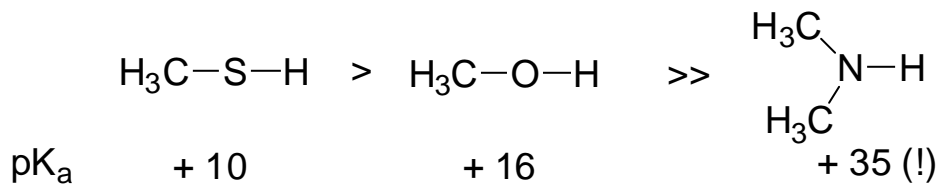
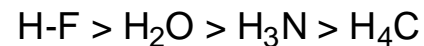


# Aciditäts-Konstanten

OC 3.9  
Koert

pK<sub>a</sub>

Bei X-H Verbindungen nimmt mit steigender Elektronegativität von X die Acidität zu.  
S kann negative Ladung besser delokalisieren.

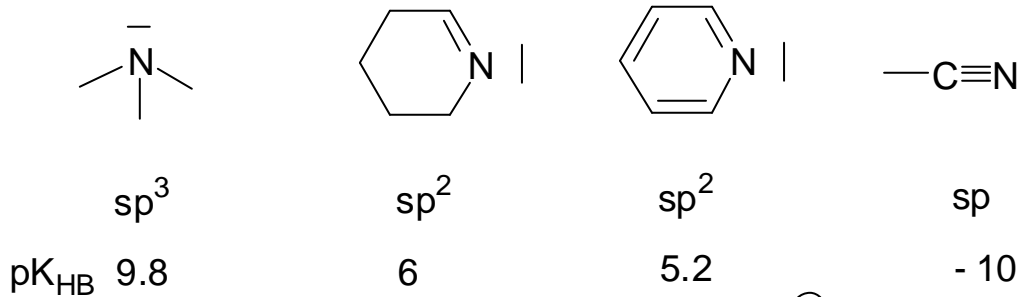




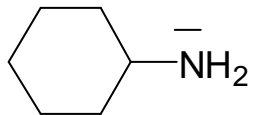
# Faktoren, die die Basizität von Aminen beeinflussen

OC 3.10  
Koert

← zunehmende Basizität

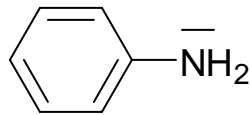


geringerer  
s-Charakter am N  
-> höhere Basizität



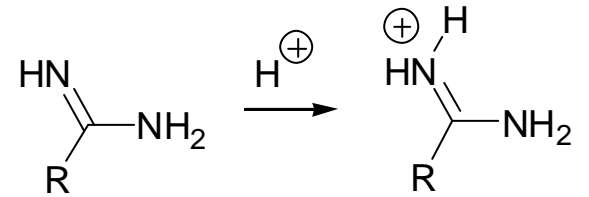
$pK_{HB} \ 11$

basischer als



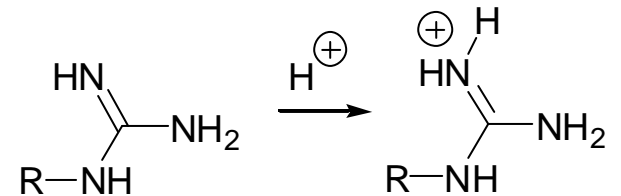
$pK_{HB} \ 4.6$

e-Paar ist über den  
 $\pi$ -Aromat delokalisiert



Amidin  $pK_{HB} \ 12.5$

Amidinium



Guanidin  $pK_{HB} \ 13$

Guanidinium

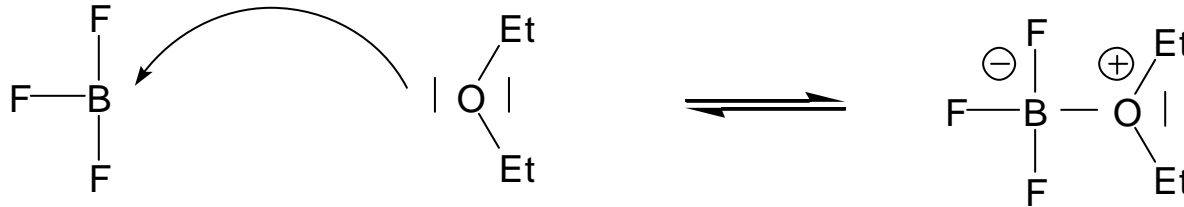
## Azidität

## Basizität

G. N. Lewis:

Lewis Säure = Elektronenpaar-Akzeptor

Lewis Base = Elektronenpaar-Donator



**Lewis Säure**

**Lewis Base**

Lewis Addukt

"Komplex"

Elektronenpaar-Lücke  
freies-p-Orbital

nicht-bindendes e-Paar  
einsames e-Paar

**Elektrophil**

**Nukleophil**

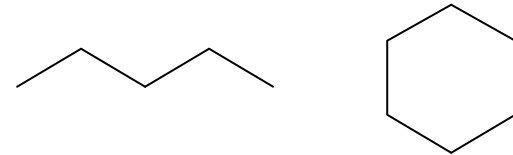
"gebogener Pfeil" - Formalismus: von der Elektronenquelle zum Elektronenabfluß!

Dieser Pfeil beschreibt die Bewegung von Elektronen (Bindungselektronen, Bindungen), nicht von Atomen!

# Alkane

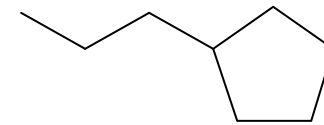
Gesättigte Kohlenwasserstoffe  
(bezüglich der experimentellen Aufnahme von H<sub>2</sub>)

Konnektivität:



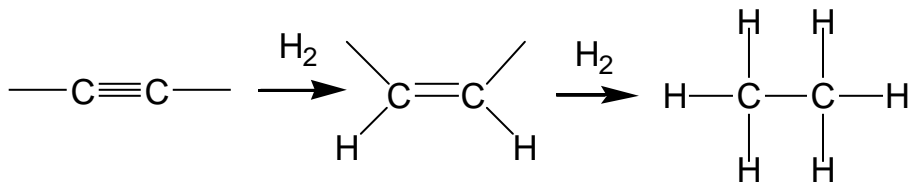
Kette

Ring



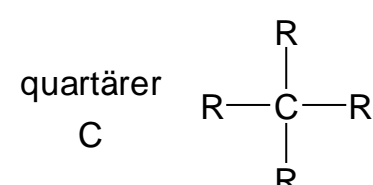
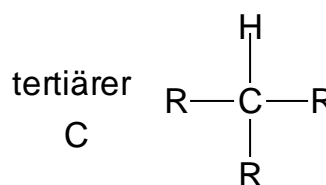
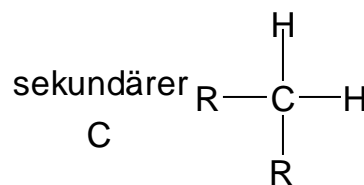
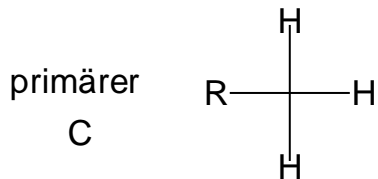
Kette + Ring

Alkin -> Alken -> Alkan



Nomenklatur:

Zahl der C's:	1	2	3	4	5	6	7	8	9	10
Alkan	Methan	Ethan	Propan	Butan	Pentan	Hexan	Heptan	Octan	Nonan	Decan
Alkyl	Methyl	Ethyl	Propyl	Butyl	Pentyl	Hexyl	Heptyl	Octyl	Nonyl	Decyl

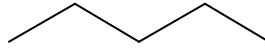
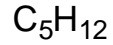


# Alkane

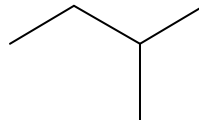
OC 5.2  
Koert

Gleiche Summenformel, aber unterschiedliche Konnektivität -> Konstitutions-Isomere

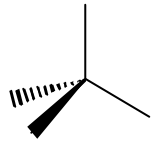
Unterschiedliches C-Gerüst:



n-Pentan  
(Unverzweigte Kette)

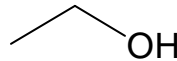
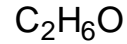


2-Methylbutan  
(Verzweigte Kette)

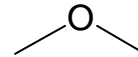


2,2-Dimethylpropan

Unterschiedliche funktionelle  
Gruppen:

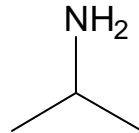
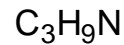


Ethanol

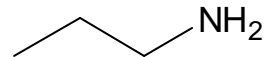


Dimethylether

Unterschiedliche Positionen  
der funktionellen Gruppen:



Isopropylamin



n-Propylamin

# Alkane

OC 5.3  
Koert

Nomenklatur

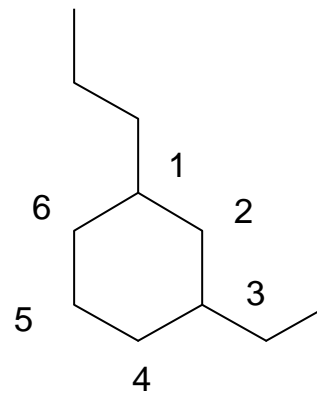
Trivialnamen  
wissenschaftliche Namen  
eindeutig -> IUPAC

Prefix - Stamm - Suffix

Wo sind welche  
Substituenten?

Wieviele  
C-Atome?

Welche ist die Haupt-  
funktionelle Gruppe?

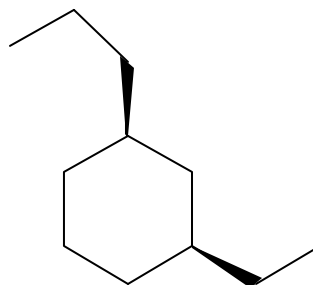


3-Ethyl-1-propylcyclohexan

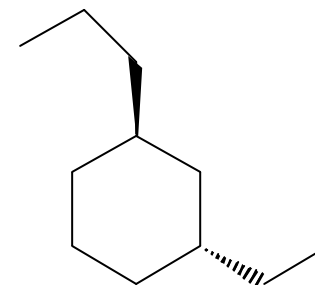
alphabetische Reihenfolge der Prefixe

Gleiche Summenformel, gleiche Konnektivität, aber unterschiedliche Strukturen -> Stereoisomere

cis-trans Isomerie bei  
Cycloalkanen



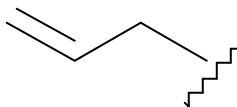
*cis*-3-Ethyl-1-propylcyclohexan



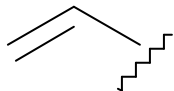
*trans*-3-Ethyl-1-propylcyclohexan

# Nomenklatur

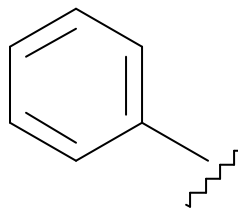
OC 5.3 B  
Koert



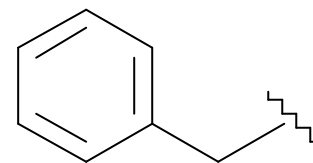
Allyl



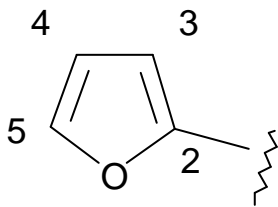
Vinyl



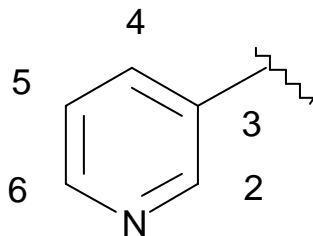
Phenyl



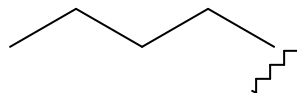
Benzyl



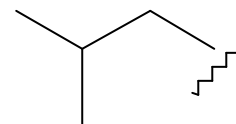
2-Furyl



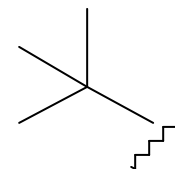
3-Pyridyl



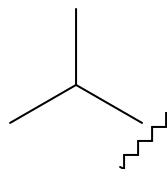
n-Butyl



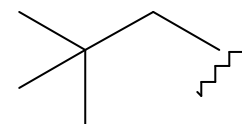
iso-Butyl



tert-Butyl



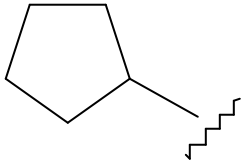
iso-Propyl



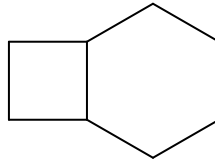
Neopentyl

# Nomenklatur

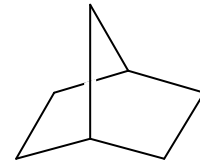
OC 5.3 C  
Koert



Cyclopentyl

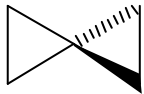


Bicyclo [4.2.0] octan

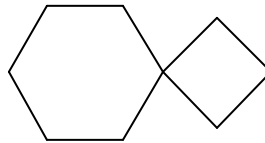


Bicyclo [2.2.1] heptan

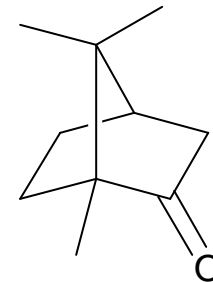
Norbornan



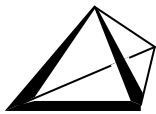
Spiropentane



Spiro [3.5] nonan



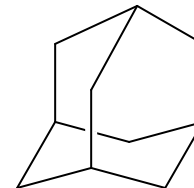
Campher



Tetrahedran  $C_4H_4$



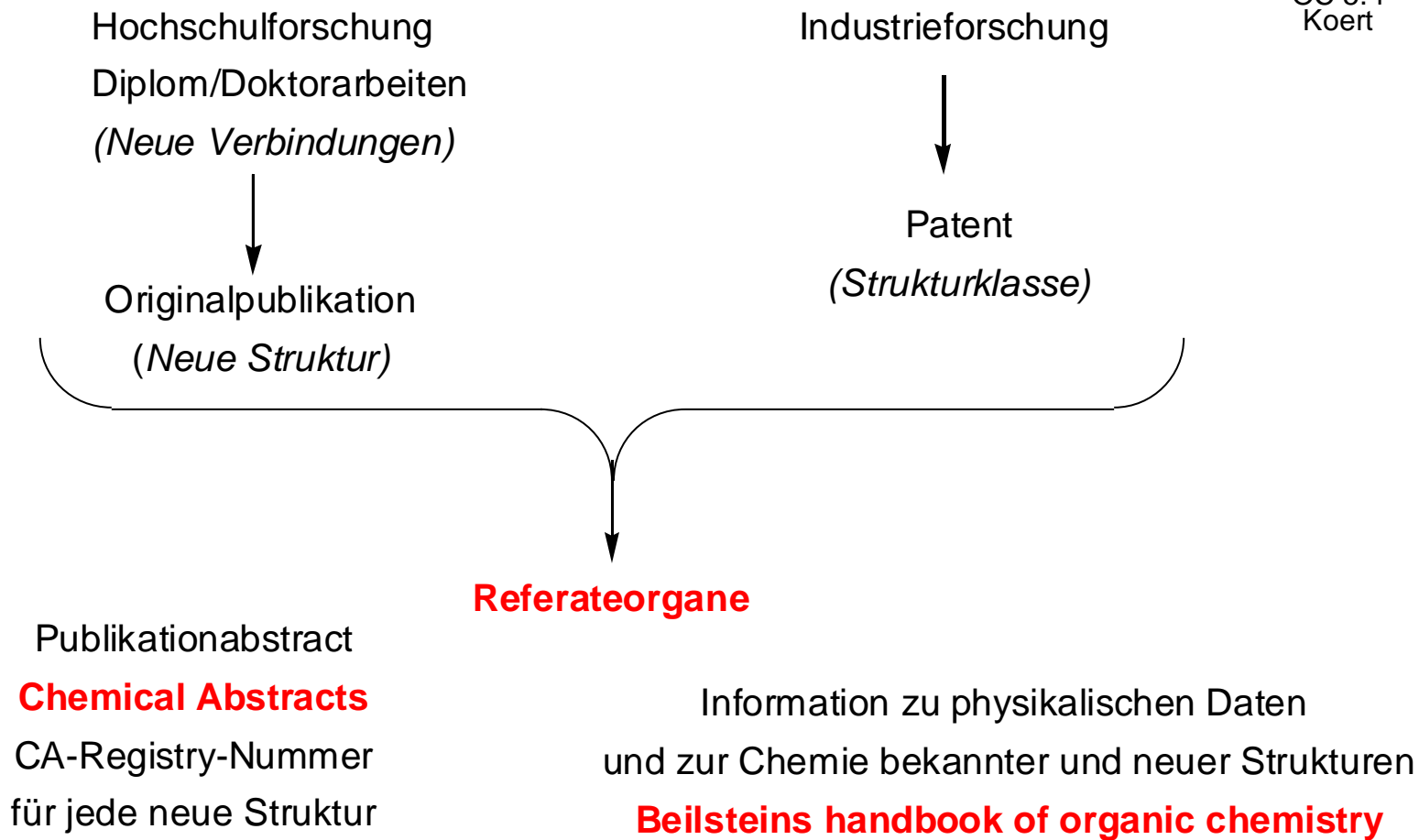
Prisman



Adamantan

# Dokumentation und Wiedergewinnung von chemischem Wissen

OC 5.4  
Koert





**Chemical Abstracts**

**Sci-Finder**  
**CAS-Online**

Alle Strukturen im **Registry-File**  
Struktursuche  
Substruktursuche

Alle abstracts im **CA-File**  
(bibliographische Daten)

**Beilsteins handbook of organic chemistry**

**Crossfire X-Fire**

in-house-Datenbank  
Struktur/Substruktursuche

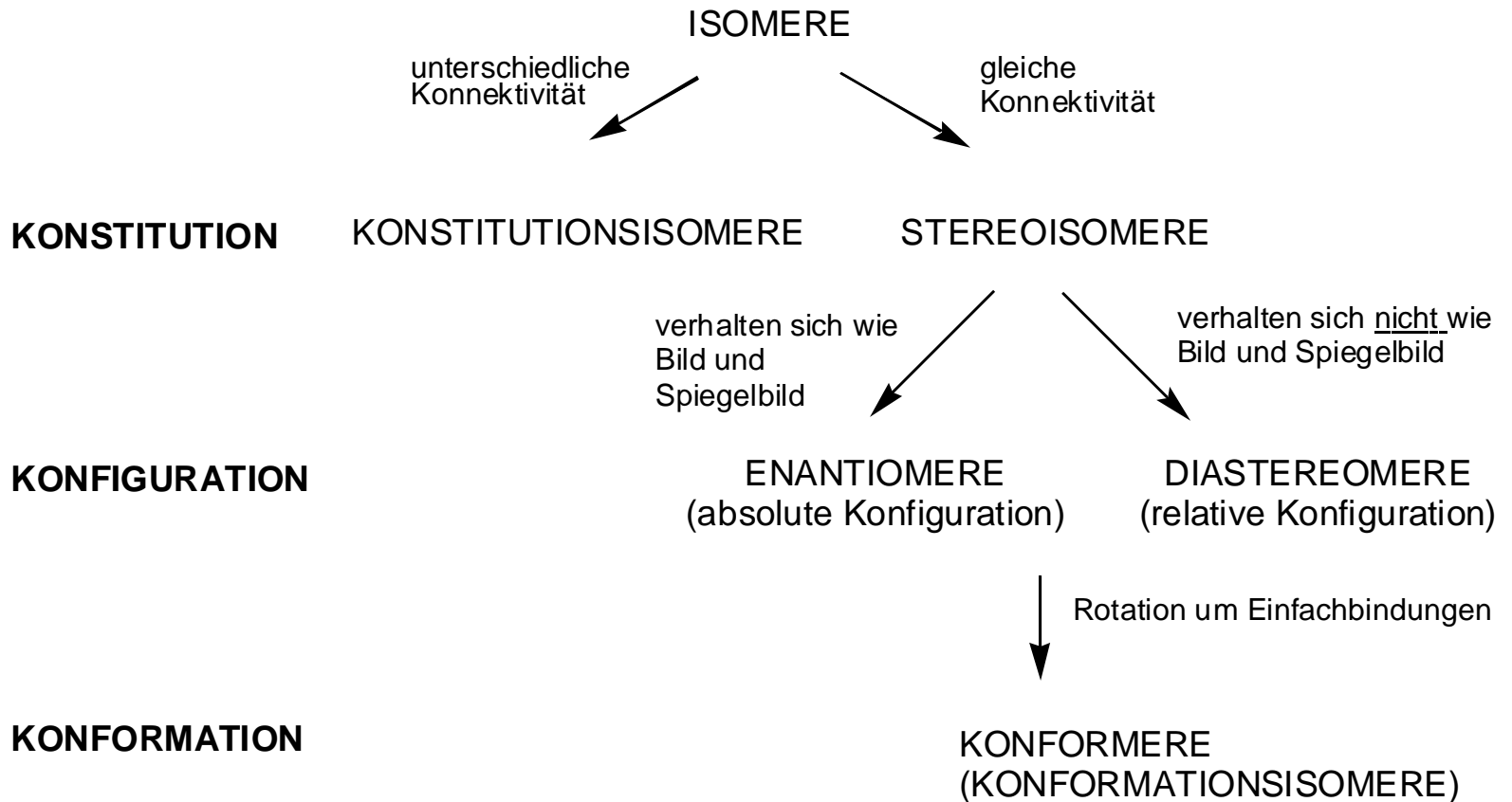
**Alle Röntgenstrukturen:**

Cambridge structure database (CSD)

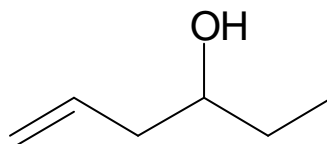
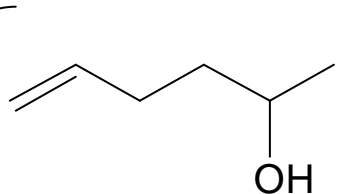
Brookhaven Protein data base

in house Datenbank  
Struktur/Substruktursuche

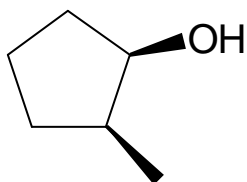
Chemie in drei Dimensionen: Stereochemie



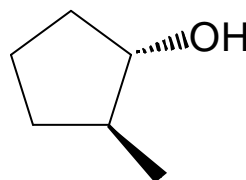
$C_6H_{12}O$



Konstitutionsisomere  
(Konstitution)

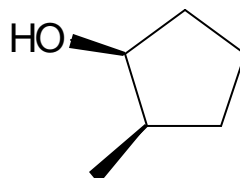
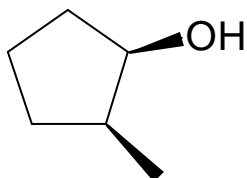


cis



trans

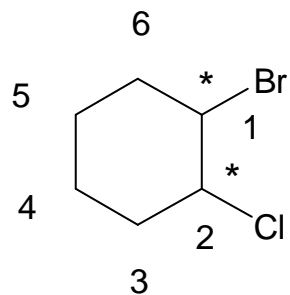
Diastereomere  
(Unterschiedliche relative  
Konfiguration)  
verhalten sich nicht  
wie Bild und  
Spiegelbild



Enantiomere  
(Gleiche relative aber  
unterschiedliche absolute  
Konfiguration)  
verhalten sich wie Bild  
und Spiegelbild

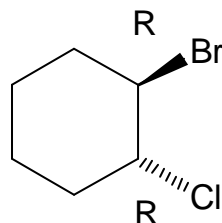
# Stereochemie

OC 6.3  
Koert

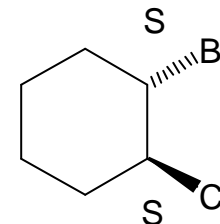


1-Brom-2-chlor-cyclohexan

Relative Konfiguration:  
trans

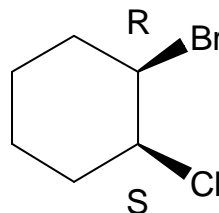


(1R,2R)-1-Brom-2-chlor-cyclohexan

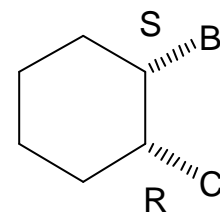


(1S,2S)-1-Brom-2-chlor-cyclohexan

Relative Konfiguration:  
cis



(1R,2S)-1-Brom-2-chlor-cyclohexan



(1S,2R)-1-Brom-2-chlor-cyclohexan

2 Stereozentren  $\longrightarrow$

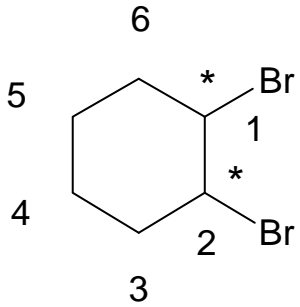
formale Maximalzahl an  
Stereoisomeren:  $2^2 = 4$

CIP-Nomenklatur für die absolute Konfiguration

formale Maximalzahl an  
Stereoisomeren =  $2^n$

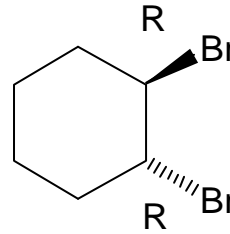
n = Anzahl der Stereozentren oder stereochemisch aktiven Doppelbindungen

# Stereochemie

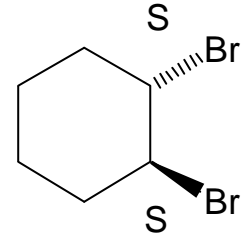


1,2-Dibromcyclohexan

Relative Konfiguration:  
trans

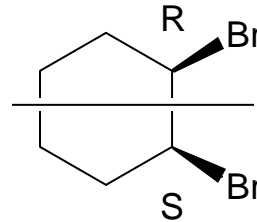


(1R,2R)-1,2-Dibromcyclohexan



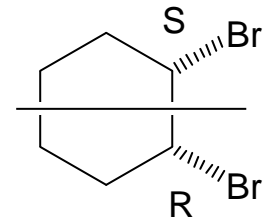
(1S,2S)-1,2-Dibromcyclohexan

Relative Konfiguration:  
cis



(1R,2S)-1,2-Dibromcyclohexan

identisch



(1S,2R)-1,2-Dibromcyclohexan

2 Stereozentren



formale Maximalzahl an  
Stereoisomeren:  $2^2 = 4$

Spiegelebene  
innerhalb des Moleküls



Meso-Verbindung

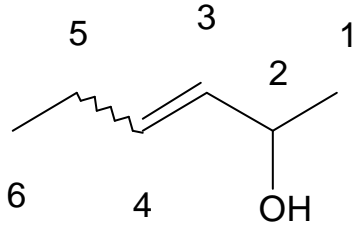
reale Maximalzahl: 3

eine meso-Verbindung (cis), ein Enantiomerenpaar (trans)

# Stereochemie

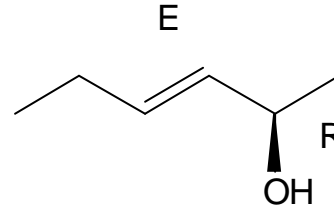
OC 6.5  
Koert

Stereochemisch aktive Doppelbindungen  
E,Z-Nomenklatur

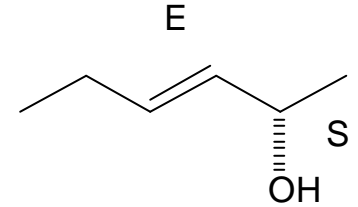


Hex-3-en-2-ol

Relative Konfiguration:  
E

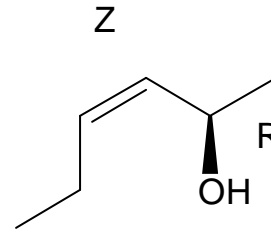


(2R,3E)-Hex-3-en-2-ol

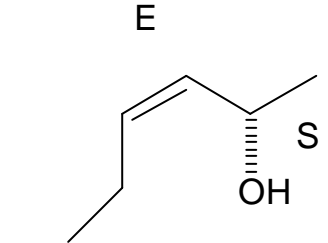


(2S,3E)-Hex-3-en-2-ol

Relative Konfiguration:  
Z



(2R,3Z)-Hex-3-en-2-ol



(2S,3Z)-Hex-3-en-2-ol

1 Stereozentrum →  
1 stereochemisch  
aktive Doppelbindung

formale Maximalzahl an  
Stereoisomeren:  $2^2 = 4$

reale Maximalzahl: 4

ein Enantiomerenpaar (E), ein Enantiomerenpaar (Z)

# Stereochemie, Chiralität, Symmetrie

OC 6.6  
Koert

Chiralität: Objekte, die sich in Bild und Spiegelbild unterscheiden, nennt man chiral. (Lord Kelvin)

Auch Molekülstrukturen können chiral sein. Das Molekül kommt dann in Form zweier Enantiomere vor.

Enantiomorphe Objekte

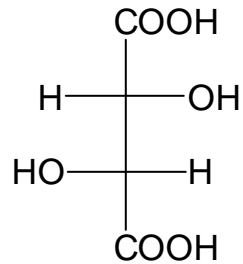
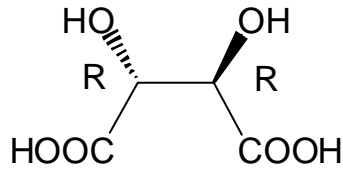
Dreieck mit 3 verschiedenen Ecken in 2D

Tetraeder mit vier verschiedenen Substituenten in 3 D.

Zusammenhang zwischen Symmetrie und Chiralität:

Genauer Gebrauch des Begriffs Symmetrie -> Symmetrieoperationen,  
Symmetrieelemente,  
Symmetriepunktgruppen

## Chiralität - Weinsäure

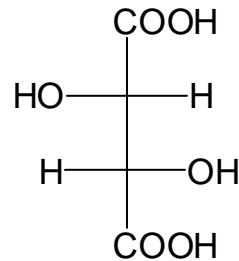
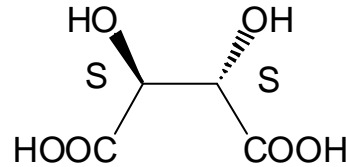


(+)-L-Weinsäure

$$[\alpha]_D^{20} = + 12.0$$

Schmp. 168-170 °C

natürlich vorkommende Fruchtsäure



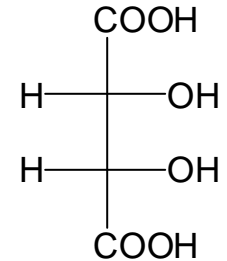
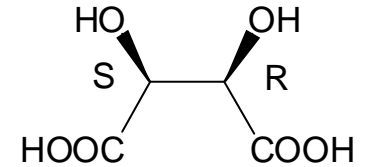
(-)-D-Weinsäure

$$[\alpha]_D^{20} = - 12.0$$

Schmp. 168-170 °C

Traubensäure: Racemat

Trennung der enantiomorphen Kristalle des Natrium-Ammoniumsalzes durch L. Pasteur 1848  
1874 van't Hoff und Le BEL Tetraedermodell



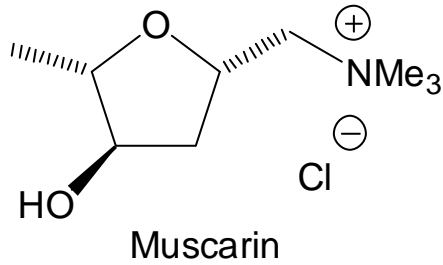
meso-Weinsäure

$$[\alpha]_D^{20} = 0$$

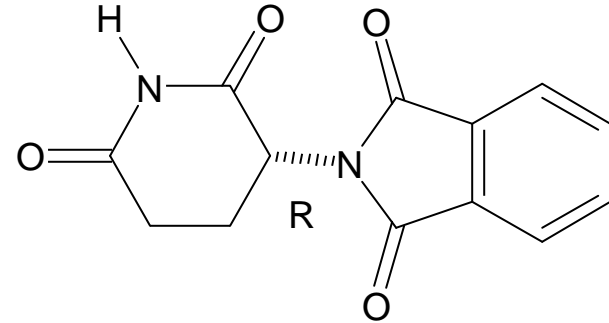
Schmp. 146-148 °C



## Eutomer und Distomer



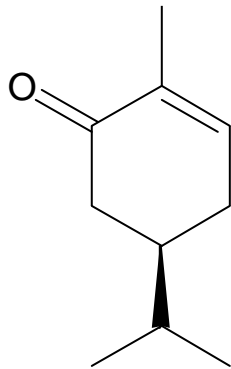
Dorothy Sayers "The document in the case"



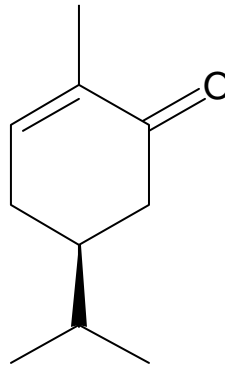
Thalidomid

R = Eutomer (Schlafmittel)  
S = Distomer (teratogen)

1960 Contergan



R-(-)-Carvon  
Pfefferminz



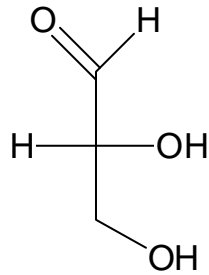
S-(+)-Carvon  
Kümmel

# Stereochemie und Zucker

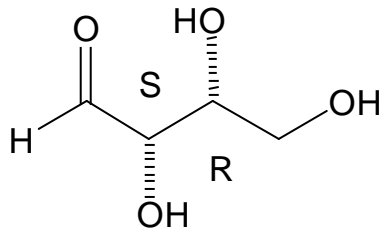
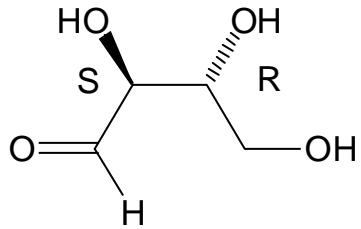
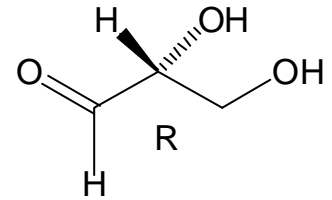
OC 7.1  
Koert

Konfiguration der Aldosen

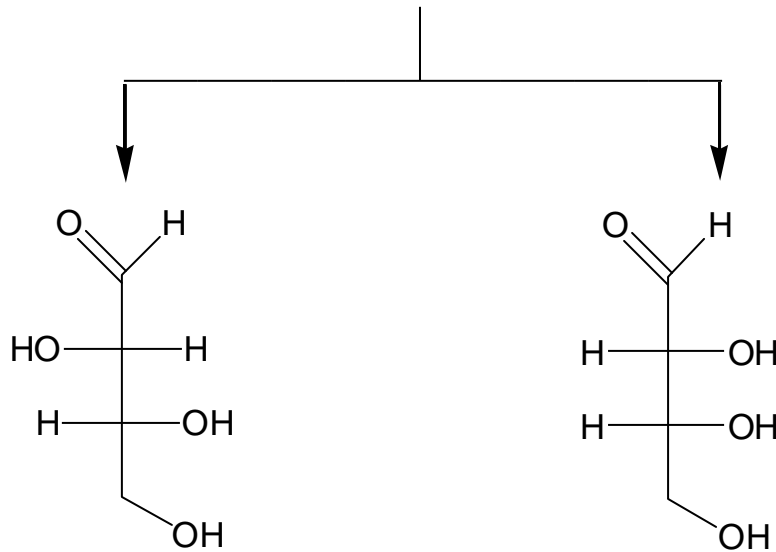
Fischer-Projektion



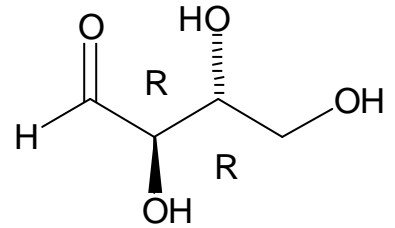
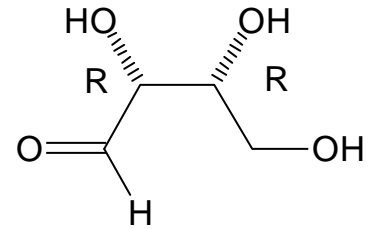
D-Glycerinaldehyd



D-Threose

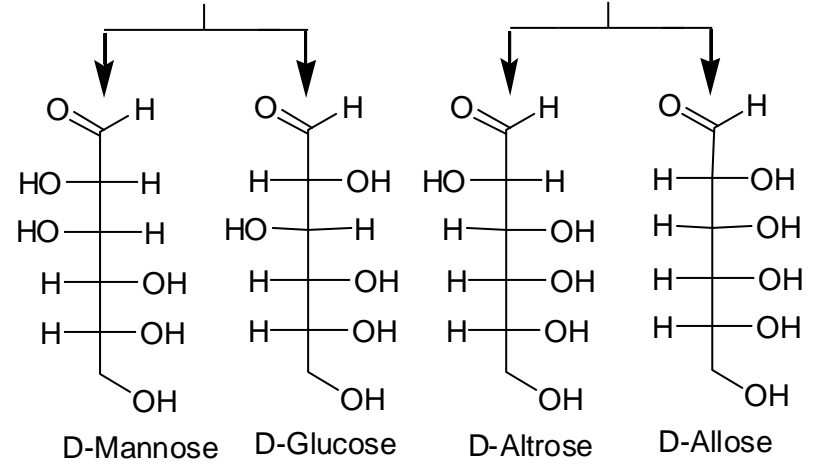
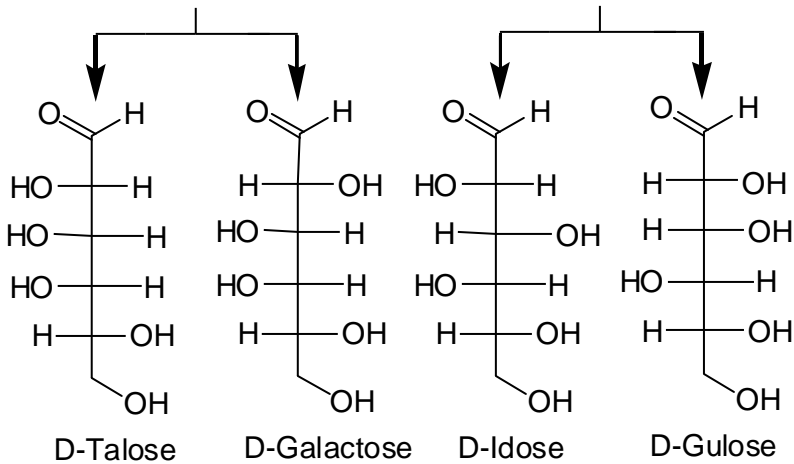
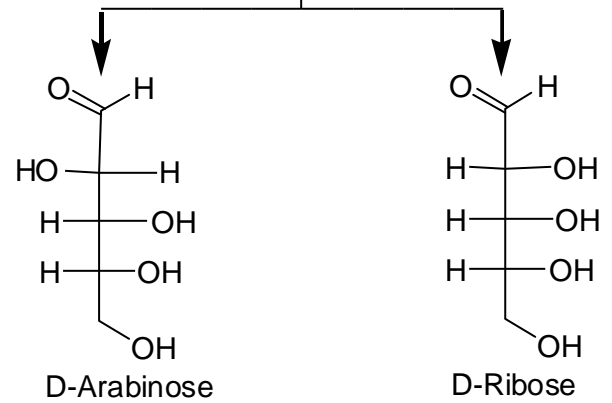
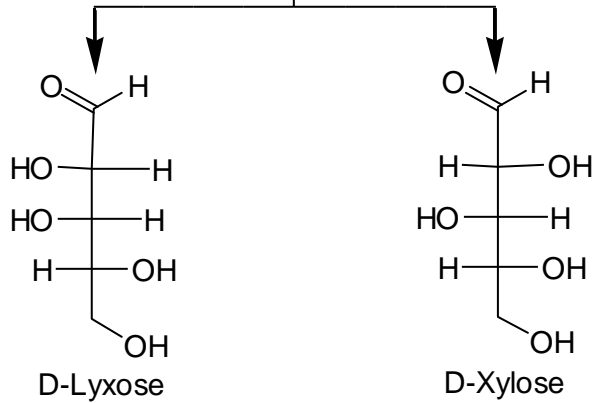
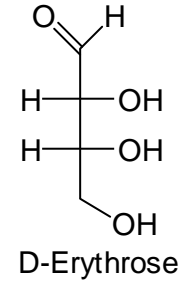
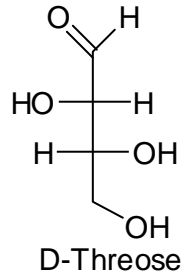


