Gattermann

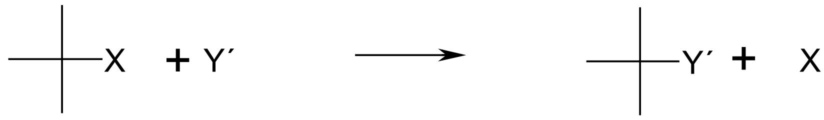
Nach der Vorlesung SS2000
von Professor M. Heuschmann

Computerabschrift von Oliver Schön

Inhaltsverzeichnis

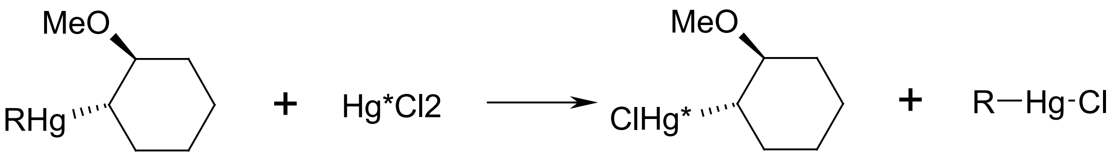
1 Aliphatische Substitution

1.1 Allgemein:



1.2 Elektrophile Substitution S_E

Y hat Elektronenlücke; Lewis –Säure



cis cis

1.3 Radikalische Substitution S_R

Y hat ungepaartes Elektron; Radikal

$$\left.\begin{array}{l} R-H+Cl^{\cdot} \rightarrow R^{\cdot}+HCl \\ R^{\cdot}+Cl_2 \rightarrow Cl^{\cdot}+R-Cl \end{array}\right\rangle Radikalkette$$

1.4 Nukleophile Substitution S_N

Y hat freies Elektronenpaar

$\mathrm{I: R-I + |OH^- \rightarrow R-OH + |I^-}$

$\mathrm{II: R-I + |NMe_3 \rightarrow R-NMe_3^+ + I^-}$

$\mathrm{III: R-NMe_3^+ + |OH^- \rightarrow R-OH + |NMe_3}$

$\mathrm{IV: R-NMe_3^+ + |SH_2 \rightarrow RSH_2^+ + NMe_3}$

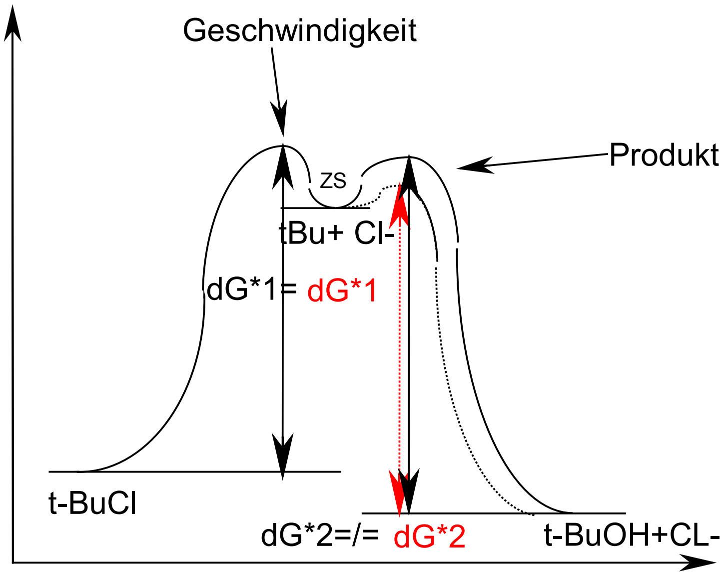
$$S_N$$

$\mathrm{S_N 1}$ $\mathrm{S_N 2}$

$$\mathrm{R-X \Leftrightarrow R^+ + X^- \xrightarrow{+Y^-} R-Y+X^- \quad \| \quad Y| \rightarrow R-X \rightarrow [Y \cdots R \cdots X]^{\ddagger} \rightarrow R-Y+X|}$$

1.4.1 Kinetik

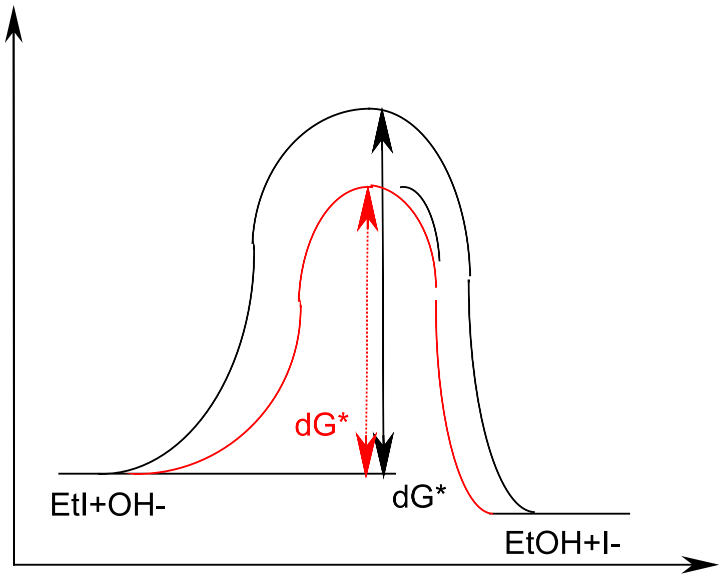
S_N1



S_N2

$$CH_3-CH_2-I \xrightarrow{H_2O} CH_3-CH_2-OH+HI$$

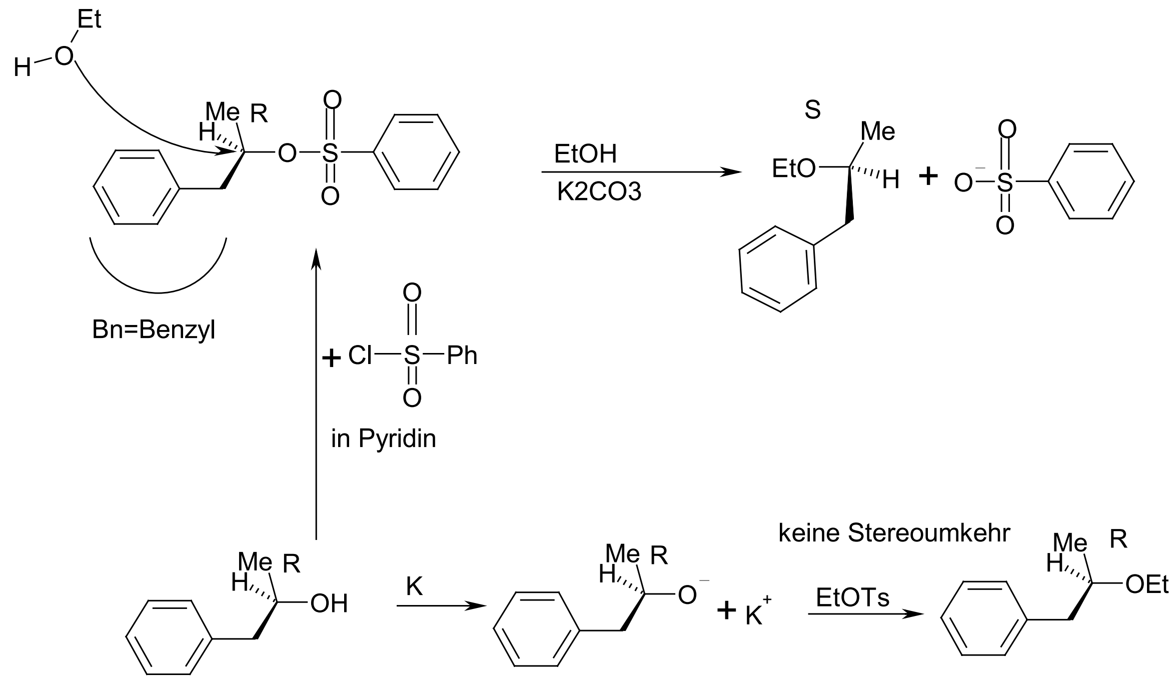
$$RG=-\frac{d[EtI]}{dt}=k[EtI]*[OH^-]$$

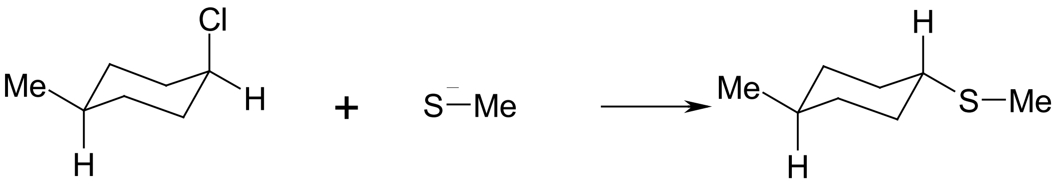


1.4.2 Stereochemie

S_n2: <u>Walden-Umkehr</u>

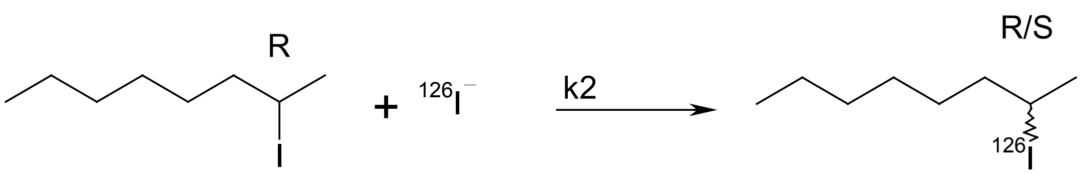
Bei S_n2 Reaktionen wird das Stereozentrum geändert, die Stereochemie dreht sich um.





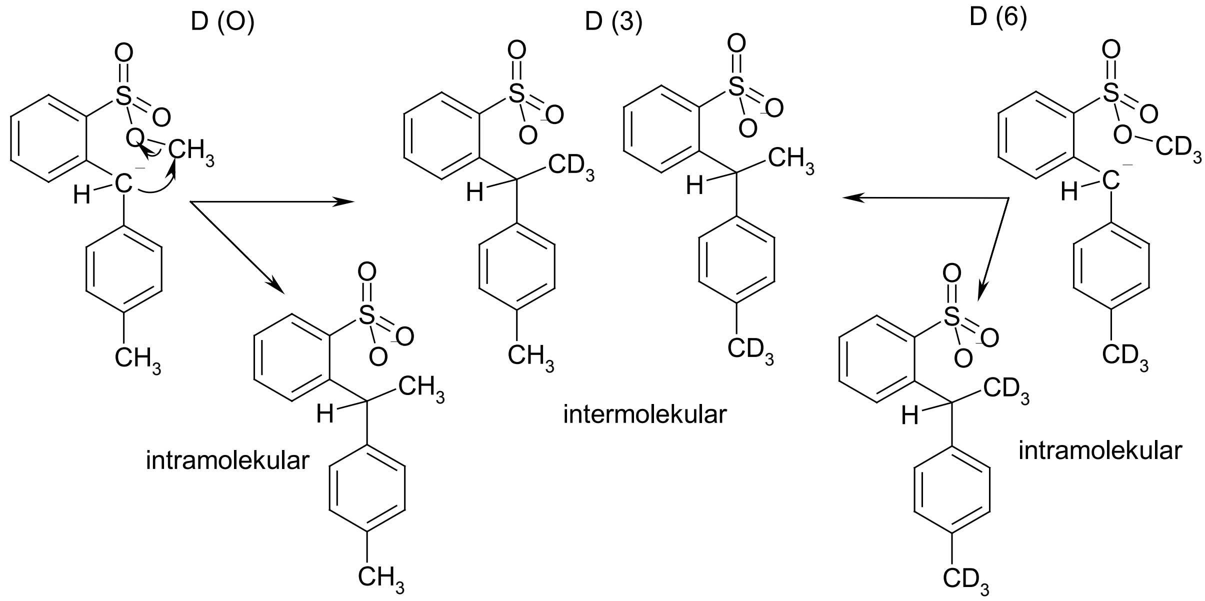
cis

trans



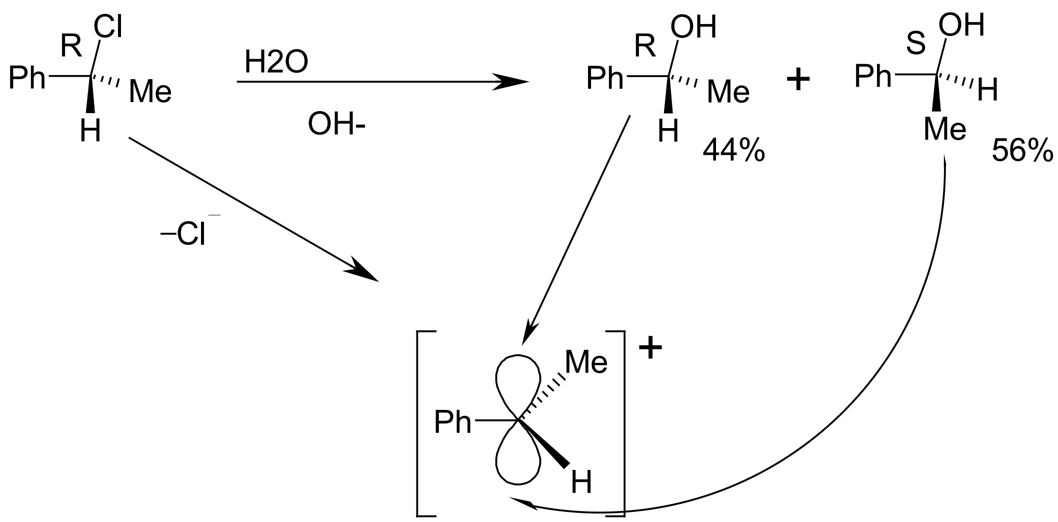
k2(^{126}I-Einbau): 2,88*10^{-5} l/mol*s
k(Racemisierung): 6,00*10^{-5} l/mol*s
Die Racemisierung ist doppelt so schnell wie die Abfangreaktion des Iodids: 50/50 Gemisch der R und S Enantiomere entsteht.

1.4.3 Racemisierungen

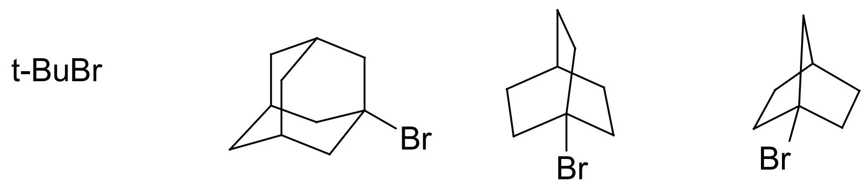


Einsetzen eines D0:D6 = 1:1 Gemisches
Statistisch: 1:2:1
S_N2 nur bei ca. 180°C !!

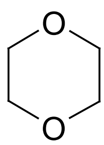
S_N1:



In H2O/Dioxan
30/70
Bp=100°C



1 10^{-3} 10^{-6} 10^{-12}

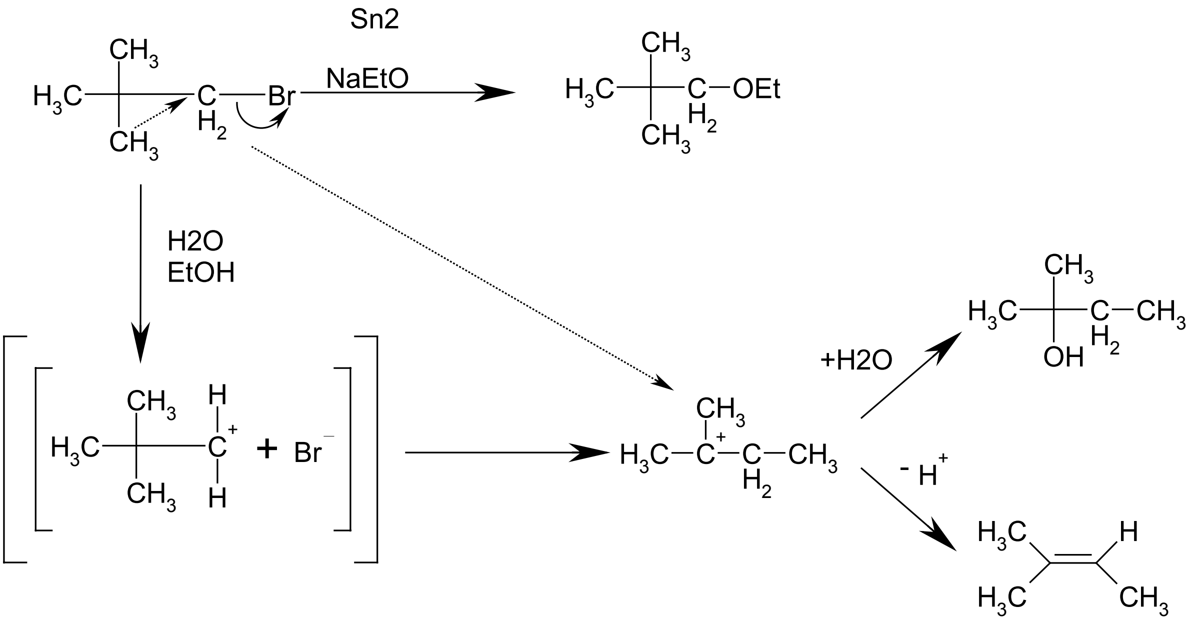
Dioxan=


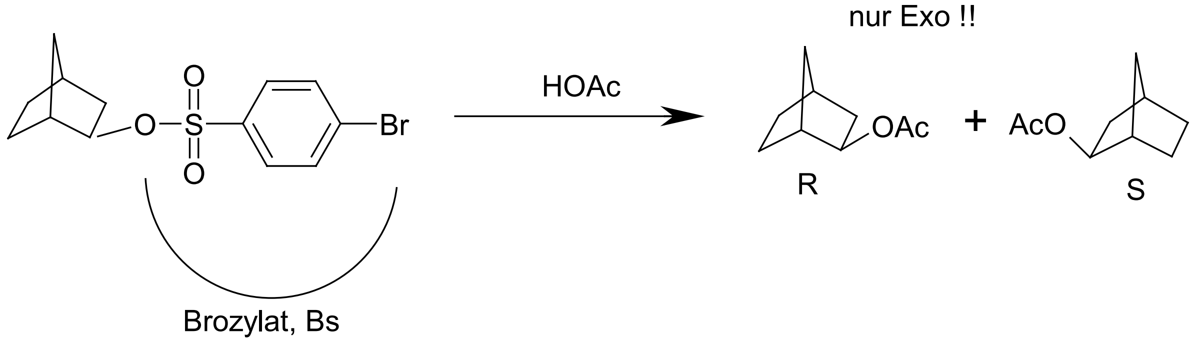
Cerbeniumion schlechter Planar => Sn1 sterisch unmöglich
Rückseitenangriff behindert => Sn2 sterisch unmöglich

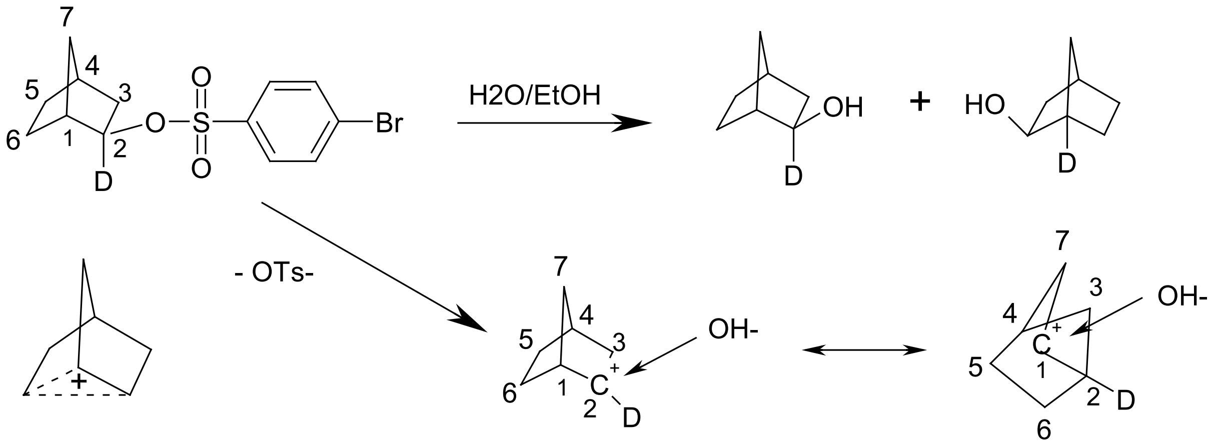
1.4.4 Umlagerung

Wagner-Meerwein-Umlagerung:

Es bilden sich durch Wasserstoff oder Alkylverschiebung stabilere Carbeniumionen:







Carboniumion: 5-fach gebunden einfach positives C-Atom

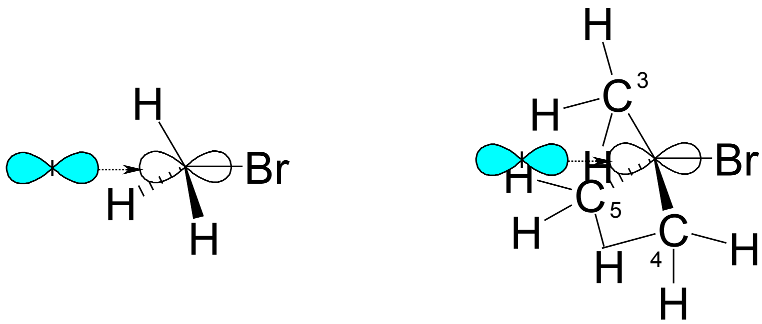
Carbeniumion: 3-fach gebunden einfach positives C-Atom

1.5 S_n2 - Reaktion

1.5.1 Struktur des Substrats

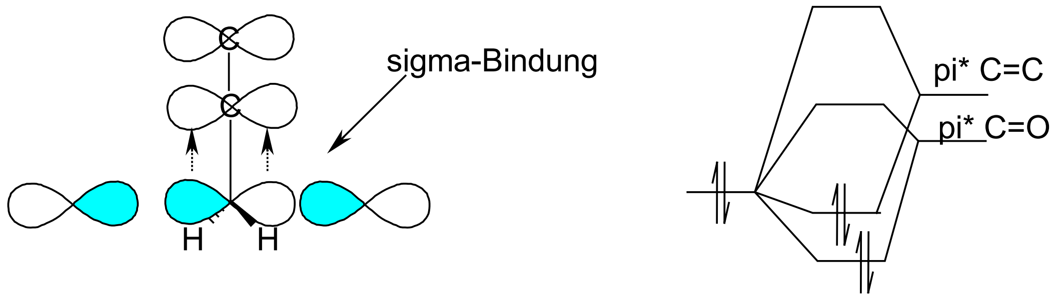
R-Bn + I^- → R-I + Bn^-

R	K(rel)
H_3C	145
$(CH_3)_3C$	<0,001



Es tritt sterische Hinderung auf wenn nicht annähernd ein 180° Winkel gegeben ist.
Grad der Hinderung ist abhängig von der Stellung des Substituenten:
α,β stark χ schwach δ gar nicht

C=C Bindung in α-Stellung



1.5.2 Nukleophile Agens

Nukleophilie →Kinetik(k)
Basizität →Thermodynamische Größe (K)

Swain-Gleichung

$$R-X+Y^- \xrightarrow[\text{MeOH}]{k} R-Y+X^-$$

$$\lg\left(\frac{k}{k_0}\right)=n*s \qquad R-X=Me-I \Rightarrow s\equiv 1 \quad k_0 : Y^- = MeOH$$

Nukleophile: $MeO^- > PhO^- > MeCOO^- > MeOH$
pKa 15,7 9,9 4,75 -1,5

Korrelation am gleichen Zentralatom:
Elektronenzug : langsamer Elektronenschub: schneller

$F^- < Cl^- < Br^- < I^-$
$RO^- < RS^- < RSe^-$
PSE von Oben→Unten

$R_3C^- > R_2N^- > RO^- > F^-$ sterischer Solvateffekt

Jenks α-Effekt

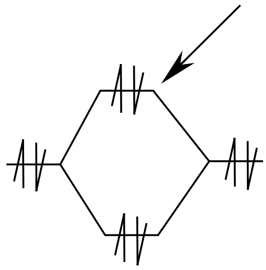
Das Atom in α-Position hat ebenfalls ein freies Elektronenpaar.

$H_2\overline{N}-\overline{N}H_2; H\overline{\underline{O}}-\overline{N}H_2 >> \overline{N}H_3$

α α

$H\overline{\underline{O}}-\overline{\underline{O}}H >> H_2\overline{\underline{O}}$

Reaktiver, da höhere Energie



Ambidente Nukleophile:

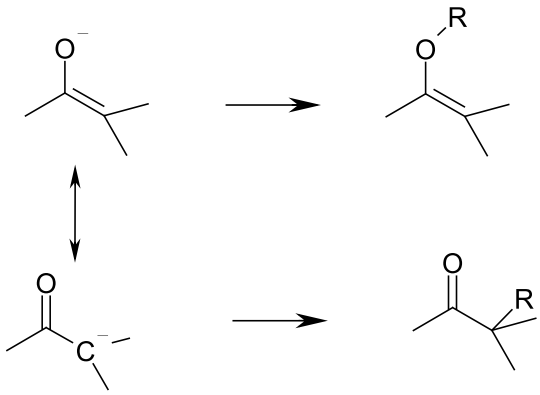
Cyanat: $^{-}\overline{\underline{N}}=C=\overline{\underline{O}} \rightarrow R-\overline{N}=C=\overline{\underline{O}}$ Isocyanat

$|N\equiv C-\overline{\underline{O}}|^{-} \rightarrow R-\overline{\underline{O}}-C\equiv N|$ Cyanat

Thiocyanat: $^{-}\overline{\underline{N}}=C=\overline{\underline{S}} \rightarrow R-\overline{N}=C=\overline{\underline{S}}$ Isothiocyanat

$|N\equiv C-\overline{\underline{S}}|^{-} \rightarrow R-\overline{\underline{S}}-C\equiv N|$ Thiocyanat

Cyanide:
$R-X+CN^{-} \rightarrow R-C\equiv N| + R-N^{+}\equiv C|^{-}$
$R-N^{+}\equiv C|^{-} \xrightarrow{H^{+}} R-N^{+}H_3 + HCO_2H$
Isocyanide sind Säurelabil



Peason HSAB

Harte Säuren $H^{+}; Li^{+}; BF_3; CO_2; SO_3$

Grenzfälle $R_3C^{+}; BR_3; Zn^{2+}; SO_2$

Weiche Säuren $R-S^{+};:CH_2; Pd^{2+}; Hg^{2+}; I^{+}; I_2$

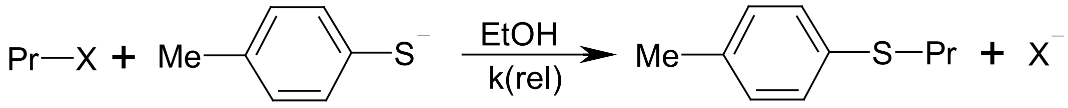
Harte Basen $F^{-}; Cl^{-}; RO^{-}; R-OH; NH_3; CO_3^{2-}; Ac^{-}, NO_3^{-}$

Grenzfälle $Br^{-}; SO_3^{2-}; NO_2^{-}; Py; N_3^{-}$

Weiche Basen $H^{-}; I^{-}; R-S^{-}; SCN^{-}; R_3P^{-}; \text{Benzol}; H_2C=CH_2; CN^{-}$

$R-N^{+}\equiv C|^{-} \xleftarrow{Ag^{+};Cu^{+}} R-Br+CN^{-} \xrightarrow{Na^{+};K^{+}} R-C\equiv N|$

1.5.3 Die austretende Gruppe (Abgangsgruppe)



X	k
I	1
Br	0,29
Cl	0,0007
OTs	0,12

$$Me - X + N_3^- \xrightarrow{k(rel)} MeN_3 + X^-$$

X⁻	k(DMF)	k(MeOH)
Cl⁻	1	0,0002
Br⁻	460	0,027
I⁻	3100	0,03

Schlechte Abgangsgruppen: $OH^-; RO^-; R_2N^-; N_3^-$

Mäßige Abgangsgruppen: $CN^-; NR_3; ArS^-$

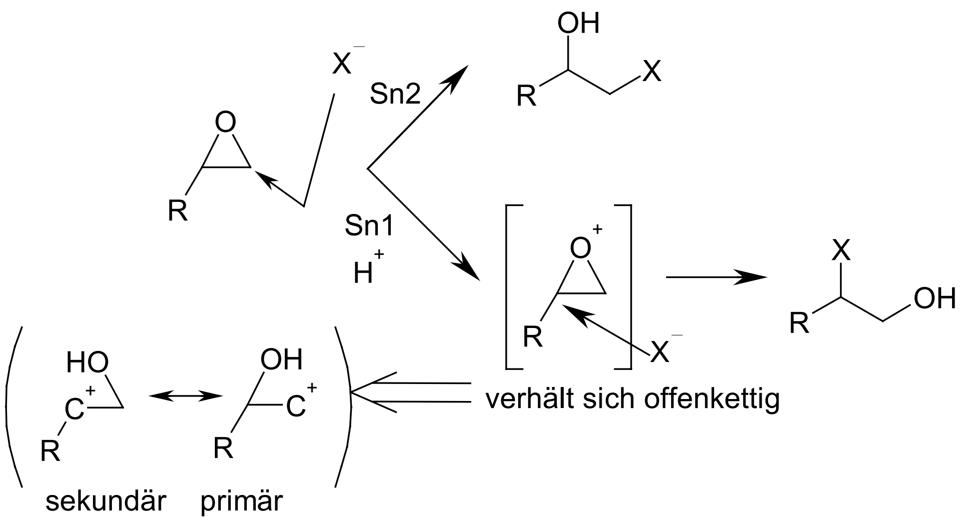
Gute Abgangsgruppen: $I^-; Br^-; Cl^-; H_2O;$ $SR_2; RSO_3^-; CF_3CO_2^-$

Sehr gute Abgangsgruppen: $CF_3SO_3^-; C_4F_9SO_3^-$
Triflat(TfO-);Nonaflat

$$R - OH + X^- \xrightarrow{\text{keine Reaktion}} R - X + OH^-$$
$$R - OH + H^+ \rightarrow R - OH_2^+$$
$$R - OH_2^+ + X^- \rightarrow R - X + H_2O$$
$$R - OH \xrightarrow[\text{Py}]{\text{TsCl}} R - O - Ts \xrightarrow{+NEt_3} R - N^+Et_3 + TsO^-$$

Etherspaltung:

$$H_3C - CH_2 - O - CH_3 \xrightarrow{HI} H_3C - CH_2 - O^+H - CH_3 + I^- \rightarrow H_3C - CH_2 - OH + I - CH_3$$



Thioether: $R^* - S - R \xrightarrow{R-X} R - S^+RR^* + X^- \xrightarrow{Nu^-} Nu - R^* + R_2S$

1.5.4 Solvenseffekte

$$MeI + X^- \xrightarrow[k(rel)]{Sn2} MeX + I^-$$

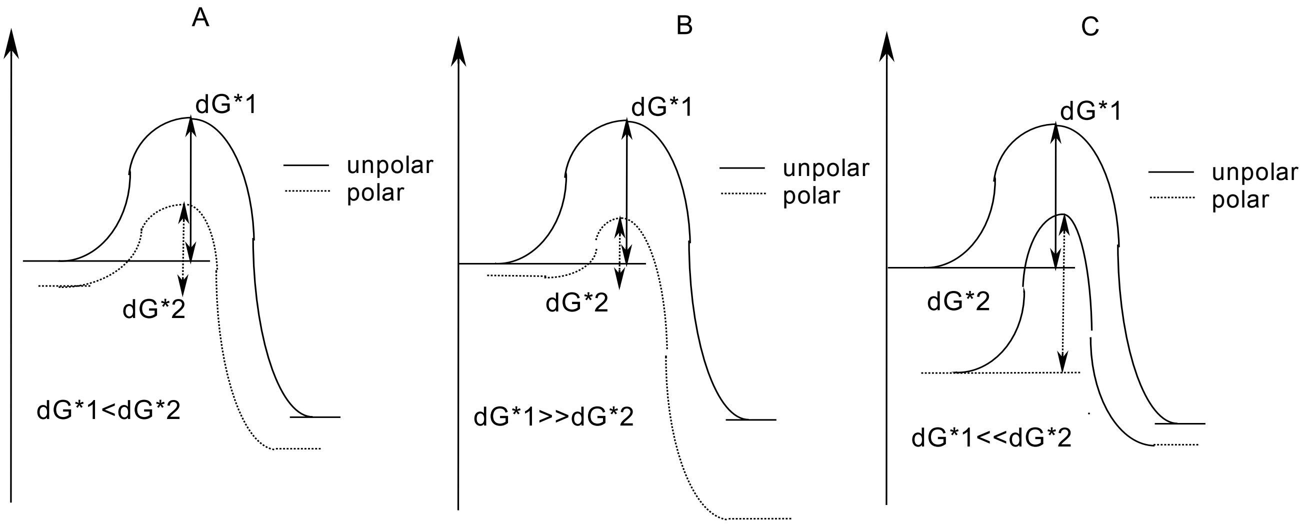
X	k(MeOH)	k(DMF)
Cl	1	$1{,}2*10^6$
Br	20	$6{,}0*10^5$
SeCN-	4000	$6{,}0*10^6$

grundlegende Reaktionstypen

A: $R-X+Y^- \rightarrow R-Y+X^-$; $R-X^+ + Y \rightarrow R-Y^+ + X$ keine Änderung der Netoladung

B: $R-X+Y \rightarrow R-Y^+ + X^-$ Erhöhung der Nettoladung

C: $R-X^+ + Y^- \rightarrow R-Y+X$ Verringerung der Nettoladung



Beispiele

A $\quad MeI + Cl^- \xrightarrow{k(rel)} \begin{cases} H_2O : 1 \\ H_2O/EtOH : 2 \end{cases}$

B $\quad Et-I + NEt_3 \xrightarrow{k(rel)} \begin{cases} Hexan : 1 \\ PhCN : 2200 \end{cases}$

C $\quad Me_3S^+ + OH^- \xrightarrow{k(rel)} \begin{cases} EtOH : 22000 \\ H_2O : 1 \end{cases}$

Dipolare aprotische Lösemittel sind ideal für Sn2!
Sie bilden „nackte Anionen“ ohne Solvathülle→kleinere und damit bessere Nukleophile

$$Bu-Br + N_3^- \xrightarrow{k(rel)} Bu-N_3 + Br^-$$

MeOH	1
DMSO	1300
DMF	2800
Acetonitril	5000
HMPT	200000

Gasphasenreaktion: $H_3C-Br + X^- \xrightarrow{k(rel)} H_3C-X + Br^-$

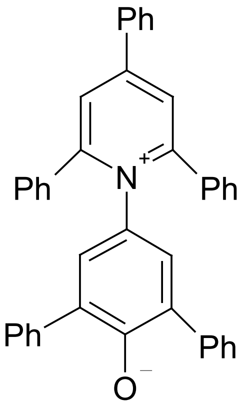
OH^-	158
OMe^-	60
F^-	50
MeS^-	12
CN^-	1,7
Cl^-	1

keine Solvathülle→ je kleiner, je besser

In Gasphase ist die reale Größe für die Nucleophilie entscheidend: $F^- > Cl^- > Br^-$

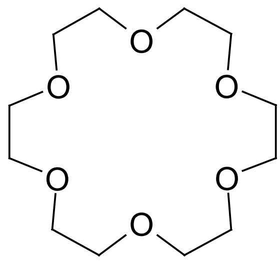
$OH^- > RO^- > RS^-$

ET-Werte: Maß für die Polarität eines Lösemittels (ETn: normiert)



Farbigkeit der Verbindung hängt sehr stark von der Polarität des Lösemittels ab, da
HOMO → LUMO
Polar → unpolar
angeregter Zustand immer unpolar
→ΔΔE ist Maß für Polarität

Besondere Lösemittel: Kronenether (hier [18]Krone 6)



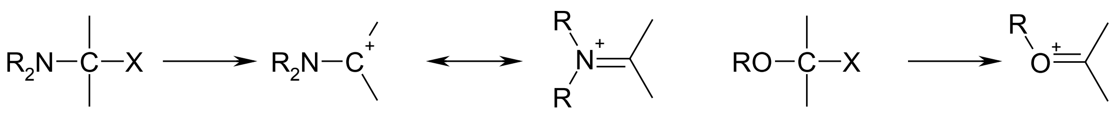
Phasen-Transfer-Katalyse: ($R > C_4$)
Meist mit Tetrabutylammoniumsalzen ($R_4N^+X^-$)
Eingesetzt $Bn-Cl(löslich CH_2Cl_2) + NaCN(löslich H_2O)$

$H_2O + NaCl$ $\quad R_4N^+CN^- + NaCl \Leftrightarrow R_4N^+Cl^- + NaCN$ $\quad R_4N^+ + Cl^-$
$\Uparrow$ $\quad \Uparrow$
Phasengrenze——————————————————
$\Downarrow$ $\quad \Downarrow$
CH_2Cl_2 $\quad Bn-Cl + R_4N^+CN^- \rightarrow$ $\quad Bn-CN + R_4N^+Cl^-$