D-Erythrose

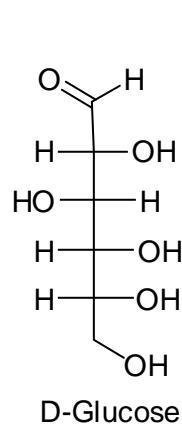


# Stereochemie und Zucker

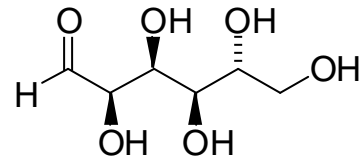
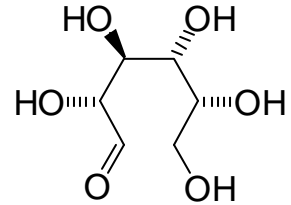
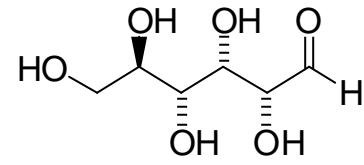
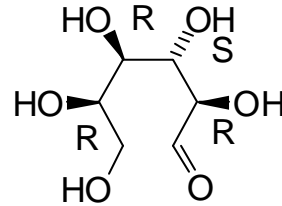
OC 7.2  
Koert



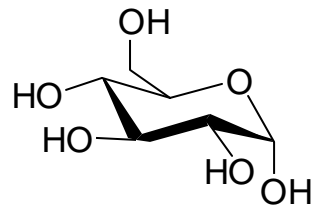
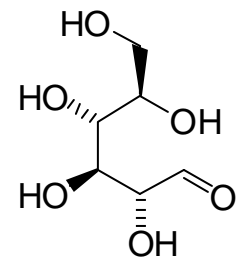
## Aldosen



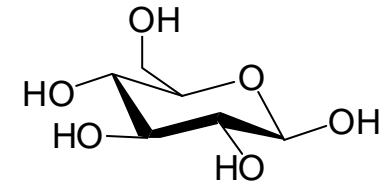
Fischer Projektion



Halbacetalschluß zur  
pyranoiden Form

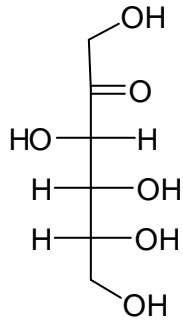


$\alpha$ -Anomer



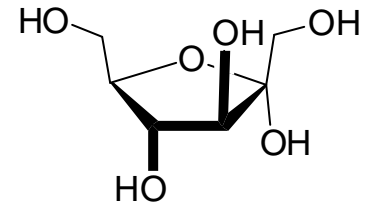
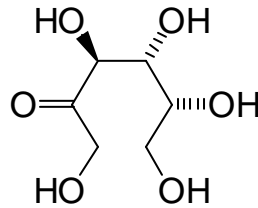
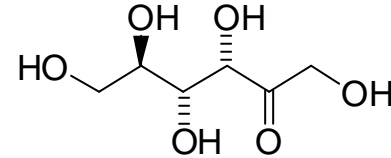
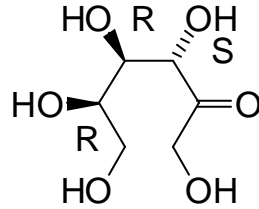
$\beta$ -Anomer

## Ketosen



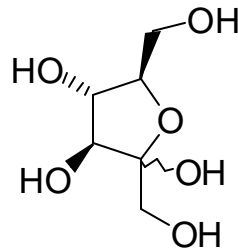
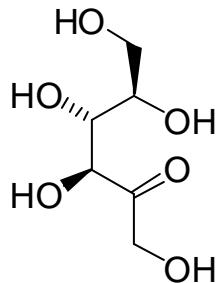
D-Fructose

Fischer Projektion

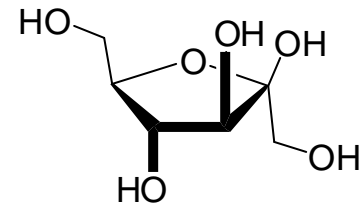


$\alpha$ -Anomer

Halbacetalschluß zur  
furanoiden Form

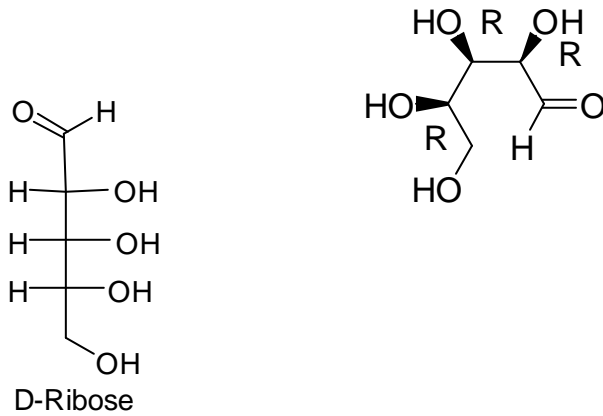


D-Fructofuranose

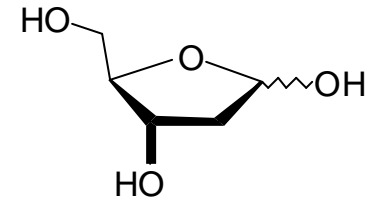
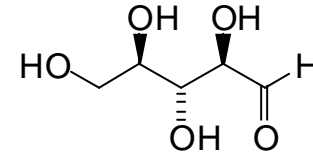
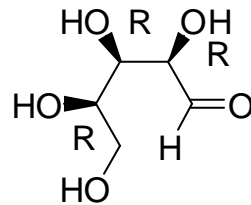


$\beta$ -Anomer

## Aldopentosen

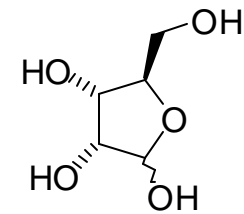
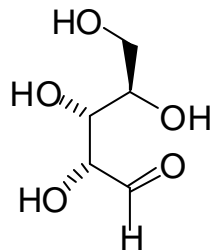


Fischer Projektion

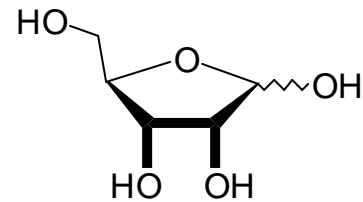


2-Desoxy-D-Ribofuranose

Halbacetalschluß zur  
furanoiden Form



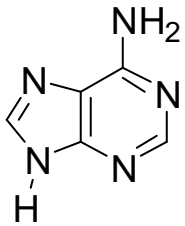
D-Ribofuranose



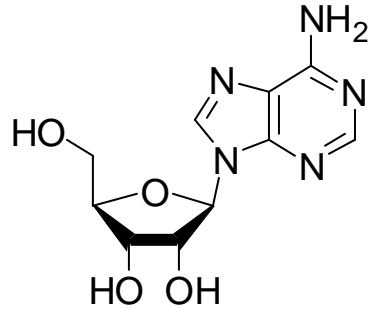
# Nukleoside

OC 7.6  
Koert

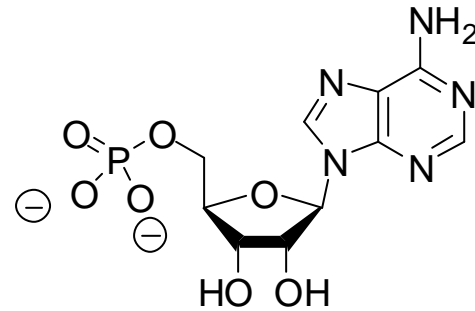
## Purin-Basen



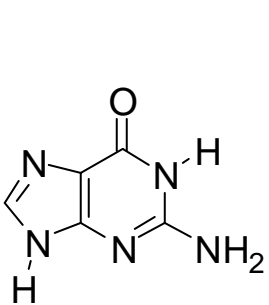
Adenin



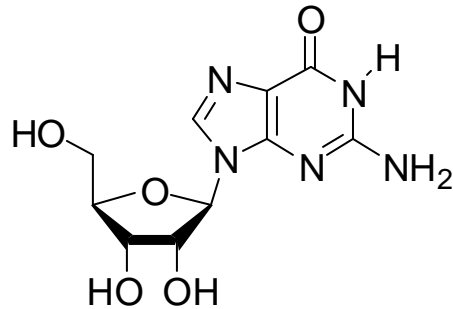
Adenosin



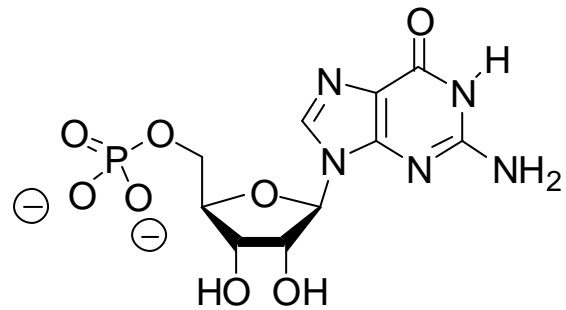
Adenosinmonophosphat



Guanin



Guanosin

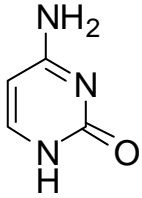


Guanosinmonophosphat

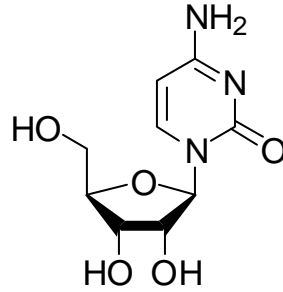
# Nukleoside

## Pyrimidin-Basen

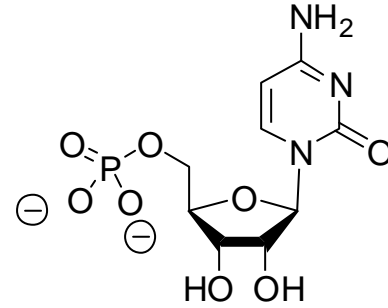
OC 7.7  
Koert



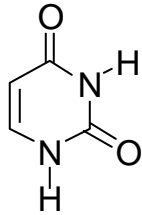
Cytosin



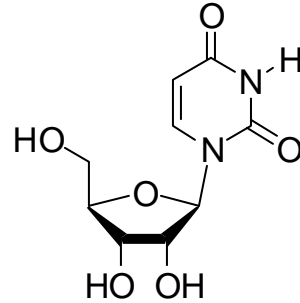
Cytidin



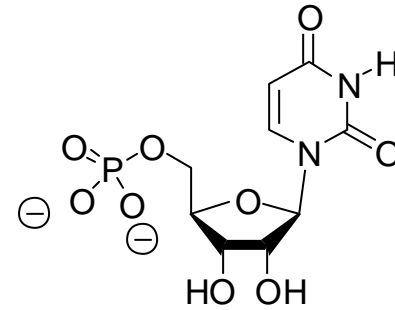
Cytidinmonophosphat



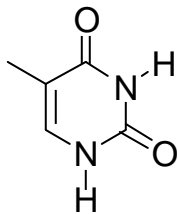
Uracil



Uridin

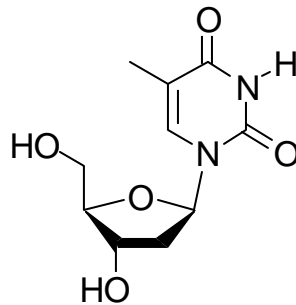


Uridinmonophosphat



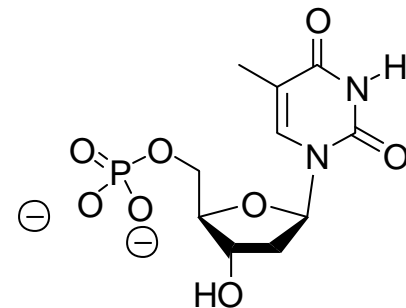
Thymin

Thymin



Thymidin

Thymidin

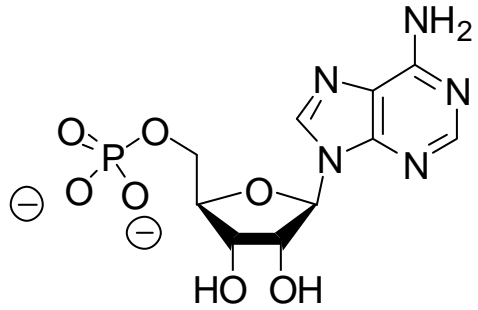


Thymidinmonophosphat

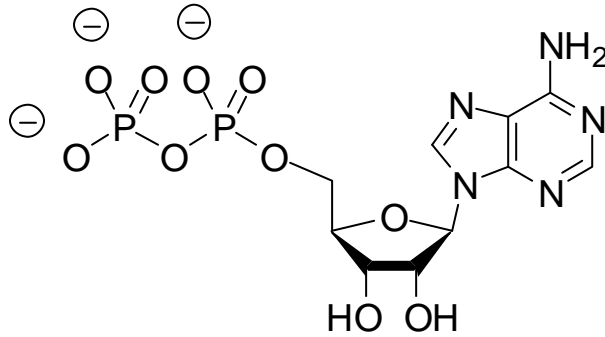


# Nukleotide

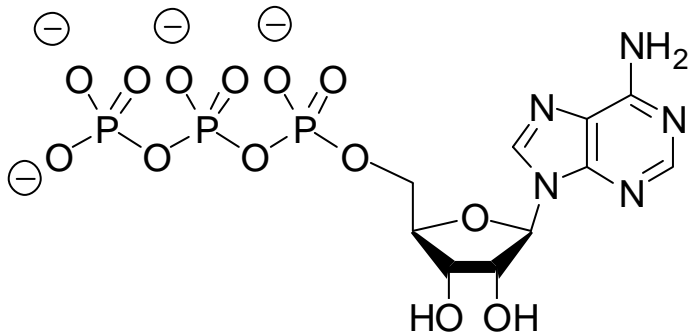
OC 7.8  
Koert



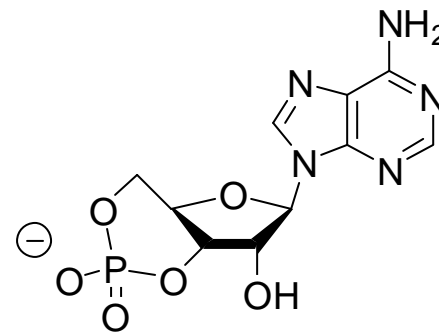
Adenosinmonophosphat AMP



Adenosindiphosphat ADP



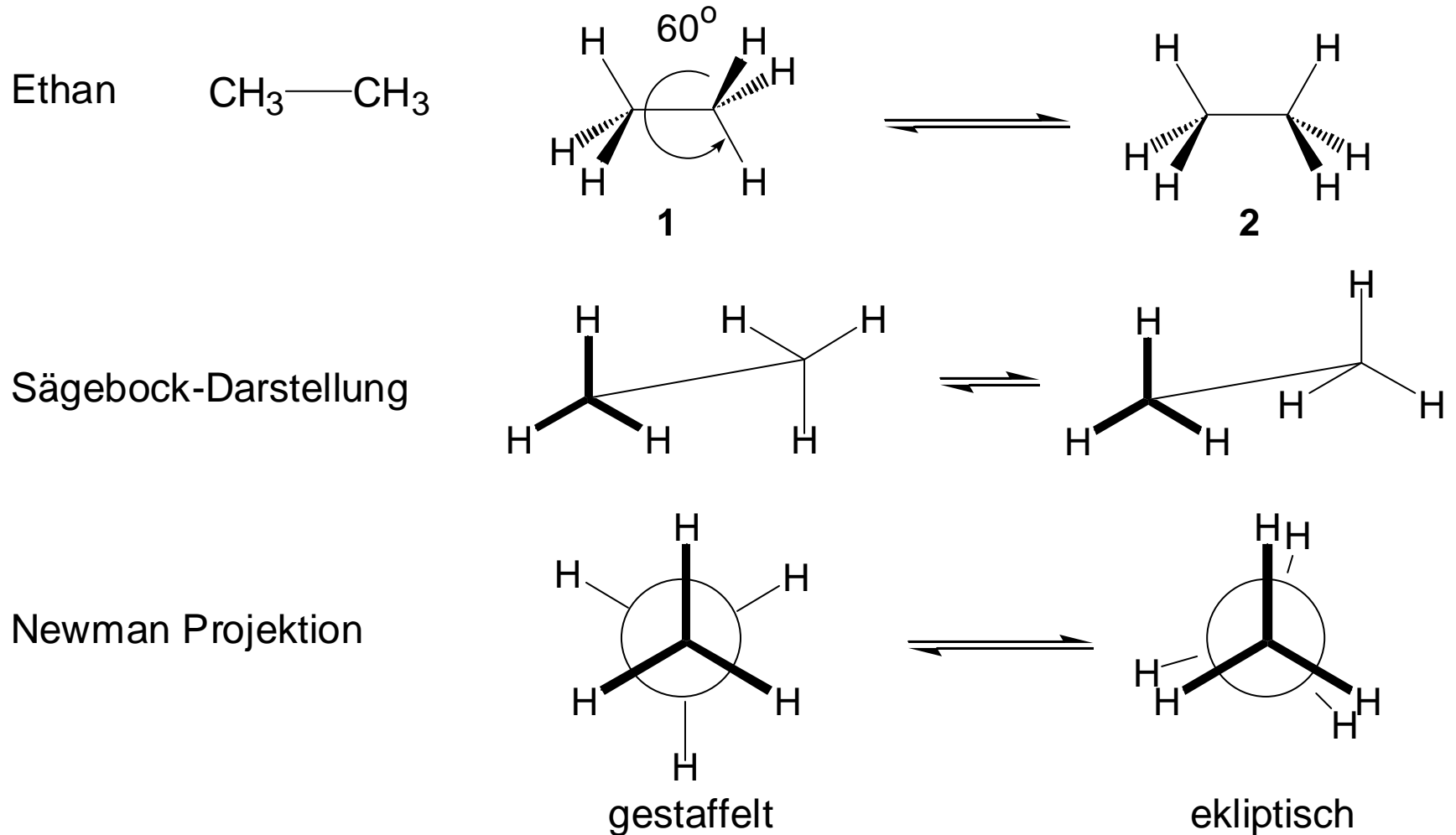
Adenosintriphosphat ATP



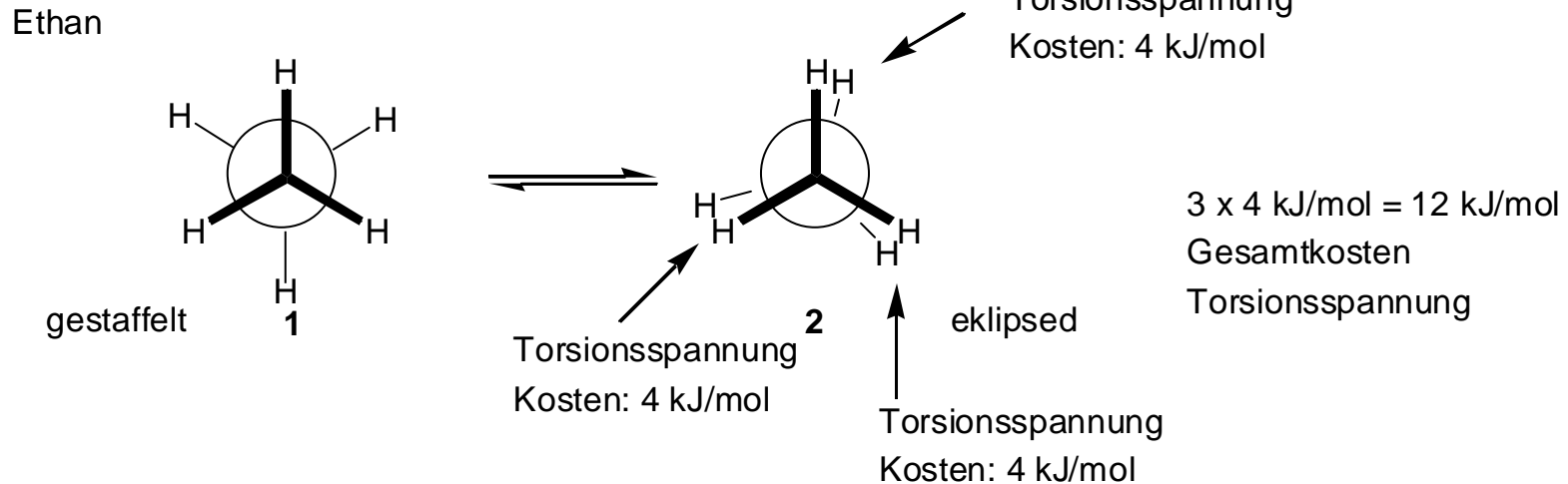
cyclisches Adenosinmonophosphat cAMP

# Konformation

Rotation um Einfachbindungen -> verschiedene Konformationen,  
Konformationsisomere = Konformere



Energiedifferenzen zwischen Konformeren: welches ist stabiler?

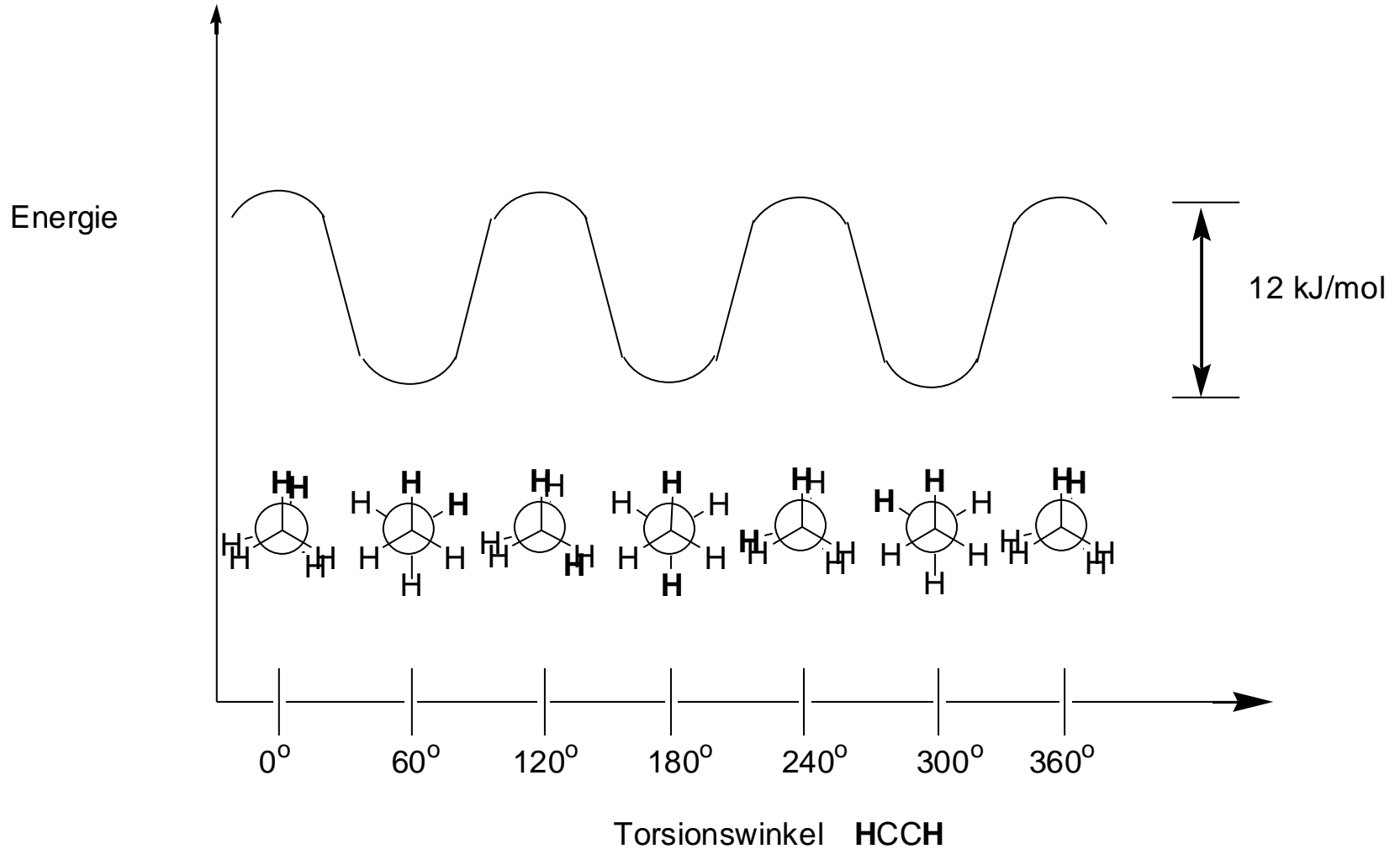


Die ekliptische-Konformation von Ethan liegt 12 kJ/mol über der gestaffelten Konformation.

Die gestaffelte Konformation ist um 12 kJ/mol stabiler als die ekliptische-Konformation.

Die Torsionsspannung beruht auf den leichten, abstossenden Wechselwirkungen zwischen den Elektronenwolken der CH-Bindungen.

Energiedifferenzen zwischen einzelnen Konformeren - Konformationsanalyse

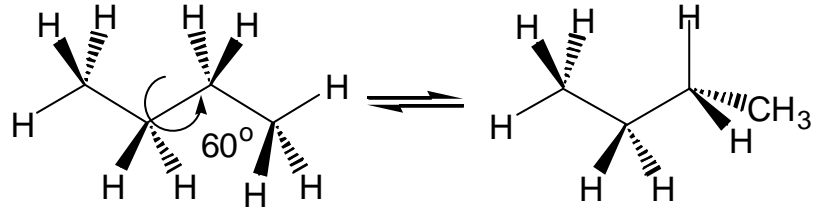


Ein Diagramm: potentielle Energie des Ethans aufgetragen gegen den HCCH-Torsionswinkel



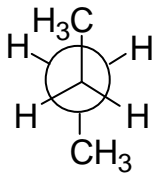
# Stereochemie

Butan  
H-H , H-C und  
C-C Wechselwirkungen



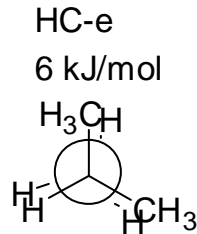
Torsionswinkel

**H<sub>3</sub>CCCCH<sub>3</sub>**



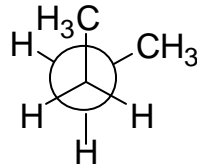
180°  
anti

0 kJ/mol



120°

16 kJ/mol

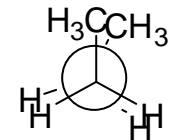


60°  
gauche

4 kJ/mol

CC-s  
(gauche)  
4 kJ/mol

CC-e  
11 kJ/mol



0°  
syn

19 kJ/mol

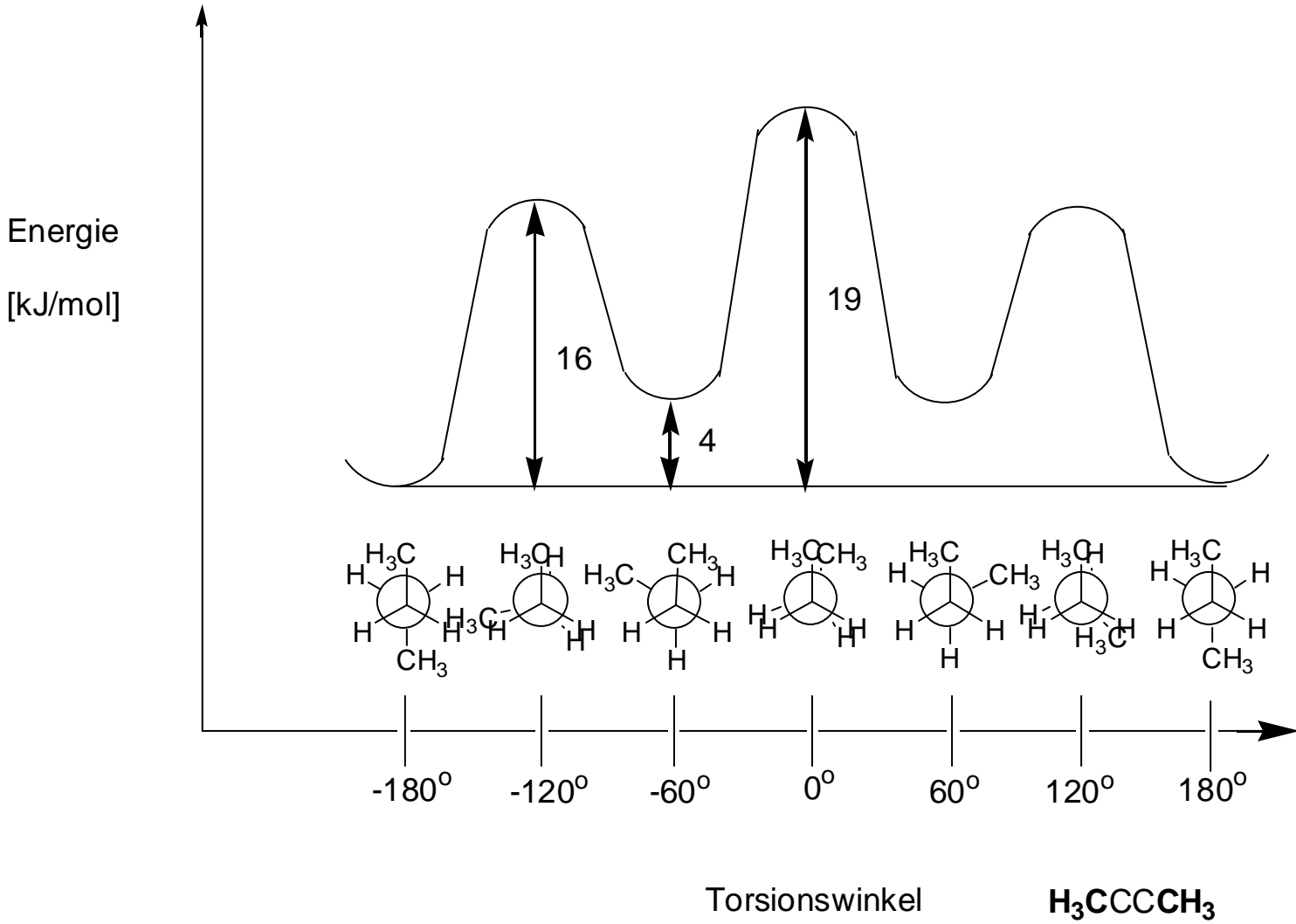
HH-e  
4 kJ/mol

HC-e  
6 kJ/mol



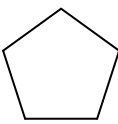
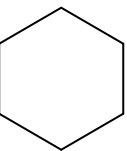
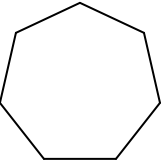
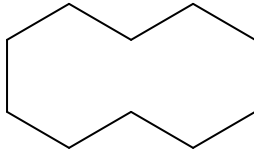
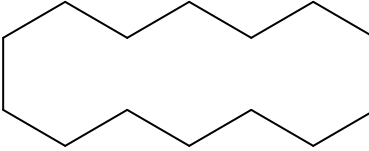
HH-e  
4 kJ/mol

HH-e  
4 kJ/mol

# Konformationsanalyse von Butan



Von Ketten zu Ringen: Stabilität von Cycloalkanen -> Konformation von Cycloalkanen

	offene Kette				
Verbrennungswärme					
(Total)	-	2092	2746	3322	3954
(pro CH <sub>2</sub> )	659	697	686	664	659
Ringspannung					
(per CH <sub>2</sub> )	0	38	27	5	0
(Total)	0	114	108	25	0
[kJ/mol]					
					
		4638	6639	9226	
		663	664	659	
		4	5	0	
		28	50	0	

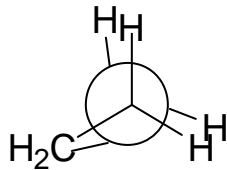
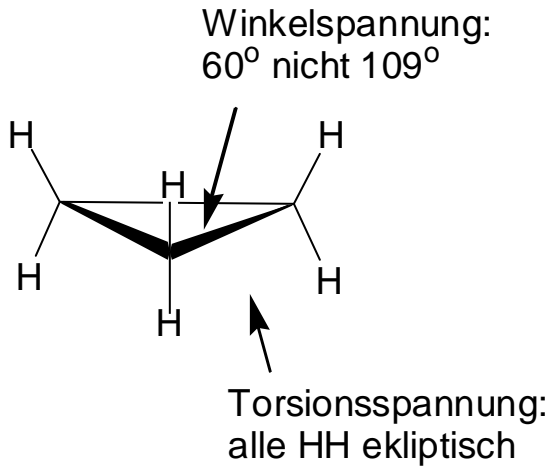


# Konformation von Cycloalkanen

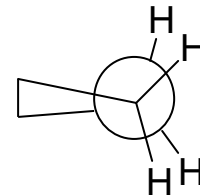
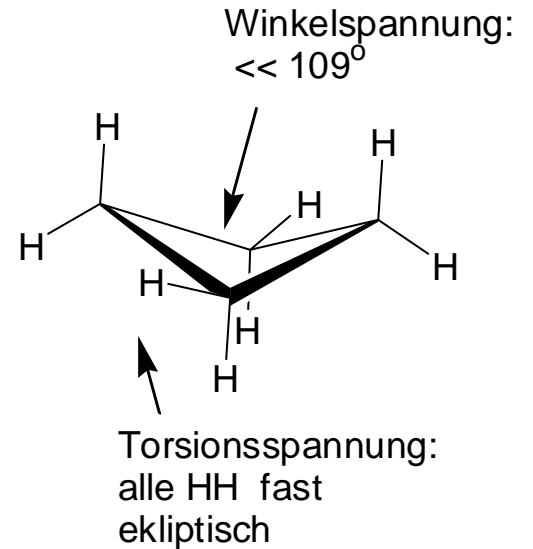
## Ringspannung (Winkelspannung + Torsionsspannung)



Cyclopropan



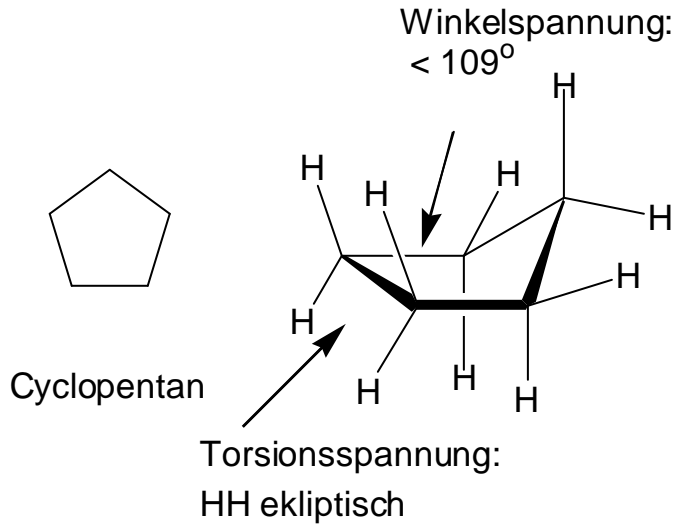
Cyclobutan



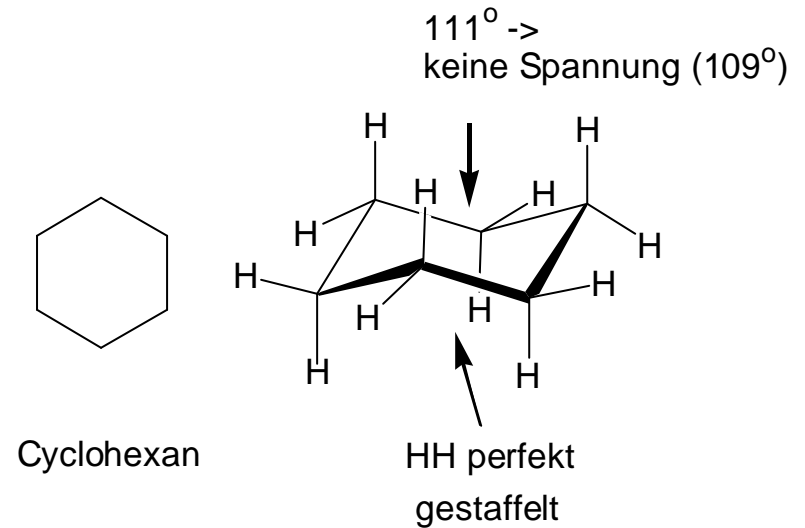
# Konformation von Cycloalkanen

## Ringspannung (Winkelspannung + Torsionsspannung)

OC- 8.9  
Koert



Briefumschlag-Konformation



Sessel-Konformation

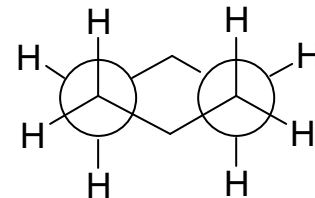
Ringgröße und Ringspannung:

kleine Ringe (3,4) Winkel- und Torsionsspannung

normale Ringe (5,6,7) wenig Spannung

mittlere Ringe (8,9,10,11) transannuläre Spannung

große Ringe (12 und größer) vergleichbar mit offenen Ketten, keine Spannung

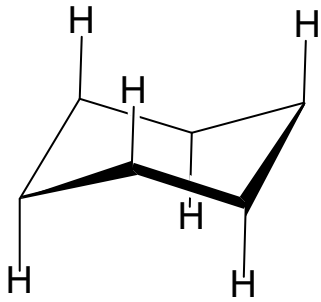


# Sesselkonformation von Cyclohexan

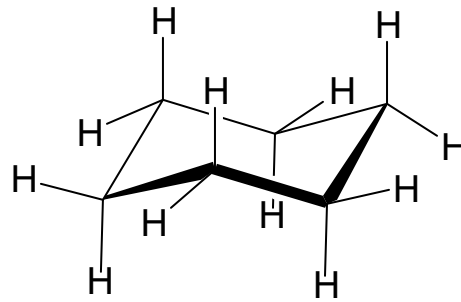
OC 8.10  
Koert

**Axiale**

Wasserstoffsubstituenten

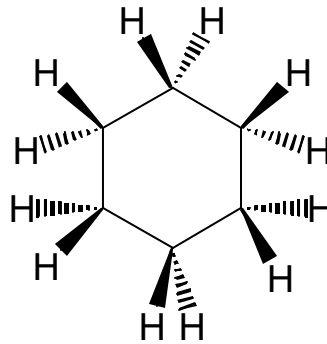
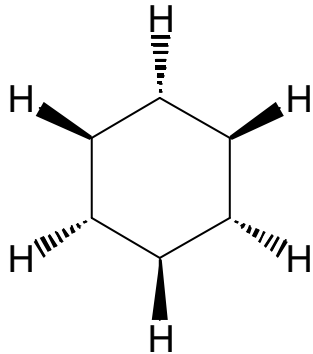
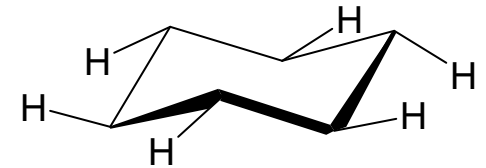


Seitenansicht

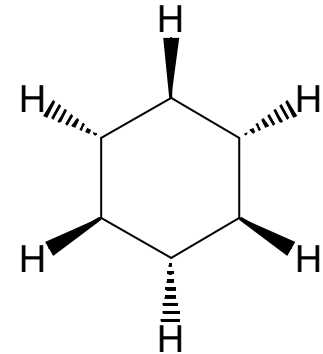


**Equatoriale**

Wasserstoffsubstituenten



Draufsicht



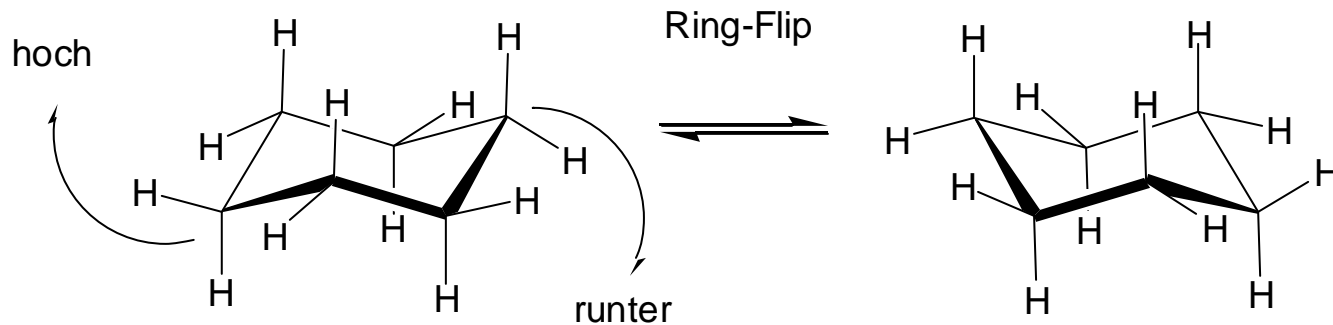
# Sesselkonformation von Cyclohexan

## Konformationale Mobilität

OC 8.11  
Koert

Bei Raumtemperatur sind keine 2 Arten von H-Substituenten beobachtbar

Ein Ring-Flip des Cyclohexan-Sessels wandelt axiale und equatoriale Positionen ineinander um.