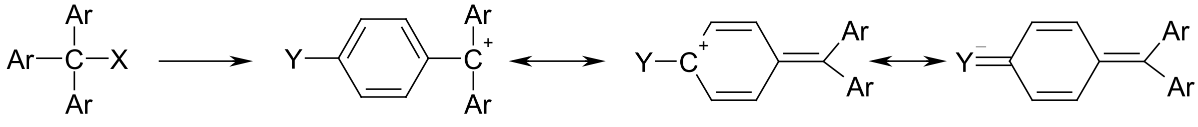
1.6 S_n1 - Reaktion

1.6.1 Die Struktur des Substrat

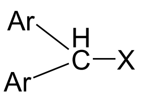
sehr rasch



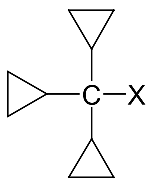
all Oktett

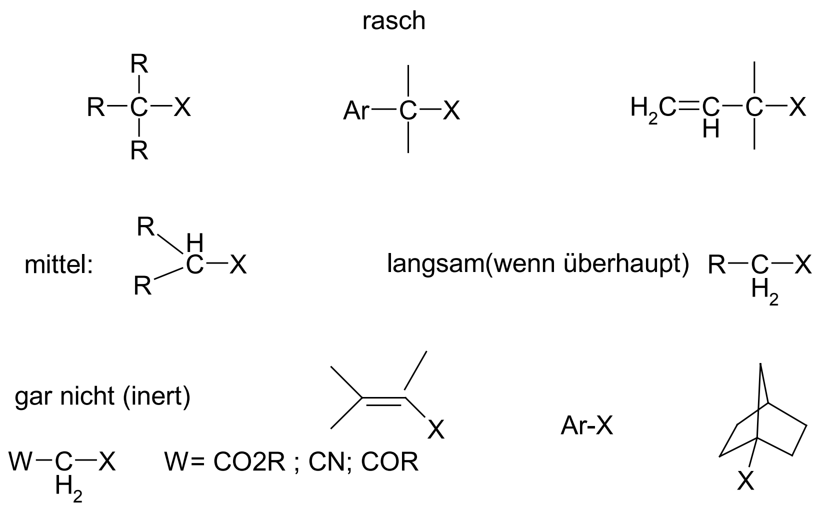


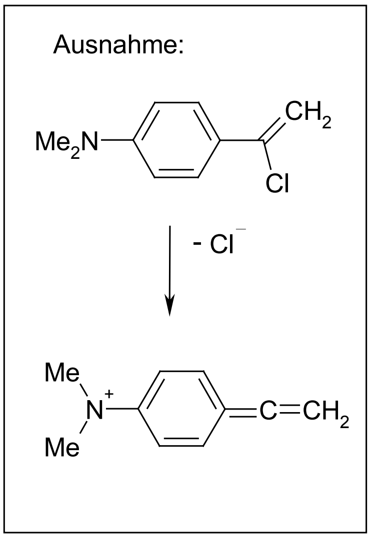
Trityl, wenn Ar=Phe



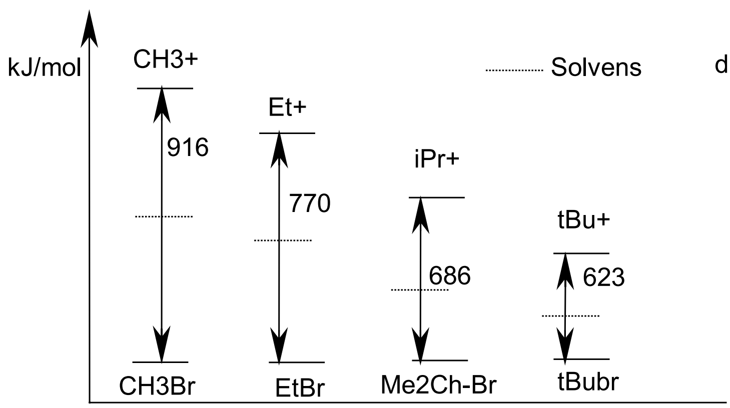
Benzhydryl

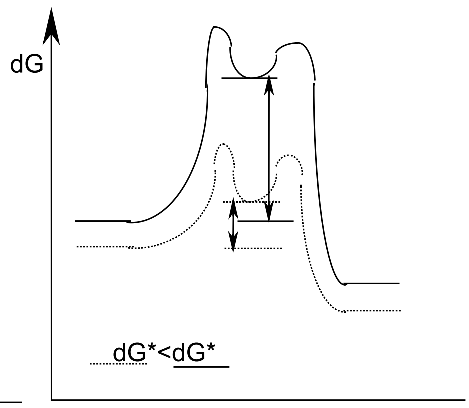






Lösemitteleinfluß:





tBu-Br + H2O $\xrightleftharpoons{k(rel)}$ tBuOH+HBr

Aceton/H2O (90:10) 1
H2O 400000

Sterische Beschleunigung:
$(tBU)_3C-CL > Me_3-Cl$

↑ sterischer Druck im Carbeniumion (120°) geringer als in der Ausgangsverbindung(109°)

1.6.2 Carbeniumionen in Lösung

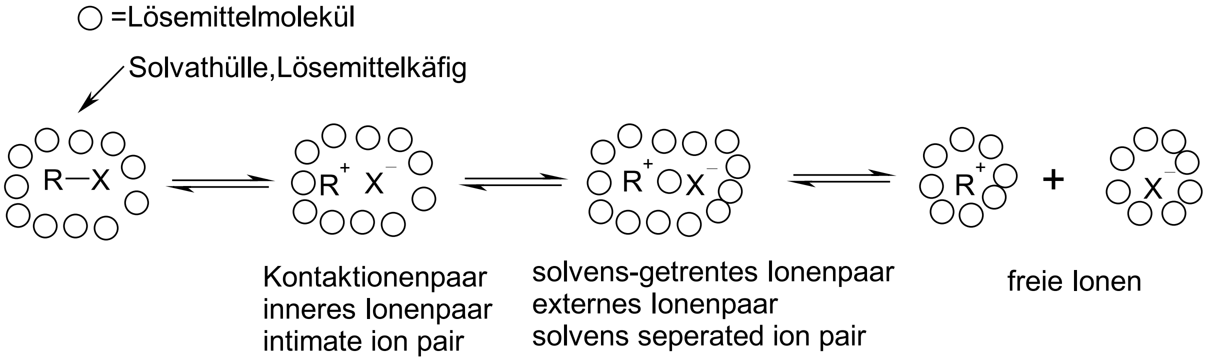
$$\text{Carbo}-\text{Kation}\left\langle \begin{matrix}\text{Carbeniumionen}(sp^2;\text{planar})\\ \text{Carboniumionen}(sp^3)\end{matrix}\right.$$

Supersaures Medium:

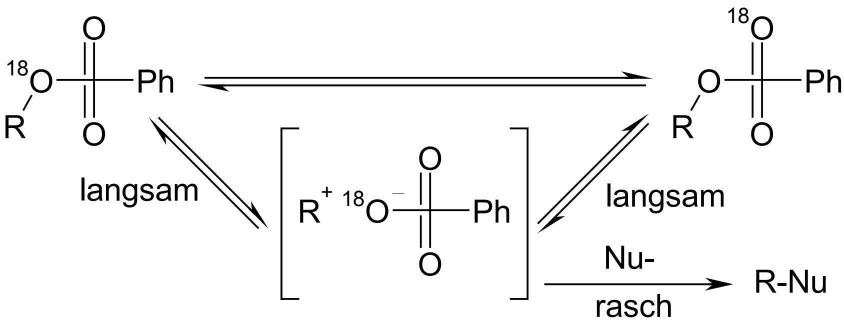
$$\text{TBuCl}\xrightarrow[\text{flSO}_2;-60°]{FSO_3H+SbF_5} Me_3C^+ + [SbF_5Cl]^-$$

13C δ= +335 ppm

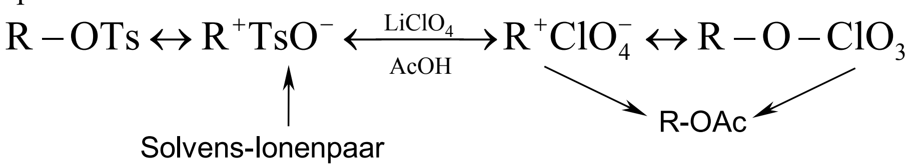
nur Carbeniumionen in diesem Bereich; sonst C bei 0-250 ppm



Isomerisierung

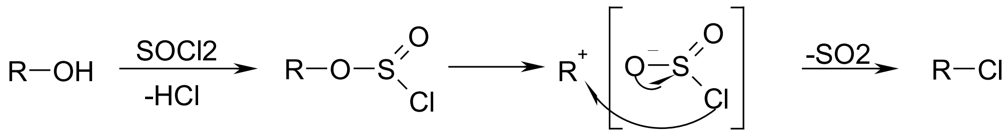


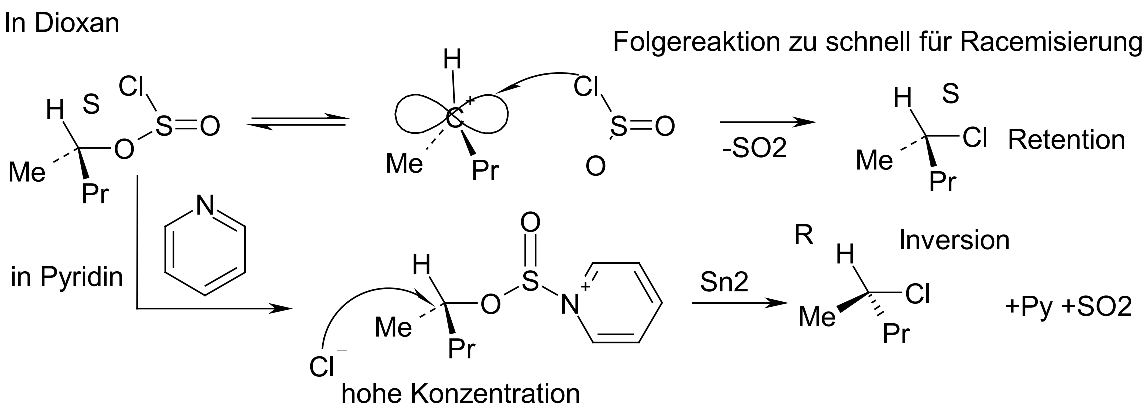
Spezieller Salzeffekt



1.6.3 Intramolekulare S_n-Reaktionen $S_n i$

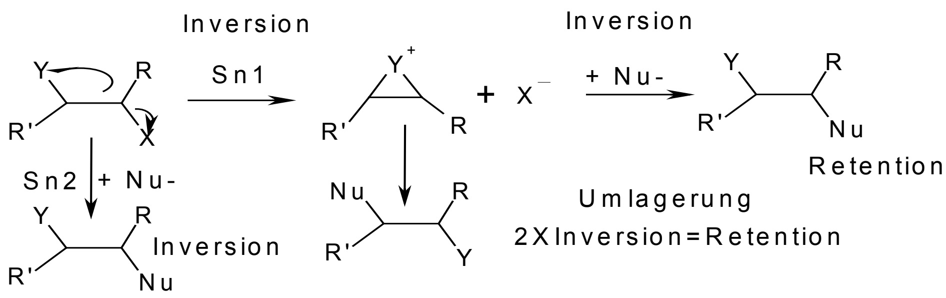
Thionylchlorid $SOCl_2$ Sulfonylchlorid: SO_2Cl_2

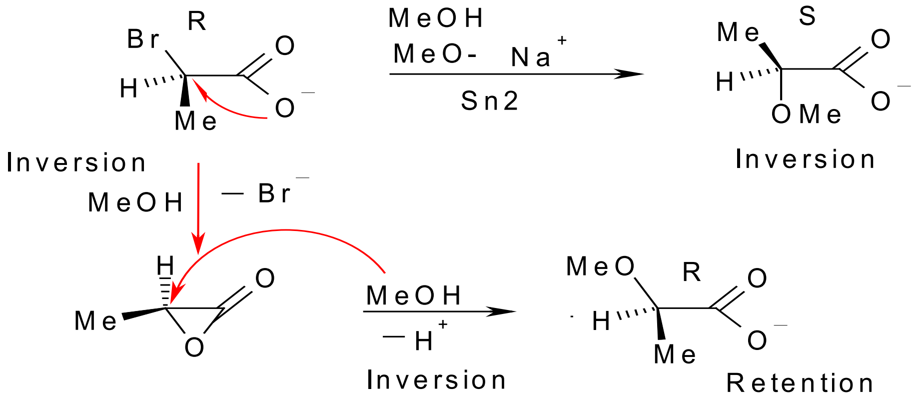




1.6.4 Nachbargruppeneffekte

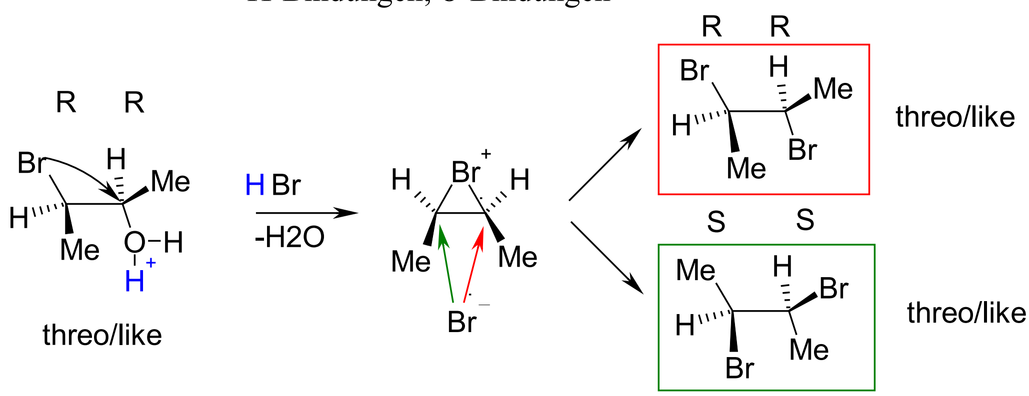
1. Erhöhte Reaktionsgeschwindigkeit 2. Retention

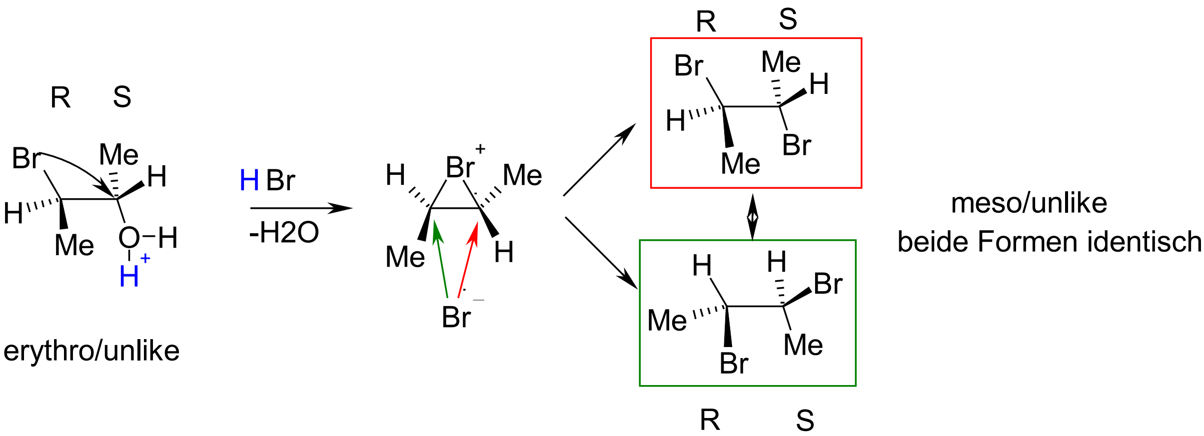


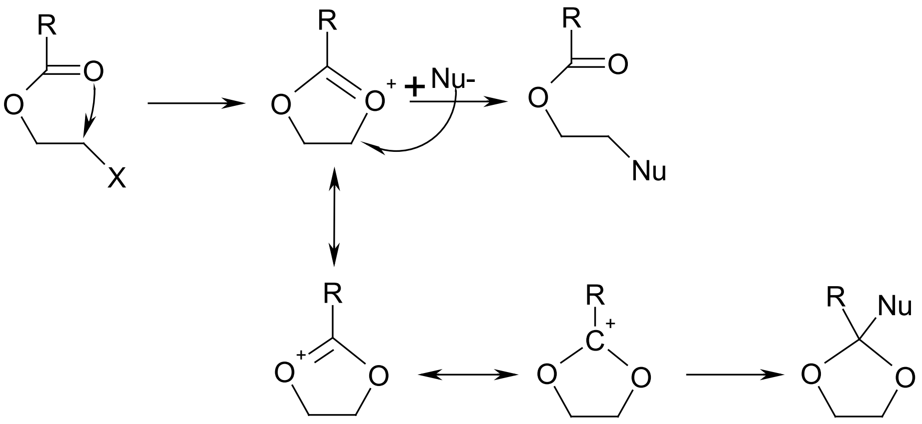


Nachbargruppen: $CO_2^-; O-CO-R; O-R; OH; O^-; NR_2; SR; S^-; I; Br$

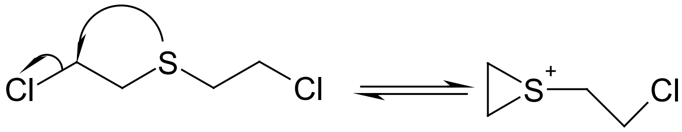
Π-Bindungen; σ-Bindungen

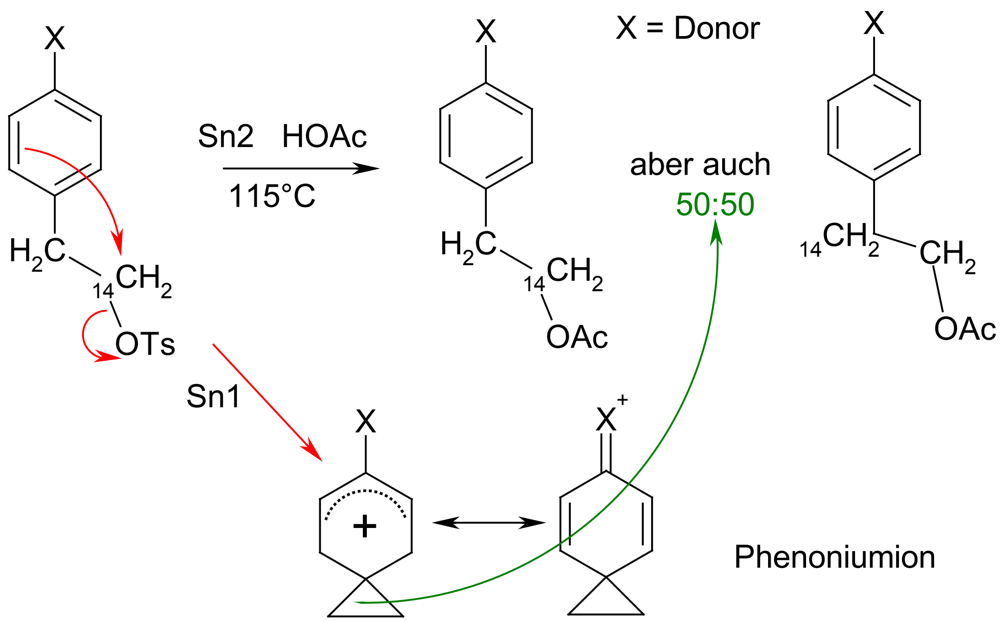




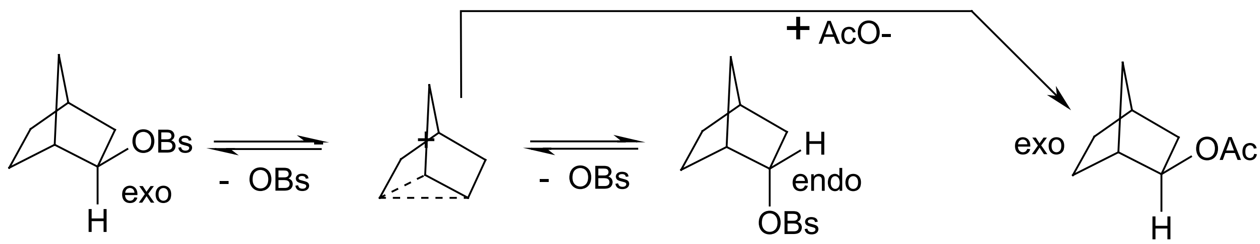


Die Wirkung des Kampfgases S-LOST beruht auf einem Nachbargruppeneffekt.