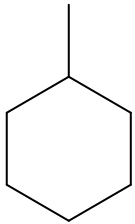
Energiebarriere für den Ring-Flip = 44 kJ/mol

-> schnell bei RT (RT-Barriere = 100 kJ/mol)

-> nur eine zeitlich gemittelte Struktur beobachtbar;

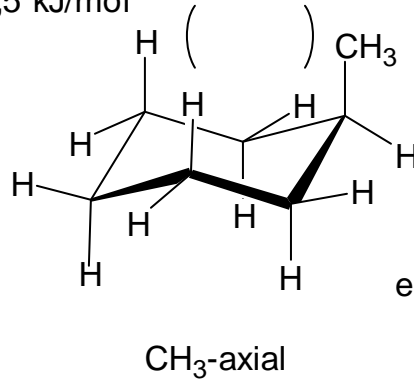
ohne unterscheidbare axiale und equatoriale Positionen.

# Konformationsanalyse substituerter Cyclohexane

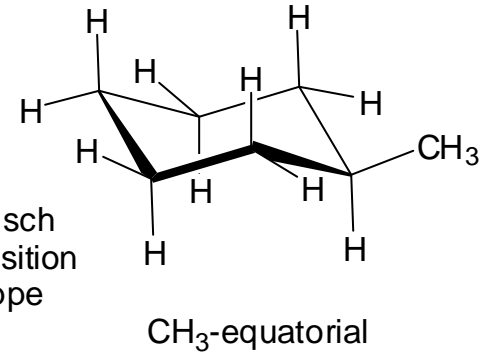


Methylcyclohexan

1,3 diaxiale Spannung  
von 7,5 kJ/mol



Ring-Flip

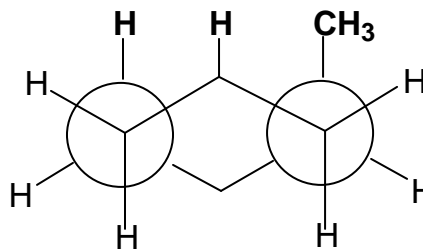


schneller Austausch  
eine gemittelte Position  
der Methyl-Gruppe  
beobachtbar

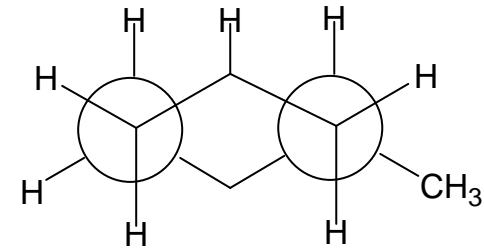
Welches Konformer ist stabiler?

Energiedifferenz bei 25°C (KJ/mol)    Stabileres Isomer (%)    Weniger stabiles Isomer (%)

0	50	50
2,7	75	25
5,4	90	10
7,3	95	5
11,4	99	1
17,1	99.9	0.1



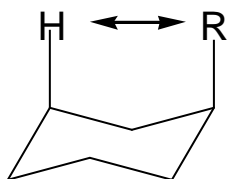
1,3 diaxiale Spannung von 7,5 kJ/mol  
-> 2 x C,C -gauche = 2 x 4 kJ/mol



keine Spannung in der  
equatorialen Position

# Konformationsanalyse substituierter Cyclohexane

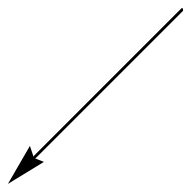
Einfluß des Substituenten R



sterisch anspruchsvoller  
-> mehr Spannung

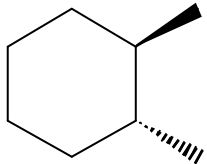
Konformationsanker

R	HR -1,3-diaxiale Spannung (kJ/mol)
CH <sub>3</sub>	3,8
CH <sub>2</sub> CH <sub>3</sub>	4,0
CH(CH <sub>3</sub> ) <sub>2</sub>	4,6
C(CH <sub>3</sub> ) <sub>3</sub>	11,3
Br	1,0
OH	2,1
C <sub>6</sub> H <sub>5</sub>	6,3
CN	0,4

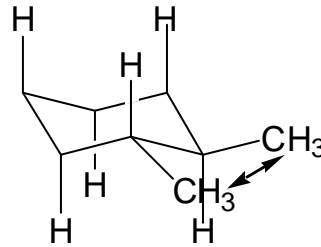


$$2 \times 11,3 = 22,6 \text{ kJ/mol} \quad \rightleftharpoons \quad > 99,9 : 0,1$$

# Konformationsanalyse 1,2-disubstituierter Cyclohexane

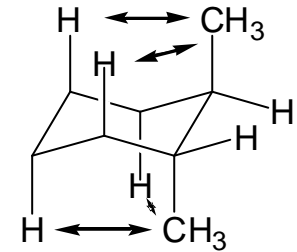


trans-1,2-Dimethylcyclohexan



diequatorial

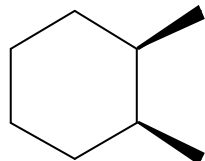
eine gauche Wechselwirkung  
4 kJ/mol Spannungsenergie



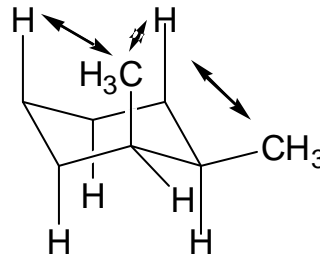
diaxial

vier 1,3 diaxial  
Wechselwirkungen 16 kJ/mol

$\Delta E = 12 \text{ kJ/mol} \rightarrow$  Gleichgewicht von 99:1 zu  
Gunsten des diequatorialen Konformers.

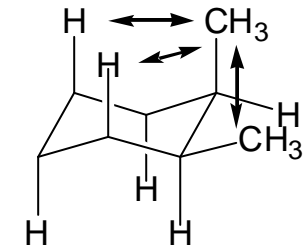
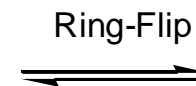


cis-1,2-Dimethylcyclohexan



axial-equatorial

eine gauche Wechselwirkung  
zwei 1,3 diaxial Wechselwirkungen  
11,6 kJ/mol Spannungsenergie



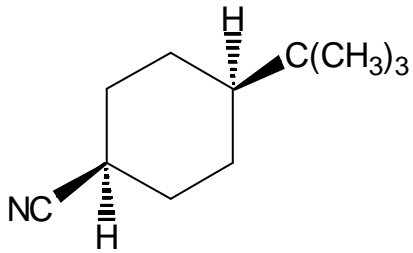
equatorial-axial

eine gauche Wechselwirkung  
zwei 1,3 diaxial Wechselwirkungen  
11,6 kJ/mol Spannungsenergie

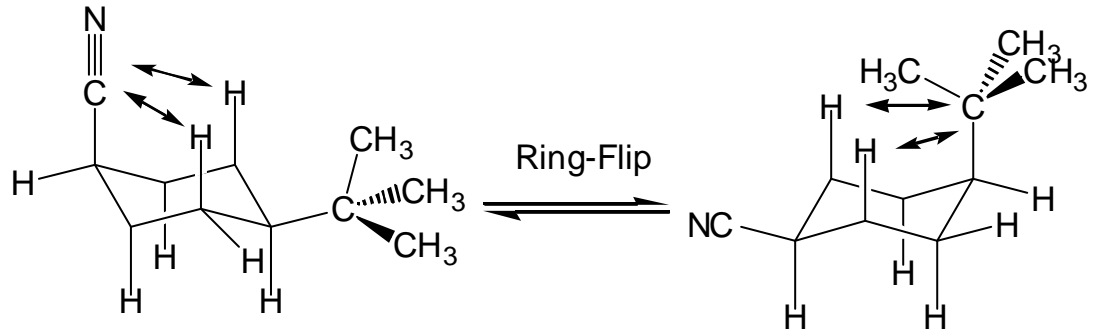
$\Delta E = 0 \text{ kJ/mol} \rightarrow$  50:50 Gleichgewicht.

# Konformationsanalyse disubstituierter Cyclohexane

OC 8.15  
Koert



*cis*-1-tert-Butyl-4-cyanocyclohexan



CN-axial; t-Butyl-equatorial  
zweimal 1,3 diaxial H-CN  
 $2 \times 0.4 = 0.8$  kJ/mol sterische Spannung

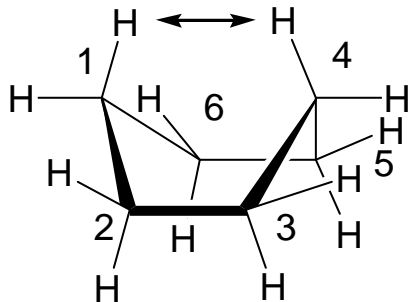
CN-equatorial; t-Butyl-axial  
zweimal 1,3 diaxial H-t-Bu  
 $2 \times 11.3 = 22.6$  kJ/mol sterische Spannung

$\Delta E = 21.8$  kJ/mol  $\rightarrow$  Gleichgewicht liegt größer 99.9 : 0.1 zu Gunsten der equatorialen t-Bu-Gruppe.

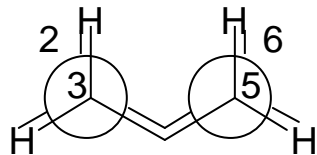


## Cyclohexan-Wanne (Boot)

keine Winkelspannung aber 29 kJ/mol über dem Sessel



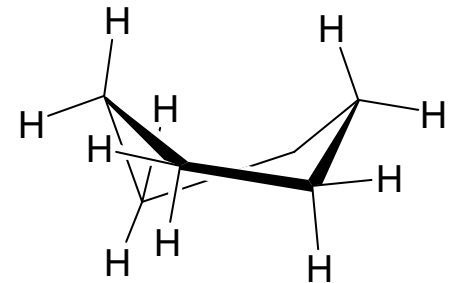
Sterische Abstoßung  
zwischen den Hs  
an C1 und C4  
Torsionsspannung an  
C2-C3 and C5-C6



Vier Paare von ekliptischen Wasserstoffen

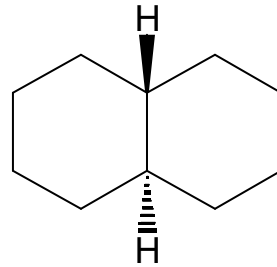
## Twist-Boot

keine Winkelspannung aber 23 kJ/mol  
über dem Sessel



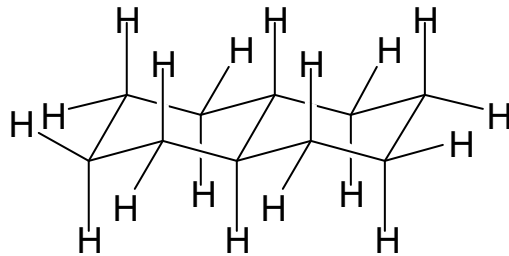
# Konformationsanalyse polycyclischer Moleküle

verknüpfte Cyclohexanringe

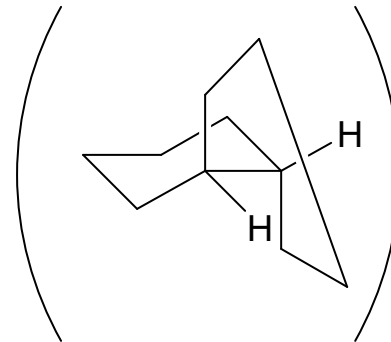
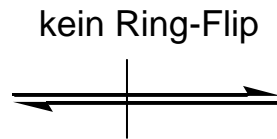


*trans*-Decalin

starres Molekül  
nur eine Vorzugs-  
konformation



keine 1,3 diaxiale Spannung  
im Molekül



unmögliche  
molekulare  
Architektur

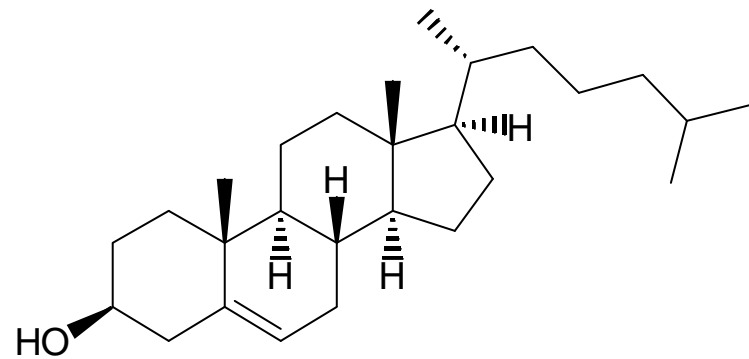
# Konformationsanalyse polycyclischer Moleküle

OC 8.18  
Koert

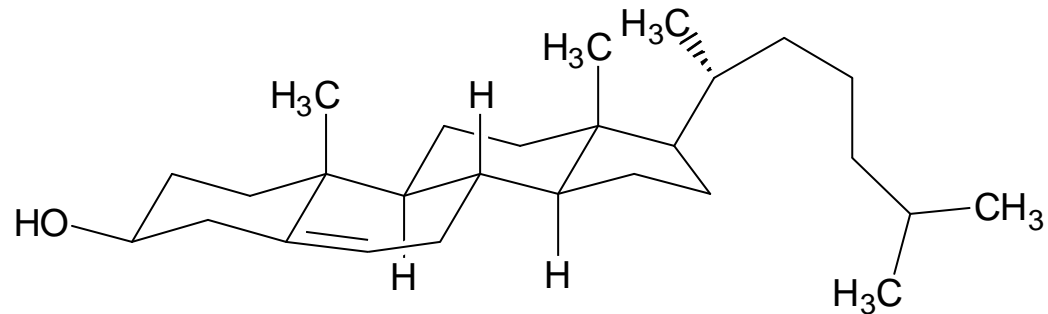
starres Molekül auf der strukturellen Basis  
von trans-Decalinen als perfekter Schlüssel  
für ein Enzym-Schloß  
-> molekulare Erkennung

Emil Fischer: Schlüssel-Schloß-Prinzip

Steroide



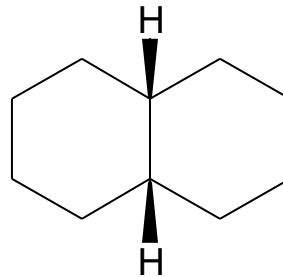
Cholesterol



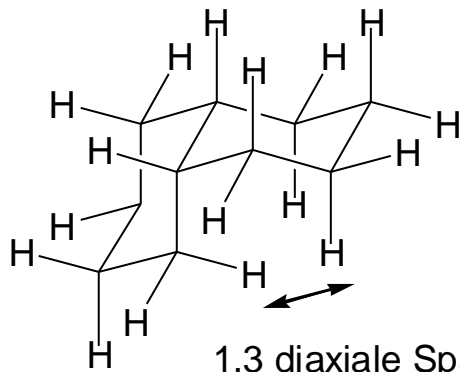
# Konformationsanalyse polycyclischer Moleküle

OC 8.19  
Koert

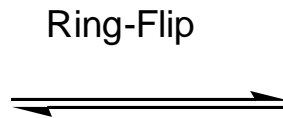
verknüpfte Cyclohexanringe



*cis*-Decalin  
ein flexibles Molekül

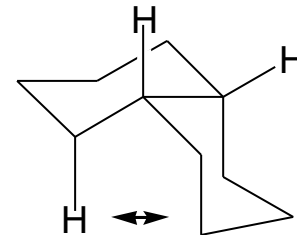


1,3 diaxiale Spannung



50 : 50

10 kcal

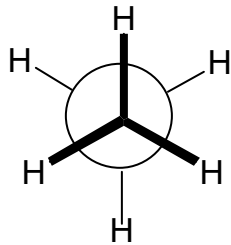


1,3 diaxiale Spannung

# Konformationsanalyse Heteroatome und freie Elektronenpaare

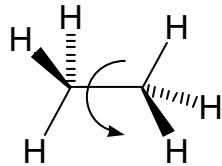
OC 8.20  
Koert

Ethan

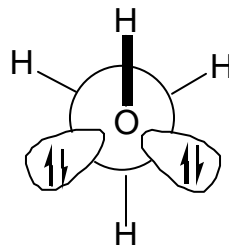


12.0

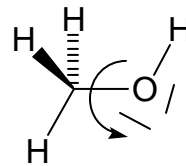
Energiedifferenz zur  
ekliptischen Konformation  
(kJ/mol)



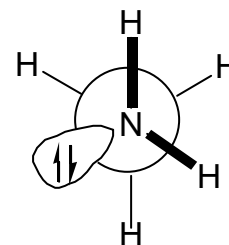
Methanol



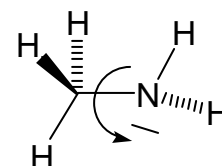
4.5



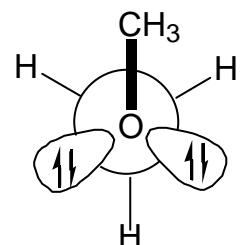
Methylamin



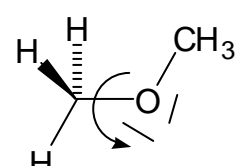
8.3



Dimethylether

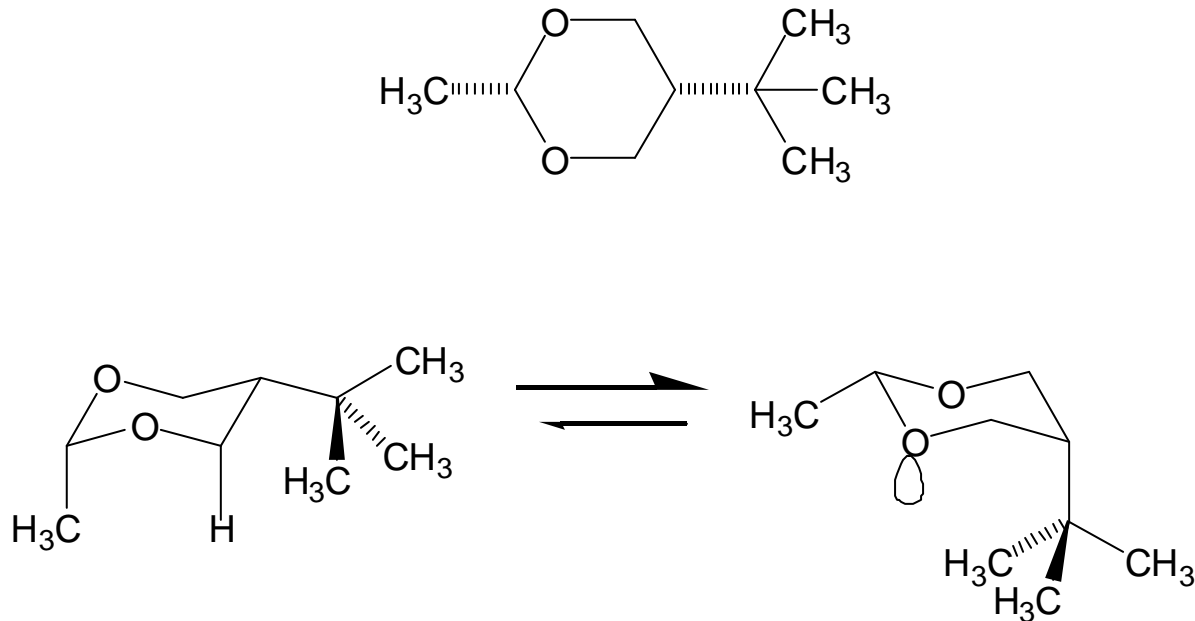


11.3



# Konformationsanalyse Heteroatome und freie Elektronenpaare

OC 8.21  
Koert



Die 1,3 diaxiale Wechselwirkung zwischen Methyl und H ist energetisch ungünstiger als die 1,3 diaxiale Wechselwirkung zwischen tert-Butyl und dem freien Elektronenpaar am Sauerstoff. In diesem Fall besetzt daher die tert-Butylgruppe die axiale Position und nicht die Methylgruppe.

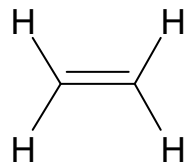
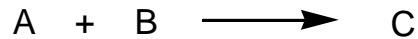
# Organische Reaktionen

## Ein Überblick

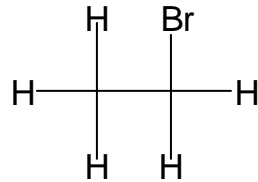
OC 10.1  
Koert

### Additionsreaktionen

addieren sich zu



+ H-Br

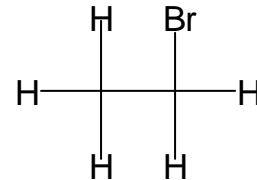


Ethylen  
(Alken)

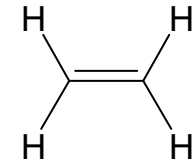
Bromoethan  
(Halogenalkan)

### Eliminierungsreaktionen

spalten sich auf in



NaOH



+ H-Br

Bromoethan  
(Halogenalkan)

Ethylen  
(Alken)

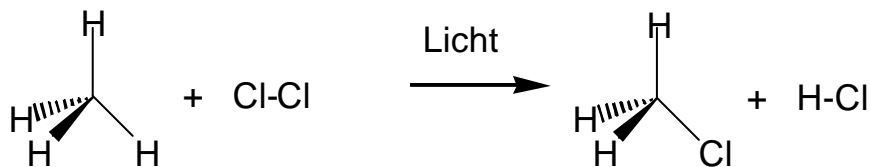
# Organische Reaktionen

## Ein Überblick

OC 10.2  
Koert

### Substitutionsreaktionen

Zwei Reaktanden tauschen Teile  
aus und ergeben zwei neue Produkte

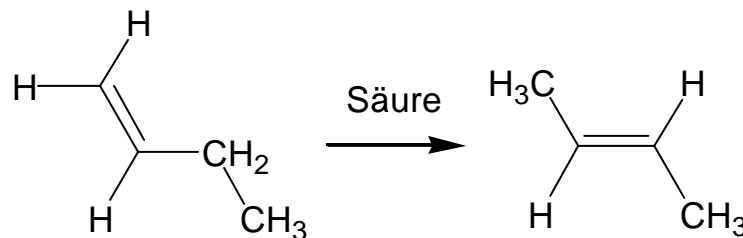


Methan  
(Alkan)

Chloromethan  
(Halogenalkan)

### Umlagerungsreaktionen

untergeht eine strukturelle  
Umorganisation



1-Buten

2-Buten



# Mechanismus: Wie eine Reaktion abläuft

Ein Mechanismus beschreibt jeden Schritt einer chemischen Umsetzung.  
(ein-, zwei- oder mehrstufig).

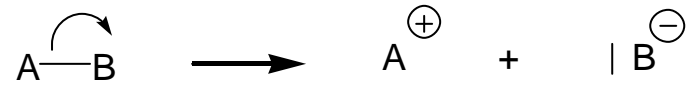
Für jeden Reaktionsschritt wird Art und Reihenfolge der Bindungen,  
die gebrochen und neu geformt werden, beschrieben. Der Mechanismus macht  
Aussagen zu den Geschwindigkeiten der Einzelreaktionen und gibt eine  
Erklärung für die Triebkraft der Reaktion.

Homolytische Bindungsspaltung



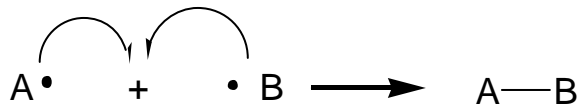
Radikal-Reaktionen

Heterolytische Bindungsspaltung

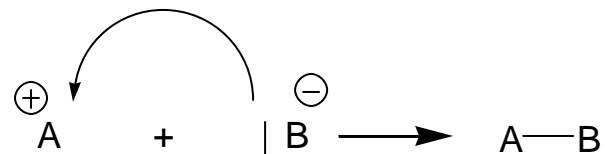


Polare Reaktionen

Homogene Bindungsbildung

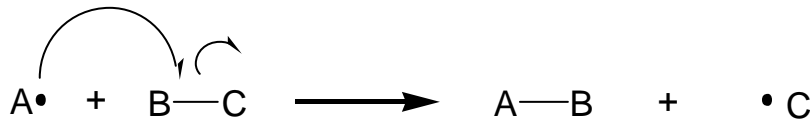


Heterogene Bindungsbildung



Triebkraft: Radikale haben eine ungerade Anzahl von Elektronen in ihrer äußeren Schale -> sie gewinnen Energie durch Ausbildung des stabilen Edelgas-Oktetts.

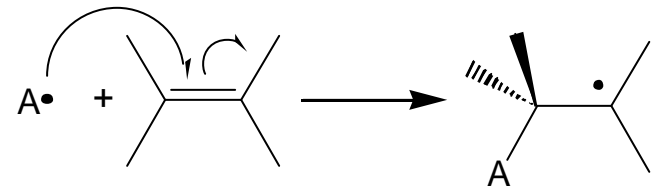
## Radikal-Substitutions-Reaktion



Reaktand-  
Radikal      Edukt

Substitutions  
Produkt      Produkt  
Radikal

## Radikal-Additions-Reaktion



Reaktand-  
Radikal      Alken  
(Edukt)

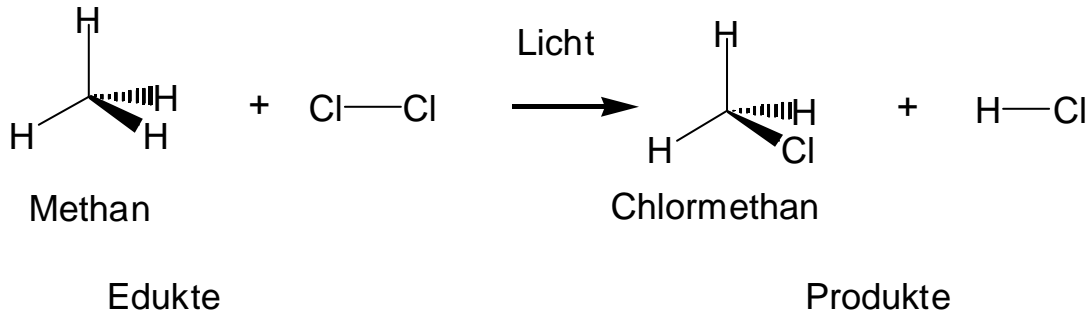
Additions-  
Produkt-  
Radikal

ausgehend von einem Radikal wird erneut ein Radikal gebildet  
-> Ketten-Reaktion

# Radikal-Reaktionen

Ein Beispiel: Die Chlorierung von Methan

-> Ozonloch



Licht:  $E = h \times \nu = h \times 1/\lambda$

$\lambda$  (nm)

E (kJ/Einstein)

UV Region  $\longrightarrow$   
Äußere  
Erdatmosphäre

100	1197
200	599
300	397
400	297
600	201
800	151

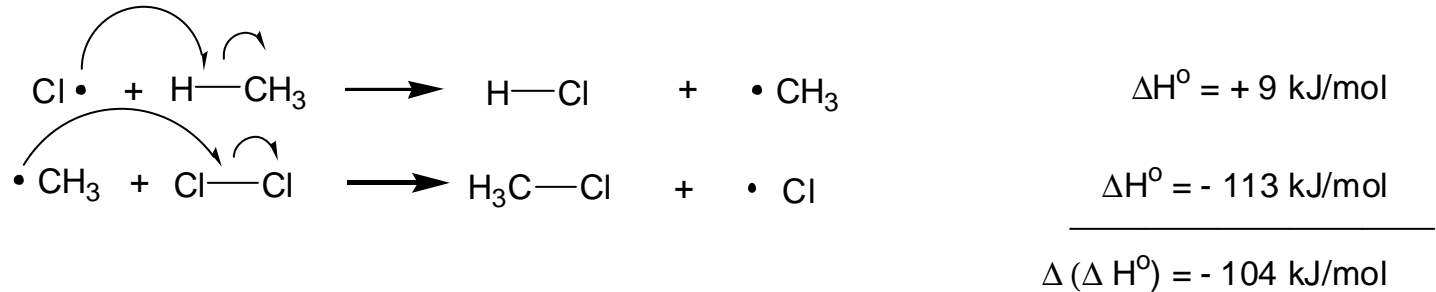
# Radikal-Reaktionen

OC 10.6  
Koert

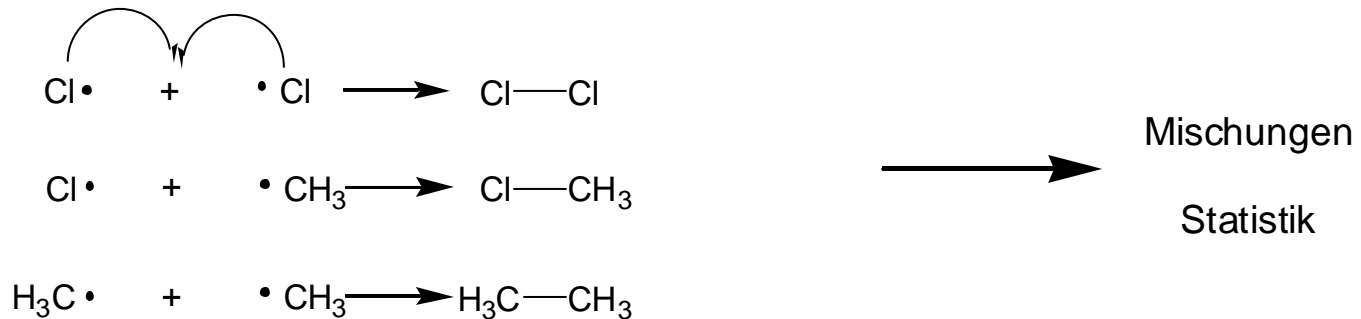
## 1) Radikalstart - die Bildung von Radikalen



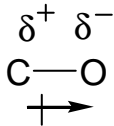
## 2) Radikalkette - Radikale gehen Substitutionsreaktionen ein



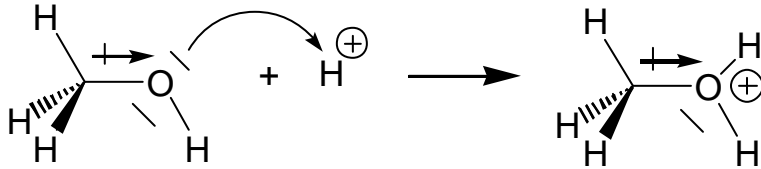
## 3) Terminierungsschritt - Rekombination von Radikalen, Kettenende



Elektronegativität -> Bindungspolarisierung



Durch Protonierung läßt sich die Bindungspolarisierung stark erhöhen.

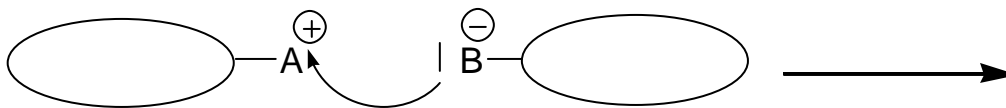


Methanol  
schwach polare C-O Bindung

protoniertes Methanol  
Methanol-Kation  
stark polare C-O Bindung

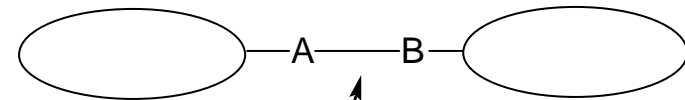
Polarität funktioneller Gruppen ->  
Reaktivität funktioneller Gruppen

Da sich ungleiche Ladungen anziehen, ist das fundamentale Charakteristikum aller polarer organischer Reaktionen, daß elektronreiche Regionen in der funktionellen Gruppe des einen Moleküls mit elektronenarmen Regionen der funktionellen Gruppe des anderen Moleküls reagieren.



Elektrophil  
(elektronenarm)

Nukleophil  
(elektronenreich)

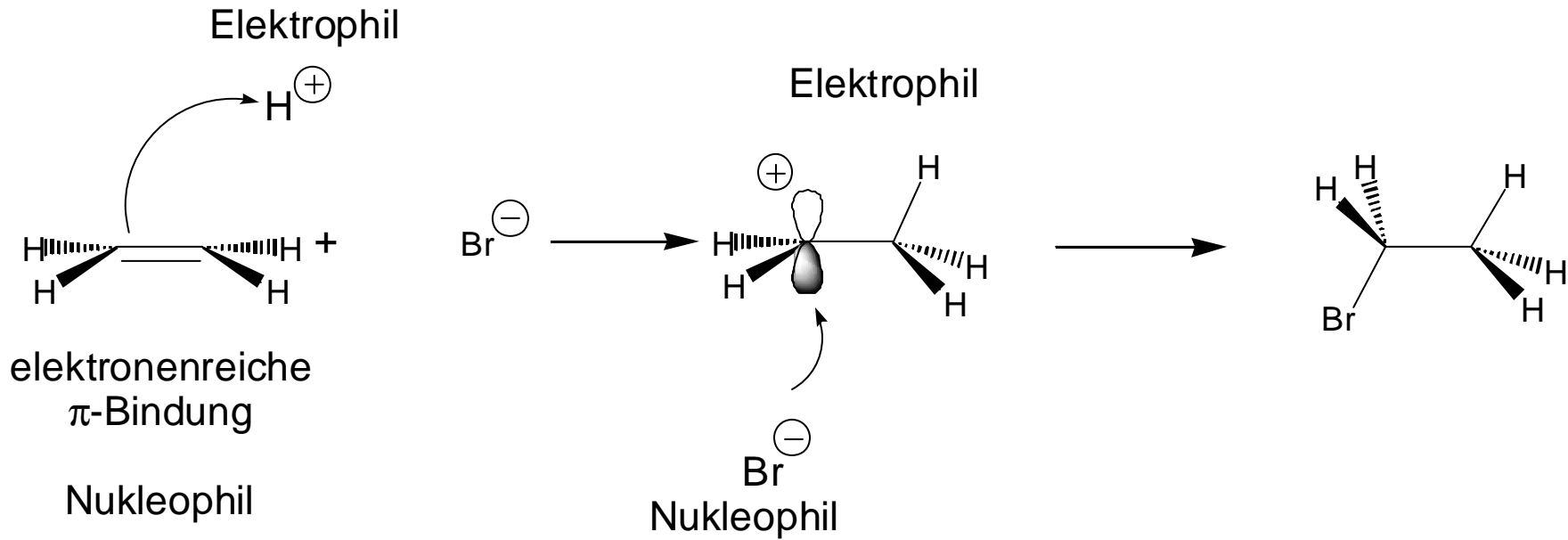


neue Bindung

# Polare Reaktionen

OC 10.8  
Koert

Beispiel: Elektrophile Addition von HBr an Alkene

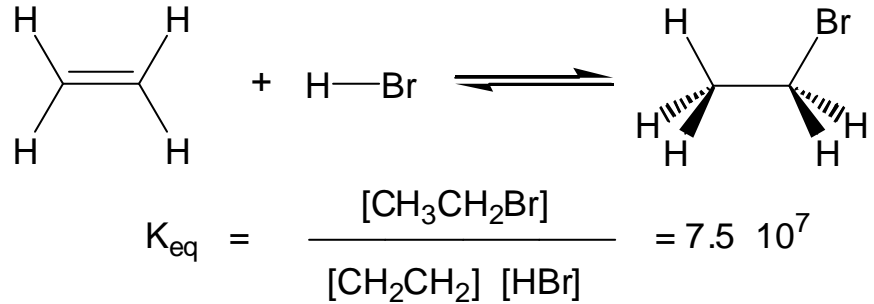


# Reaktionsgleichgewicht und Reaktionsgeschwindigkeiten

OC 10.9  
Koert



$$K_{\text{eq}} = \frac{[\text{Produkte}]}{[\text{Edukte}]} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$



Gleichgewicht liegt zu 99.999997 % auf der Produktseite.

Energiedifferenz zwischen  
Produkten und Edukten

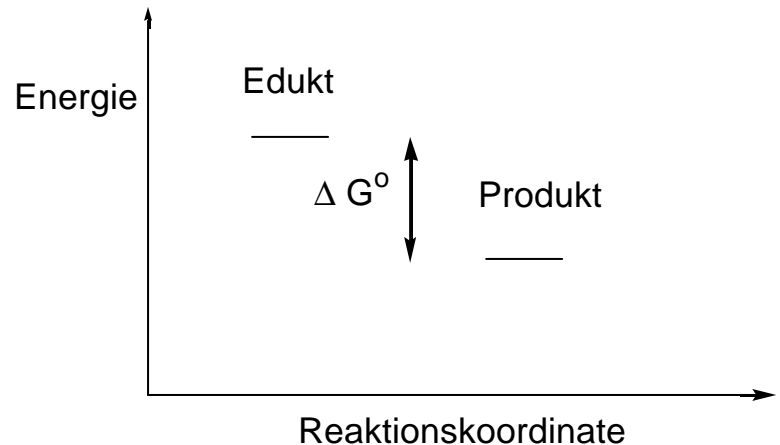
$$\Delta G^{\circ} = - RT \ln K_{\text{eq}}$$

Änderung der freien Energie

$$K_{\text{eq}} > 1 \quad \rightarrow \quad \Delta G^{\circ} = \text{negativ}$$

$$K_{\text{eq}} < 1 \quad \rightarrow \quad \Delta G^{\circ} = \text{positiv}$$

$$\Delta G^{\circ} = - (8,31 \text{ J/K mol}) 298 \text{ K} \ln (7.5 \cdot 10^7) = - 44,8 \text{ kJ/mol}$$



# Gleichgewichte und Reaktionsgeschwindigkeiten

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \quad \text{Thermodynamik}$$

$\uparrow$                        $\uparrow$   
 enthalpischer      entropischer  
 Faktor                      Faktor

$\Delta H^{\circ}$  = Änderung der freien Enthalpie -> Energiedifferenz zwischen den Bindungsstärken der gebrochenen und der neugebildeten Bindungen

Bindungsspaltung kostet Energie, Bindungsbildung liefert Energie.

$\Delta H^{\circ}$  negativ -> exotherme Reaktion      oft gilt  $\Delta G^{\circ} = \Delta H^{\circ}$  -> der kleine Entropieterm kann  
 $\Delta H^{\circ}$  positiv -> endotherme Reaktion      vernachlässigt werden.

$\Delta S^{\circ}$  = Änderung der Entropie; betrifft die Summe der Bewegungsfreiheitsgrade der bei der Reaktion beteiligten Spezies; die "Ordnung" bzw. "Unordnung" des Systems.

A -> B + C      Zunahme an Entropie -> Zunahme an freier Energie  
 A + B -> C      Abnahme an Entropie -> Abnahme an freier Energie

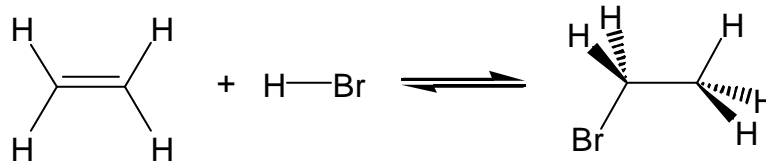
Gleichgewicht: In welche Richtung verläuft eine Reaktion? Wohin? **Thermodynamik**

Reaktionsgeschwindigkeit: Wie schnell? **Kinetik**

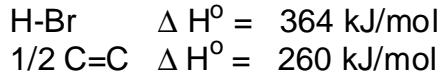


# Thermodynamik Ein Beispiel

OC 10.11  
Koert



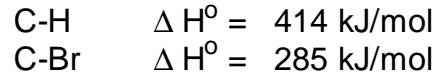
Bindungsspaltung:



---

$$\Delta H^\circ = 624 \text{ kJ/mol}$$

Bindungsbildung:



---

$$\Delta H^\circ = 699 \text{ kJ/mol}$$

Nettoänderung: Bindungsspaltung - Bindungsbildung = **-75 kJ/mol**

berechnet

$$\Delta G^\circ = -45 \text{ kJ/mol}$$

$$\Delta H^\circ = \mathbf{-84 \text{ kJ/mol}}$$

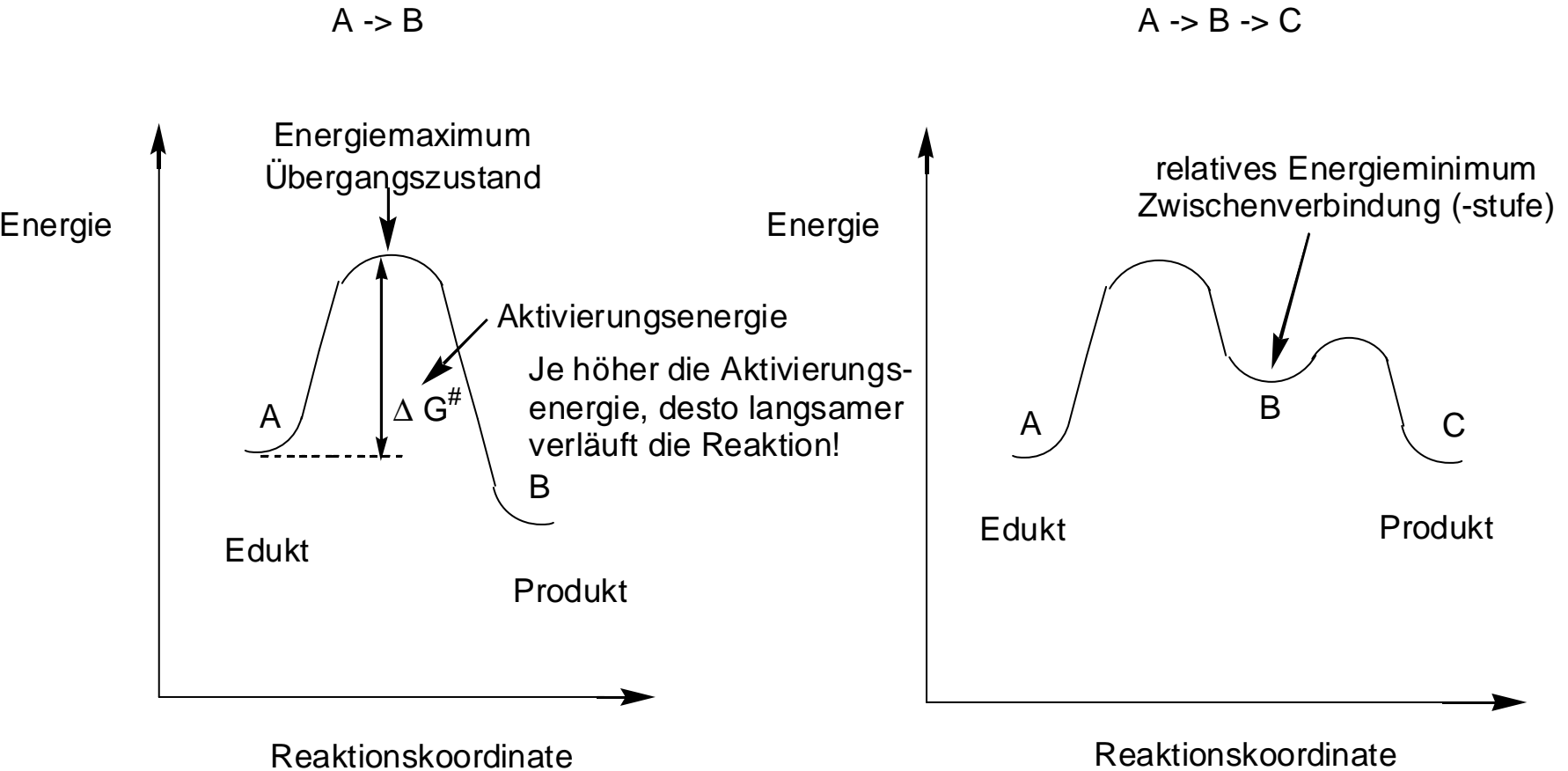
$$\Delta S^\circ = -0.132 \text{ kJ/K mol}$$

$$T = 298 \text{ K}$$

gemessen

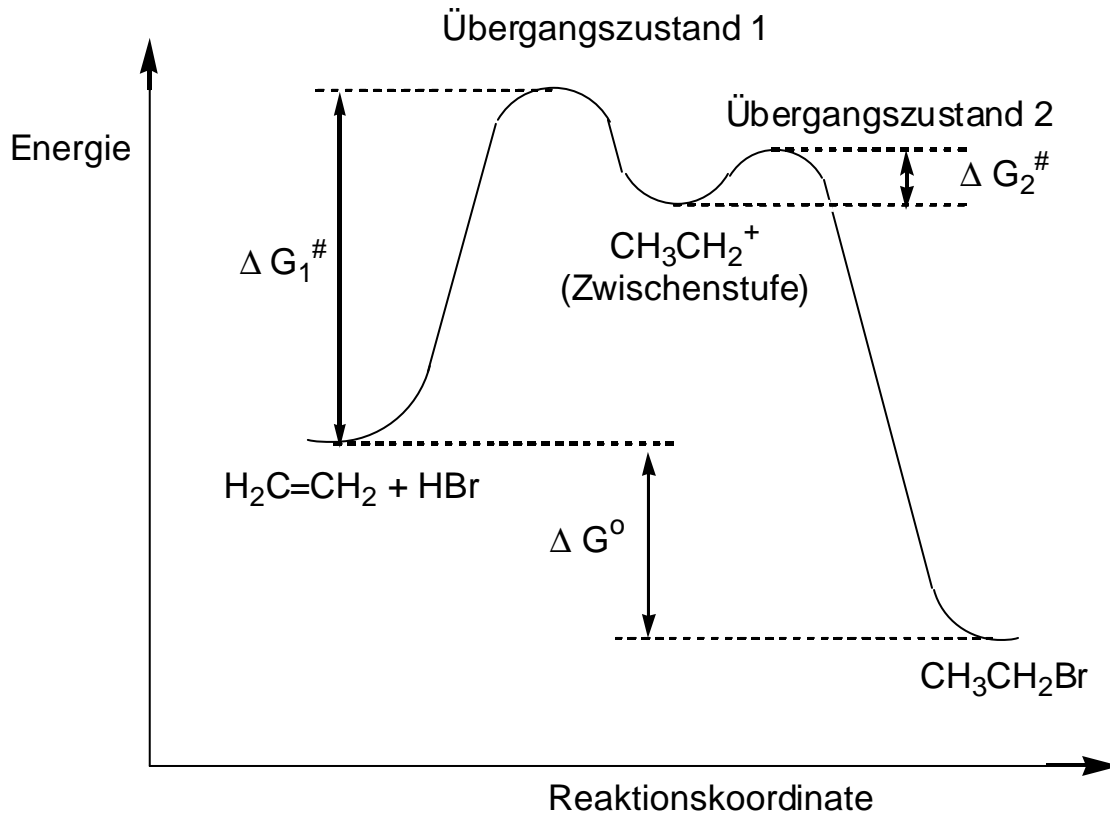
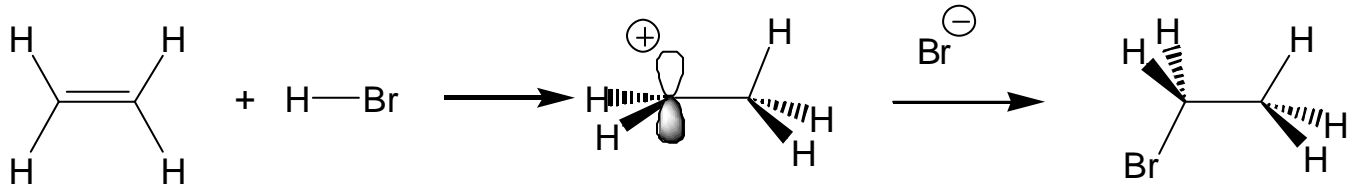
# Beschreibung einer Reaktion

## Energiediagramm und Übergangszustand

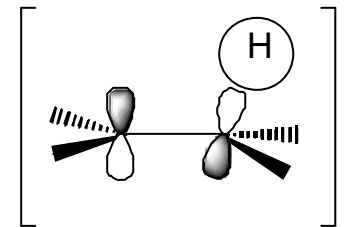


# Beschreibung einer Reaktion: Energiediagramm und Übergangszustand

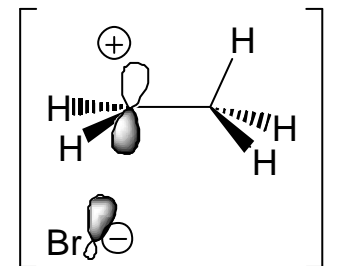
OC 10.13  
Koert



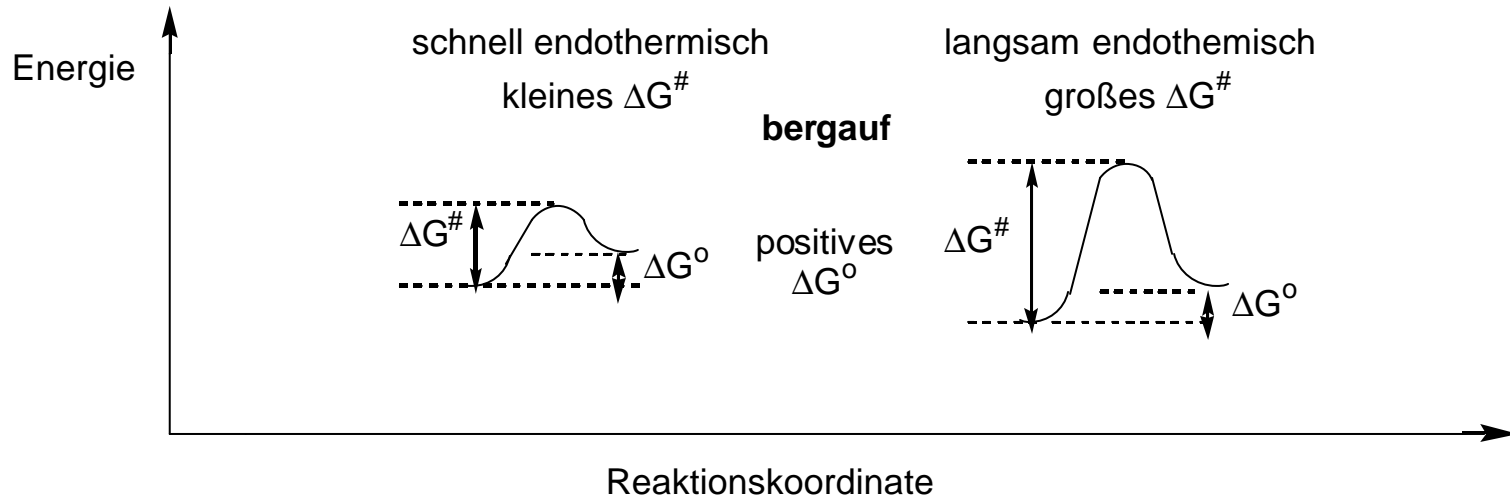
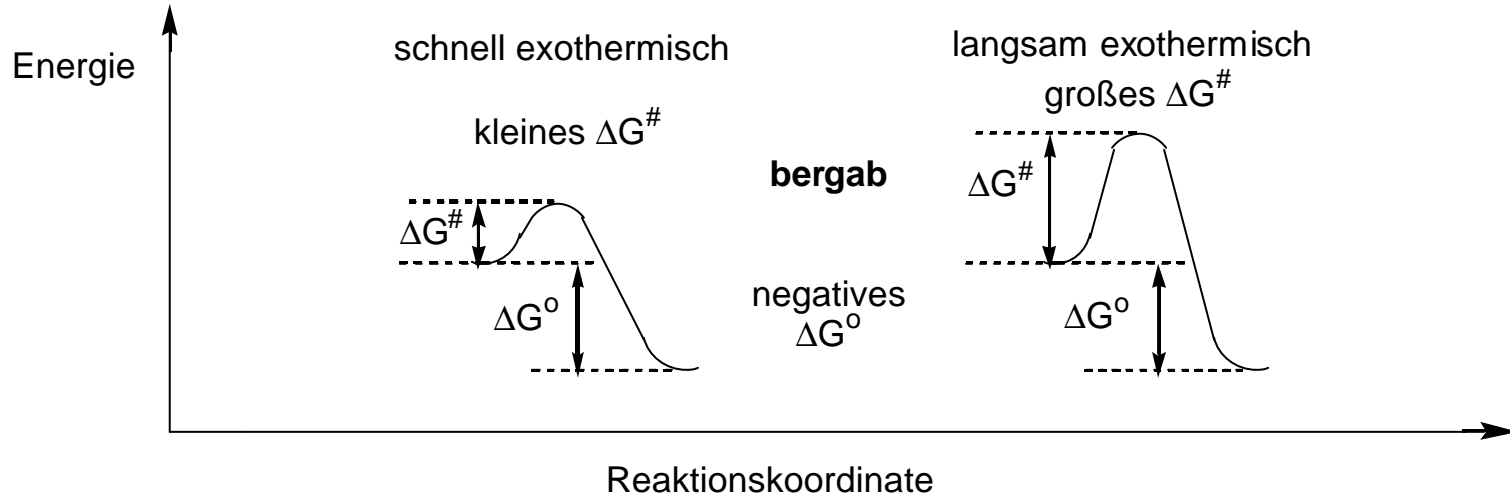
Übergangszustand 1



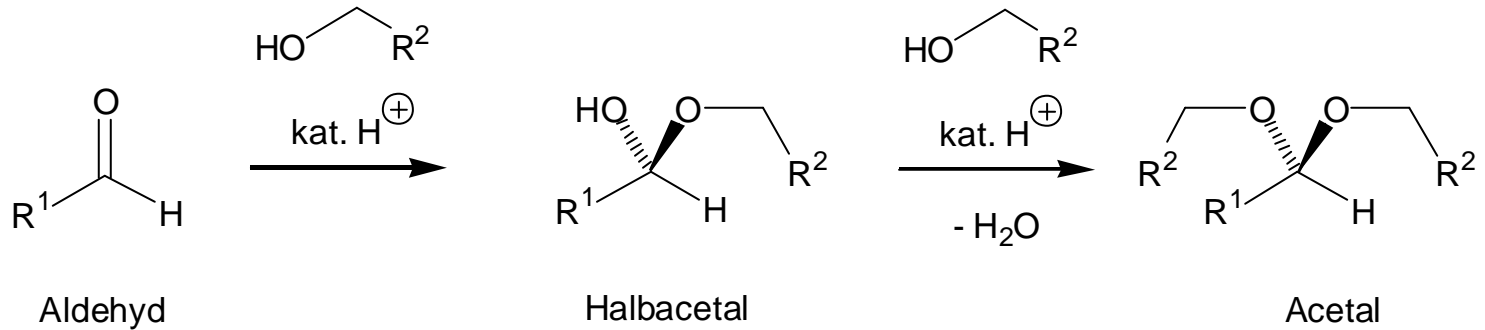
Übergangszustand 2



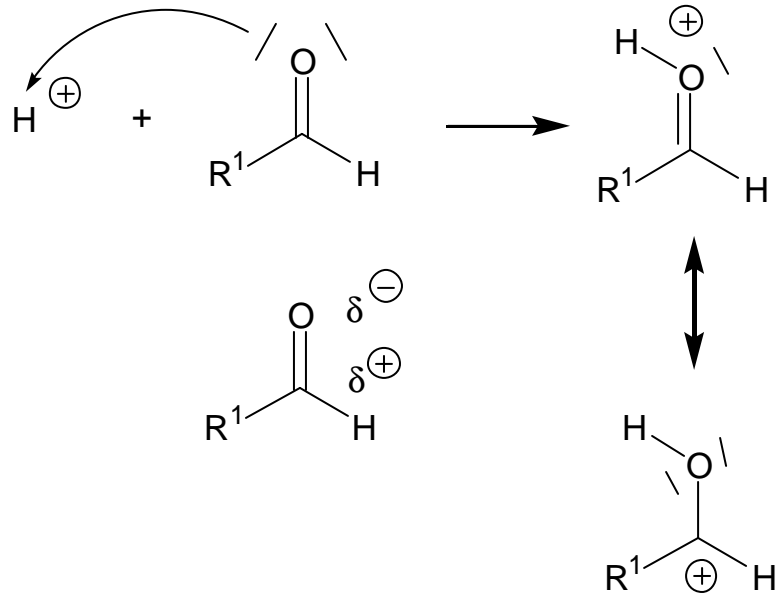
# Beschreibung einer Reaktion: Energiediagramm und Übergangszustand



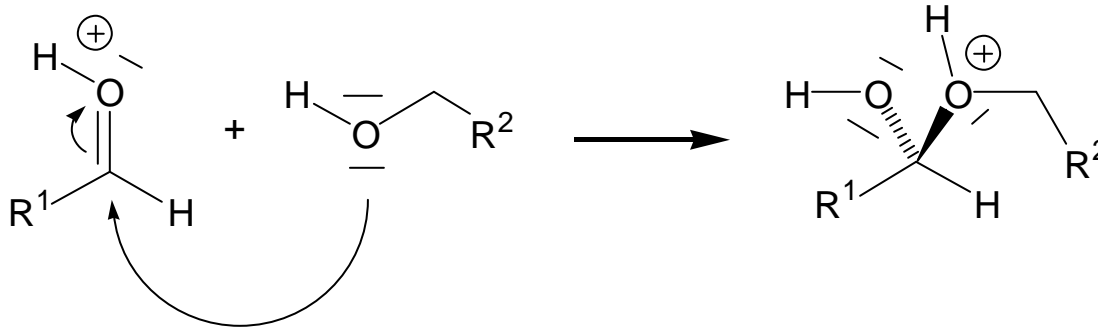
## säurekatalysierte Acetalbildung



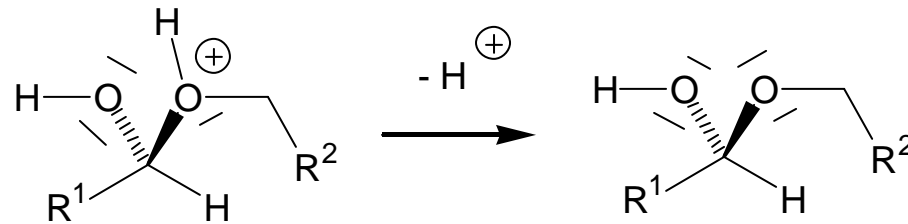
## 1. Schritt



2. Schritt



3. Schritt



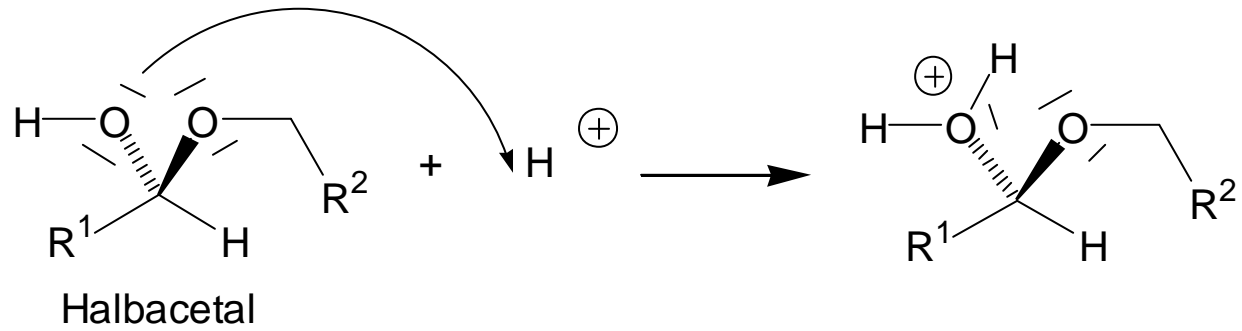
Halbacetal

Der Katalysator "Proton" wird wieder freigesetzt und geht erneut in den katalytischen Kreislauf ein.

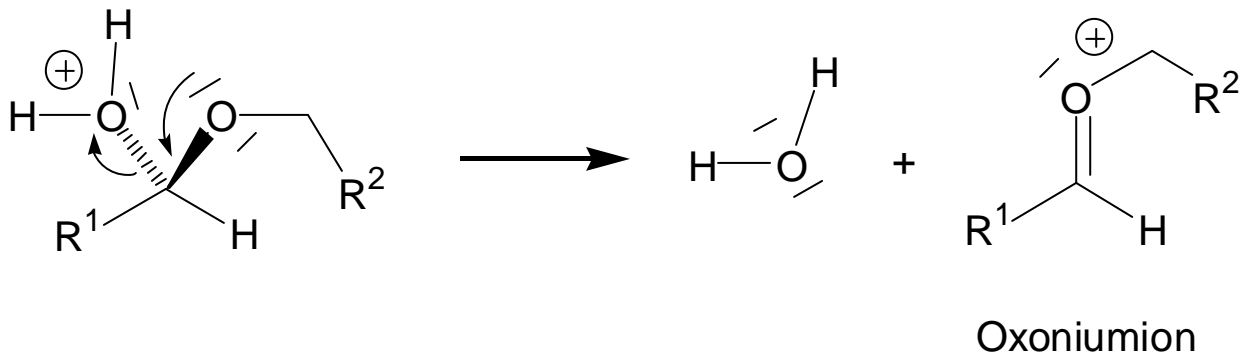
# Katalyse

OC I 11.1C  
Koert

4. Schritt



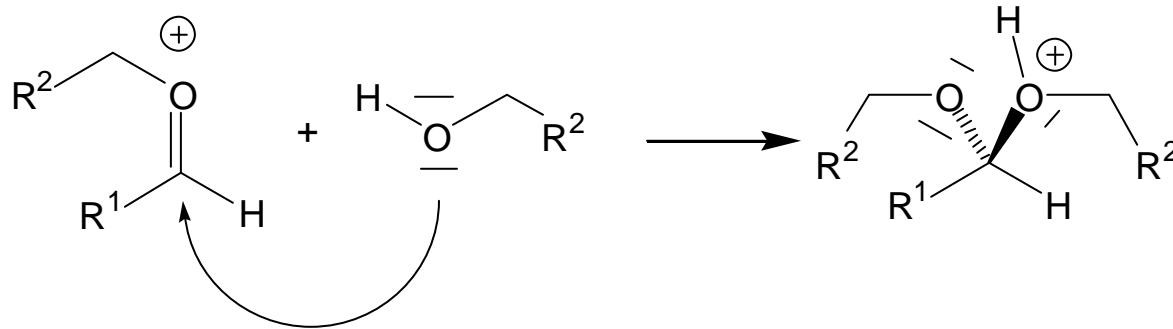
5. Schritt



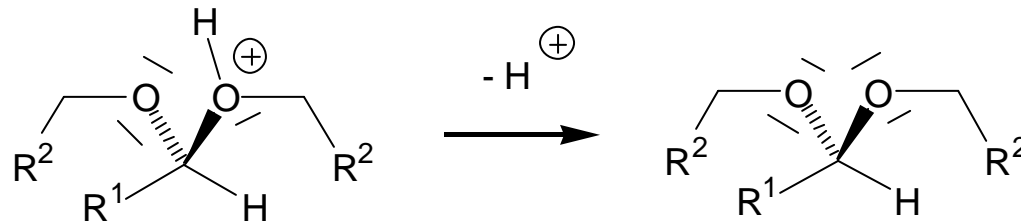
# Katalyse

OC I 11.1D  
Koert

6. Schritt



7. Schritt



Acetal

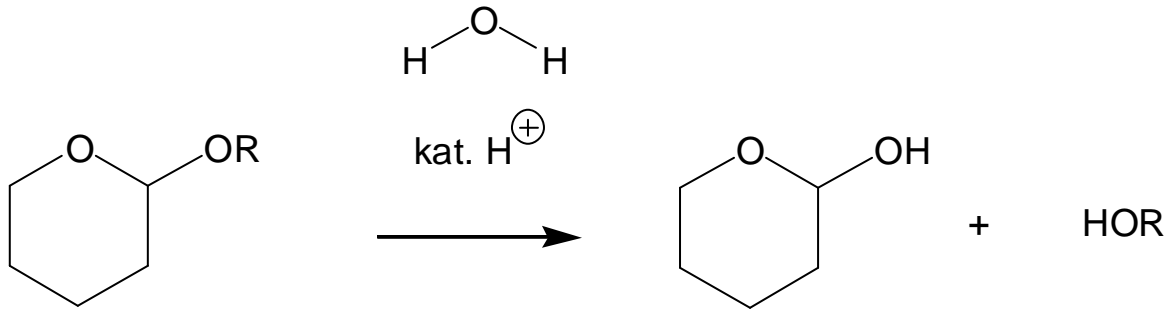
Der Katalysator "Proton" wird wieder freigesetzt und geht erneut in den katalytischen Kreislauf ein.



# Katalyse

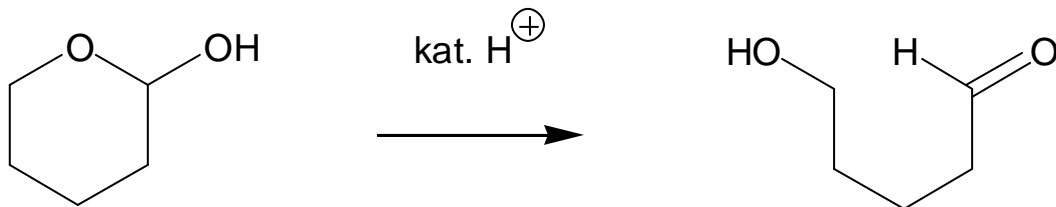
OC I 11.2A  
Koert

säurekatalysierte Acetalspaltung



Acetal

Halbacetal



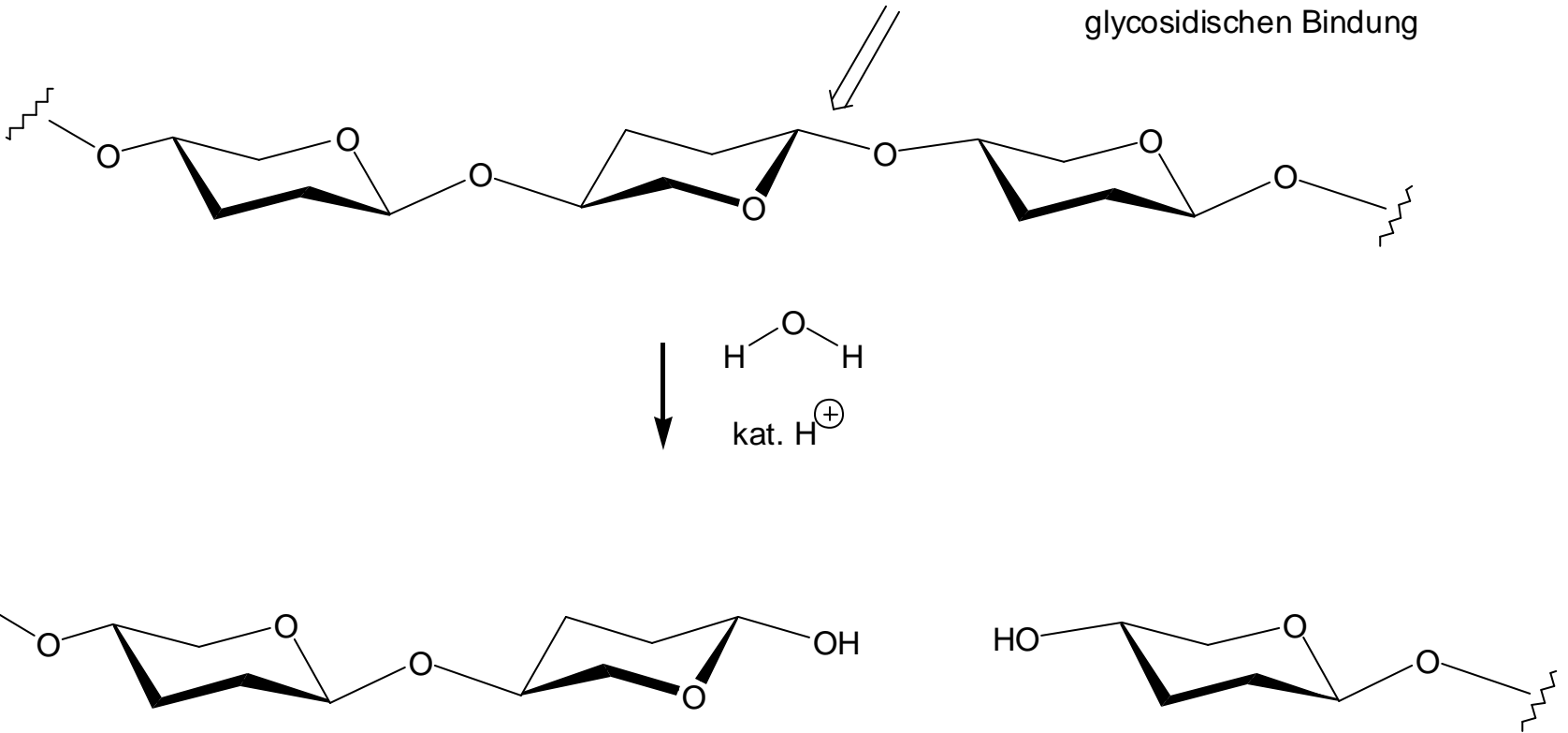
Hydroxyaldehyd

# Katalyse

OC I 11.2B  
Koert

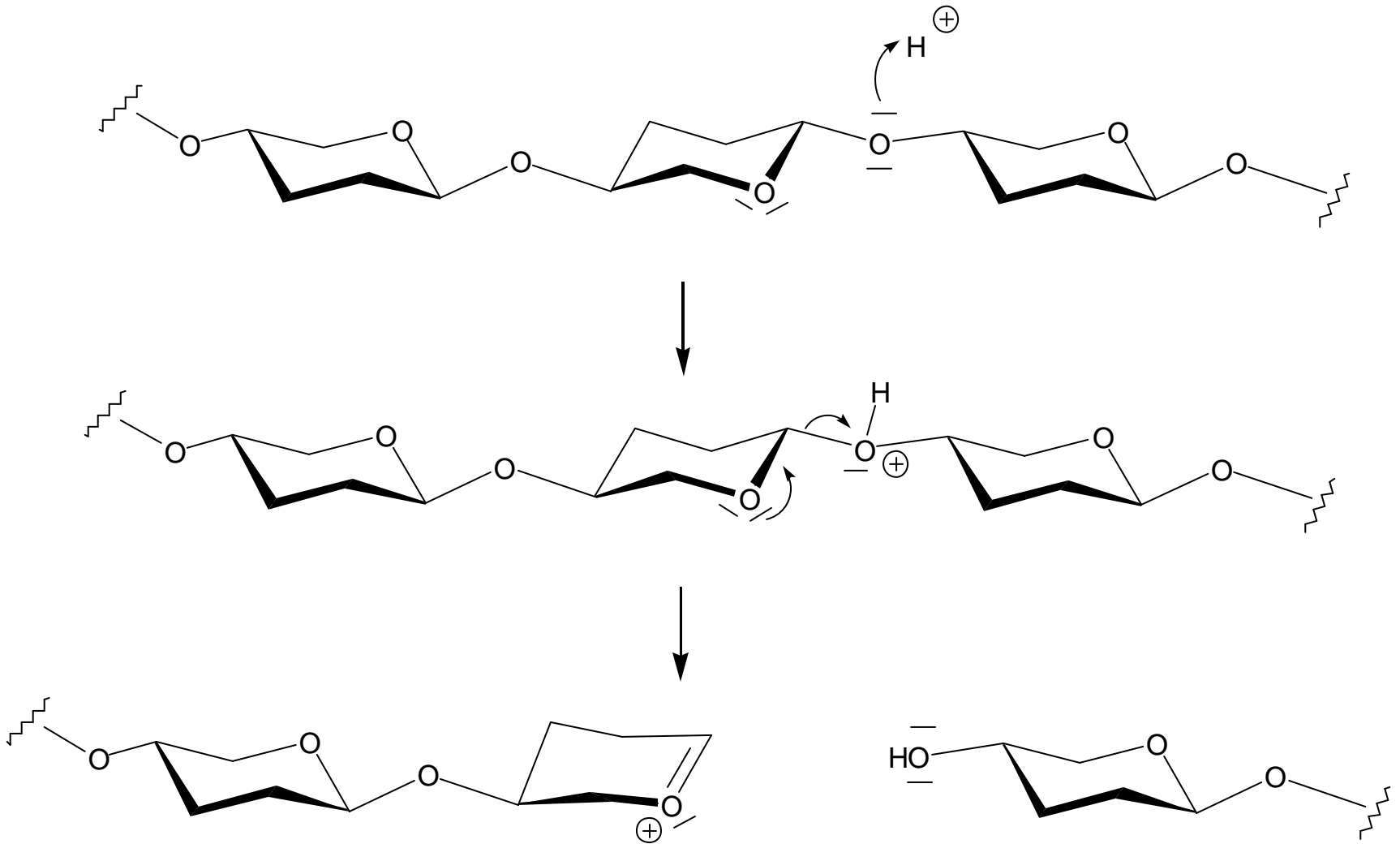
säurekatalysierte Acetalspaltung

Acetalspaltung - selektive Spaltung einer  
glycosidischen Bindung



# Katalyse

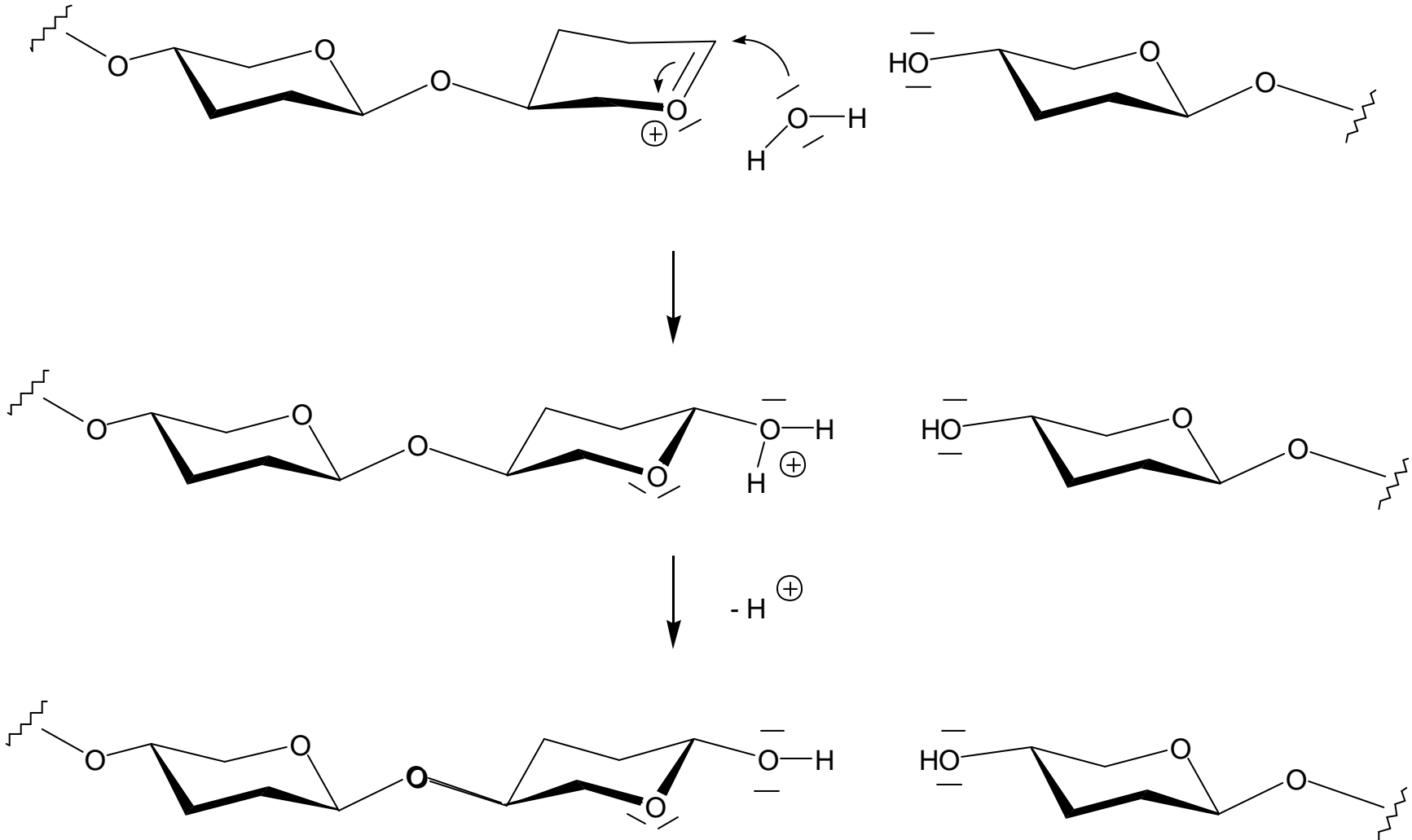
OCI 11.2C  
Koert



Oxoniumion -> Halbsessel

# Katalyse

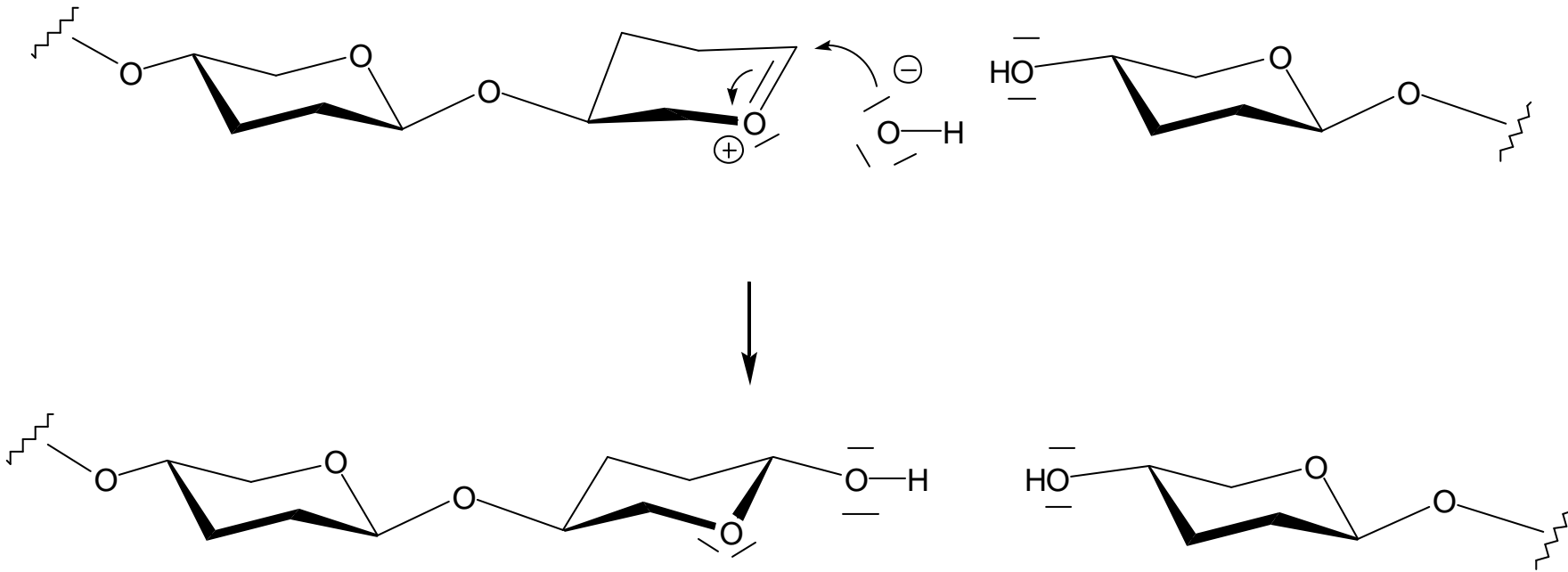
OCI 11.2D  
Koert



# Katalyse

OC I 11.2E  
Koert

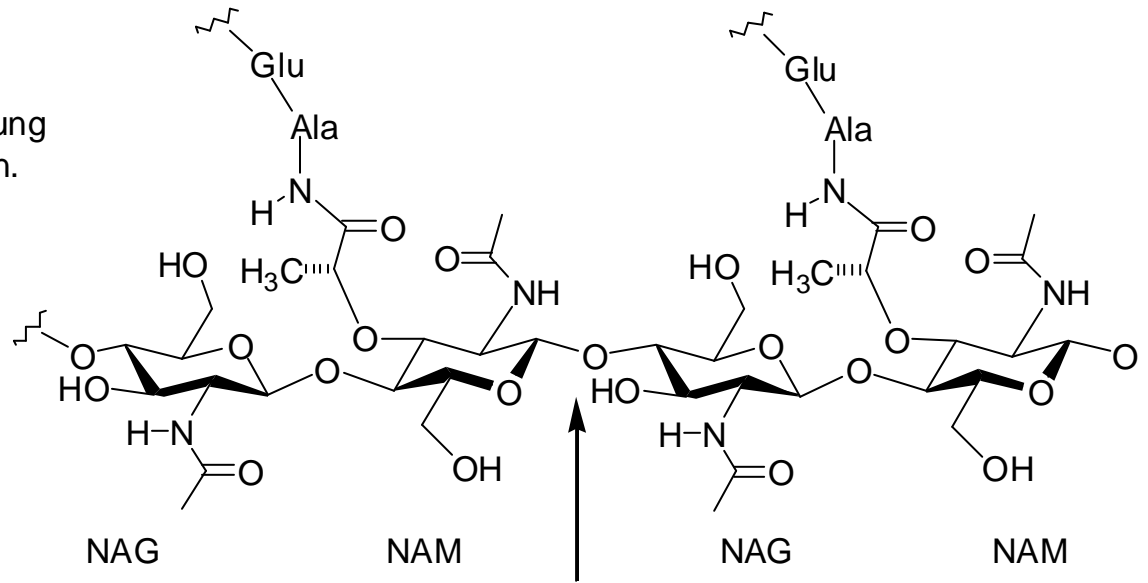
Hydroxid ist ein besseres Nukleophil als Wasser



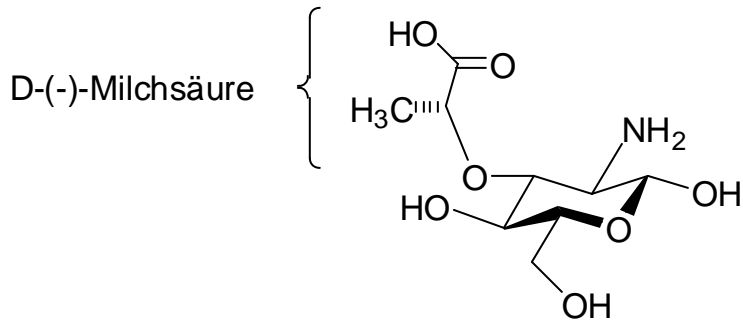
**Enzymkatalyse:**

Das Enzym Lysozym katalysiert die Spaltung der glucosidische Bindung zwischen NAM und NAG in Mureinen.