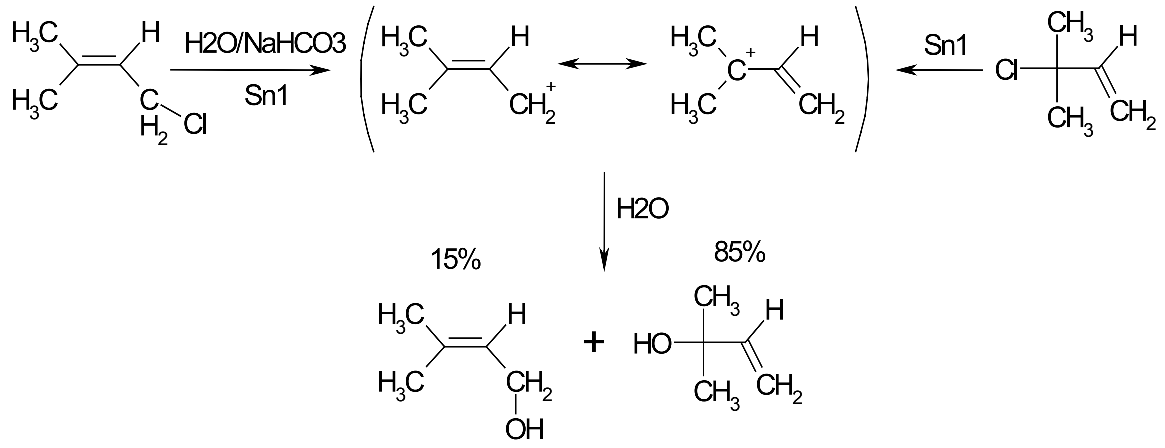


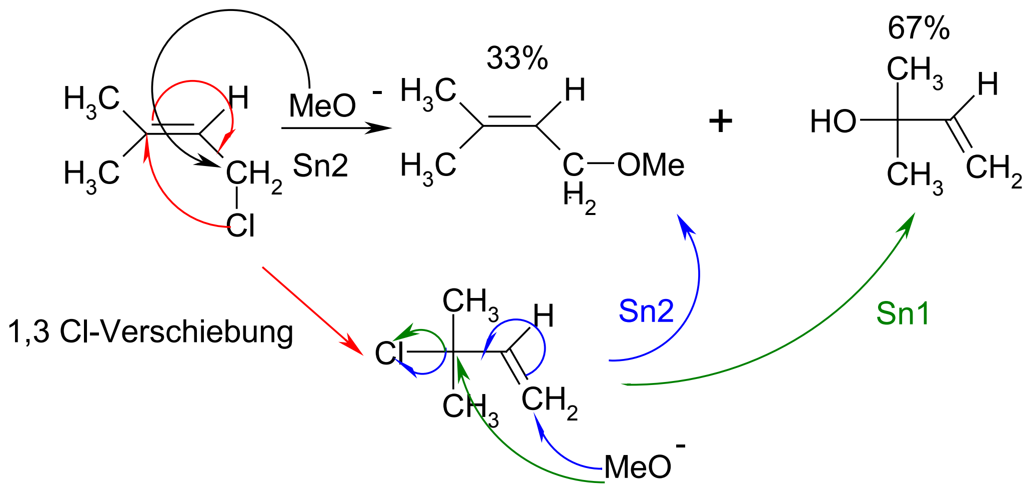


k(rel)=550 k(rel)=1

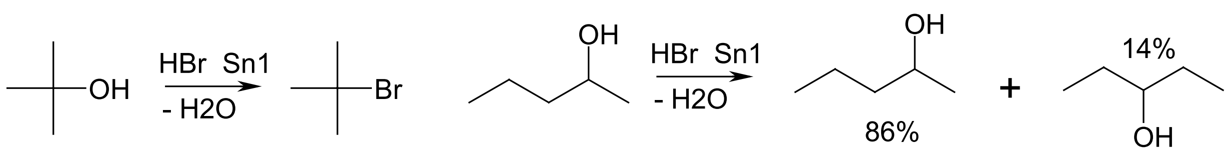


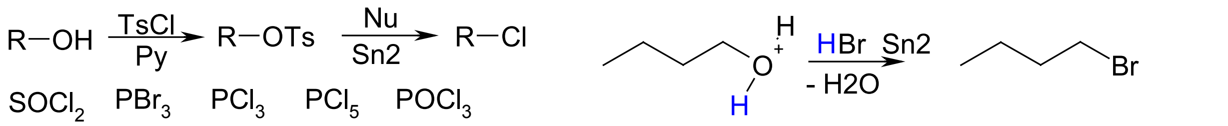
1.6.5 Allylderivate

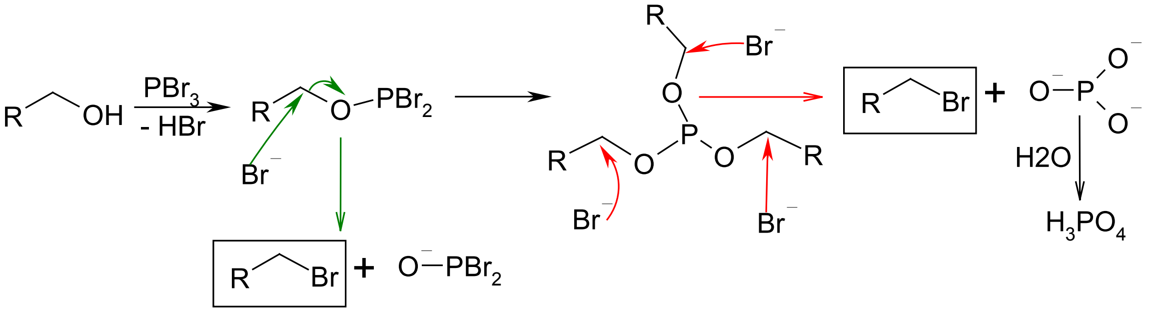




1.6.6 Präparative Aspekte







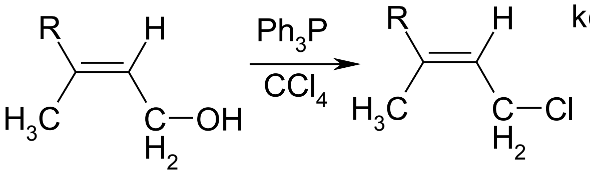
<u>Appel-Reaktion</u> (Alkohole zu Halogeniden)

$Ph_3P + CCl_4 (C_2Cl_6)$

$$Cl_3C - Cl + |PPh_3 \rightarrow CCl_3^- + Cl - P^+Ph_3$$

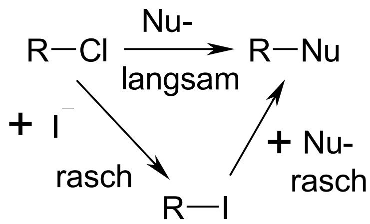
$$CCl_3^- + R - OH \rightarrow Cl_3CH + RO^-$$

$$RO^- + Cl - P^+Ph_3 \rightarrow Ph_3PCl(OR) \Leftrightarrow Ph_3P^+ - OR + Cl^- \rightarrow R - Cl + Ph_3P = O$$



keine Nebenreaktionen

Folgereaktionen: Katalyse mit Iodid

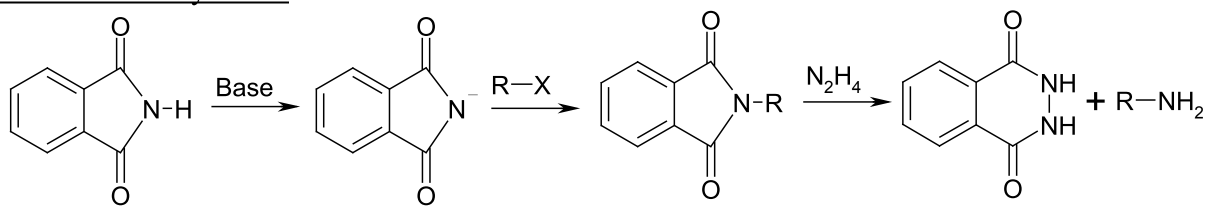


Unmöglichkeit einer „normalen“ Aminsynthese mit Sn

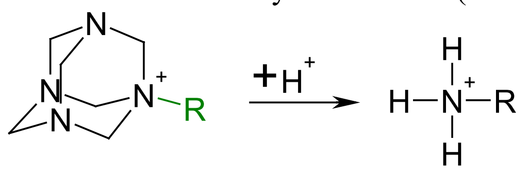
$$NH_3 \xrightarrow{R-X} R - N^+H_3 + X^- \xrightarrow{NH_3} R - NH_2 \xrightarrow[\text{rasch}]{R-X} R_2N^+H_2$$

$$\xrightarrow{NH_3} R_2NH \xrightarrow[\text{rasch}]{R-X} R_3N^+H \xrightarrow{NH_3} R_3N \xrightarrow[\text{rasch}]{R-X} R_4N^+$$

<u>Gabriel-Aminsynthese</u>:



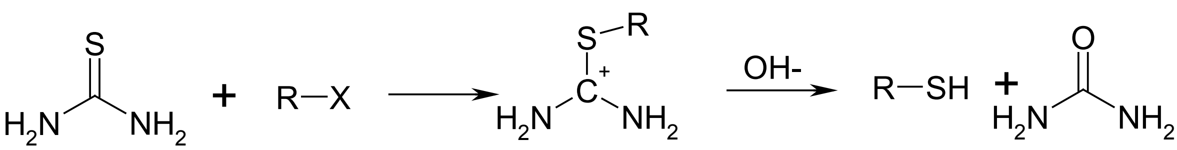
Amine aus Hexamethylentetraamin (Urotropin)



Amine aus Aziden:

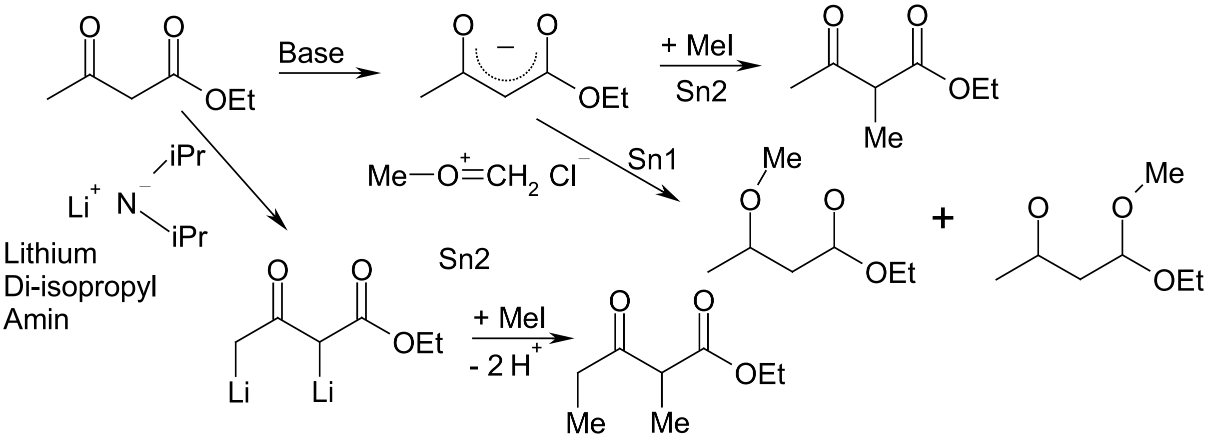
$$R - X + N_3^- \rightarrow R - N_3 \xrightarrow{H_2/Kat} R - NH_2$$

Thiole aus Thioharnstoff



1.6.7 Stabilisierungseffekte

S_n1 versus S_n2



Sn1: harte Säuren und Basen; Ladungen
Sn2: weiche Säuren und Basen; Orbitalbeteiligung

1.7 Radikalische aliphatische Substitution

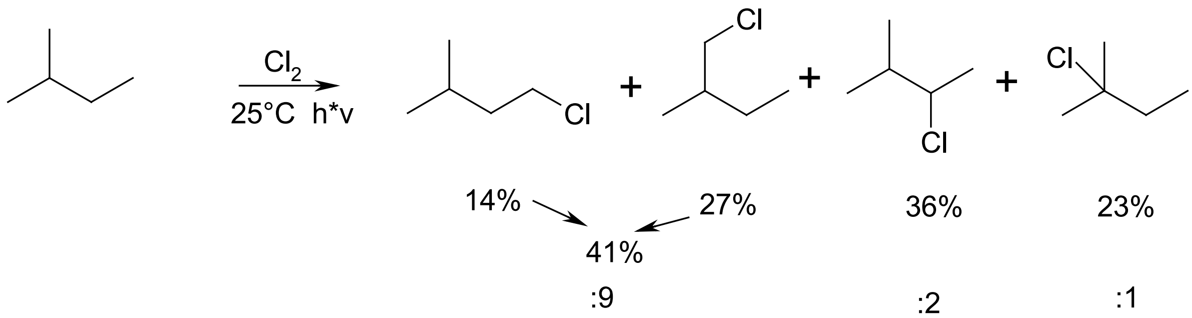
1.7.1 Halogenierungen

alle Angaben in ΔH(kJ/mol)

Phase	Reaktion	Fluor	Chlor	Brom	Iod
Start	$X-X \xleftrightarrow[\Delta]{h*v} 2X\bullet$	+37	+58	+46	+36,5
Kette 1	$X\bullet + CH_4 \rightarrow HX + \bullet CH_3$	-32	+1	+17	+33
Kette 2	$\bullet CH_3 + X_2 \rightarrow XCH_3 + X\bullet$	-72	-26	-24	-20
ΣKette	$X_2 + CH_4 \rightarrow XCH_3 + HX$	-104	-25	-7	+13
Abbruch 1	$X\bullet + \bullet CH_3 \rightarrow XCH_3$				
Abbruch 2	$H_3C\bullet + \bullet CH_3 \rightarrow C_2H_6$				

Die Reaktion mit Fluor läuft explosionsartig; bei Iod liegt das Gleichgewicht auf der falschen Seite. Praktisch durchführbar sind daher nur Chlorierungen und Bromierungen.

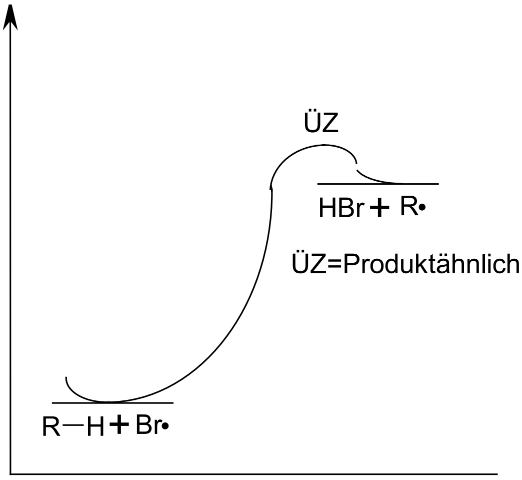
Selektivität

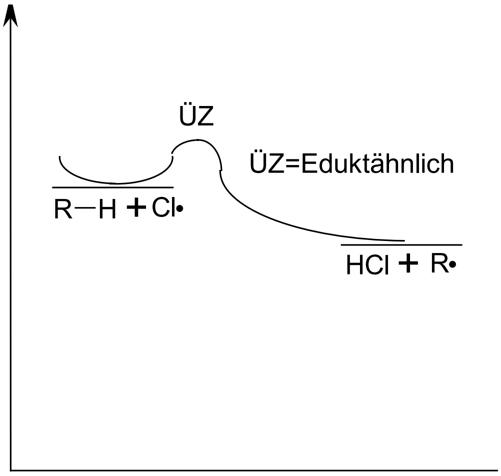


Halogen	primär	sekundär	tertiär
Chlor	1	4	5
Brom	1	250	6300
Fluor	1	1,2	1,4

→ Je reaktiver, desto unselektiver!