Mureine sind Glycanpeptide, die zum Aufbau der Zellwand von Bakterien dienen.



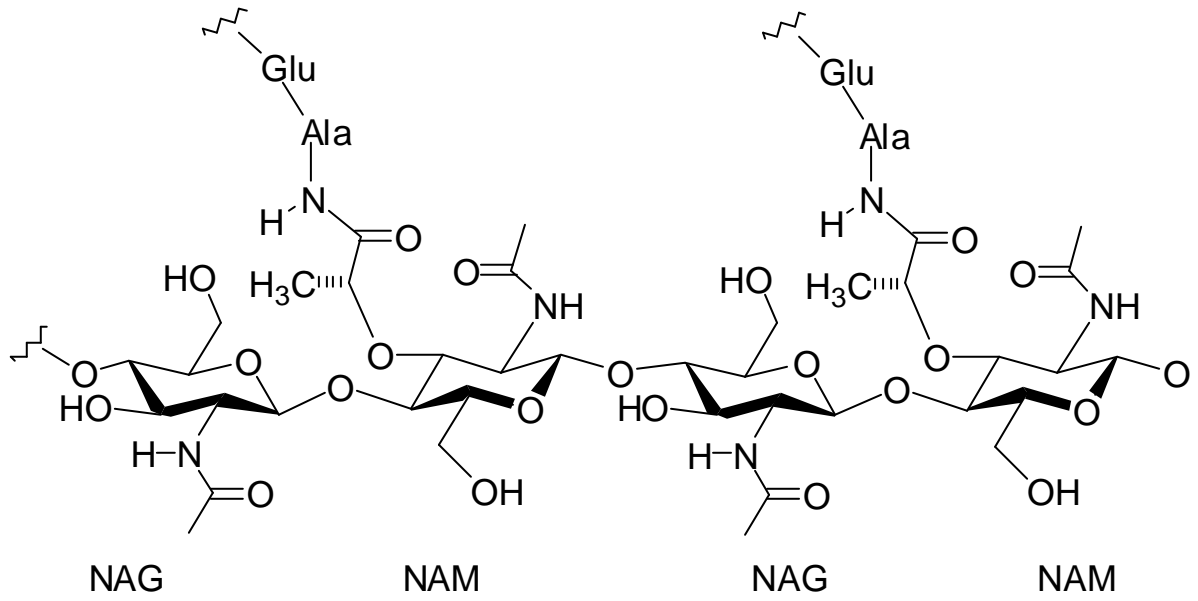
Lysozym spaltet hier



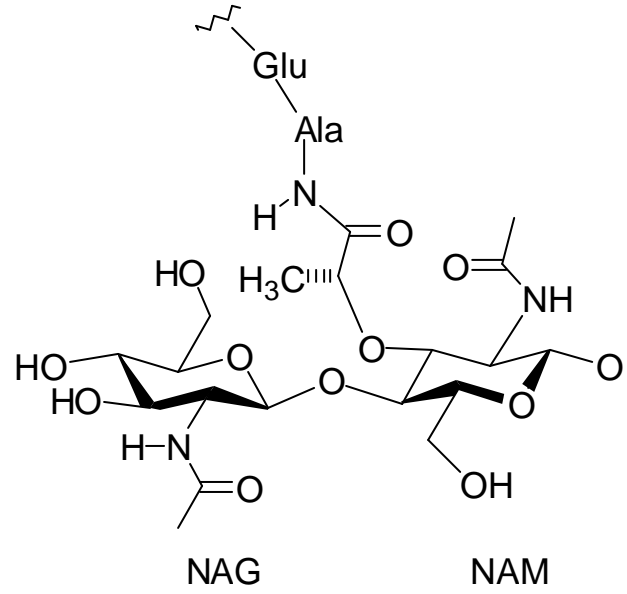
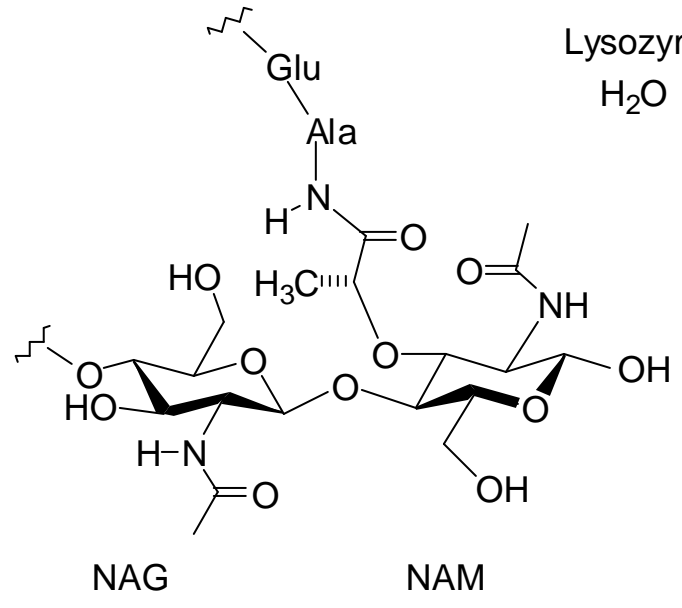
Muraminsäure

NAG = N-Acetylglucosamin

NAM = N-Acetylmuraminsäure



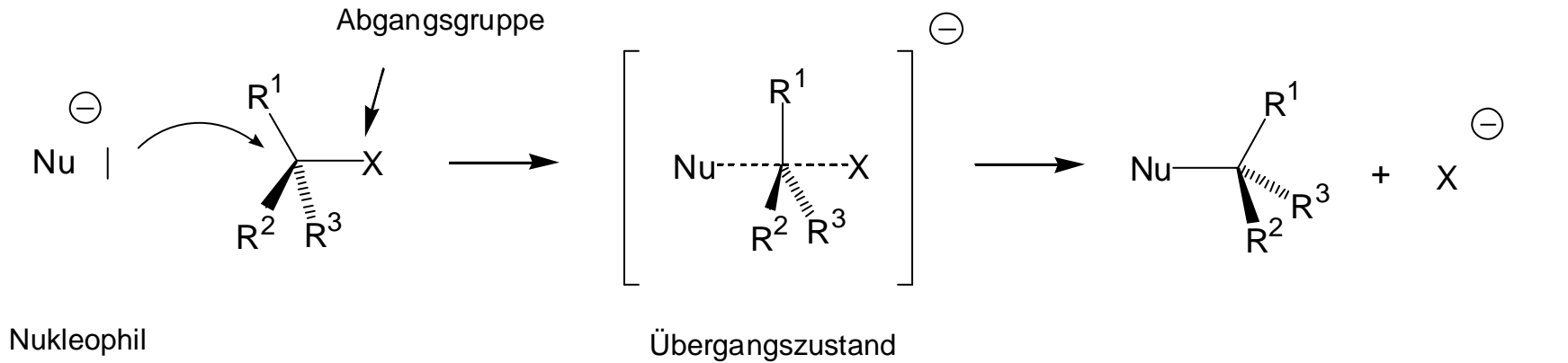
Lysozym  
H<sub>2</sub>O



# Nukleophile Substitution

OC 12.1  
Koert

## $S_N2$



einstufiger Mechanismus mit bimolekularer Kinetik

trigonal-bipyramidaler Übergangszustand mit colinearer Anordnung von Nu-C-X

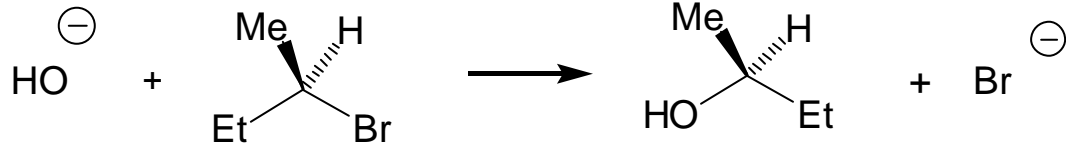
stereochemischer Verlauf: Inversion durch Rückseitenangriff (Waldensche Umkehr)



# Nukleophile Substitution

OC 12.2  
Koert

## $S_N2$

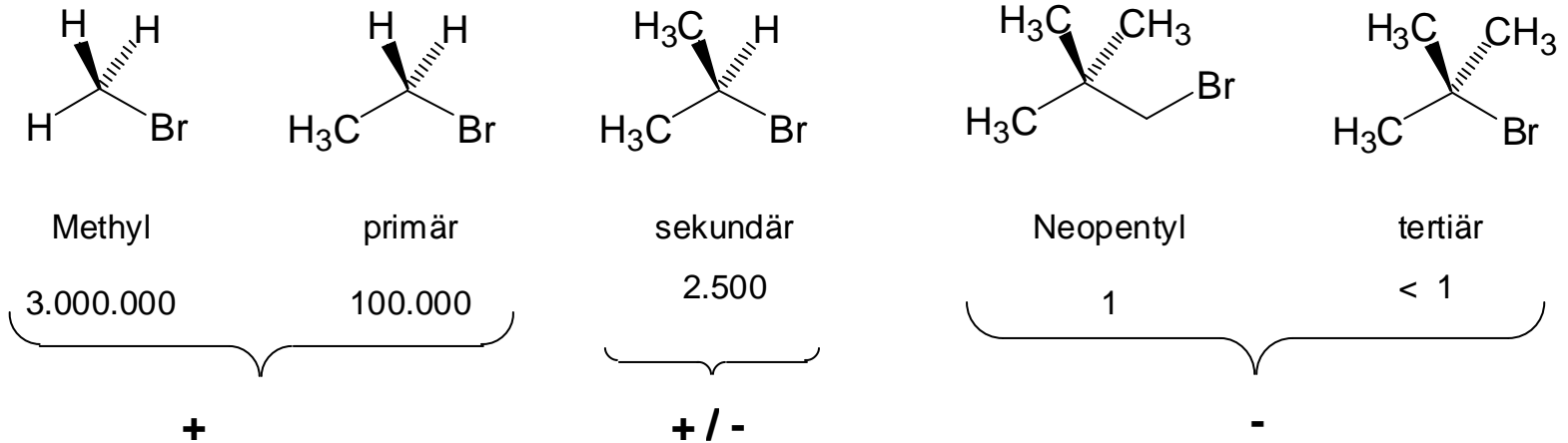


R-2-Brombutan

S-Butan-2-ol

CIP-Nomenklatur

Reaktivität des Substrats: sterische Effekte

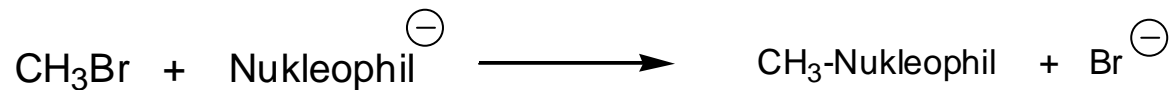


# Nukleophile Substitution

OC 12.3  
Koert

## $S_N2$

Nukleophilie



$\text{HS}^-$	$\text{CN}^-$	$\text{I}^-$	$\text{CH}_3\text{O}^-$	$\text{HO}^-$	$\text{Cl}^-$	$\text{NH}_3$	$\text{H}_2\text{O}$
125	125	100	25	16	1,0	0.7	0,001

Abgangsgruppe

$\text{TosO}^-$	$\text{I}^-$	$\text{Br}^-$	$\text{Cl}^-$	$\text{F}^-$	$\text{RO}^-$	$\text{NH}_2^-$	$\text{OH}^-$
60	30	10	0,2	0,001	fast 0		

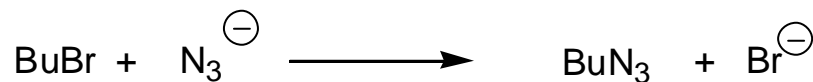
stabile Anionen sind gute Abgangsgruppen

# Nukleophile Substitution

OC 12.4  
Koert

Lösungsmittel-Einfluß

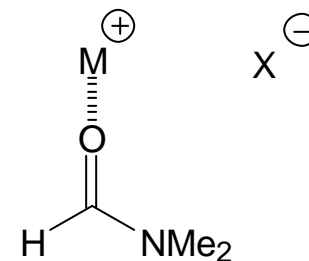
## $S_N2$



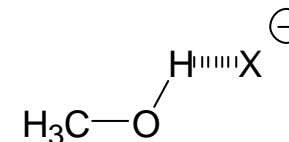
HMPA	CH <sub>3</sub> CN	DMF	DMSO	H <sub>2</sub> O	CH <sub>3</sub> OH
200	5,0	2,5	1,3	0,007	0,001

aprotische, polare Lösungsmittel begünstigen die  $S_N2$ -Reaktion

Komplexierung des Kations -> Aktivierung des anionischen Nukleophils



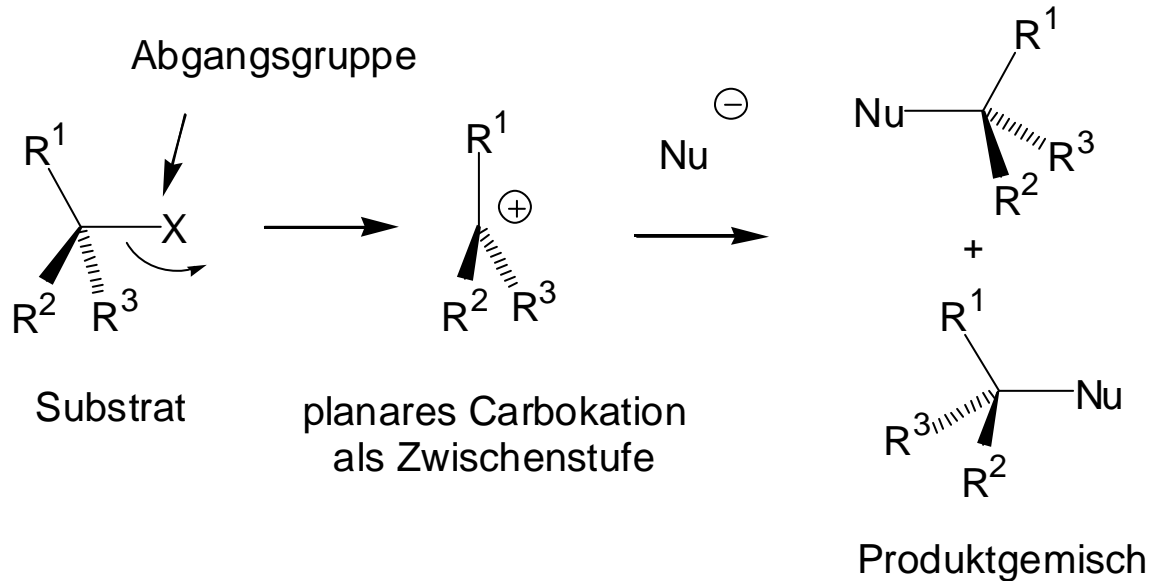
Protische Lösungsmittel solvatisieren das anionische Nukleophil und verlangsamen die  $S_N2$ -Reaktion.



# Nukleophile Substitution

OC 12.5  
Koert

## $S_N1$



zweistufiger Mechanismus

1. Schritt geschwindigkeitsbestimmend,  $RG = k [\text{Substrat}]$

kationische Zwischenstufe

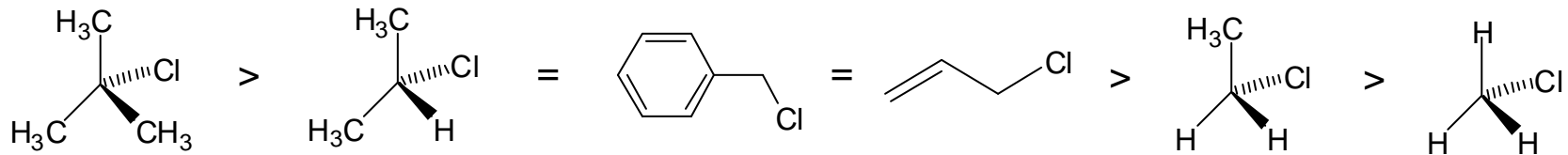
stereochemischer Verlauf: Verlust der stereochemischen Information durch planares Kation

Der geschwindigkeitsbestimmende Schritt ist die endotherme Bildung des Kations.

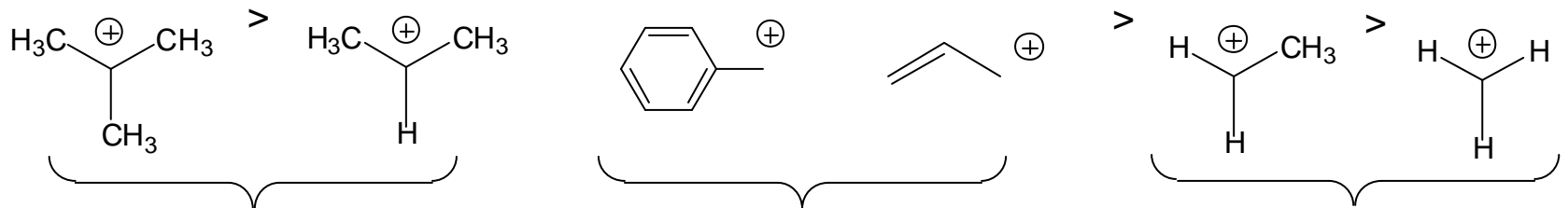
Nach dem Hammond-Postulat reflektiert die energetische Lage der Kations damit die energetische Lage des korrespondierenden Übergangszustands.

-> je stabiler das Kation, desto niedriger die Aktivierungsenergie, desto rascher die  $S_N1$ -Reaktion

## Reaktivitätsskala für $S_N1$ -Substrate



## Stabilitätsskala für Kationen



+

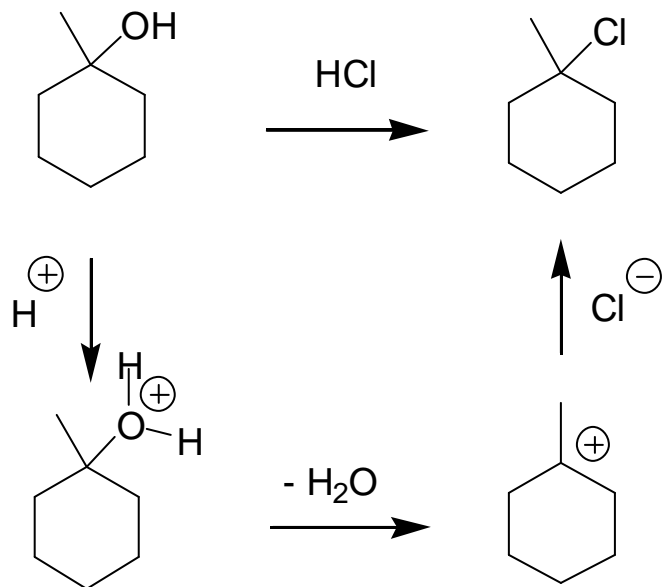
+

-

# Nukleophile Substitution $S_N1$

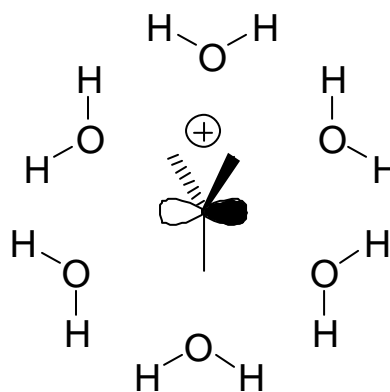
OC 12.7  
Koert

Rolle der Abgangsgruppe:



Rolle des Lösungsmittels:

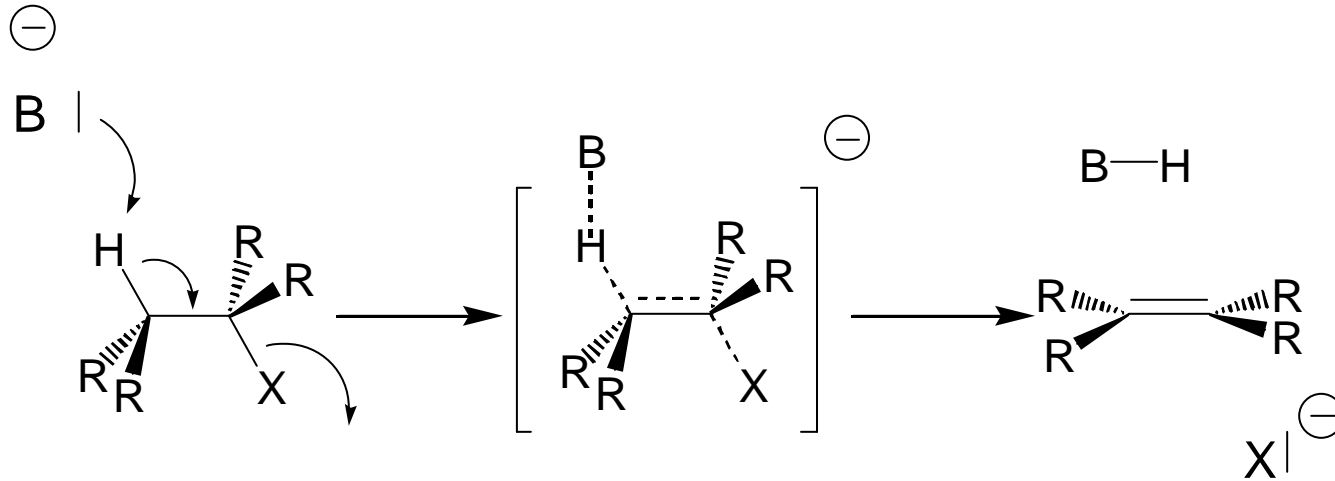
hohe Dielektrizitätskonstante fördert  $S_N1$



Hexan	1,9
Et <sub>2</sub> O	4,3
DMF	38
EtOH	24,3
H <sub>2</sub> O	80,4



Wasser	80% EtOH	40% EtOH	EtOH
100	14	0,1	0,001



konzertierter, einstufiger Mechanismus

Geschwindigkeit =  $k [\text{Base}] \times [\text{Substrat}]$  (bimolekular)

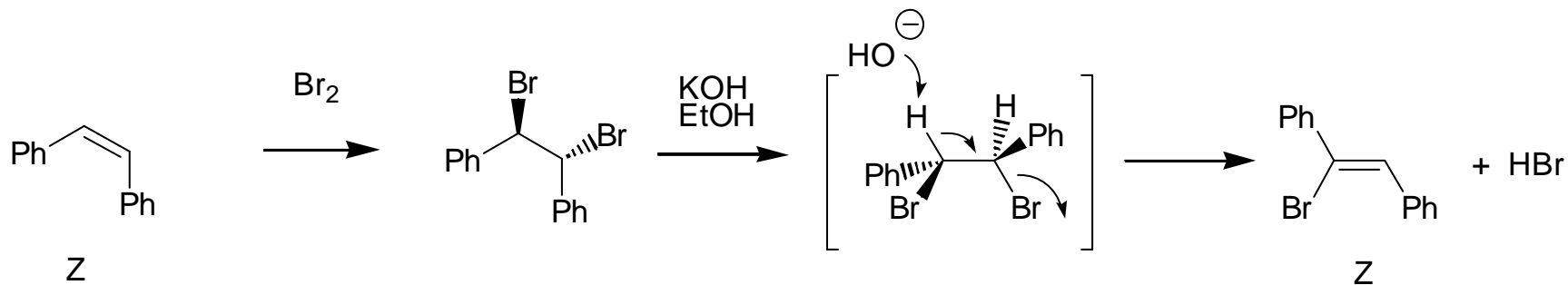
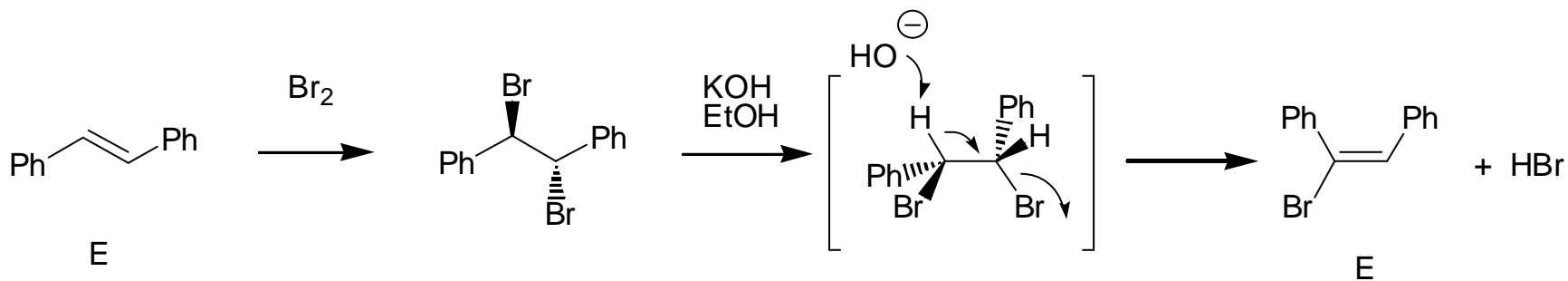
B-H-C-C-X in einer Ebene zur maximalen Überlappung der beteiligten Orbitale

antiperiplanare Anordnung von H und X am günstigsten

# Eliminierung

# E2

OC 12.9  
Koert



Anti-Addition

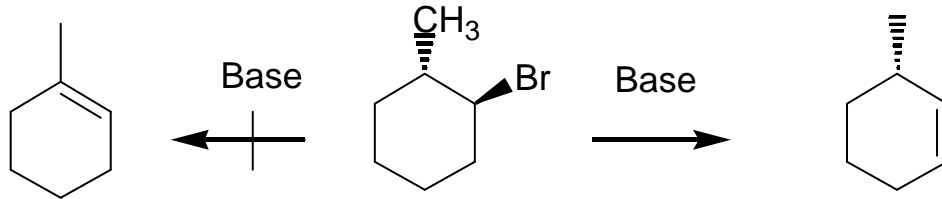
antiperiplanare  
Anordnung in der  
E2-Eliminierung



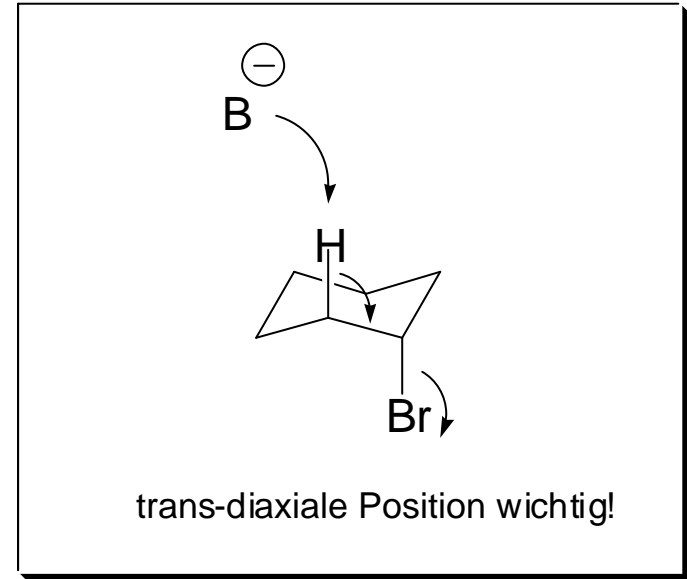
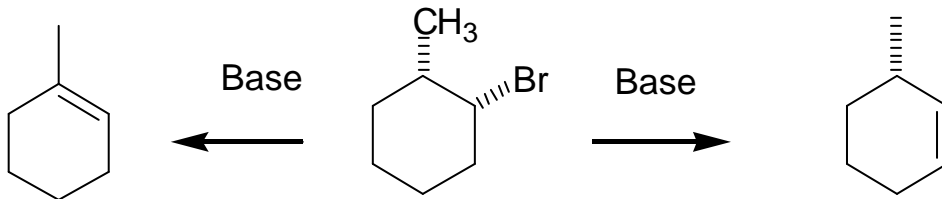
# Eliminierung

# E2

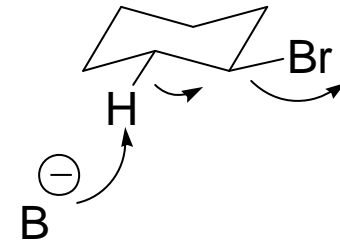
OC 12.10  
Koert



antiperiplanare Anordnung  
erfordert trans-Stellung von Br und H



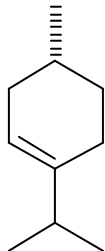
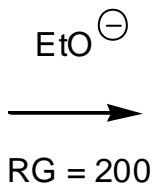
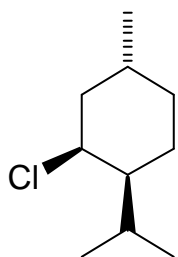
trans-diequatorial ungünstig  
keine maximale Überlappung  
der beteiligten Orbitale



# Eliminierung

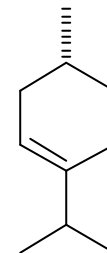
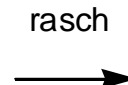
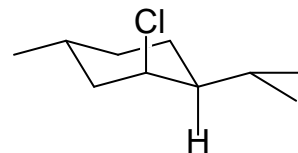
# E2

OC 12.11  
Koert

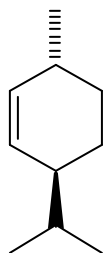
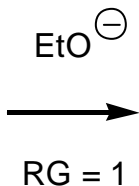
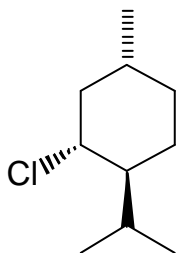


3-Menthen

Neomenthylchlorid

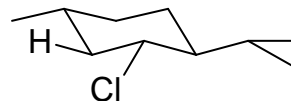


trans-diaxial schon in der  
Vorzugskonformation



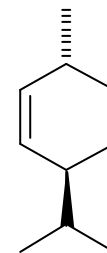
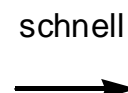
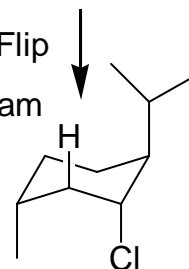
2-Menthen

Menthylchlorid



in der Vorzugskonformation  
trans-diequatoriale Anordnung

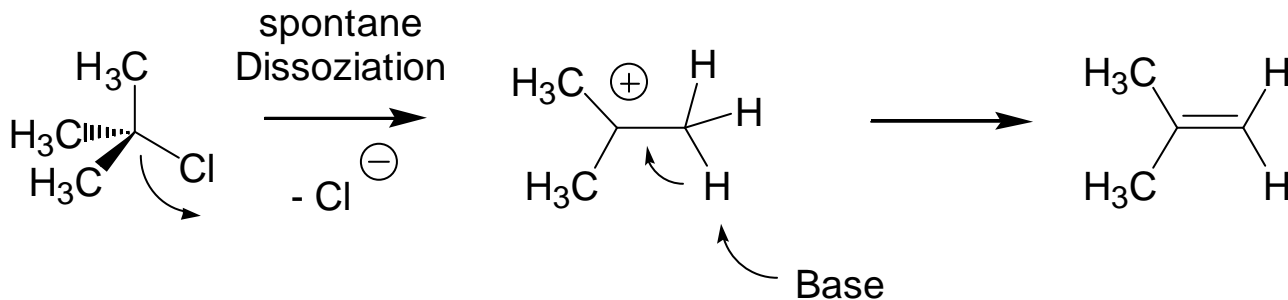
Ring-Flip  
↓  
langsam



energetisch ungünstig  
aber trans-diaxial gewährleistet

# Eliminierung E1

OC 12.12  
Koert

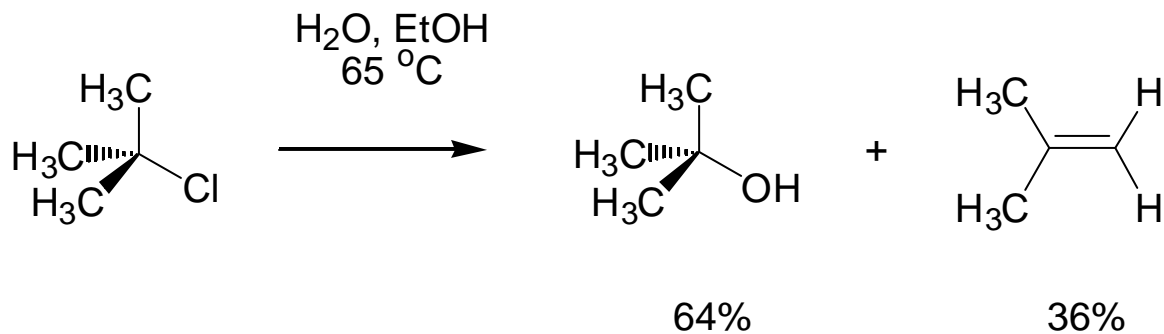


zweistufiger Mechanismus

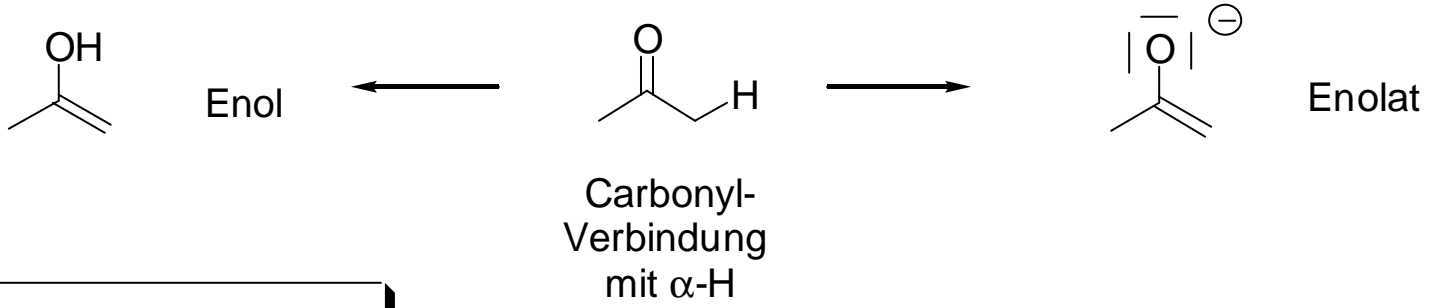
erster Schritt (Dissoziation) geschwindigkeitsbestimmend

Reaktionsgeschwindigkeit =  $k$  [Substrat] (unimolekular)