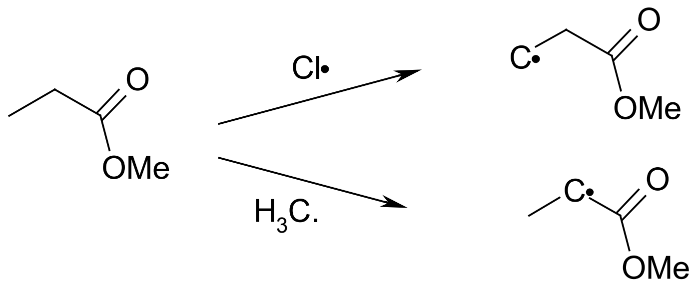
1.7.2 Hammond-Prinzip





Lösemittel	tertiär	primär
Gasphase	3,7	1
CCl_4	3,5	1
$H_3C\text{-}NO_2$	3,3	1
Dioxan	5,6	1

→kaum Lösemitteleinfluß



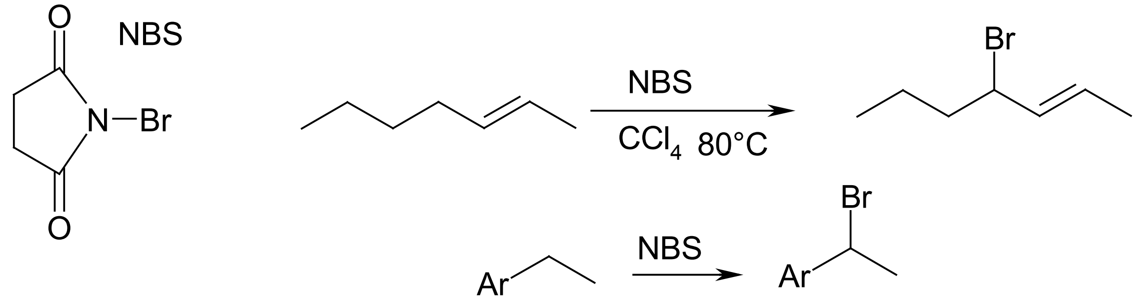
I - Effekte

1.7.3 Präparative Aspekte

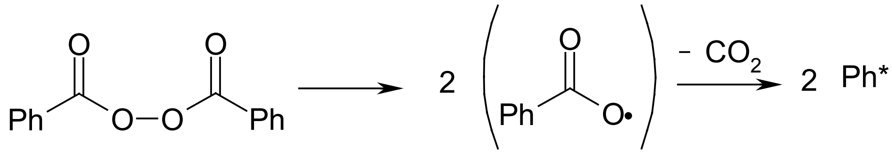
$$SO_2Cl_2 \xrightarrow{h*\nu} SO_2 + 2Cl\bullet$$
$$Cl\bullet + R-H \rightarrow R\bullet + HCl$$
$$R\bullet + SO_2Cl_2 \rightarrow R-Cl + SO_2Cl\bullet$$
$$SO_2Cl\bullet \rightarrow SO_2 + Cl\bullet$$

$$tBuOCl \xrightarrow{h*\nu} tBuO\bullet + Cl\bullet$$
$$R-H + tBuO\bullet \rightarrow tBuOH + R\bullet$$
$$R\bullet + tBuOCl \rightarrow tBuO\bullet + R-Cl$$
$$\text{prim : sek : tert} \quad = \quad 1 : 12 : 44$$

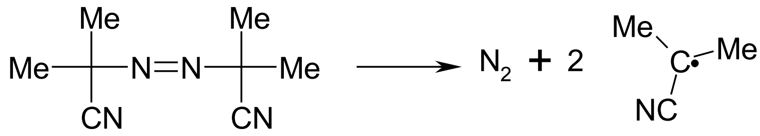
Bromierung mit N-Bromsuccinimid (NBS)



Radikalstarter



AIBN = AzobisIsoButyronitril



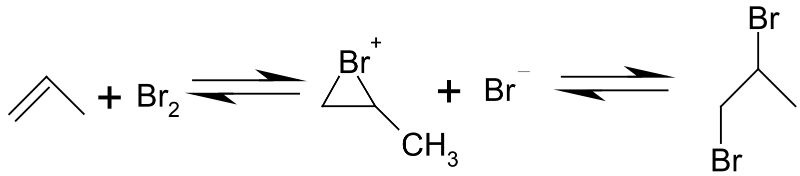
Start: $Ph\bullet + NBS \rightarrow Ph-NBS + Br\bullet$

$Br\bullet + H_2C=CH-CH_3 \rightarrow HBr + H_2C=CH-CH_2\bullet$

Kette: $HBr + NBS \rightarrow Br_2 + NBS-H$ 3 Schritte !!

$H_2C=CH-CH_2\bullet + Br_2 \rightarrow H_2C=CH-CH_2-Br + Br\bullet$

Bei normaler Bromzugabe erfolgt Addition an C=C Bindung



→ Brom(radikal)konzentration klein halten

Sulfonierung

$$R-H + SO_2 + O_2 \xrightarrow{h*\nu} R-SO_3H$$

$$R\bullet + SO_2 \rightarrow R-SO_2\bullet$$

$$R-SO_2\bullet + O_2 \rightarrow R-SO_2-O-O\bullet$$

$$R-SO_2-O-O\bullet + R-H \rightarrow R\bullet + R-SO_2-O-OH$$

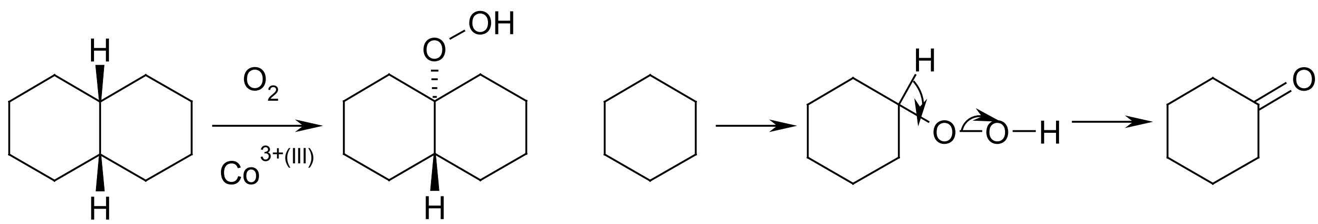
Sulfochlorierung Druck!!

$$R-H + SO_2 + Cl_2 \xrightarrow{h*\nu} R-SO_2-Cl$$

Aufoxidation (Schwermetallkatalysiert)

Start
$$Co(II) + O_2 \rightarrow Co(III)-O-O\bullet$$
$$Co(III)-O-O\bullet + R-H \rightarrow Co(III)-O-OH + R\bullet$$

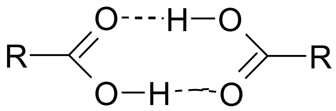
Kette
$$R\bullet + O_2 \rightarrow R-O-O\bullet$$
$$R-O-O\bullet + R-H \rightarrow R-O-OH + R\bullet$$



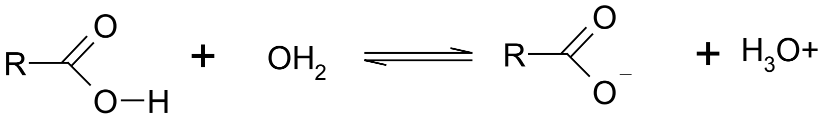
2 Carbonsäuren und Derivate

2.1 Eigenschaften

Dimerbildung



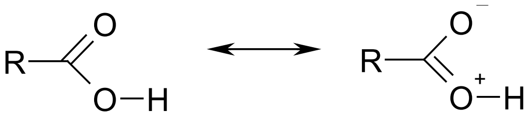
Dissoziation

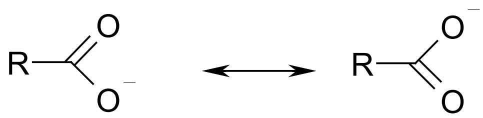


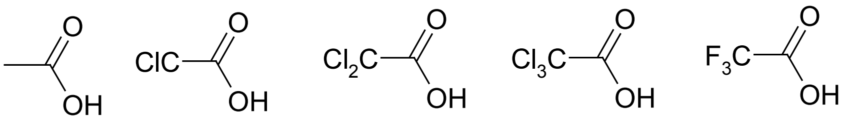
Säurestärke: $K_S = K_A = \frac{[R-CO_2^-]*[H_3O^+]}{[R-COOH]}$ K_A ca. 10^{-5} →pK_A ca. 5

Zum Vergleich: Alkohole $R-OH + H_2O \leftrightarrow R-O^- + H_3O^+$ pK_A ca. 16

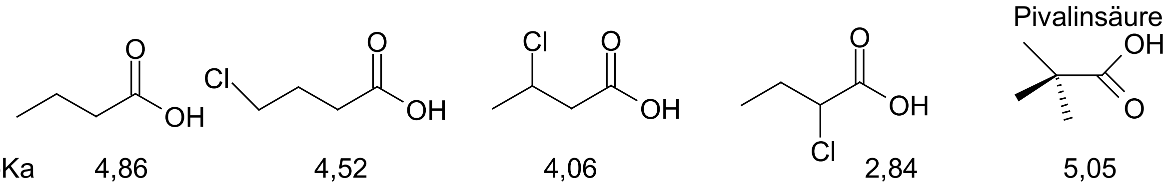
Grund: Mesomeriestabilisierung des Anions, daher O-H Bindung geschwächt







pKa 4,76 2,86 1,29 0,65 -0,6



pKa 4,86 4,52 4,06 2,84 5,05

2.2 Hammett-Gleichung

(Verknüpfung von Thermodynamik und Kinetik)

$$\log\frac{k}{k_0} = \sigma * \rho$$

k = Geschwindigkeitskonstante einer substituierten Verbindung

k_0 = Geschwindigkeitskonstante einer unsubstituierten Verbindung

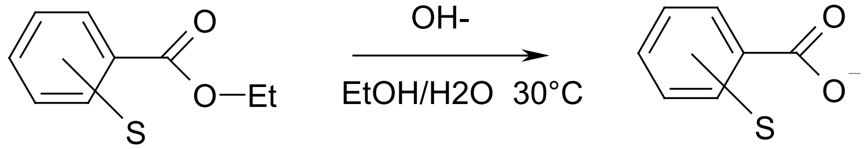
ρ = Reaktionskonstante

σ = Substituentenkonstante

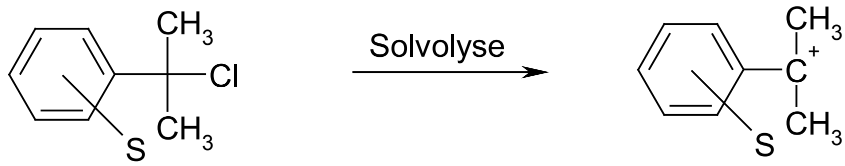
Ursprüngliche Definition: $\log\frac{k}{k_0} = \sigma$ für Reaktion

σ>0 Substituierte Säure stärker Substituent ist e^- -Donor

σ<0 Substituierte Säure schwächer Substituent ist e^- -Akzeptor σ-Werte: siehe Tabelle σ vereint I- und M- Effekte



ρ = +2,43
ρ>0 e^- -Zug beschleunigt die Reaktion
ρ<0 e^- -Schub beschleunigt die Reaktion

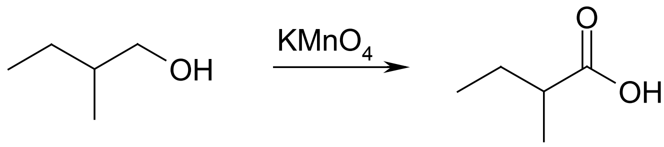


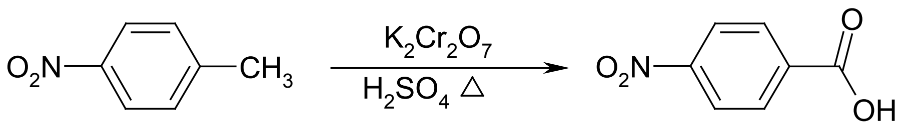
ρ = -4,63

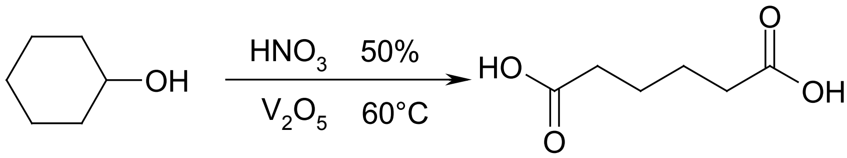
ρ ist die Steigung der Geraden der linearen Regression eines $\log(k/k_0)$ (y-Achse) gegen σ (x-Achse)
wenn |ρ|>3 dann hat die Reaktion einen ausgeprägt ionischen Charakter
dann werden anstelle von σ- Werten die σ+ oder σ- Werte verwendet