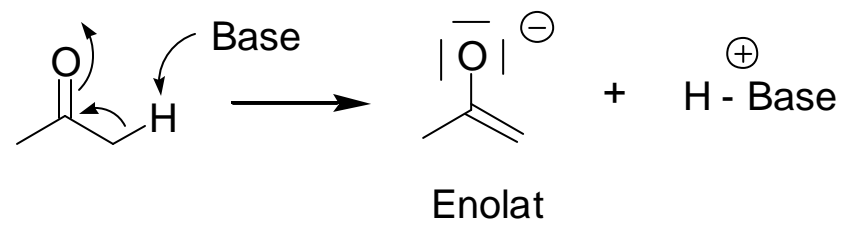
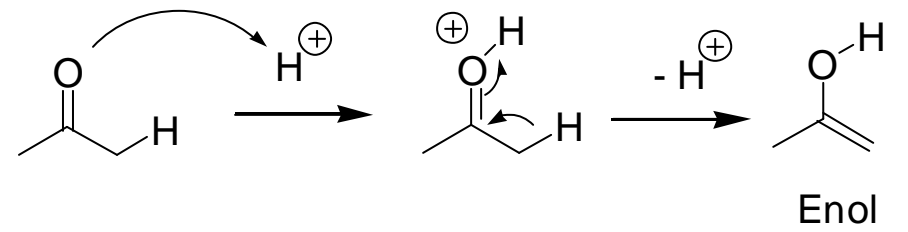
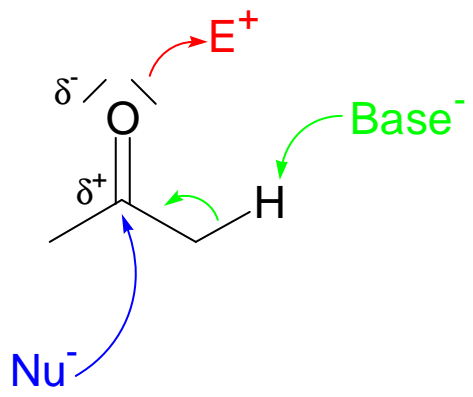
E1 begleitet of  $\text{S}_{\text{N}}1$



# Carbonylchemie



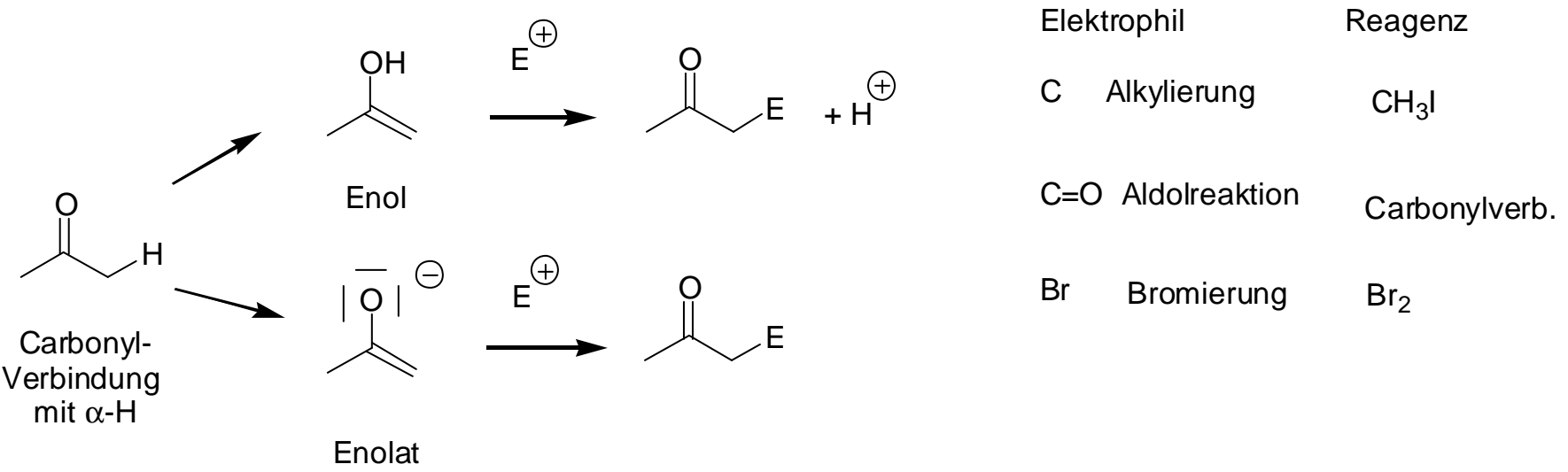
*Grundreaktionstypen von Carbonylgruppen*



# Carbonylchemie

OC 13.2  
Koert

Enole und Enolate sind gute Nucleophile



$\alpha$ -Substitution von Carbonylverbindungen  
über die entsprechenden Enole/Enolate

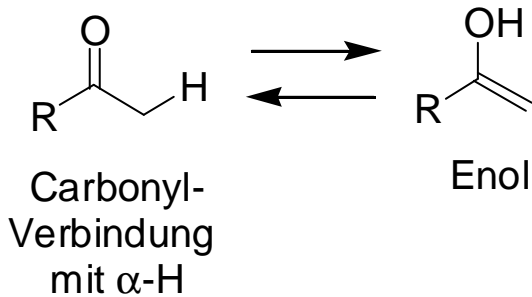
# Carbonylchemie

OC 13.3  
Koert

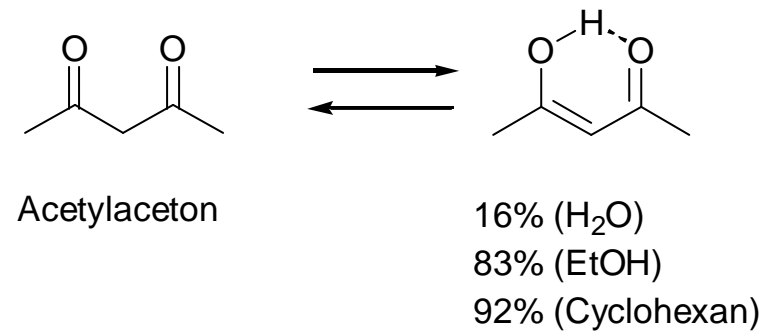
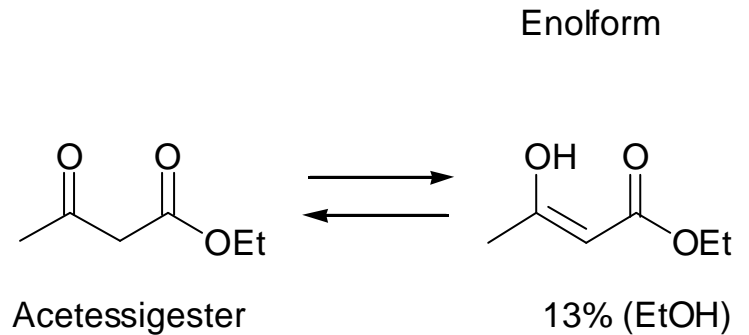
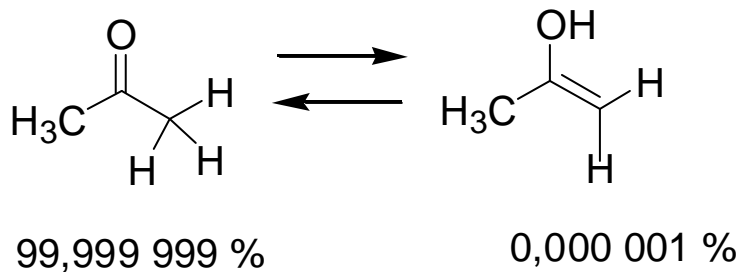
Enole und Enolate werden durch Säure-Basen-Reaktionen aus den entsprechenden Carbonylverbindungen gebildet.

-> Gleichgewichtsreaktionen

-> Acidität des  $\alpha$ -Hs.



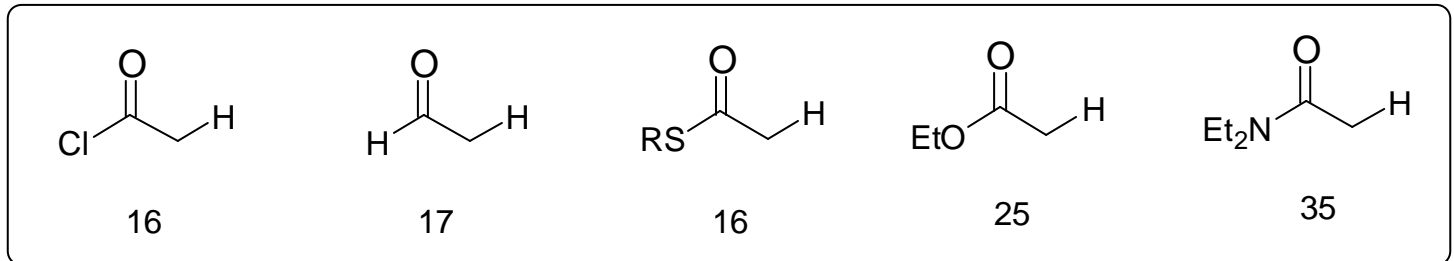
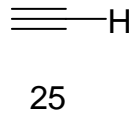
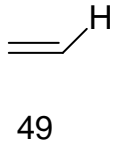
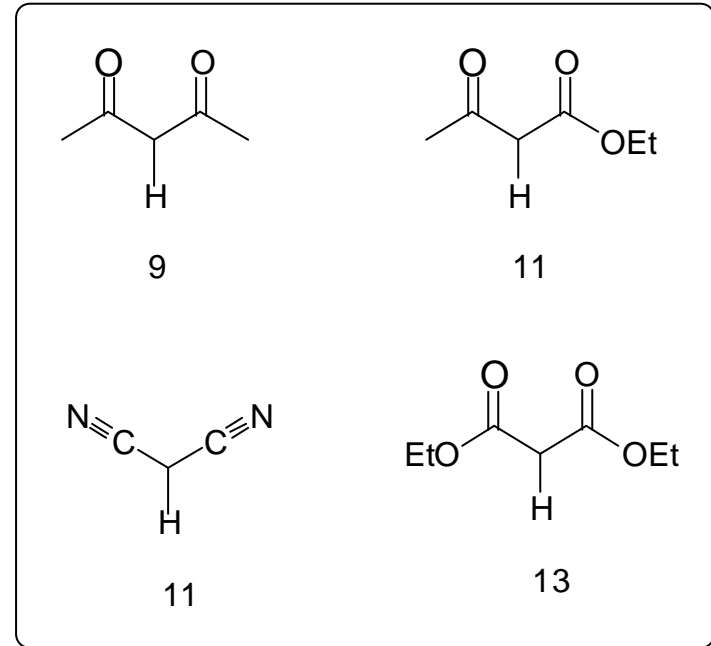
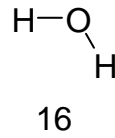
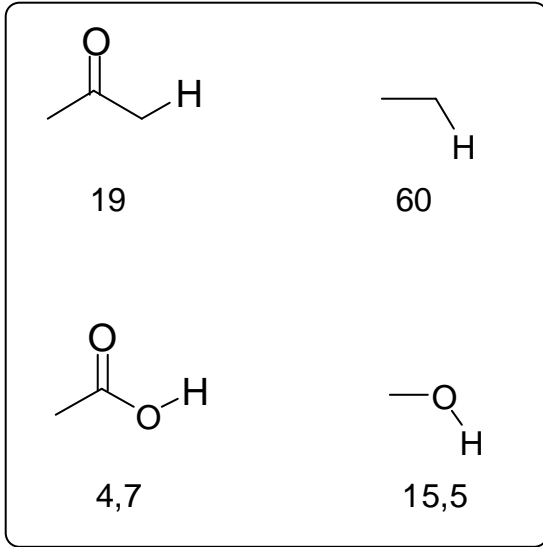
Keto-Enol-Gleichgewicht (Tautomerie)



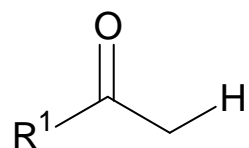
# Aciditäts-Konstanten

OC 13.4  
Koert

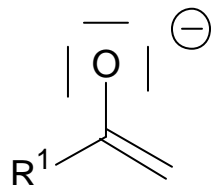
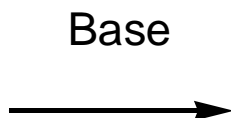
pK<sub>a</sub>



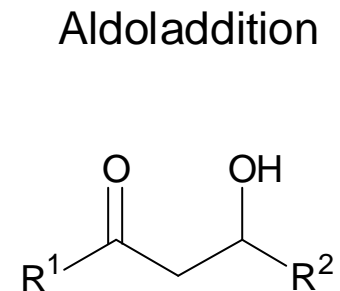
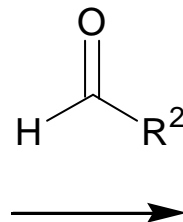
# Aldolreaktion



Carbonyl-  
Verbindung  
mit  $\alpha$ -H



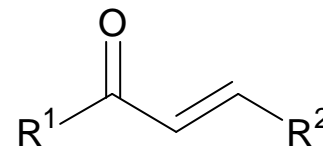
Enolat



Aldol



- H<sub>2</sub>O



Enon

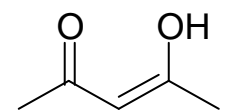
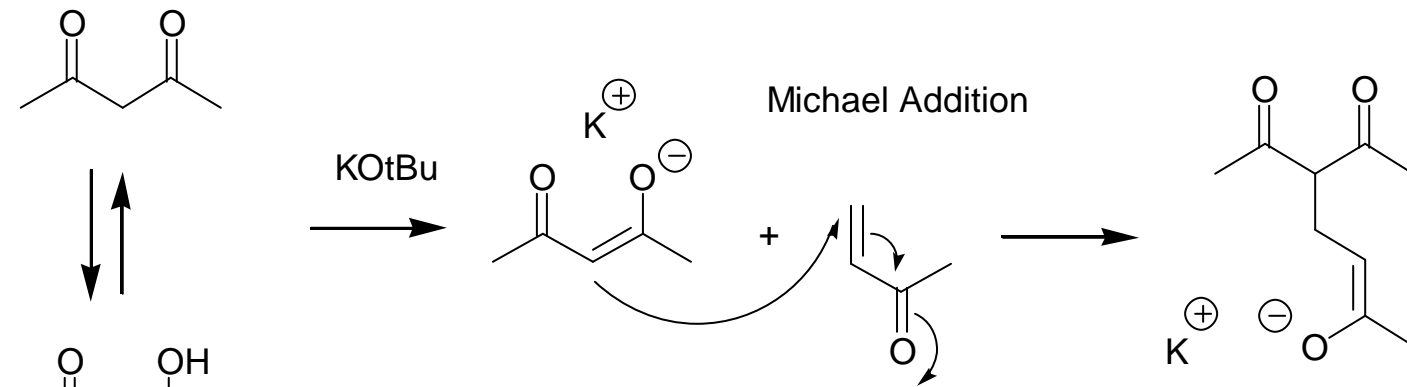
Aldolkondensation



# Carbonylchemie

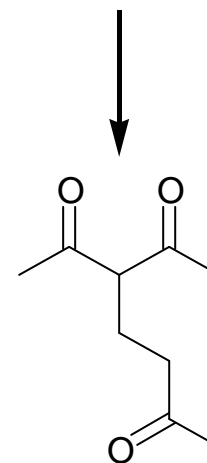
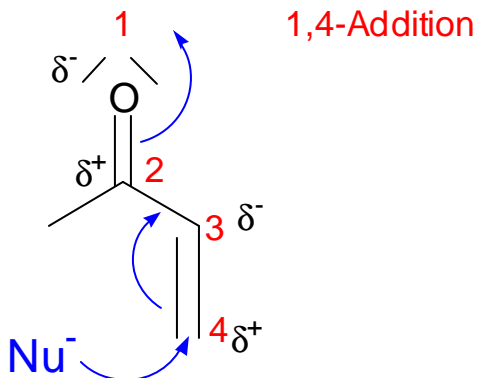
OC 13.6  
Koert

1,3-Dicarbonylverbindungen sind gute C-H acide Komponenten



vinyloge Säure

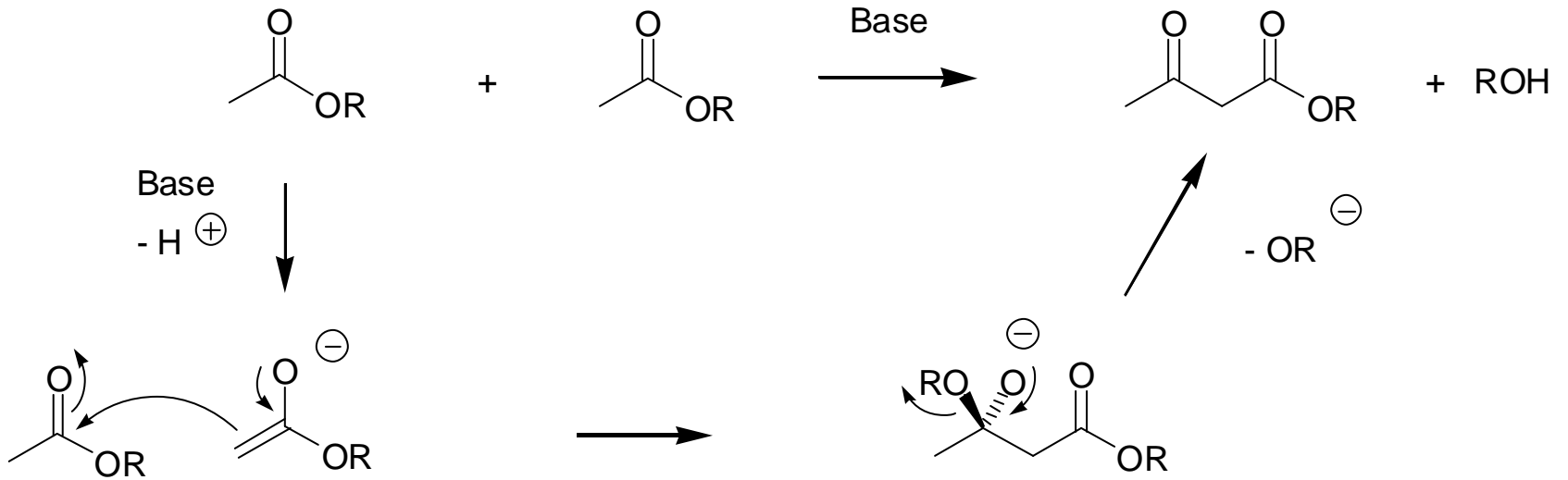
Grundreaktionsmuster  
von *a-b*-ungesättigten  
Carbonylverbindungen



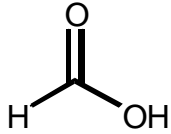
# Esterenolate

OC 13.7  
Koert

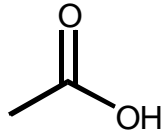
## Claisenkondensation



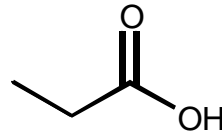
# Carbonsäuren



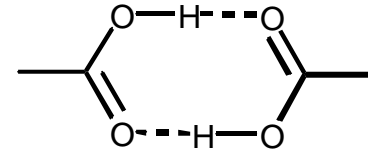
Ameisensäure



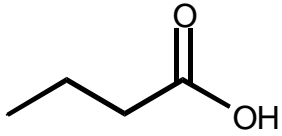
Essigsäure



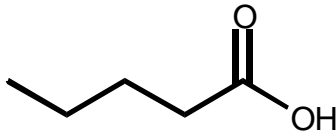
Propionsäure



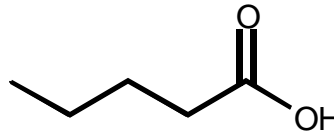
Bildung von Dimeren  
über H-Brücken



Butansäure  
(Buttersäure)

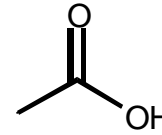


Pentansäure  
(Valeriansäure)

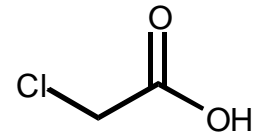


Hexansäure  
(Capronsäure)

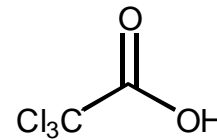
Acidität ( $pK_a$ )



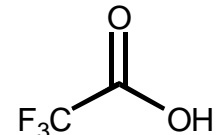
4.7



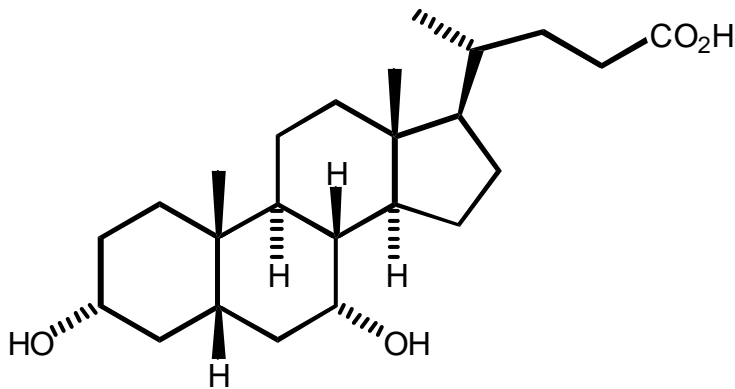
2.9



0.6



0.2



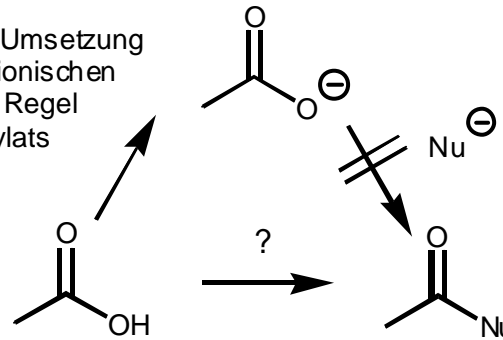
Cholsäure

Gallensäuren  
Micellenbildung

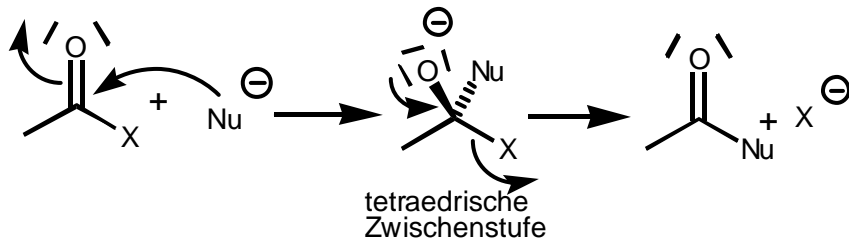
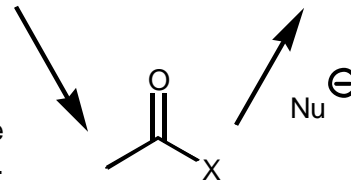
langkettige Fettsäuren

-> Fette, Lipide, Phospholipidmembran

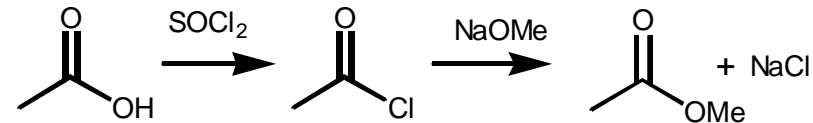
Der Versuch der direkten Umsetzung von Carbonsäuren mit anionischen Nucleophilen bleibt in der Regel auf der Stufe des Carboxylats stecken.



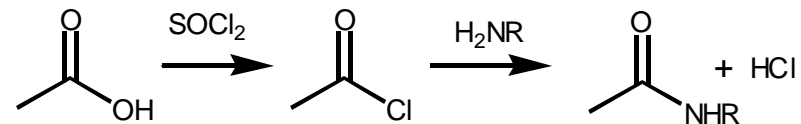
Daher wird die OH-Gruppe der Säure gegen eine bessere Abgangsgruppe ausgetauscht. Die Carbonsäure wird so für eine nukleophile Substitution aktiviert.



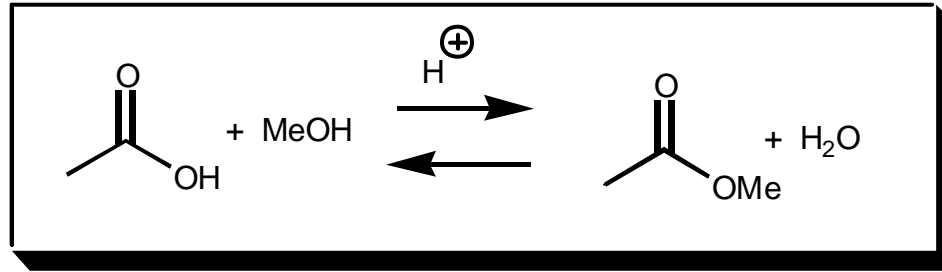
Beispiel: Säure -> Säurechlorid -> Ester



Beispiel: Säure -> Säurechlorid -> Amid

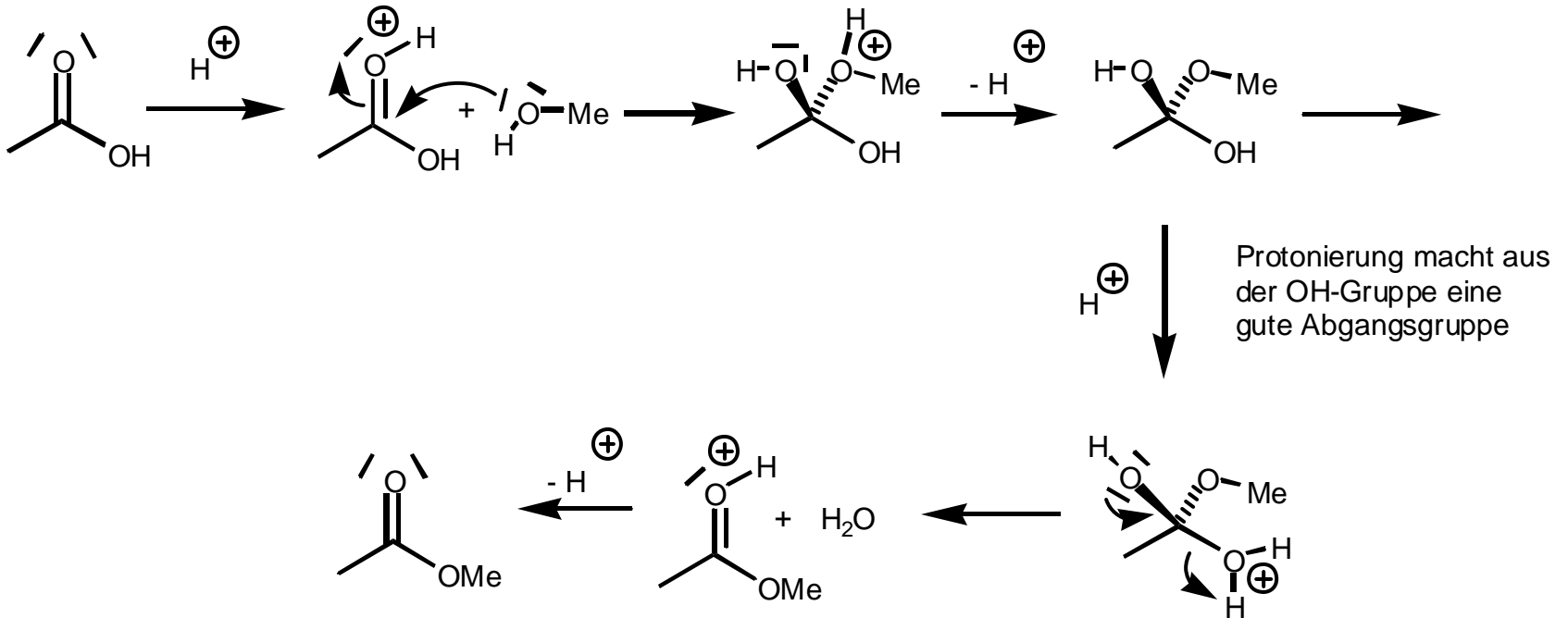


# Esterbildung unter Säurekatalyse



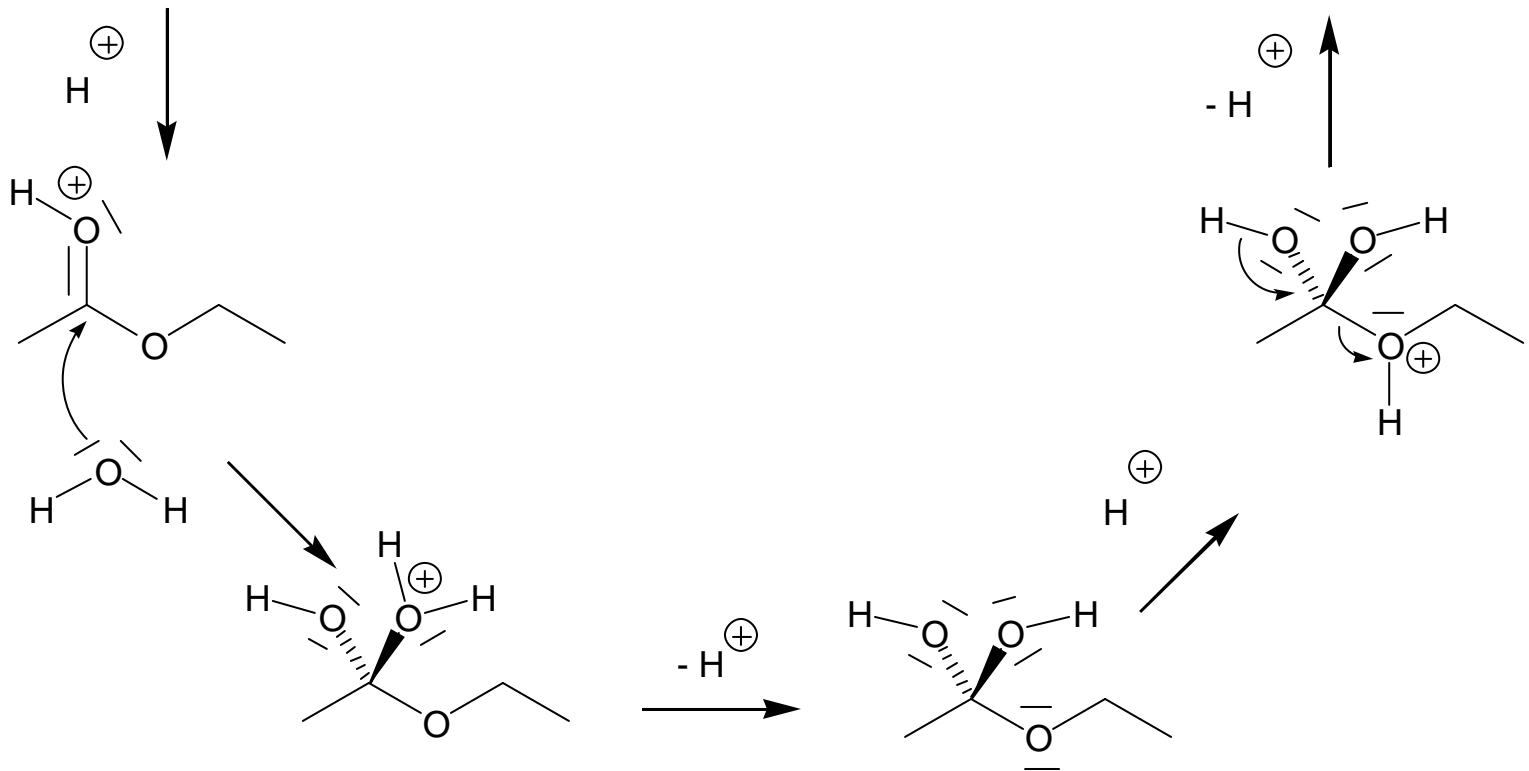
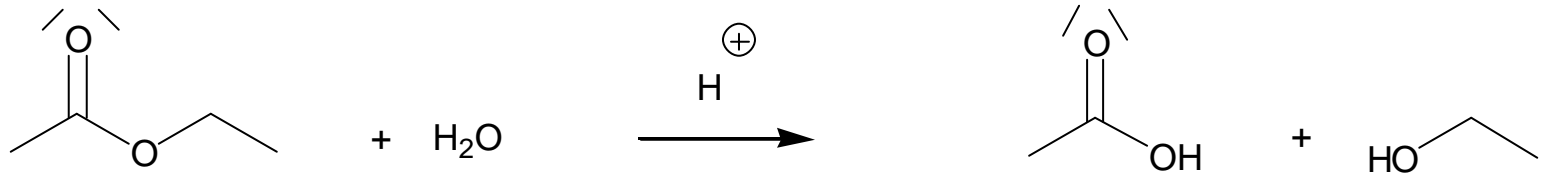
Protonierung aktiviert die Carbonylgruppe für einen nukleophilen Angriff

tetraedrische Zwischenstufe

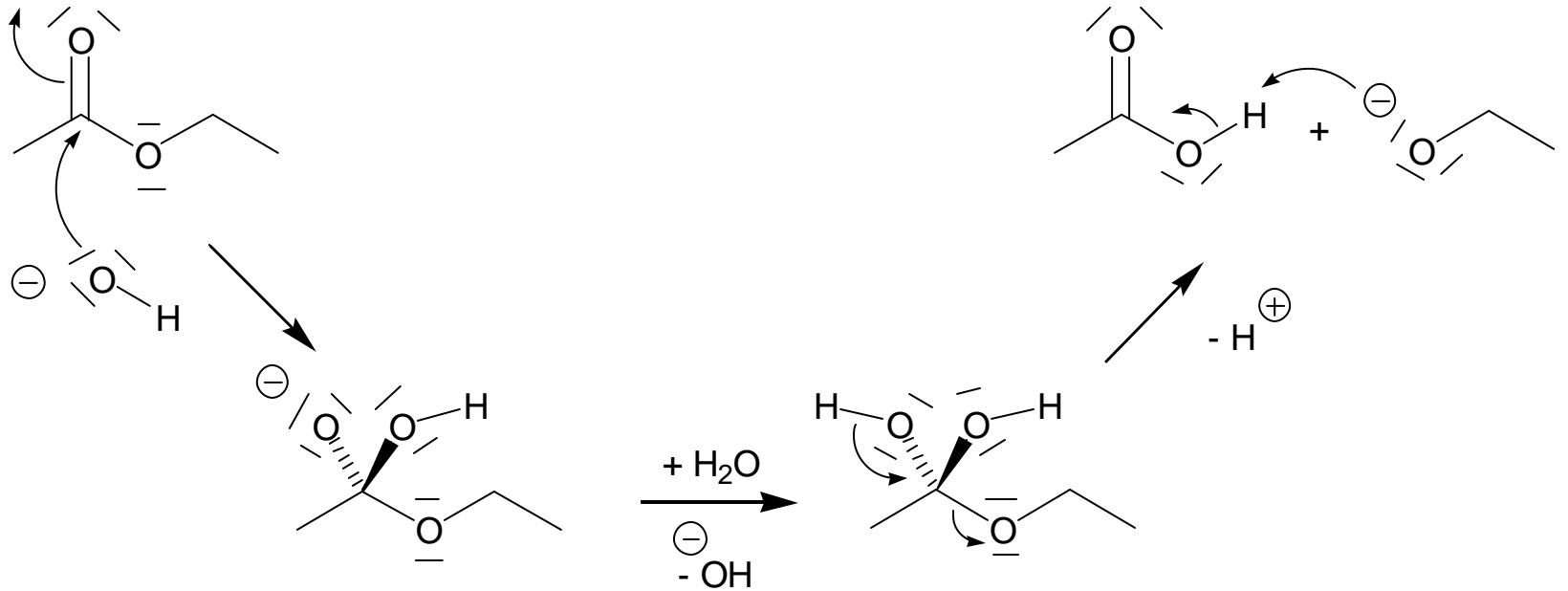
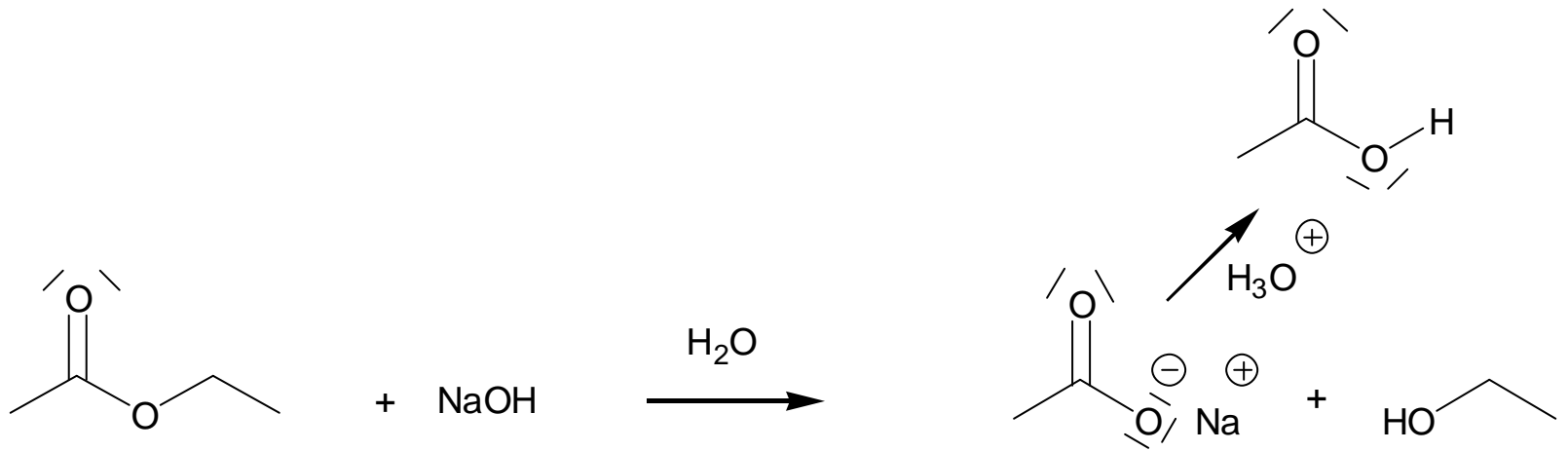


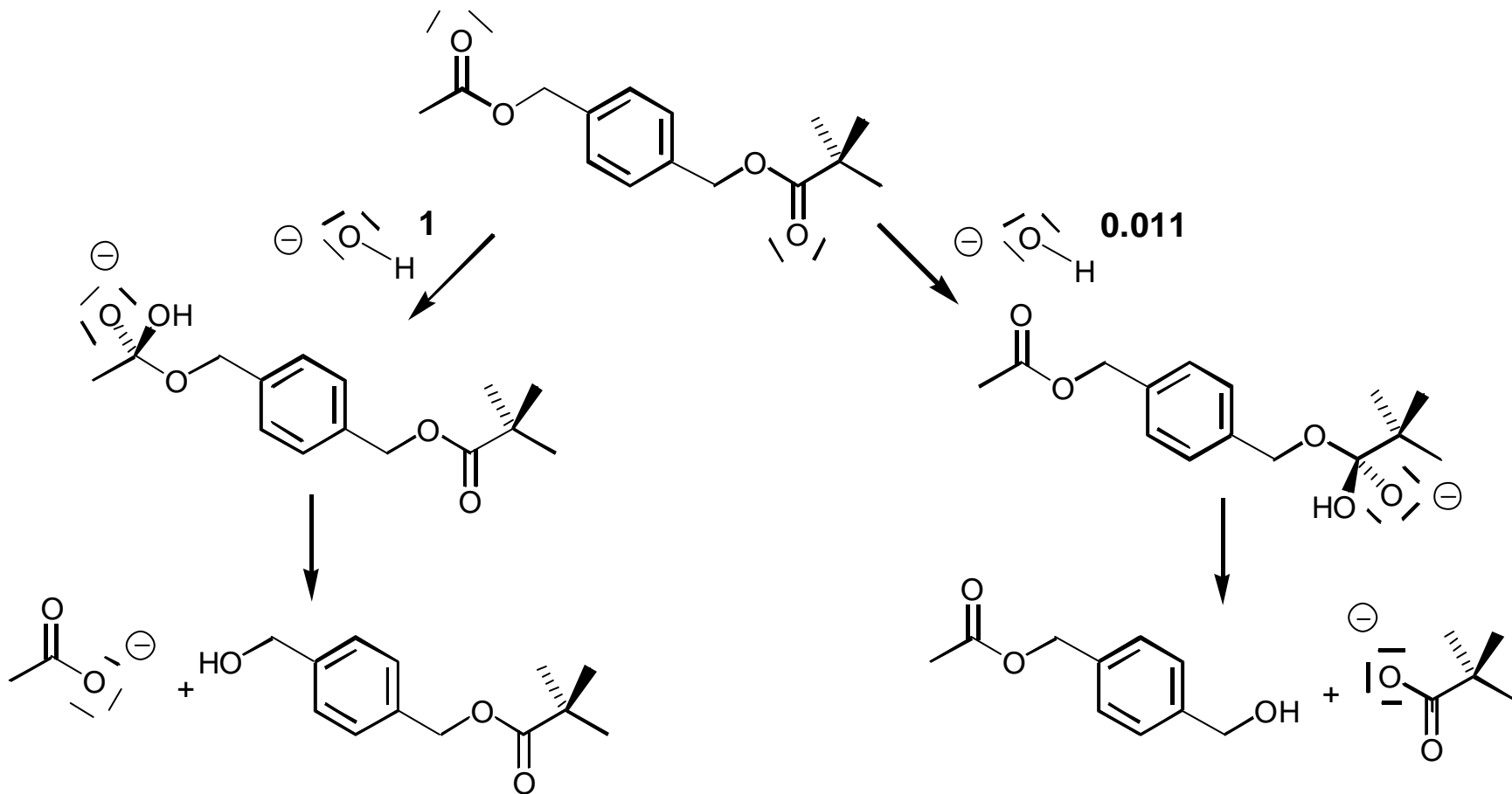
# Saure Esterhydrolyse

OC 13.11  
Koert



# Basische Esterhydrolyse

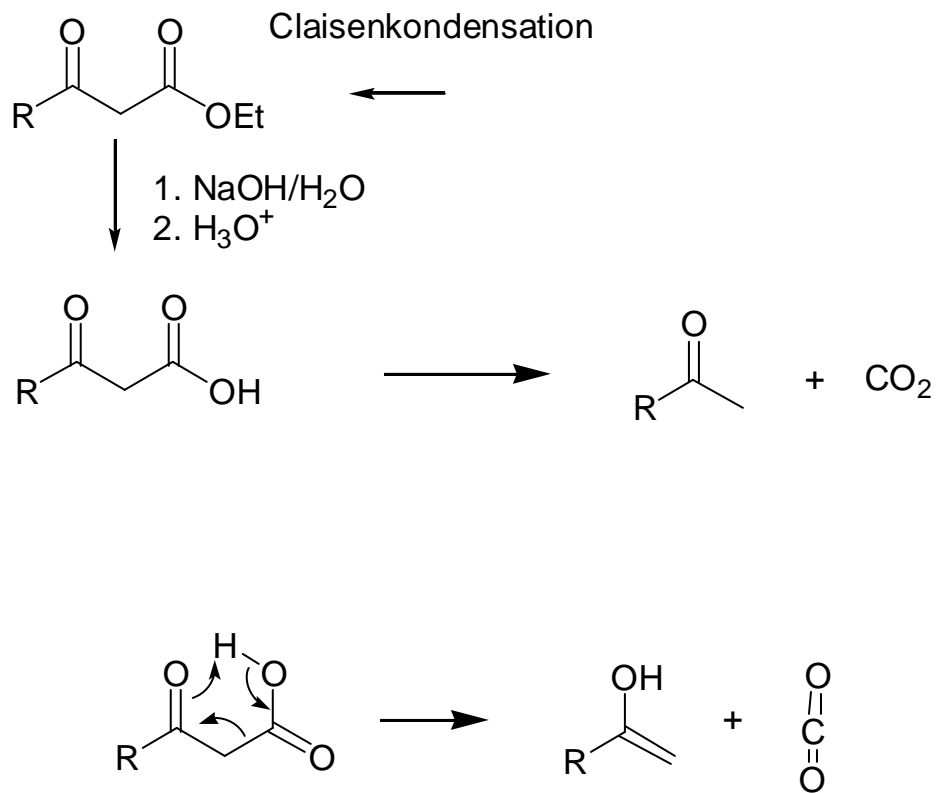




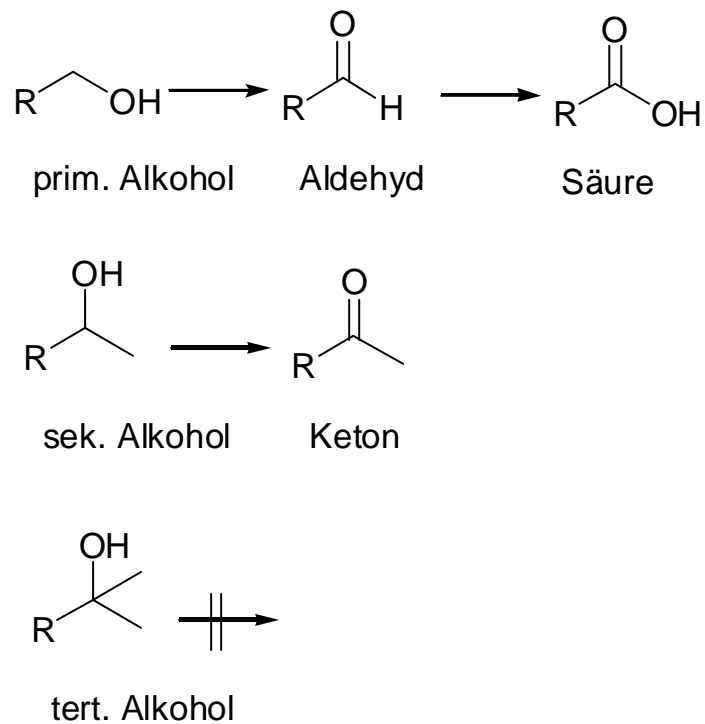
Der für den nukleophilen Angriff von  $\text{OH}^-$  sterisch besser zugängliche Essigsäureester wird schneller hydrolysiert als der sterisch abgeschirmte Ester der Pivalinsäure.