2.3 Synthesen

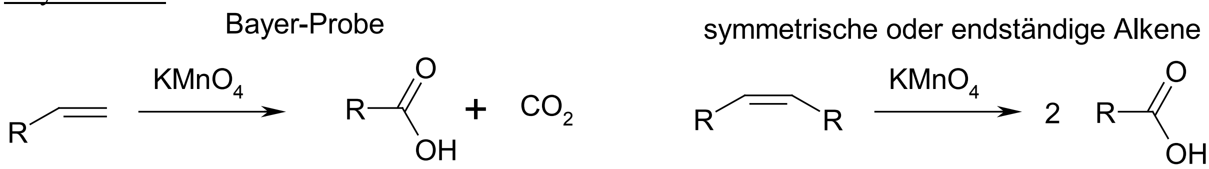
Oxidativ



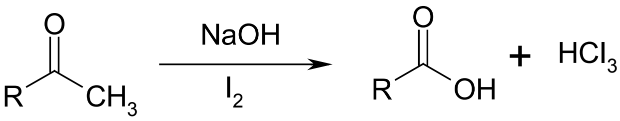




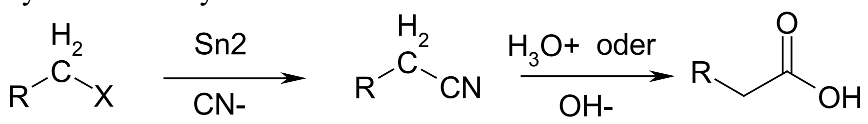
Bayer-Probe



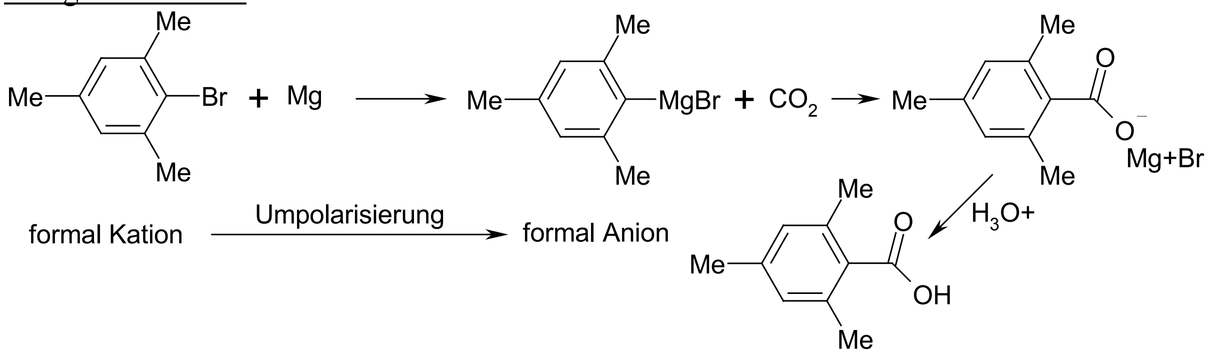
Haloform-Reaktion und Iodoform-Probe



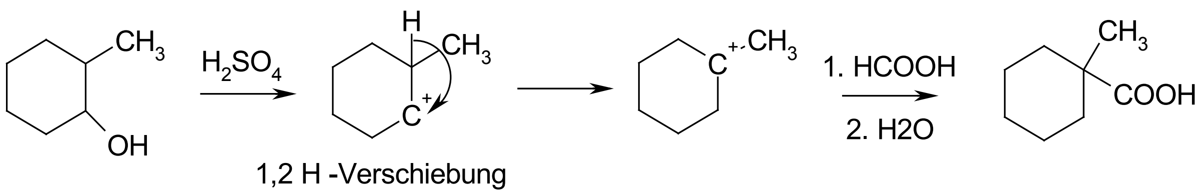
Synthese mit Cyanid



Gringard-Reaktion

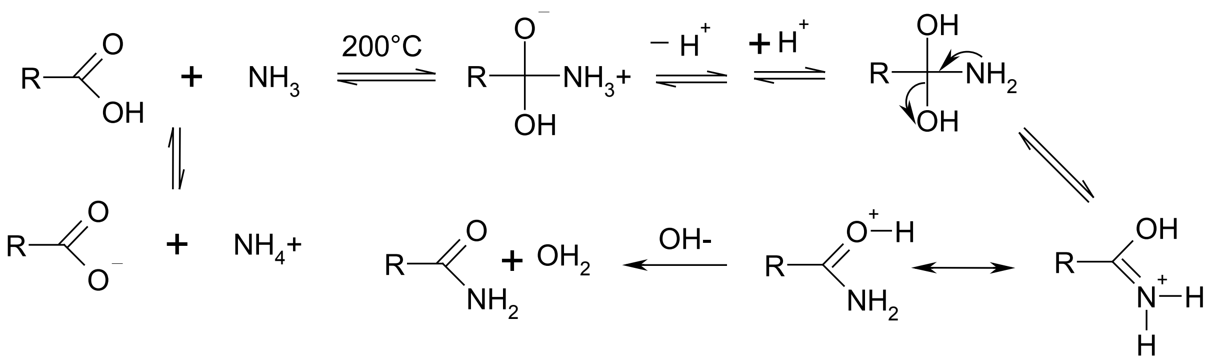


Koch-Haaf-Reaktion

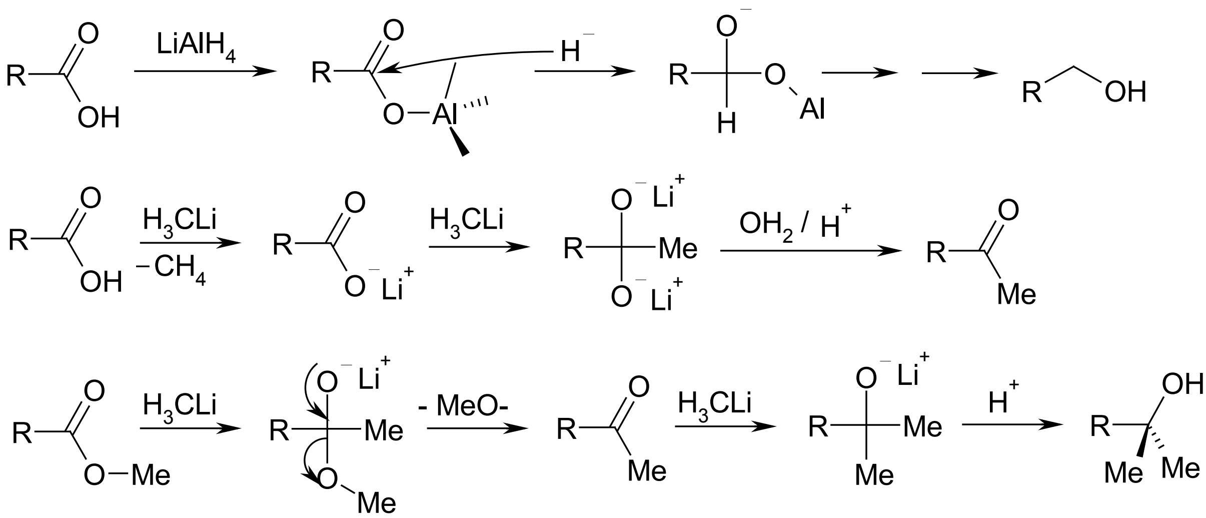


2.4 Reaktionen

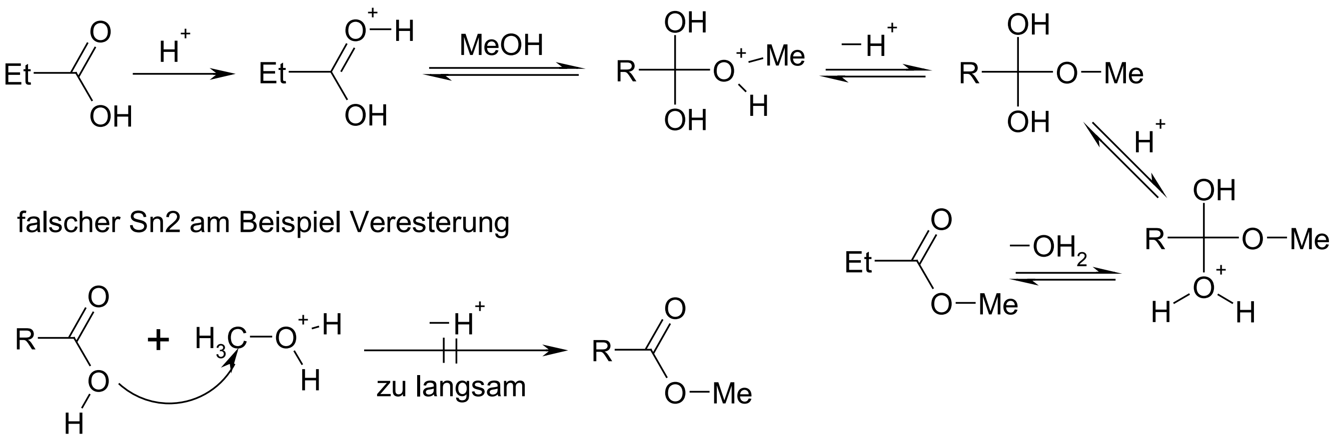
2.4.1 Mechanismen ohne Katalyse

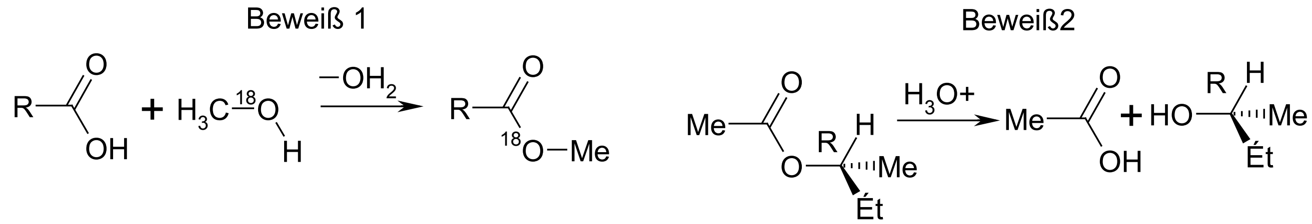


2.4.2 Reduktion und Lithiumorganyle

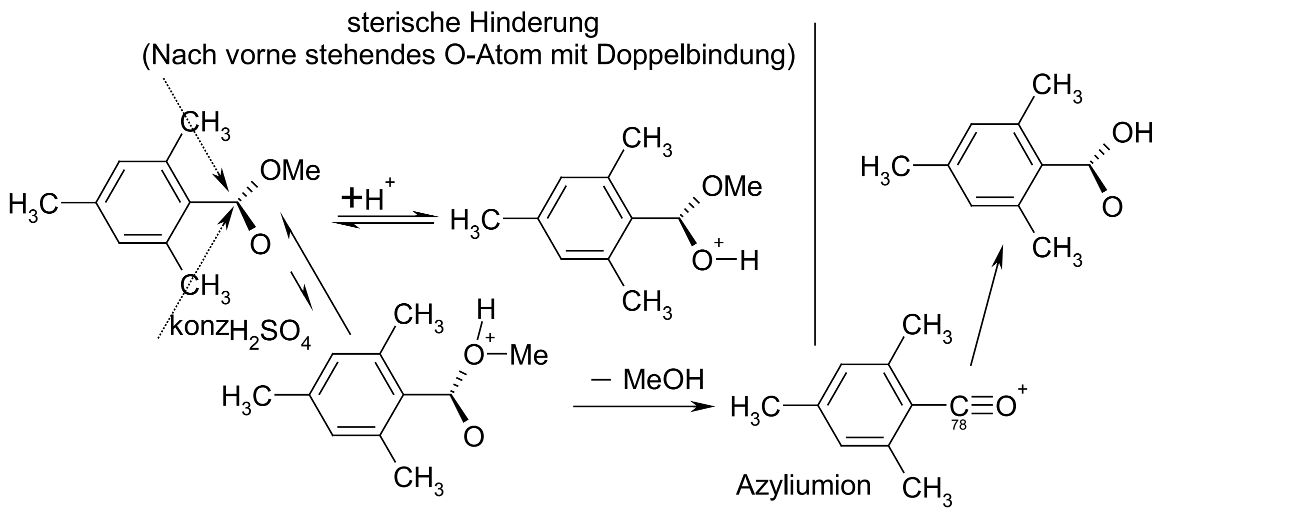


2.4.3 Säurekatalysierte Veresterung

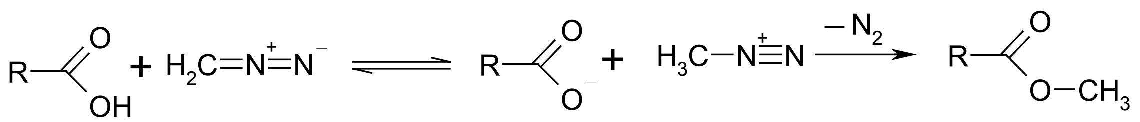




Ausnahmen:
Sterische Hinderung

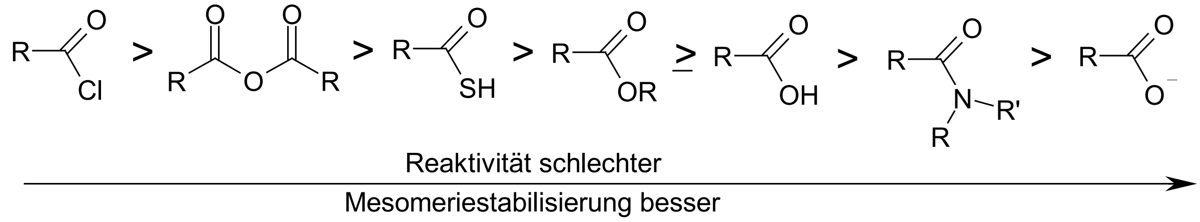


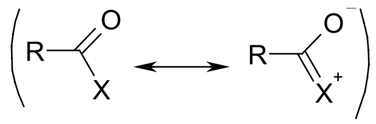
Diazoverbindungen



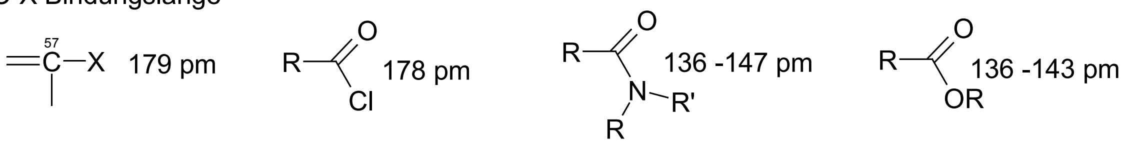
2.5 Carbonsäurederivate

2.5.1 Reaktivität



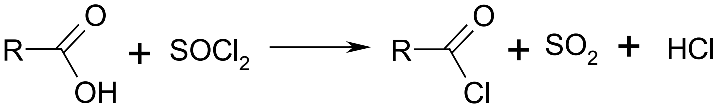


C-X Bindungslänge

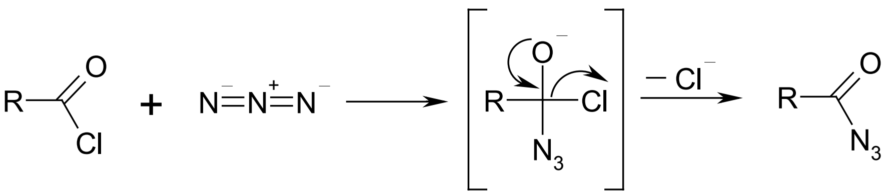


2.5.2 Carbonsäurehalogenide

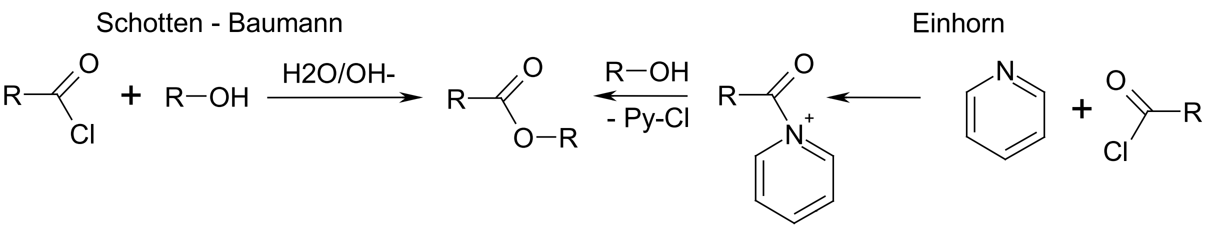
Die Reaktionen und Verfahren, welche Alkohole in Halogenide überführen, funktionieren auch bei Carbonsäuren. Zum Beispiel Thionylchlorid:



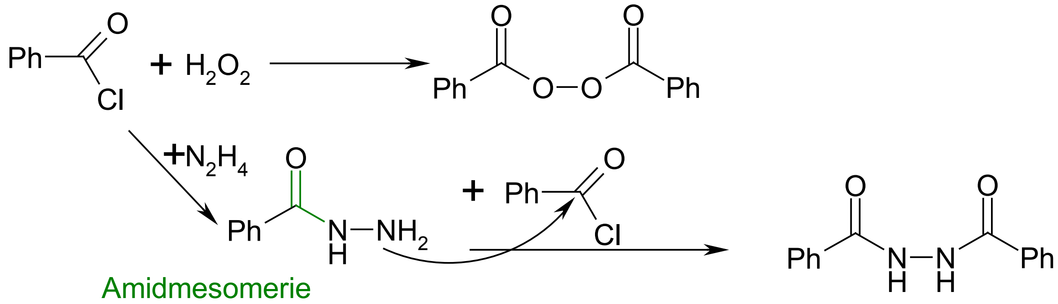
Weitere Reaktionen:



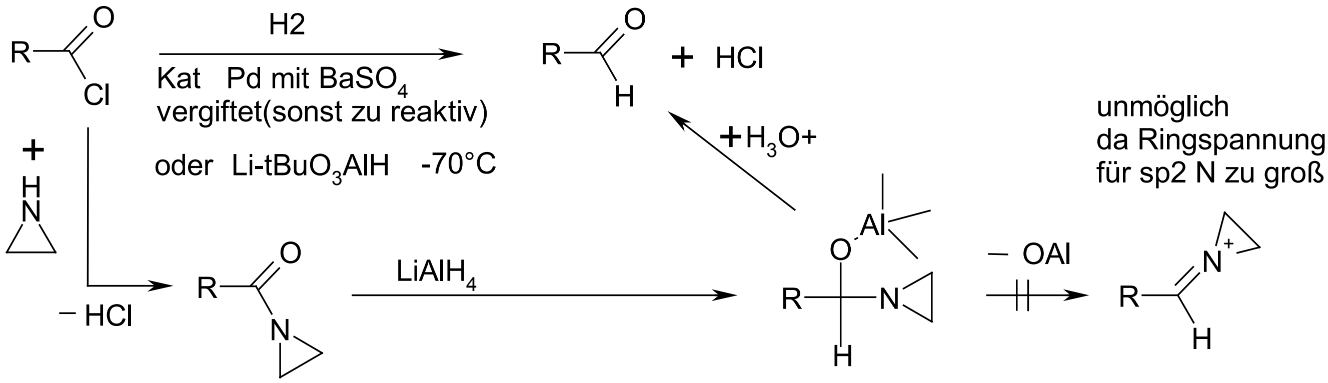
Schotten-Baumann-Reaktion und Einhorn-Reaktion



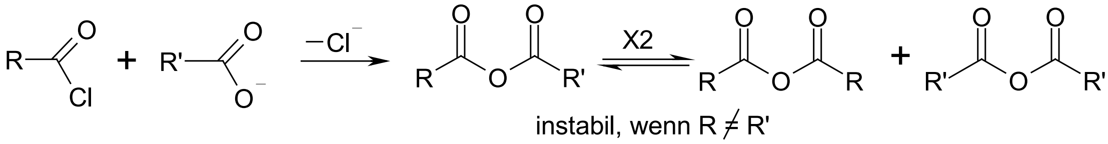
Reaktion mit H_2O_2 oder Hydrazin (α-Effekt)

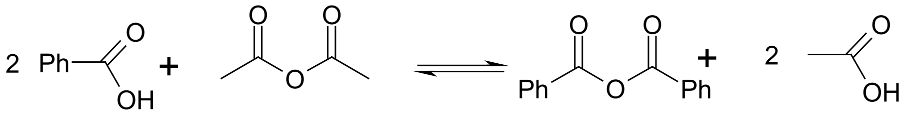


Rosenmund-Reaktion

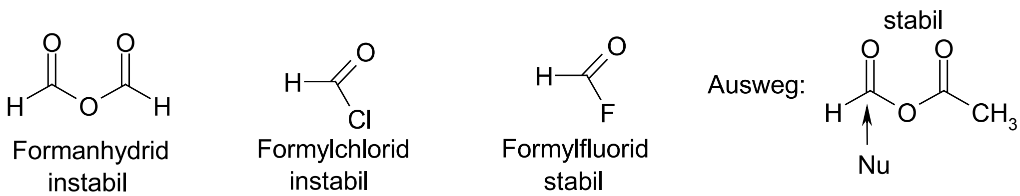


2.5.3 Carbonsäureanhydride

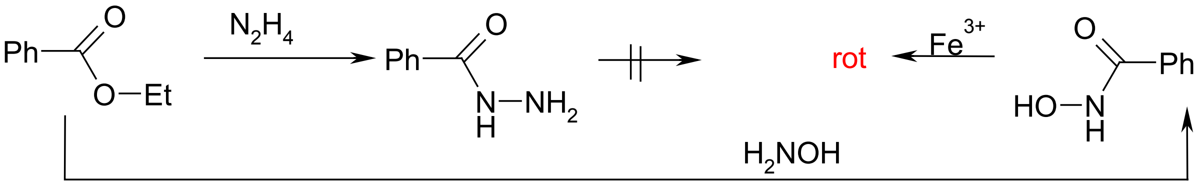




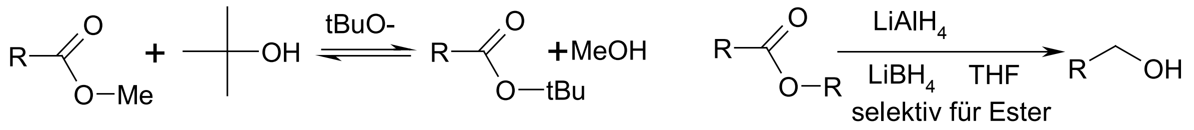
Ausnahmen:



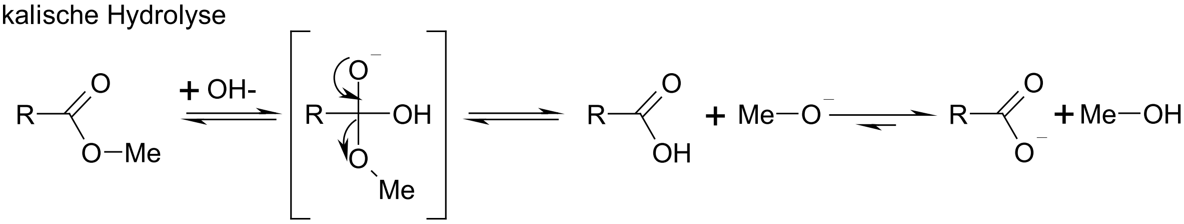
2.5.4 Carbonsäureester



Umestern

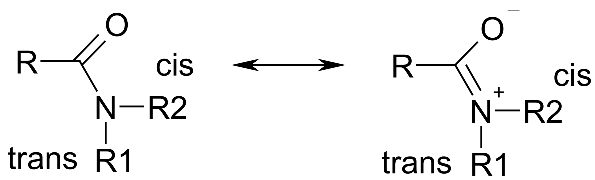


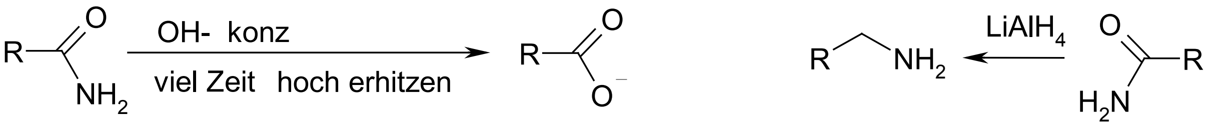
alkalische Hydrolyse



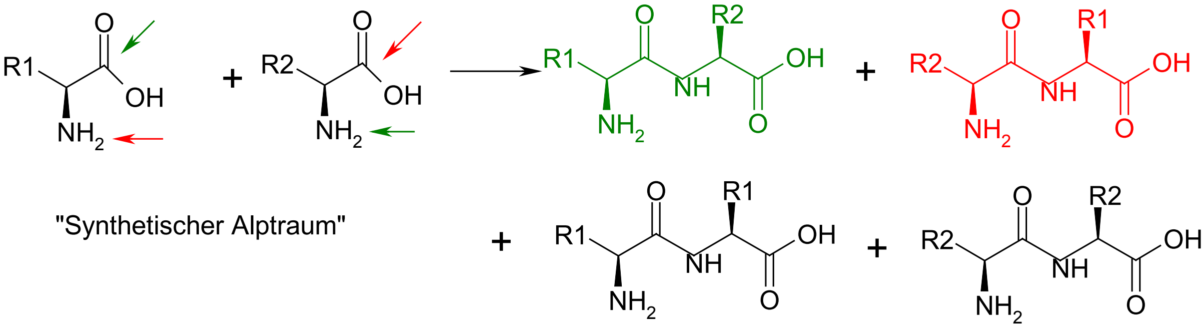
2.5.5 Carbonsäureamide

Amidmesomerie:
Rotationsbariere um die
C-N Bindung ca. 22 kcal/mol
(C-C Einfachbindung ca. 5 kcal/mol)
selbst wenn R1=R2 ist im NMR
δ R1 $\neq$ δ R2 wegen cis/trans

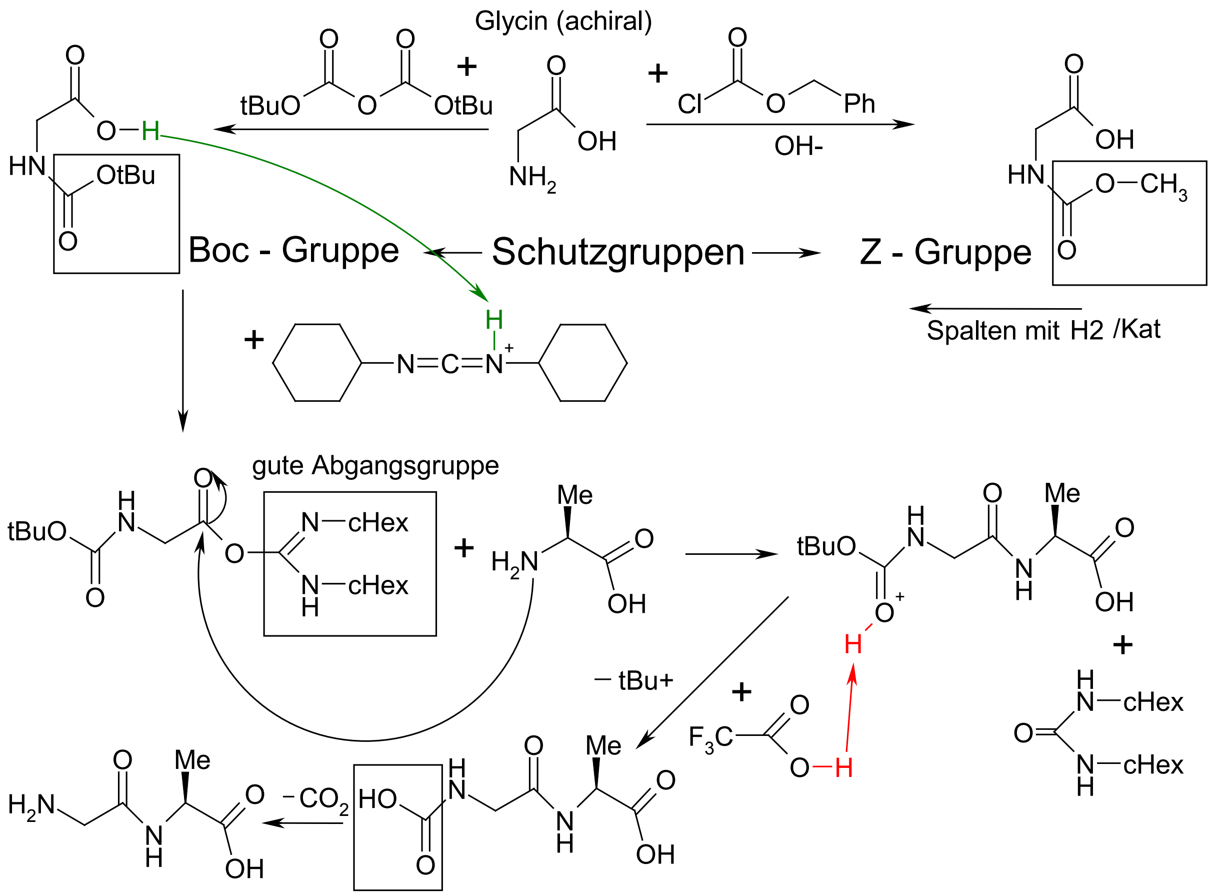




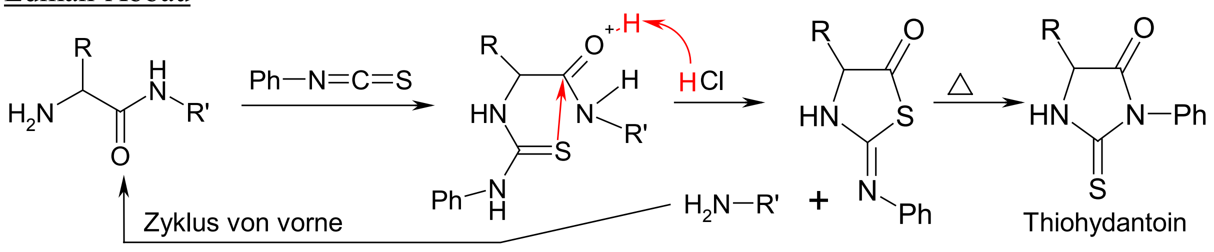
Peptide



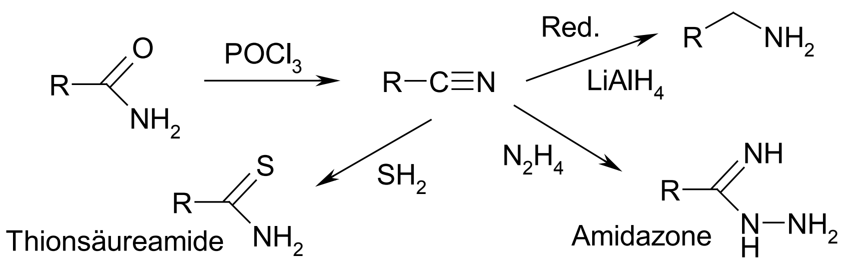
Ein Ausweg ist die Verwendung von Schutzgruppen.



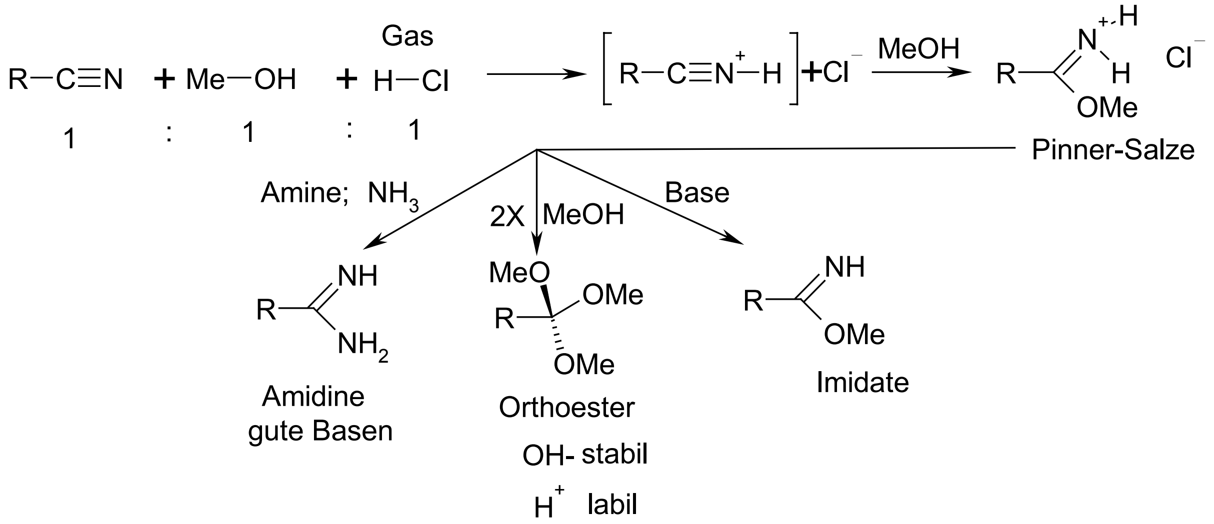
<u>Edman-Abbau</u>



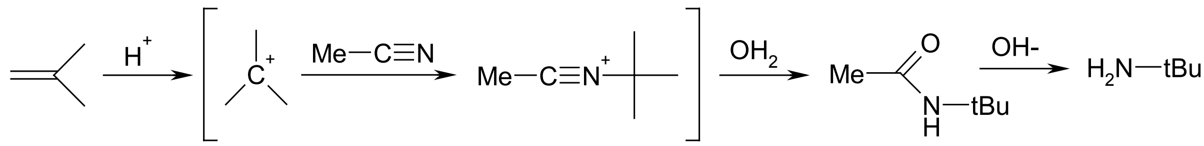
2.5.6 Nitrile



Pinner-Reaktion

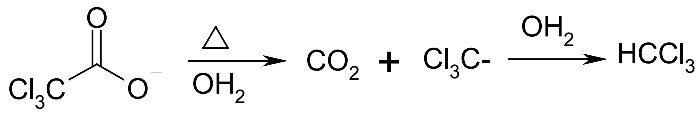


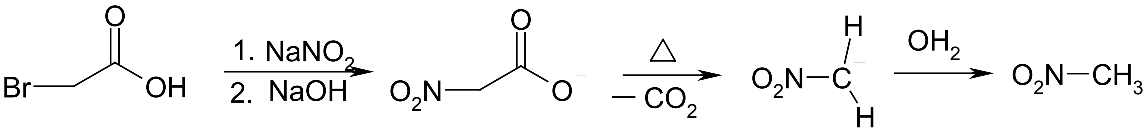
Ritter-Reaktion

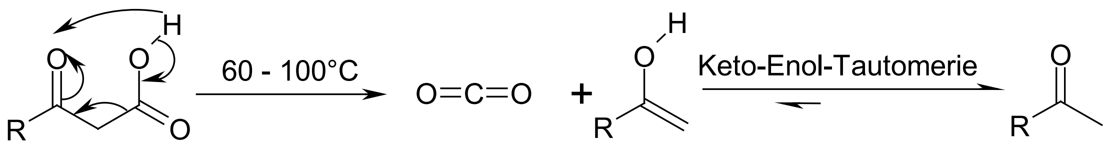


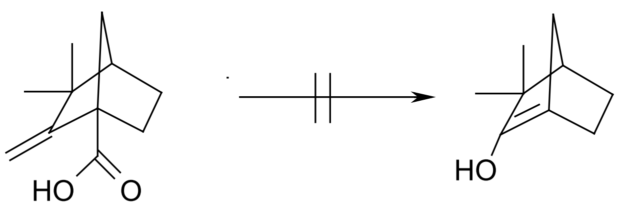
2.6 Abbaureaktionen

2.6.1 Thermische Decarboxylierung





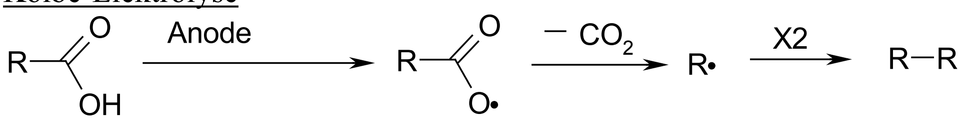




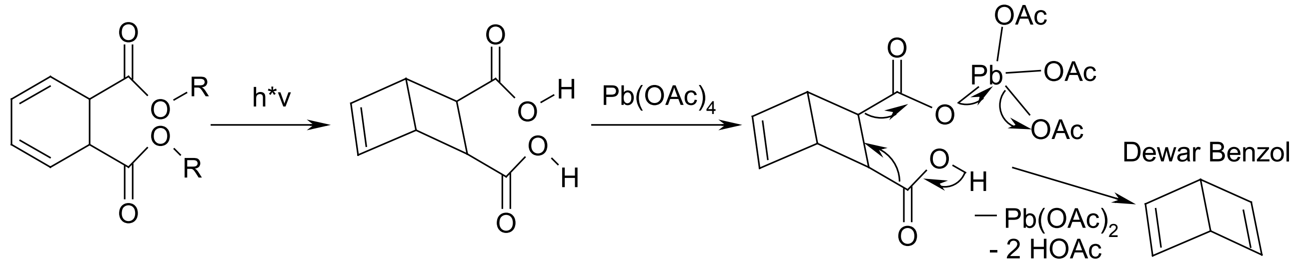
sterische Spannung
bei trans C=C zu groß

2.6.2 Elektrochemische Decarboxylierung

Kolbe-Elektrolyse

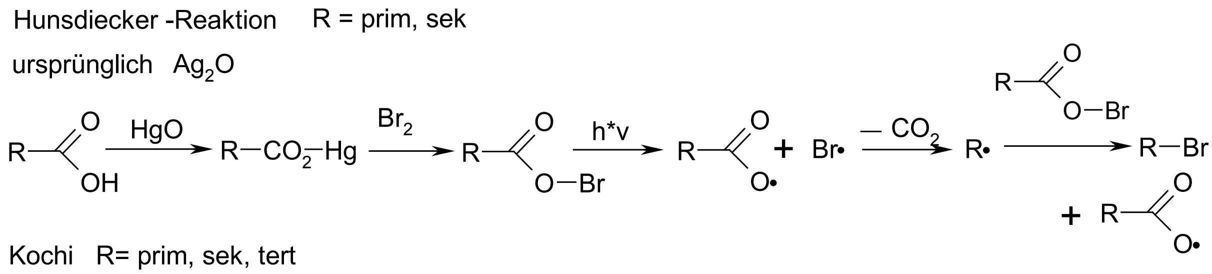


2.6.3 Oxidative Decarboxylierung

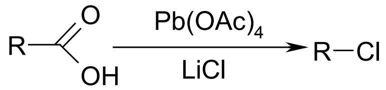


2.6.4 Abbau nach Hundsdicker

Hundsdicker-Reaktion und Kochi-Reaktion

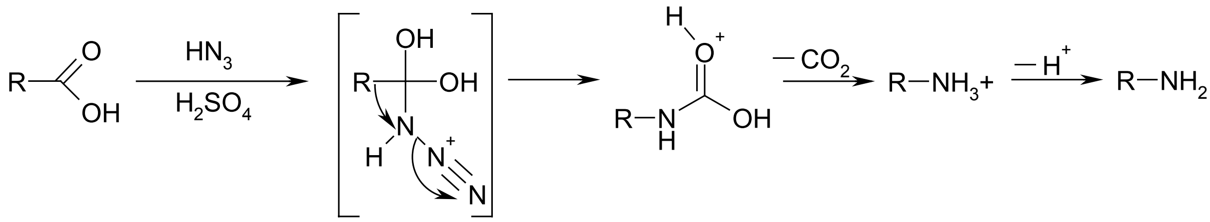


Kochi R= prim, sek, tert

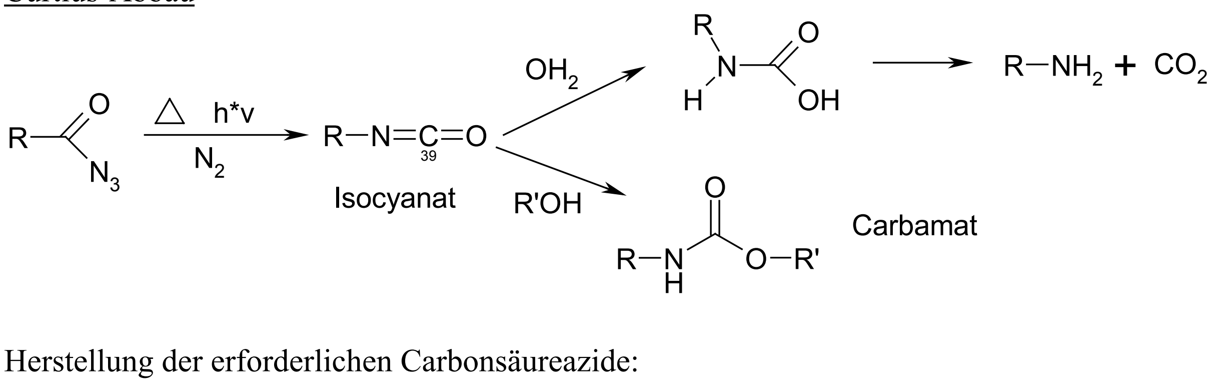


2.6.5 Schmidt, Curtis und Hoffmann-Abbau

Schmidt-Abbau



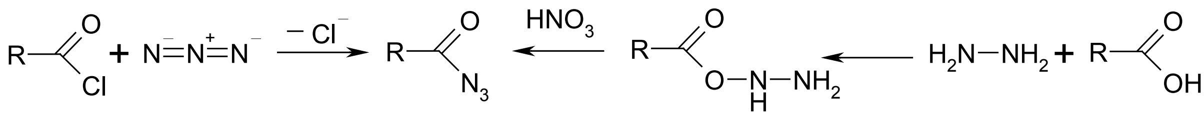
Curtius-Abbau



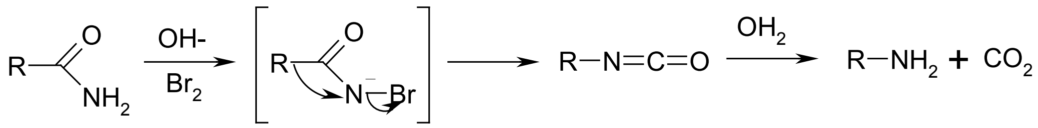
Herstellung der erforderlichen Carbonsäureazide:

aus Säurechloriden

mit Hydrazin: gutes Nukleophil, da alpha-Effekt



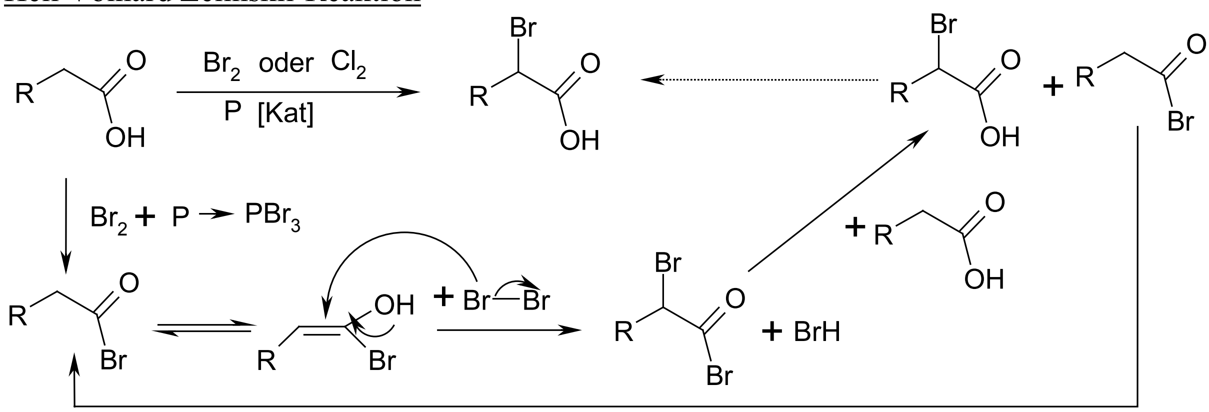
Hofman-Abbau



2.7 Reaktionen der Seitenkette

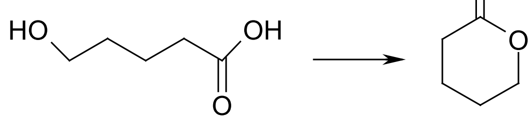
2.7.1 Hell Volhard Zelinskii

Hell Volhard Zelinskii-Reaktion

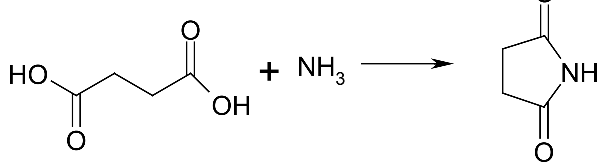


2.8 Zusatz

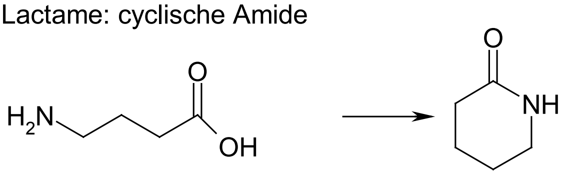
Lactone: cycliche Ester



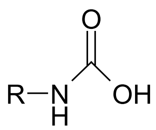
Imide: cyclisches "Azo" Anhydrid



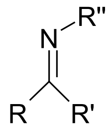
Lactame: cyclische Amide



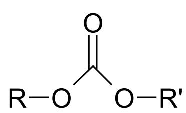
Carbamidsäure



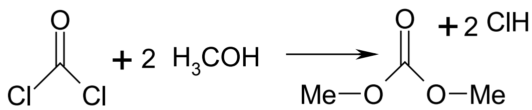
Imine



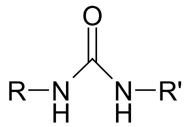
Dialkylcarbonate

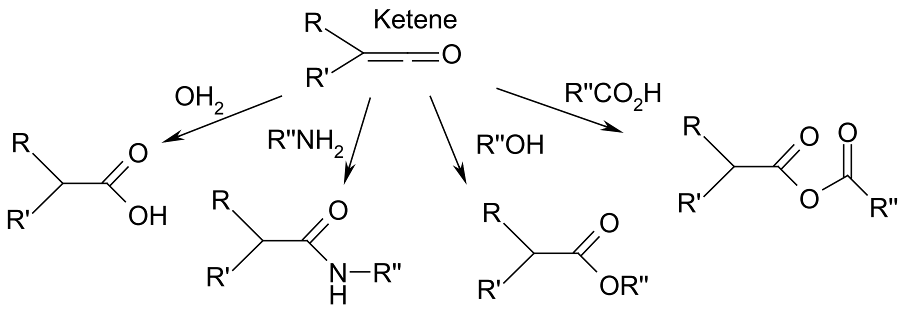


z.B.