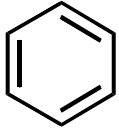
## Decarboxylierung von $\beta$ -Ketocarbonsäuren



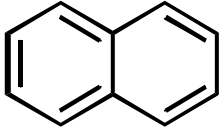
## Oxidationen



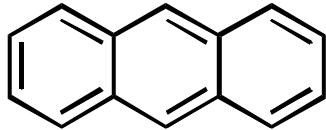
Hückel:  $4n + 2 \pi$ -Elektronen



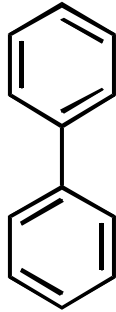
Benzol  
(Kekules Traum)



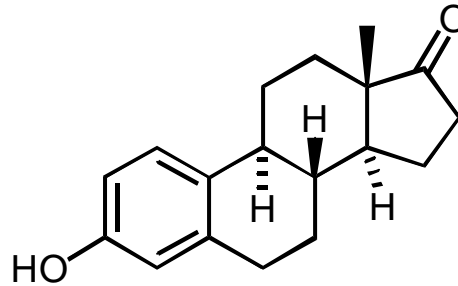
Naphthalin



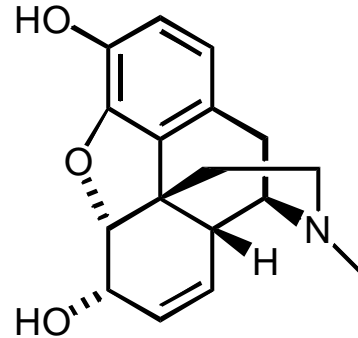
Anthracen



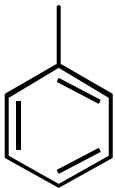
Biphenyl



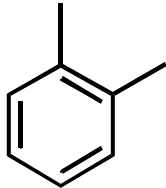
Östron



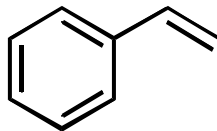
Morphin



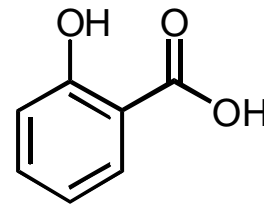
Toluol



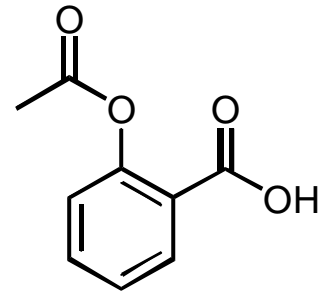
ortho-Xylol



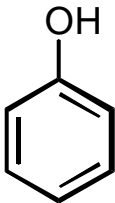
Styrol



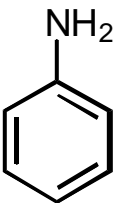
Salicylsäure



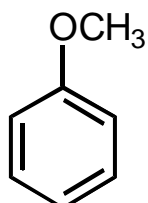
Acetylsalicylsäure  
(Aspirin)



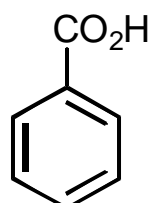
Phenol



Anilin

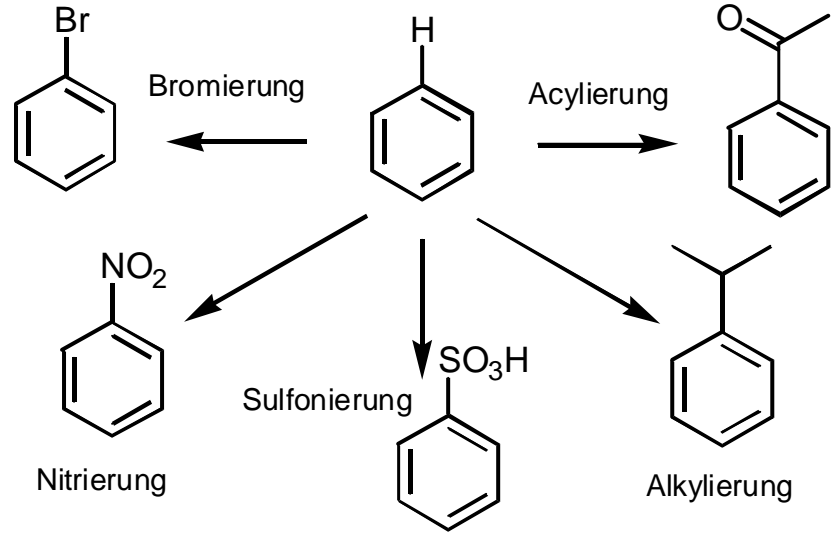
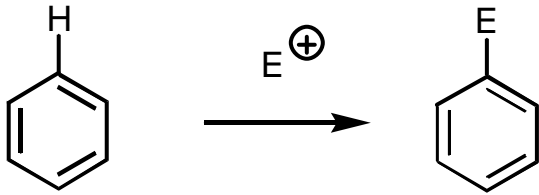


Anisol

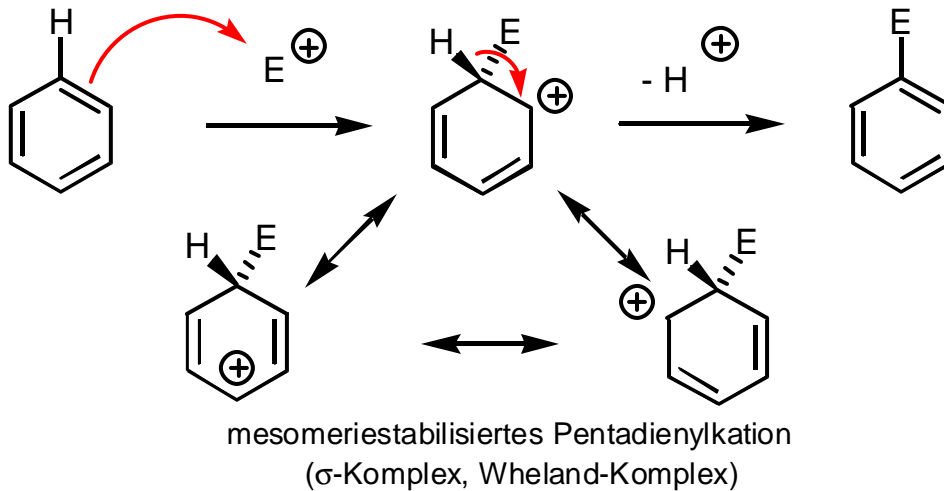


Benzoesäure

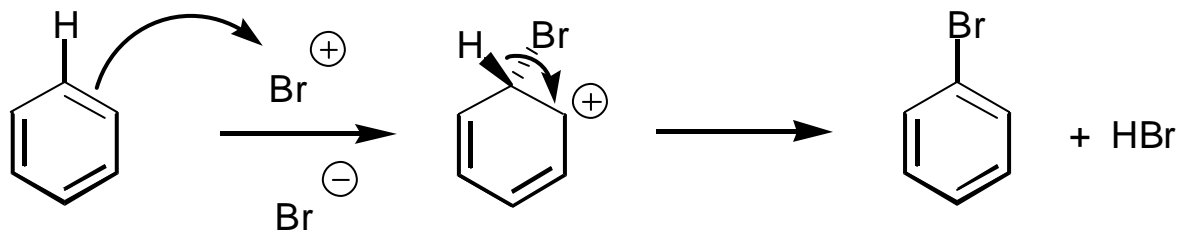
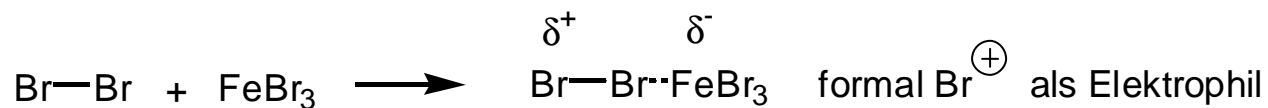
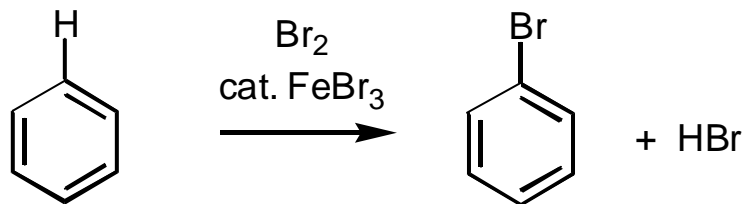
*Elektrophile aromatische Substitution*



*Allgemeiner Mechanismus der elektrophilen aromatischen Substitution*



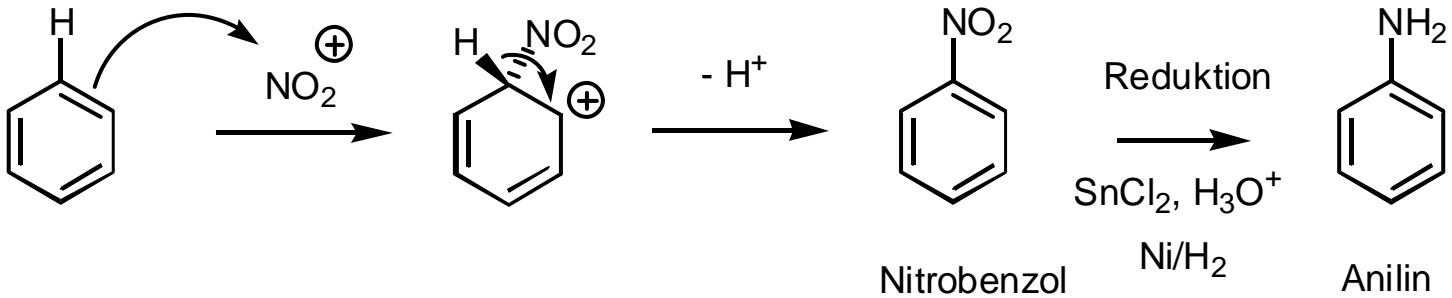
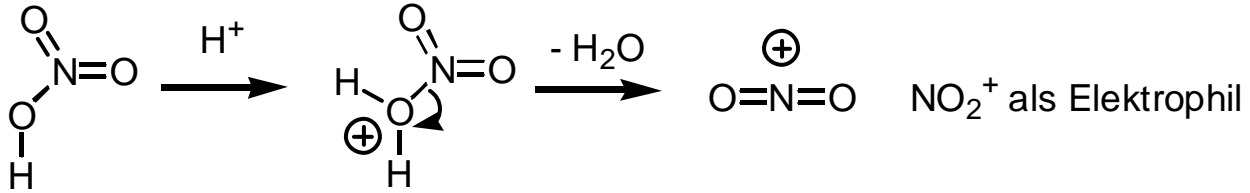
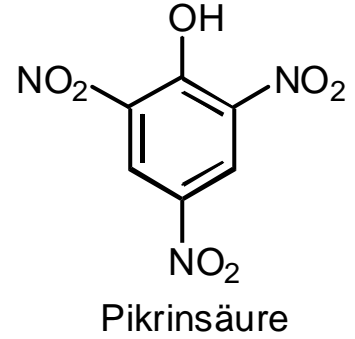
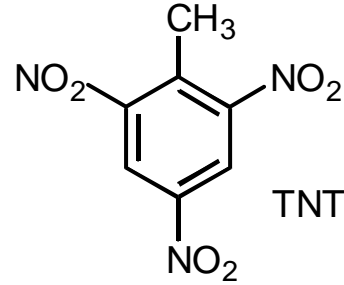
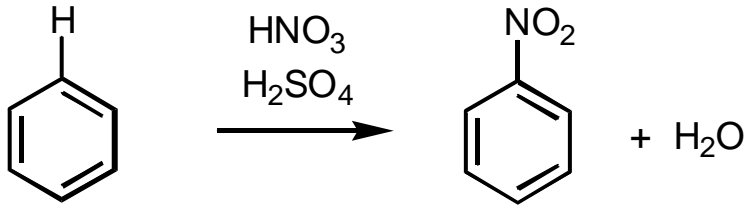
### Bromierung von Benzol



Unter Abspaltung des Protons wird das aromatische System zurückgebildet.  
Es erfolgt kein Angriff des Bromids als Nukleophil an das Carbokation.

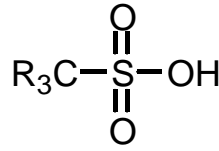
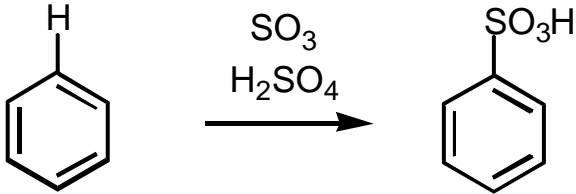
# Nitrierung von Benzol

OC 14.4  
Koert

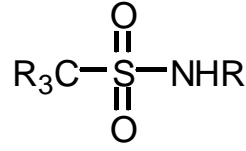


# Sulfonierung von Benzol

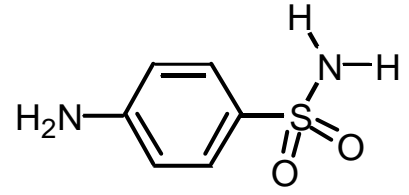
OC 14.5  
Koert



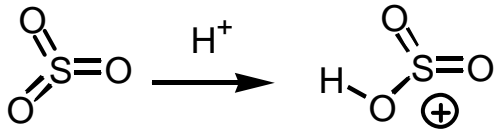
Sulfonsäure



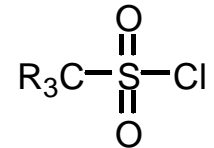
Sulfonamid



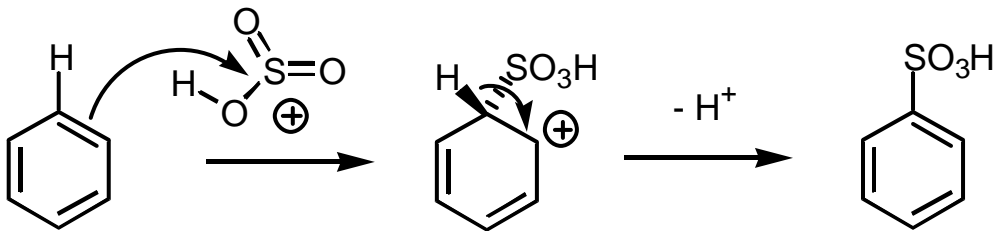
Sulfanilamid (Antibiotikum)



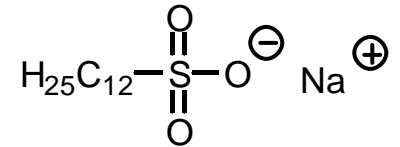
$\text{SO}_3\text{H}^+$  als Elektrophil



Sulfonsäurechlorid



Benzolsulfonsäure



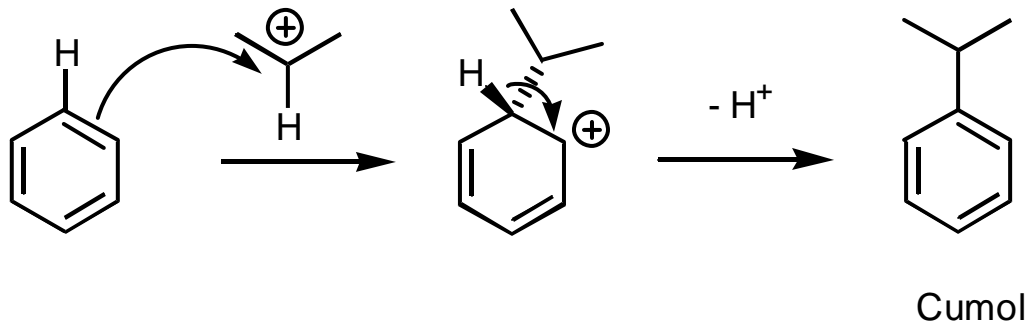
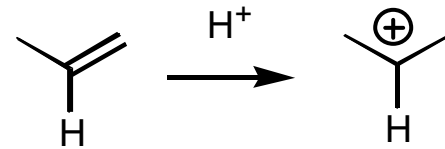
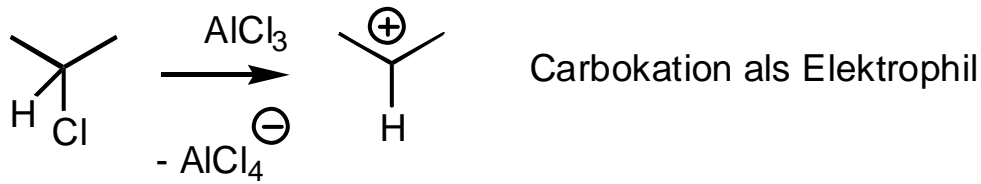
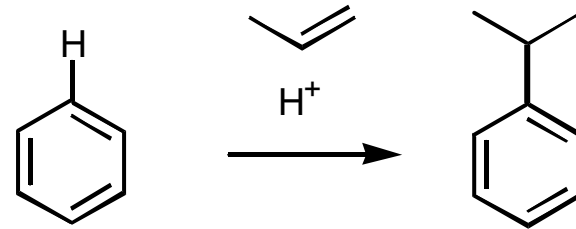
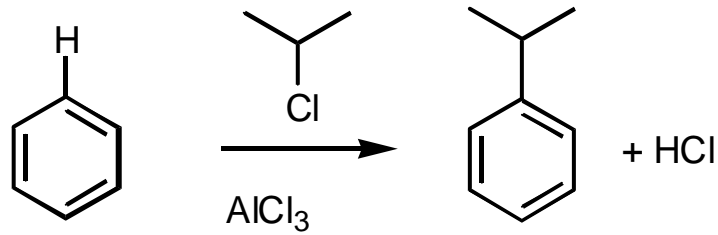
Natriumdodecylsulfat (SDS)

Detergenz

# Alkylierung von Benzol

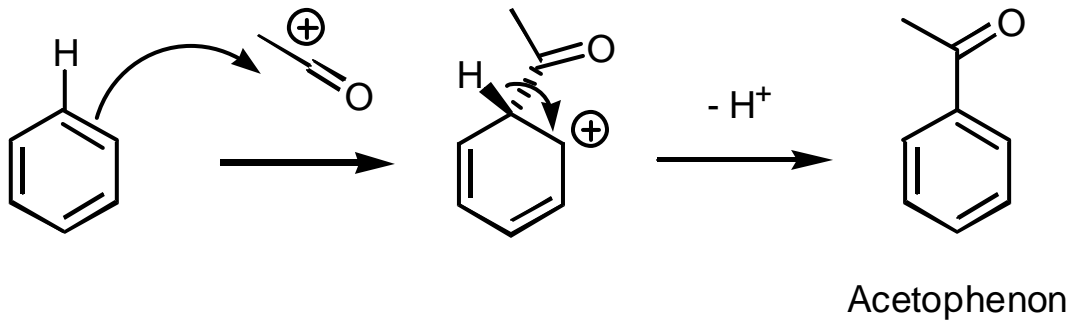
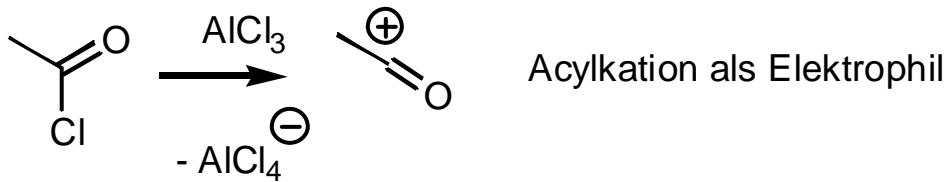
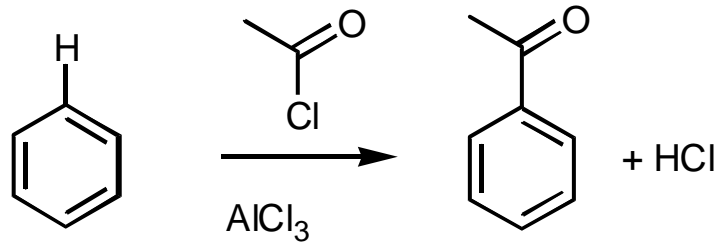
## Friedel-Crafts-Alkylierung

OC 14.6  
Koert



# Acylierung von Benzol

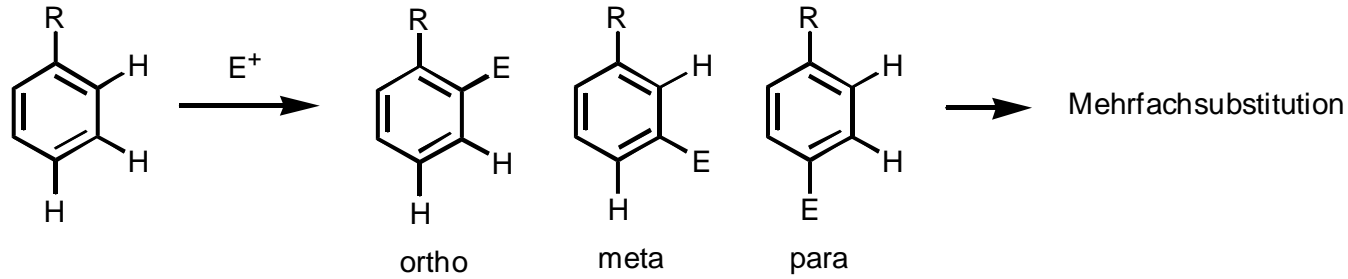
## Friedel-Crafts-Acylierung



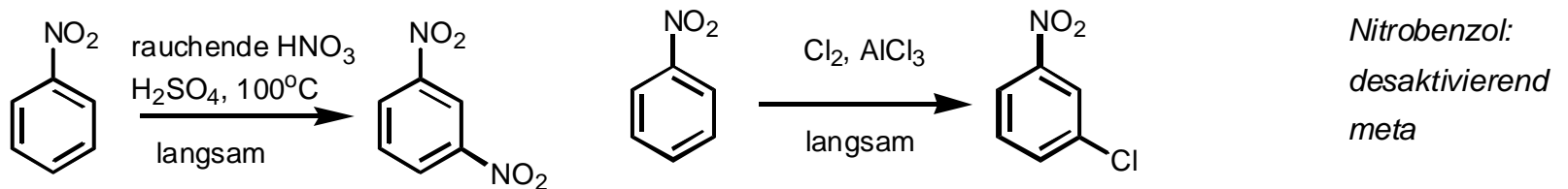
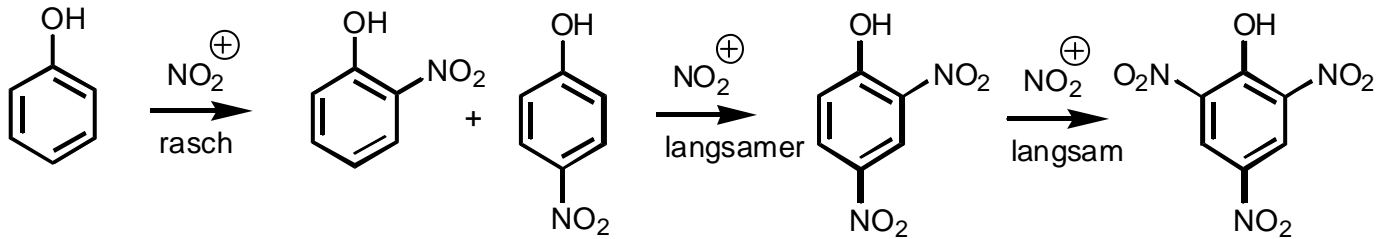
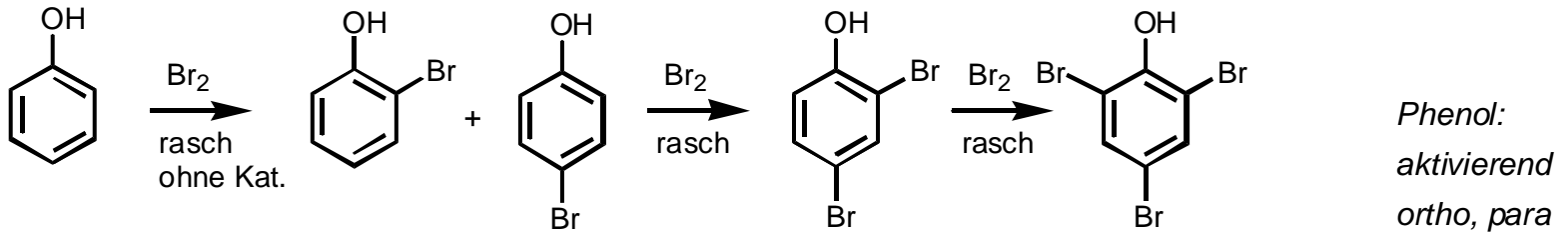


# Elektrophile aromatische Zweitsubstitution

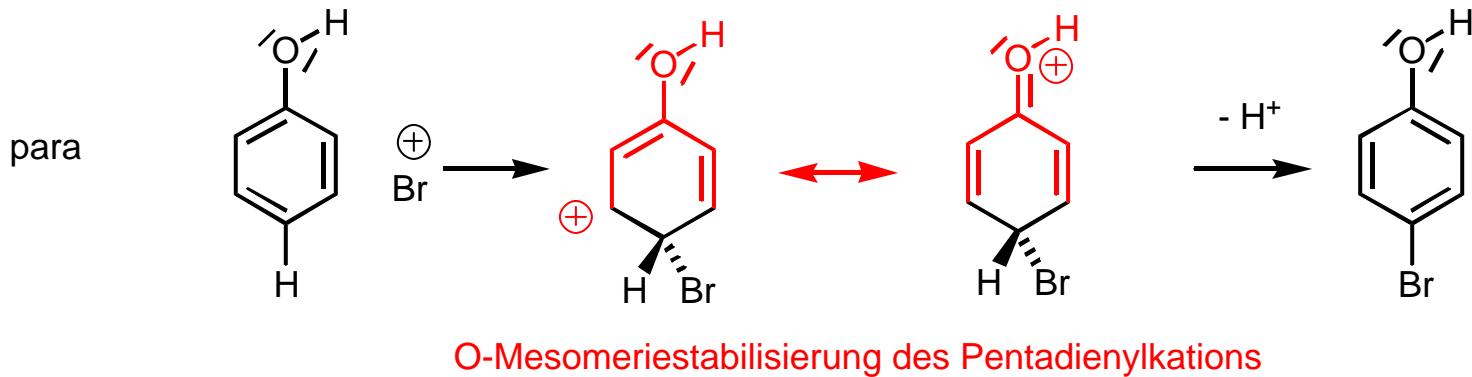
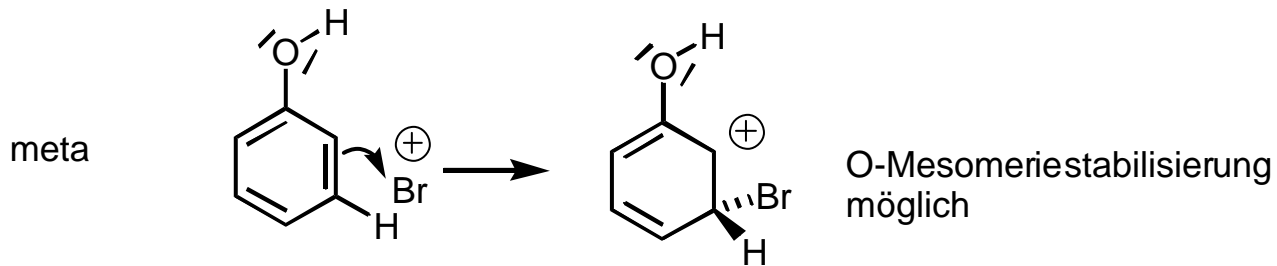
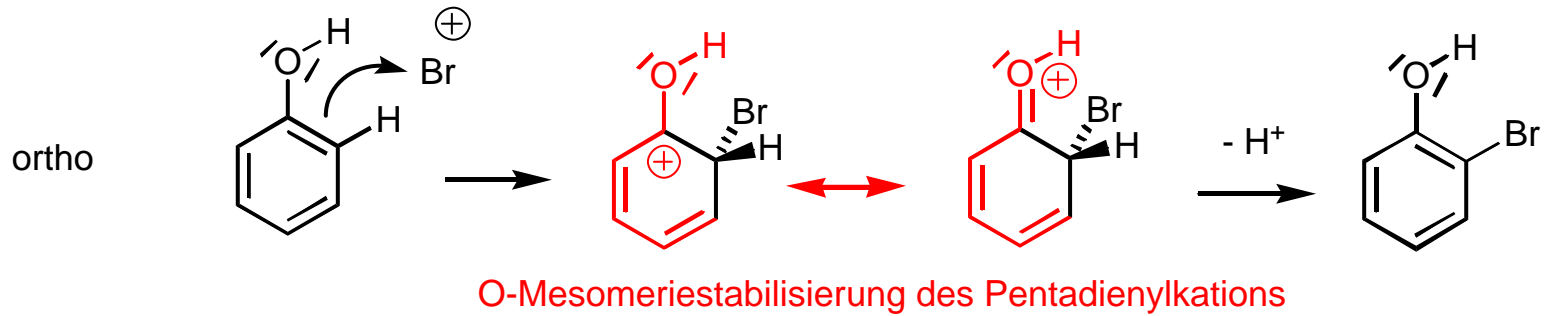
OC 14.8  
Koert



Position und Reaktionsgeschwindigkeit der Zweitsubstitution wird vom Erstsубstituenten gesteuert.



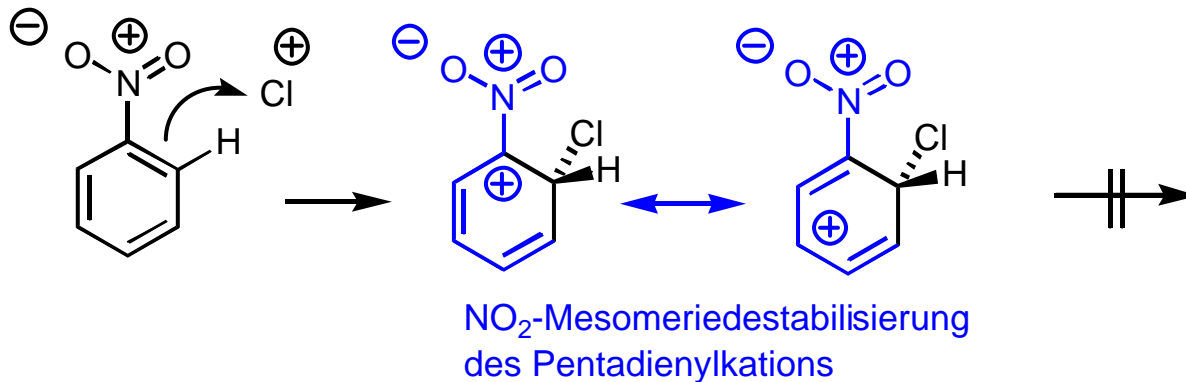
# Elektrophile aromatische Zweitsubstitution



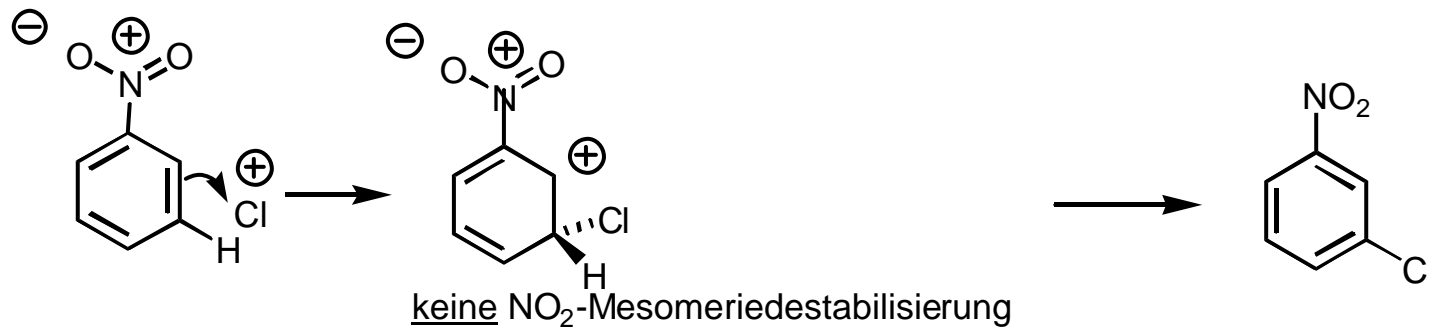
# Elektrophile aromatische Zweitsubstitution

OC 14.10  
Koert

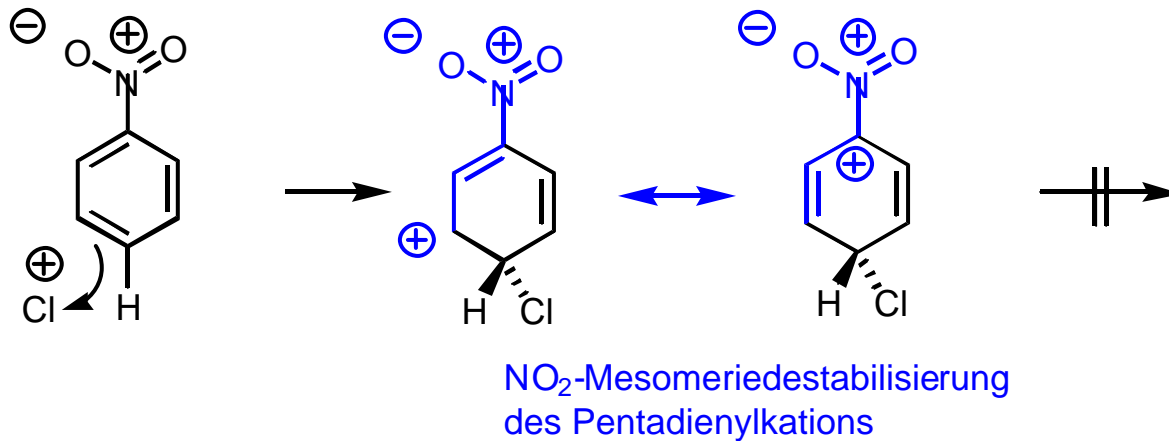
ortho



meta

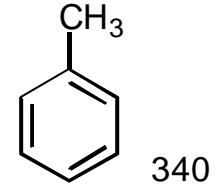
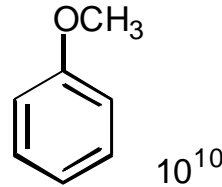
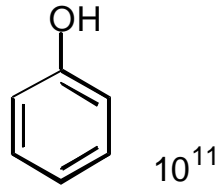
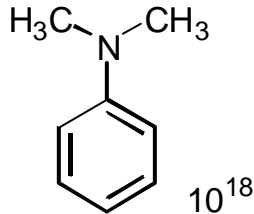


para

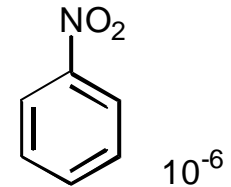
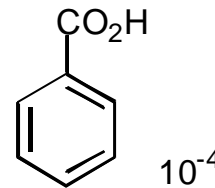
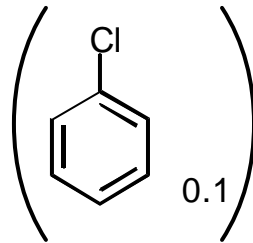
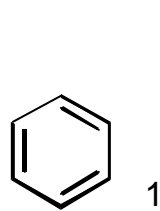


## Elektrophile aromatische Zweitsubstitution

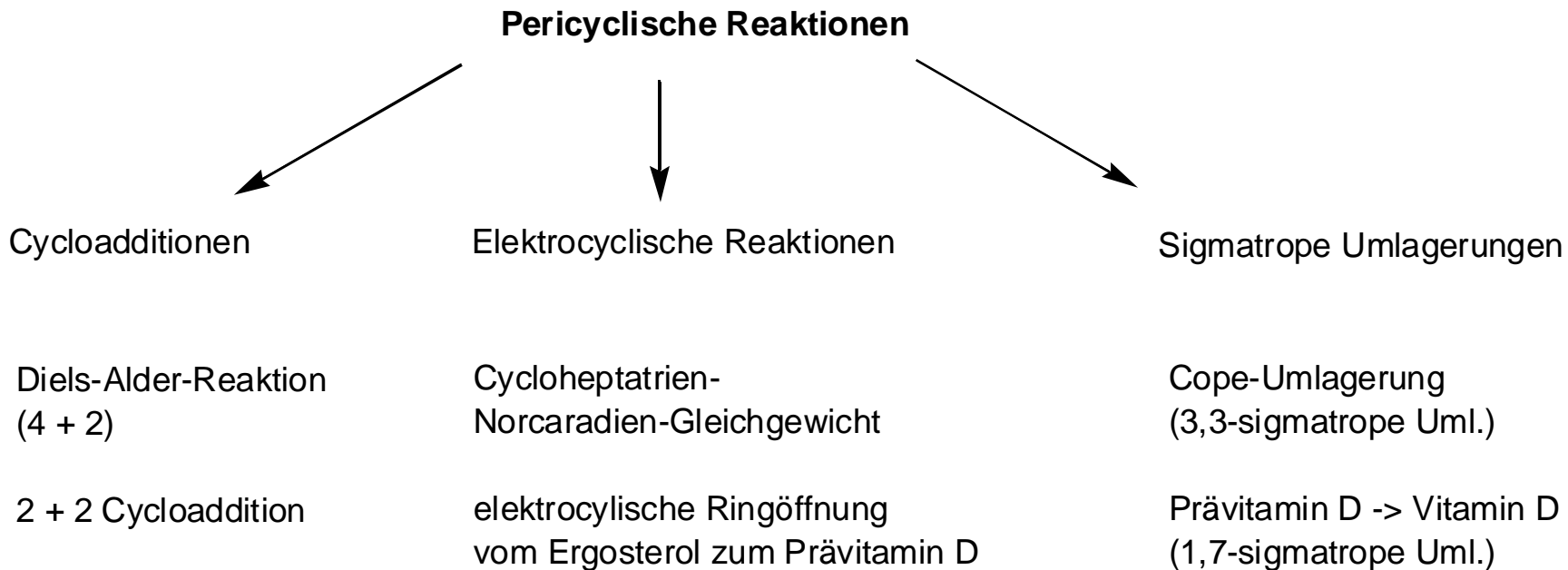
Substituenten, die die Elektronendichte im Ring erhöhen, erleichtern die Substitution in ortho und para Stellung



Relative  
Reaktions-  
geschwindigkeiten  
Benzol = 1



Substituenten, die Elektronendichte aus dem Ring herausziehen, erschweren die elektrophile Substitution. Das Elektrophil tritt langsam nur noch in die meta Position.

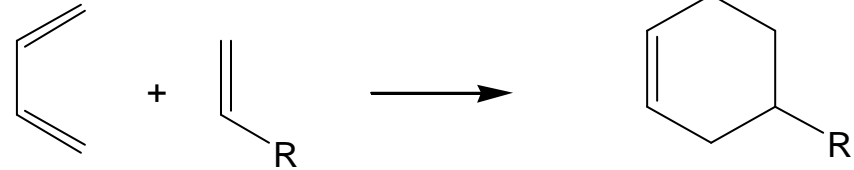


Die Woodward-Hoffmann Regeln entscheiden darüber, ob eine pericyclische Reaktion eintritt und welchen stereochemischen Verlauf sie nimmt.

Cycloadditionen

**Diels-Alder-Reaktion  
(4 + 2)**

thermisch erlaubt



Dien

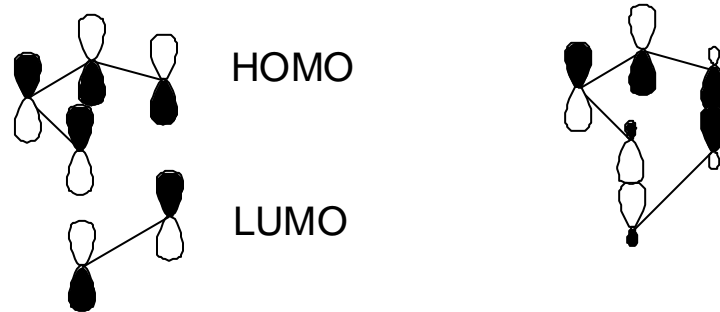
Dienophil

Diels-Alder-Addukt

Diels-Alder mit  
normalem  
Elektronenbedarf:

Dien = Donor  $\rightarrow$  HOMO

Dienophil = Akzeptor  $\rightarrow$  LUMO



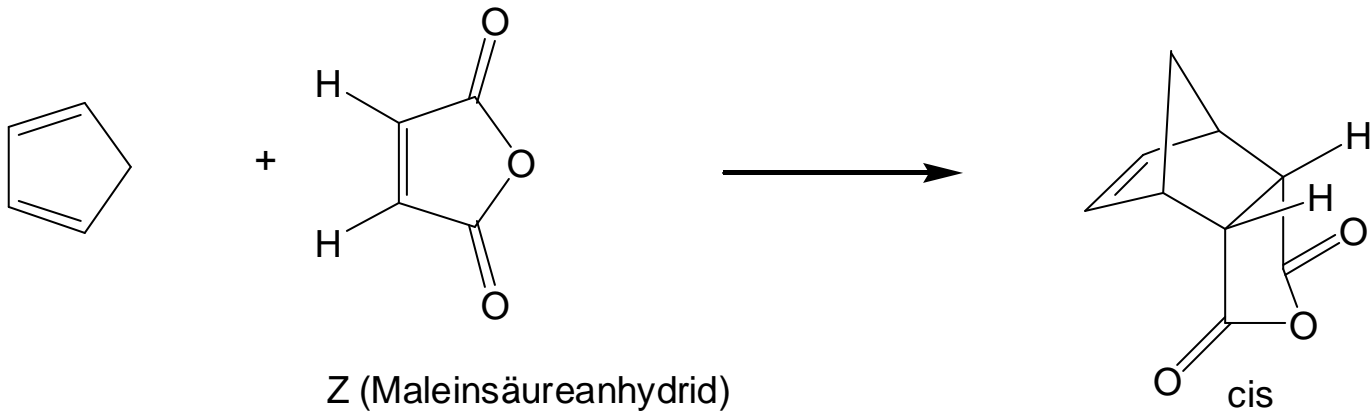
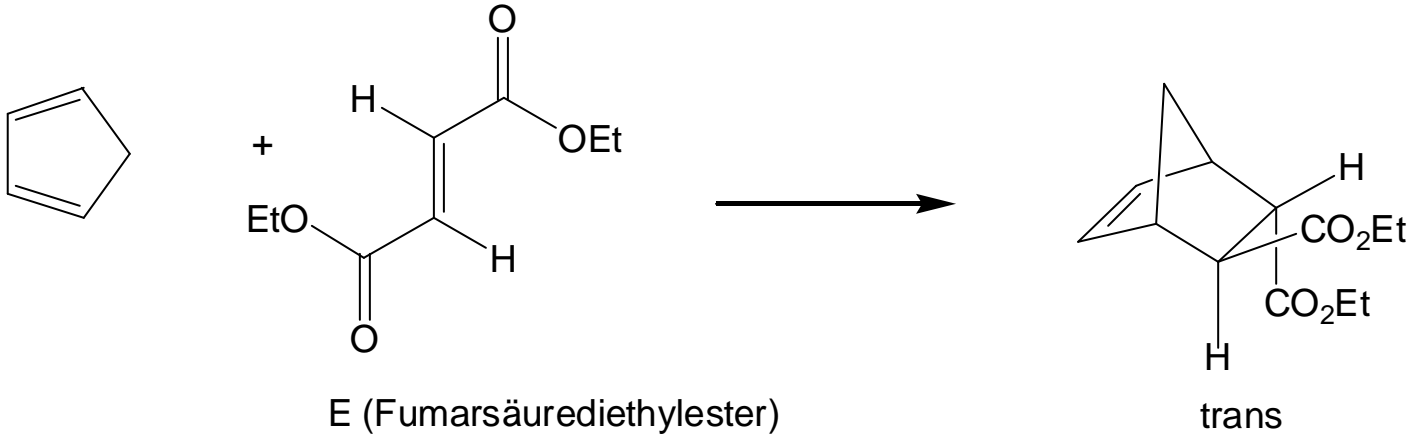
Lewisäuren, die die Elektronendichte des Dienophils herabsetzen, katalysieren die Reaktion.

Die D.A. Reaktion hat ein negatives Aktivierungsvolumen und läuft unter Druck beschleunigt ab.

Diels-Alder-Reaktion  
(4 + 2)

cis-Prinzip: Weitergabe der relativen Konfiguration vom Edukt in das Produkt

Stereochemie



# $\pi$ -Systeme pericyclische Reaktionen

OC 15.4  
Koert

Diels-Alder-Reaktion  
(4 + 2)

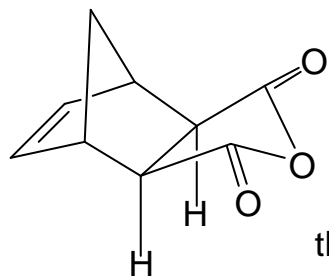
**endo** Präferenz: unter kinetischer Kontrolle stabilisieren sekundäre Orbitalwechselwirkungen den zum endo-Produkt führenden Übergangszustand.

Stereochemie

Bei höherer Temperatur gewinnt die Reversibilität der Diels-Alder Reaktion die Oberhand. Unter thermodynamischer Kontrolle wird jetzt bevorzugt das stabilere **exo**-Produkt gebildet.

**exo-Produkt**

die Anhydrid-Funktion steht auf der Seite der kleineren Brücke

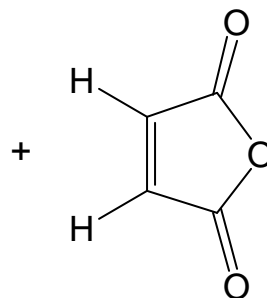


thermodynamische Kontrolle

geringere sterische Wechselwirkung im **exo-Produkt**

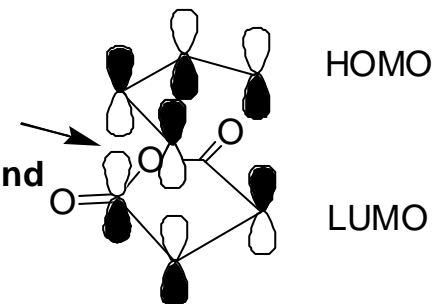
**endo-Produkt**

die Anhydrid-Funktion steht auf der Seite der größeren Brücke



kinetische Kontrolle

sekundäre Orbitalwechselwirkungen stabilisieren den **endo-Übergangszustand**

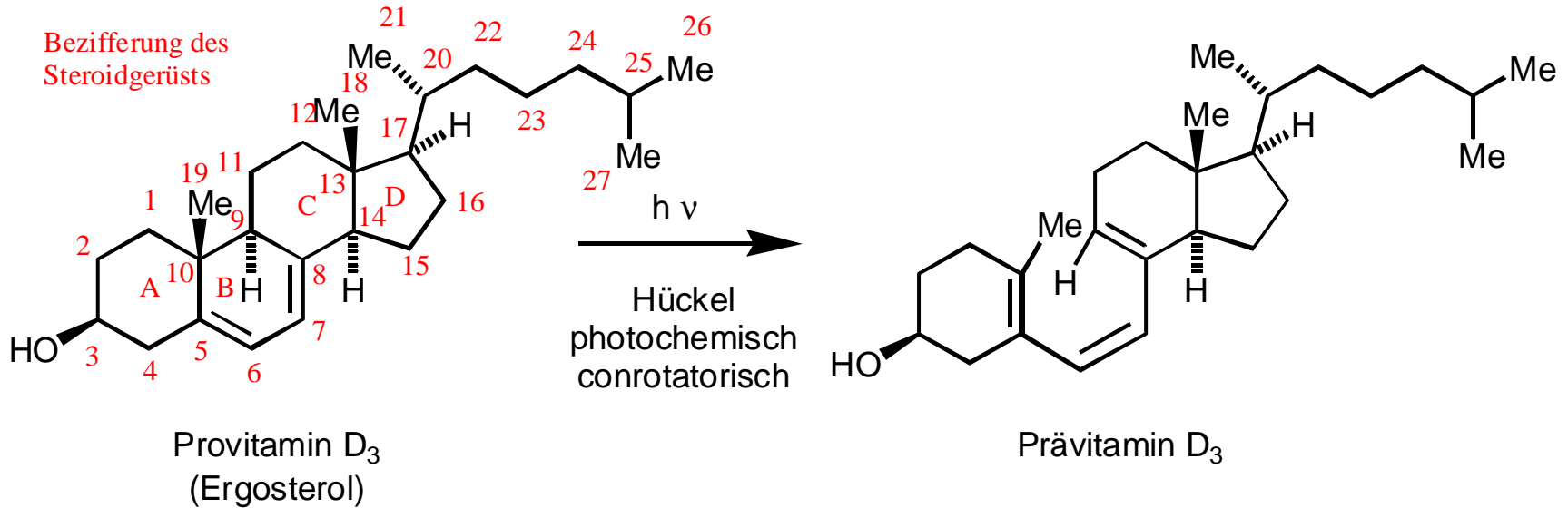




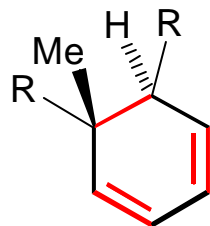
**elektrocyclische Reaktionen:**

$4n + 2$   $\pi$ -Elektronen = Hückel-System (2, 6, 10 usw.)

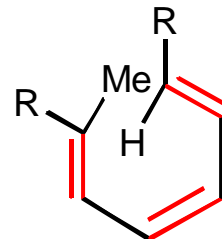
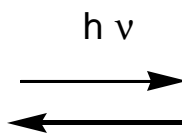
$4n$   $\pi$ -Elektronen = Möbius-System (4, 8 usw)



4  $\pi$ -Elektronen  
2  $\sigma$ -Elektronen



Cyclohexadien



Hexatrien

6 $\pi$ -Elektronen

$\pi$ -Systeme - pericyclische Reaktionen  
**elektrocyclische Reaktionen und Woodward-Hoffmann Regeln**

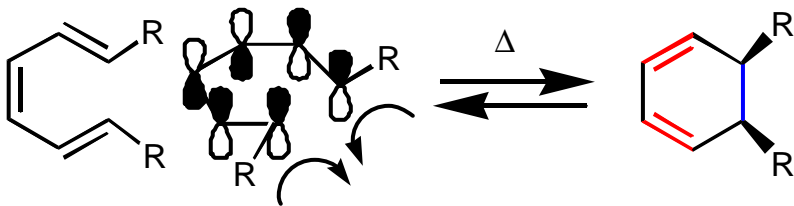
OC 15.6  
 Koert

**Hückel**

Beispiel: Hexatrien / Cyclohexadien

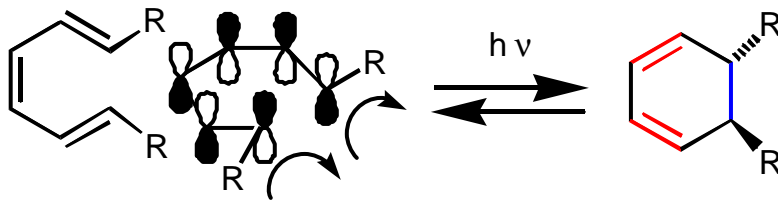
6  $\pi$ -Elektronen /  $4\pi+2\sigma$

HOMO



thermisch  
disrotatorisch

LUMO



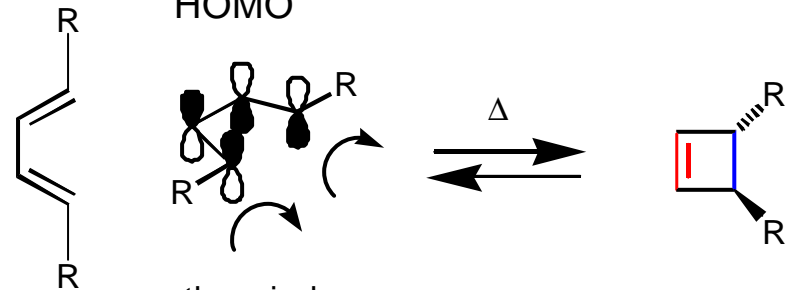
photochemisch  
conrotatorisch

**Möbius**

Beispiel: Butadien - Cyclobuten

4  $\pi$ -Elektronen /  $2\pi+2\sigma$

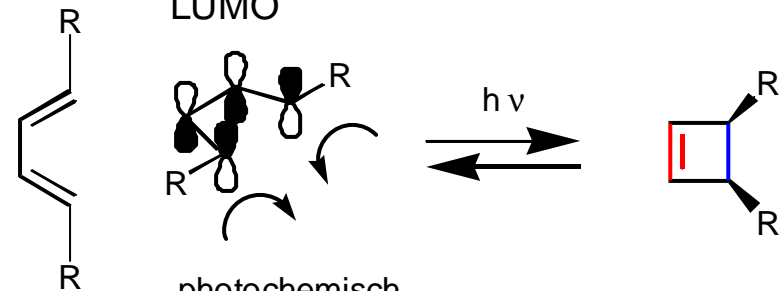
HOMO



thermisch  
conrotatorisch

*MTK =  
Möbius Thermisch  
Konrotatorisch*

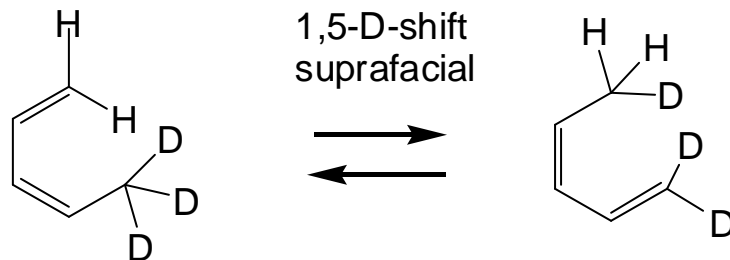
LUMO



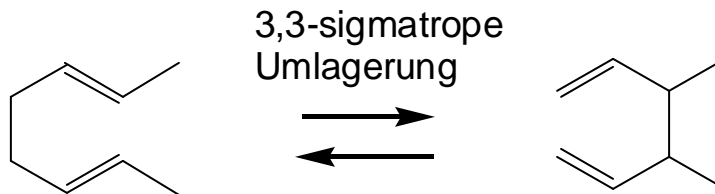
photochemisch  
disrotatorisch



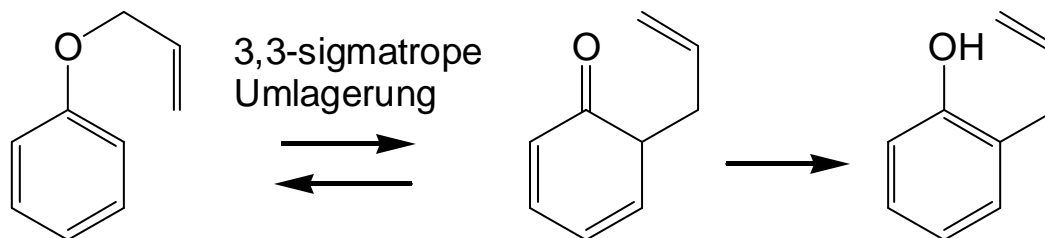
**sigmatrope Umlagerungen:**



Cope-Umlagerung



Claisen-Umlagerung

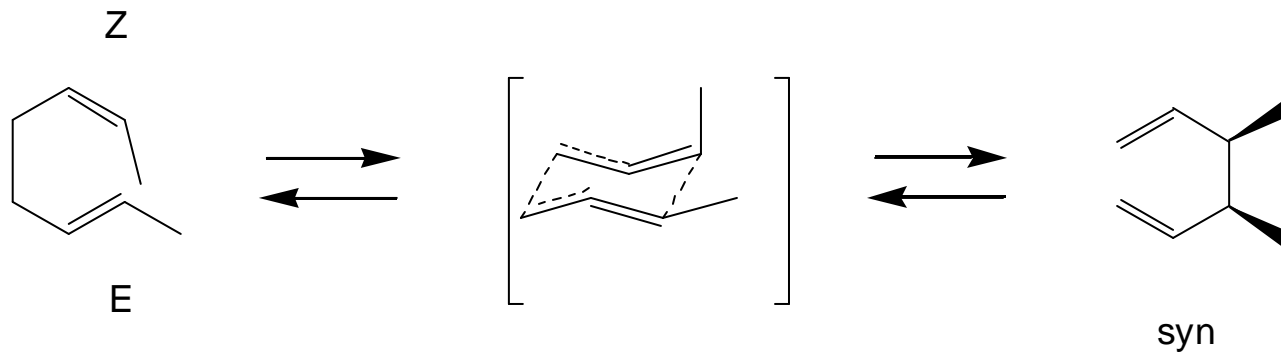
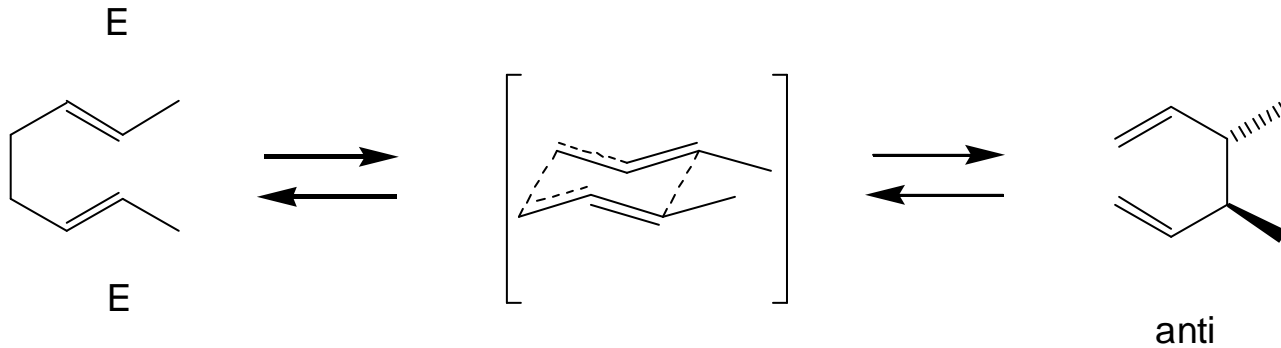


# $\pi$ -Systeme - pericyclische Reaktionen

OC 15.9  
Koert

Sigmatrope Umlagerungen:

stereochemischer Verlauf der Cope-Umlagerung über  
einen Sessel-Übergangszustand



Grundzustandschemie und Chemie  
angeregter Zustände  
(Photochemie)

elektronischer Grundzustand  
(energetisch günstigste Besetzung der Molekülorbitale, Grundzustandselektronenkonfiguration)

angeregten Zustände

Absorption von Licht mit einer Strahlungsenergie, die der Energiedifferenz zwischen Grundzustand und angeregtem Zustand entspricht, führt zu einem Wechsel des Elektrons in einen angeregten Zustand.

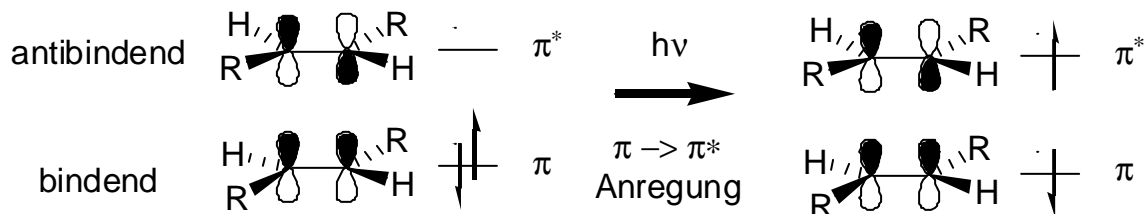
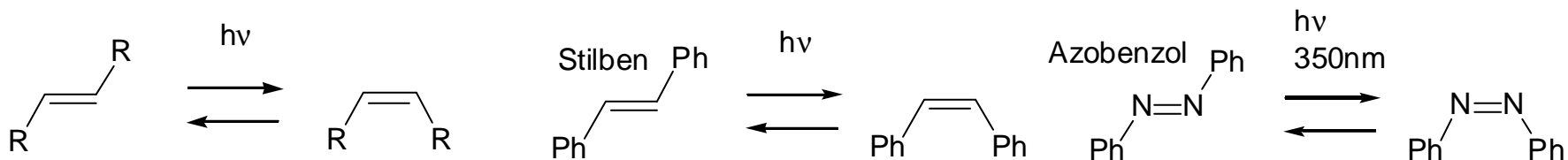
UV/VIS Spektrum

Im Moment der Anregung ( $10^{-15}$  s) werden nur die "leichten" Elektronen reorganisiert, die "schweren" Atome des Molekülgerüsts behalten die Grundzustandsgeometrie (Frank-Condon-Prinzip).

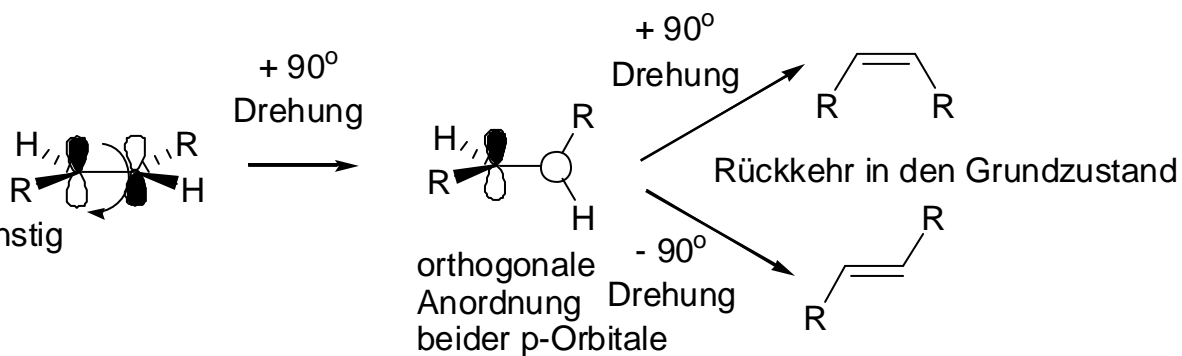
Im Moment der Anregung findet keine Spinumkehr statt.

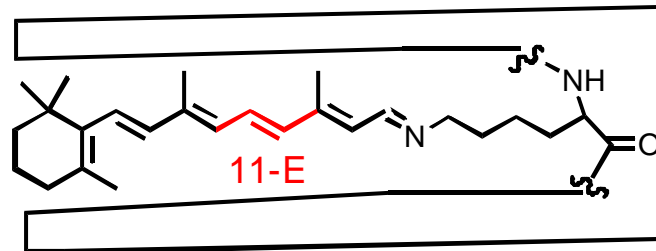
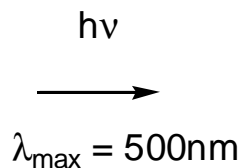
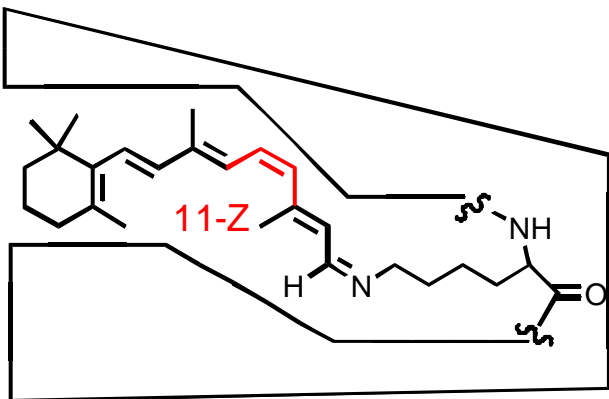
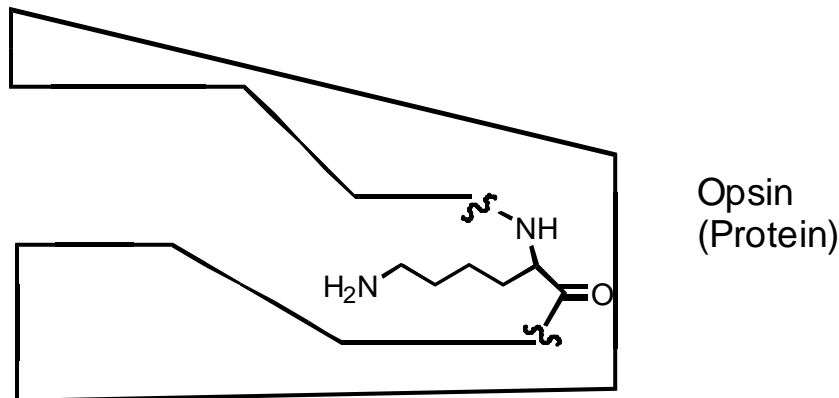
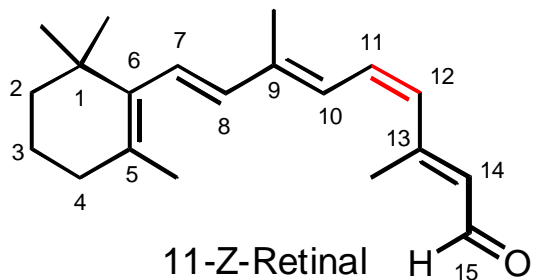
Organische Photochemie

E/Z-Isomerisierung von Doppelbindungen



Besetzung des antibindenden  $\pi^*$ -Orbitals ist energetisch ungünstig





Retinal + Opsin  $\rightarrow$  Rhodopsin (Iminbildung)

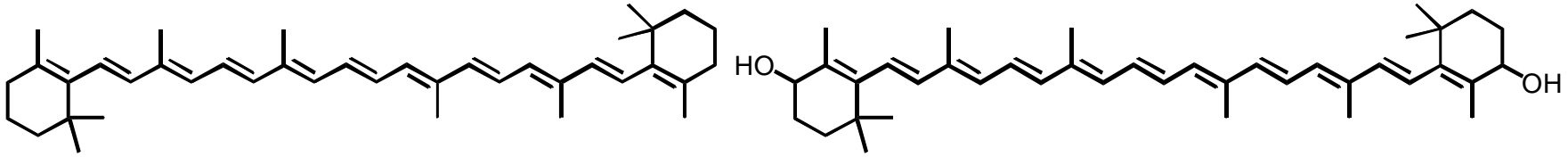
Die photochemische Z/E-Isomerisierung führt zu einer Konformationsänderung des Proteins, die über Ionenkanalöffnungen das Membranpotential des neuronalen Impulses induziert.



thermische Rückumwandlung (mehrere Stufen)

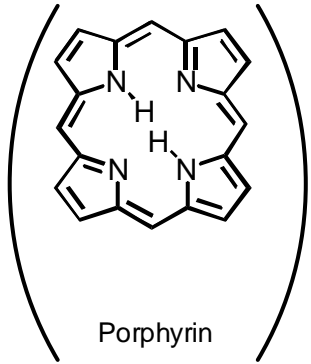


## Struktur verschiedener Blattfarbstoffe

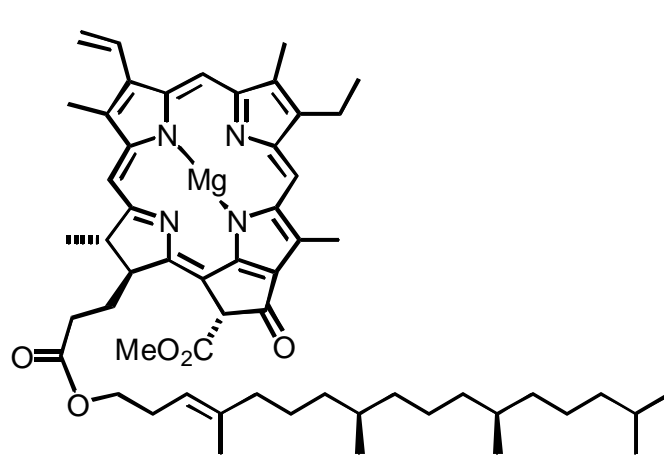


$\beta$ -Carotin

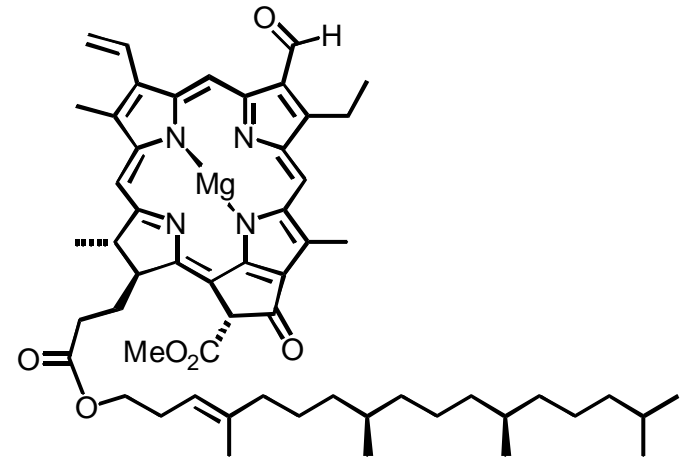
Lutein



Porphyrin

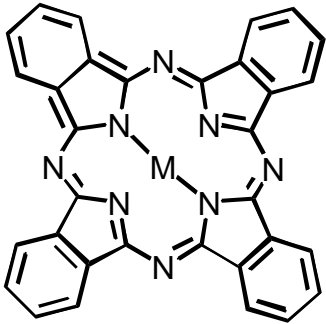


Chlorophyll a

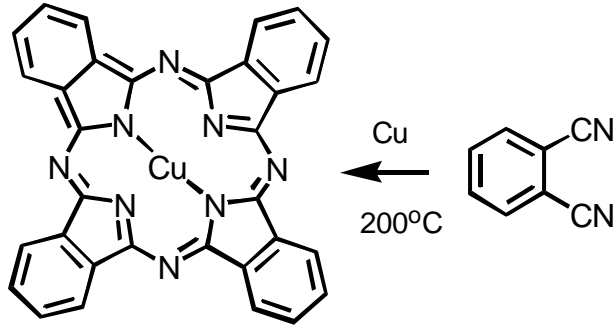


Chlorophyll b

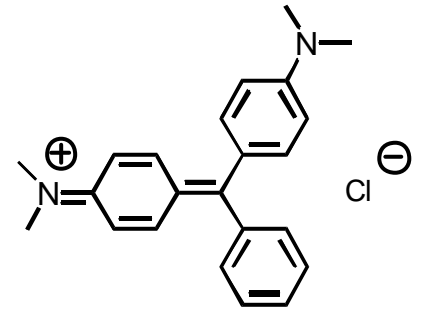
# Synthetische Farbstoffe



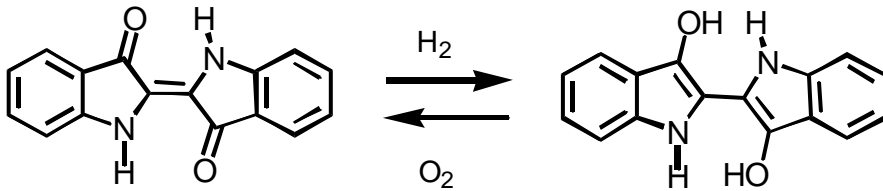
Phthalocyanin-Metallkomplexe



Phthalocyaninblau

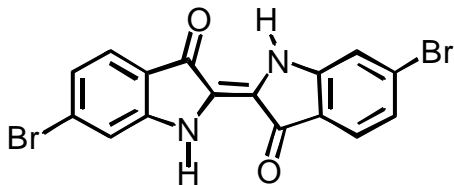


Malachitgrün  
(Triphenylmethanfarbstoff)

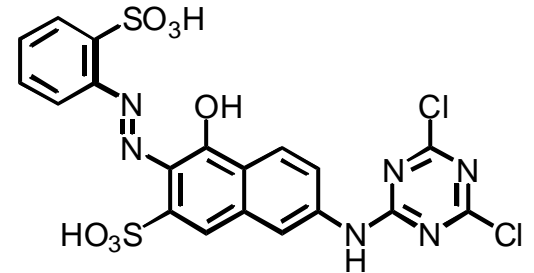


Indigo (blau)

Indigoweiß



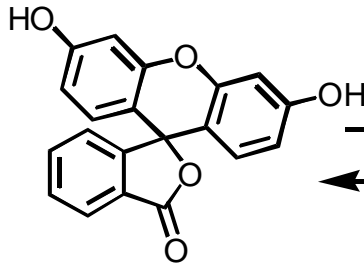
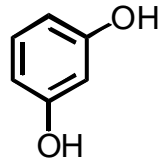
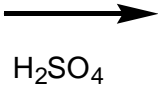
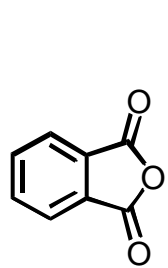
Dibromindigo (purpurrot) Purpurschnecke



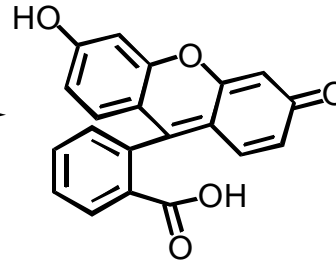
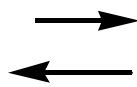
Brilliantorange  
Reaktivfarbstoff  
Azofarbstoff

# Fluoreszenzfarbstoffe, Photochemie, Lumineszenz

Resorcin



Fluorescein



chinoide Form  
des Fluoresceins

*Photochemische Prozesse:*

Lichtanregung

Carbonyl-Photochemie

Franck-Condon-Prinzip

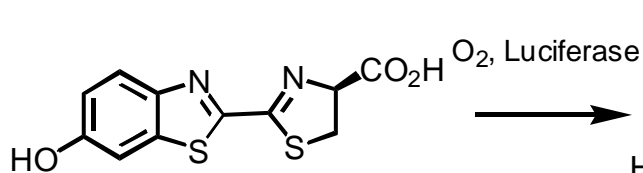
Lumineszenz

Fluoreszenz

Intersystemcrossing

Phosphoreszenz

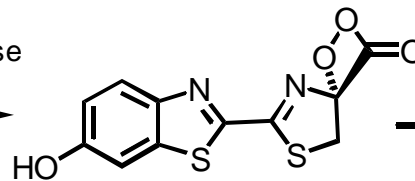
*Chemolumineszenz/Biolumineszenz*



Luciferin

(Glühwürmchen / Firefly)

$\text{O}_2$ , Luciferase



Dioxacyclobutanon