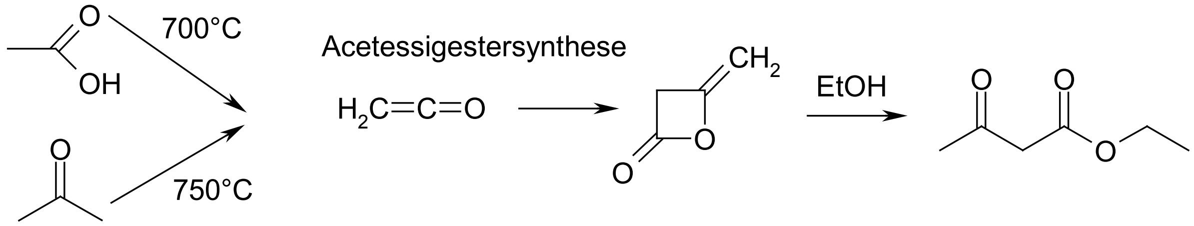


Harnstoffderivate





Acetessigestersynthese

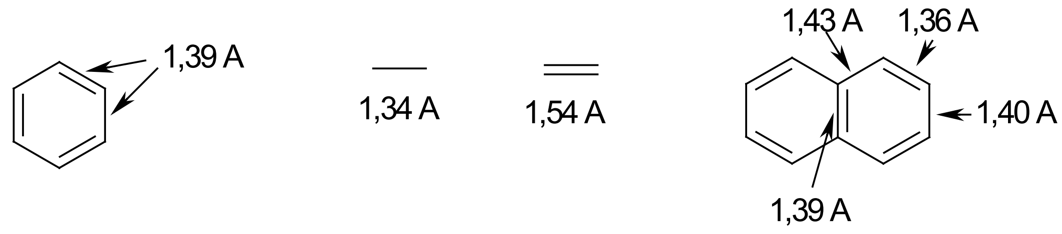


3 Aromatische Substitution

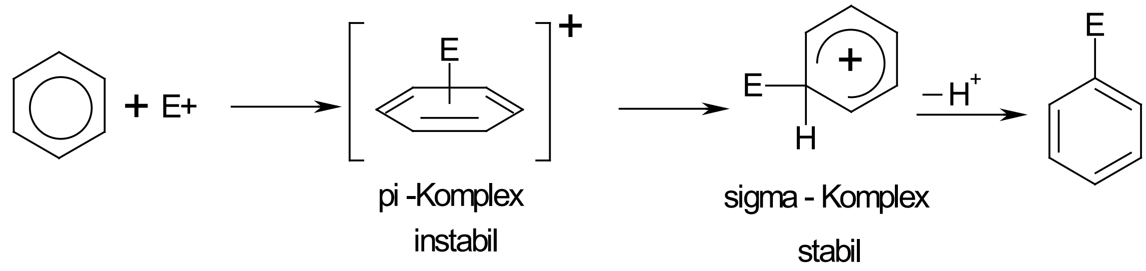
3.1 S_EAr: Mechanismus

3.1.1 σ und π Komplexe

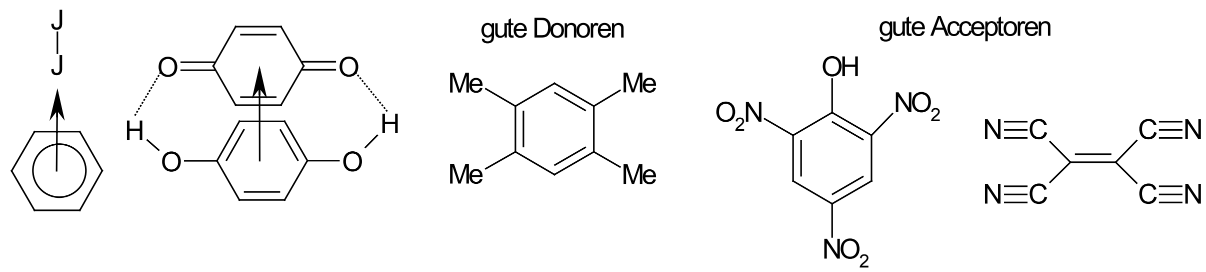
Aromaten:



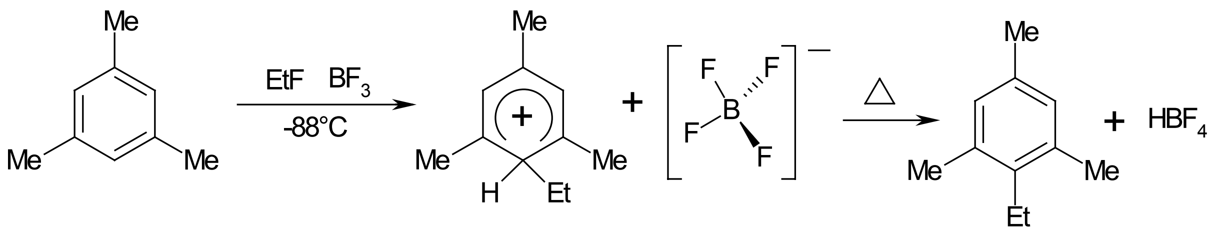
Allgemeiner Mechanismus

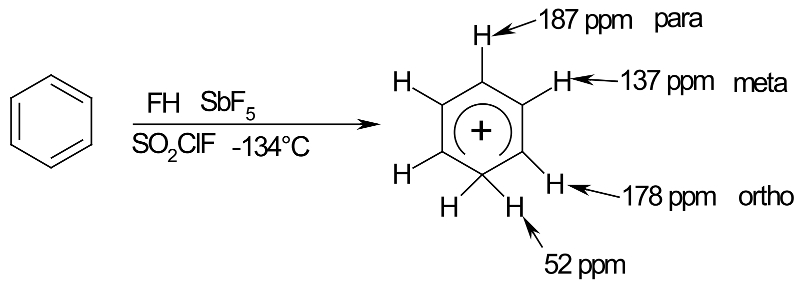


Charge-Transfer π Komplexe

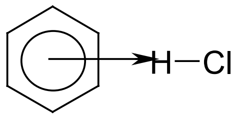


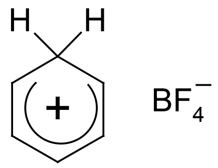
Isolierung von σ -Komplexen





3.1.2 Stabilität des σ und π Komplexes:



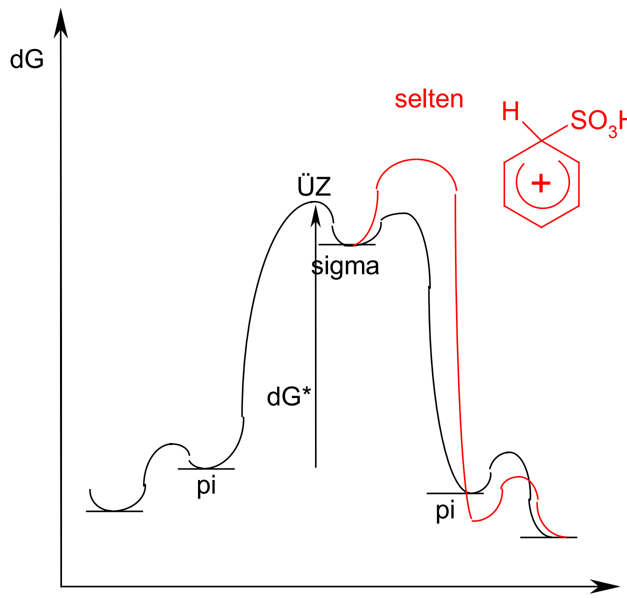


Bestimmung über UV-Spektrum

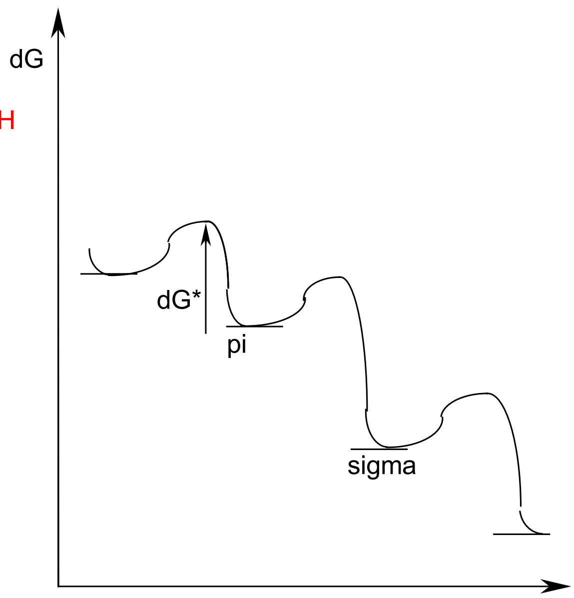
Bestimmung über Leitfähigkeit

π Komplex	σ-Komplex	Lösemittel	k(rel) in HOAc Br_2	k(rel) Sulfolan $NO_2^+ BF_4^-$
1	1	Benzol	1	1
1,5	790	Toluol	605	1,7
1,8	7900	o-Xylol	5300	1,8
2,0	1´000´000	m-Xylol	514´000	1,7

Energieprofile:



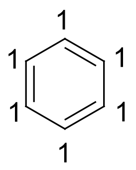
Typisch für Halogenierung und die meisten anderen Reaktionen



Typisch für Nitrierung

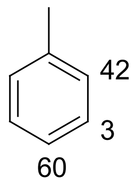
3.1.3 Partielle RG-Konstanten

Aussagen über Konkurrenzreaktionen und Produktverhältnisse



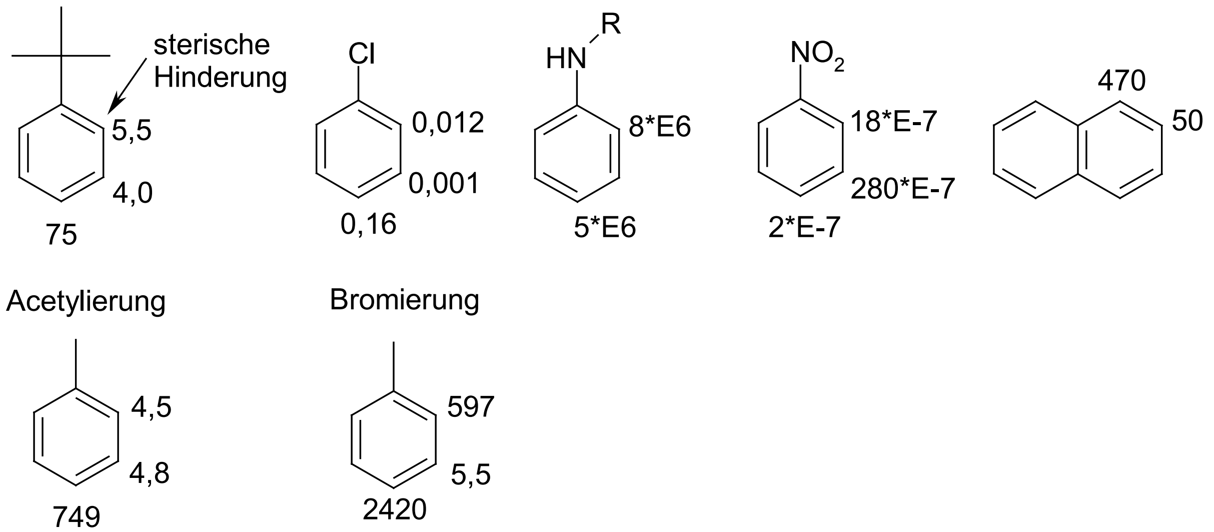
definitionsgemäß

HNO_3 /HOAc

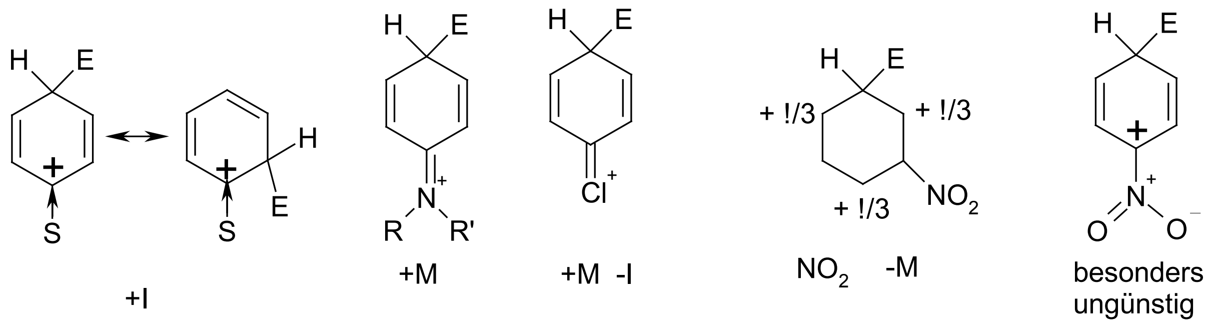


$$\frac{k(\text{Toluol})}{k(\text{Benzol})} = \frac{42{*}X2 + 3X2 + 60}{6X1} = \frac{150}{6} = 25$$

o : m : p = 42X2 : 2X3 : 60 = 56% : 4% : 40%



o, p Lenkung: +I +M Substituenten   m Lenkung: -M Substituenten (-I)



3.2 Elektrophiler Stickstoff

3.2.1 Nitrierung

Nitrierungsmittel

1.Nitriersäure: $HNO_3 : H_2SO_4 = 1:2$

$$HO-NO_2 + 2H_2SO_4 \rightarrow H_2O^+ - NO_2 + HSO_4^- + H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

Van't Hoffscher Faktor(Zahl der entstehenden Ionen) = 4

Nitroniumkation Nitrylkation NO_2^+ $O=\overset{+}{N}=O$

2. Salpetersäure über Autoprotolyse

$$3HNO_3 \Leftrightarrow NO_2^+ + H_3O^+ + 2NO_3^-$$

3. Salpetersäure und Essigsäureanhydrid

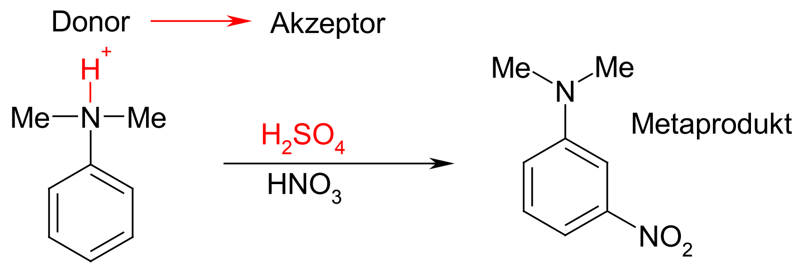
$$HNO_3 + Ac_2O \xleftrightarrow{HOAc} Ac-O-NO_2 \leftrightarrow AcO^- + NO_2^+$$

4. Nitrylterafluoroborat: $NO_2^+BF_4^-$ (Salz)

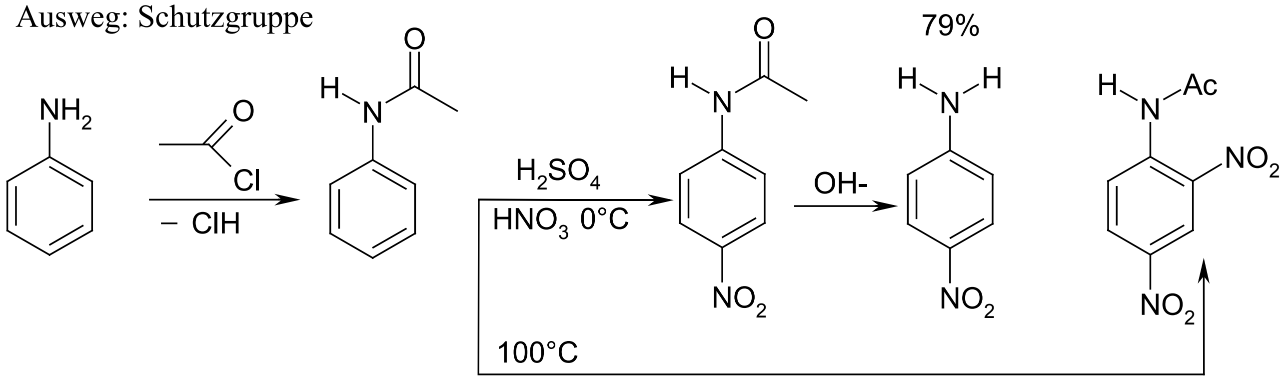
5. Carbonsäurechloride

$$Ph-COCl + AgNO_3 \rightarrow Ph-CO-O-NO_2 + AgCl\downarrow \rightarrow Ph-CO_2^- + NO_2^+$$

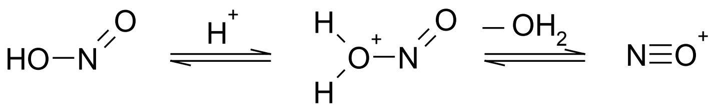
Probleme mit Nitriersäure:

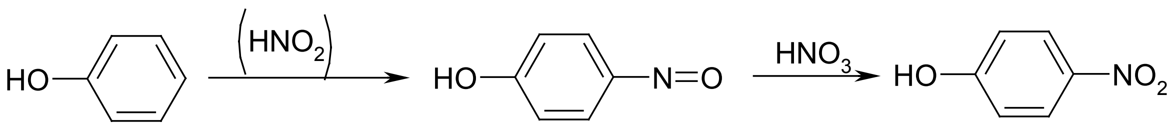


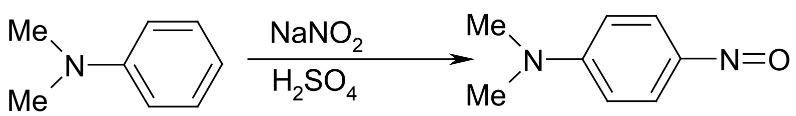
Ausweg: Schutzgruppe



3.2.2 Nitrosierung



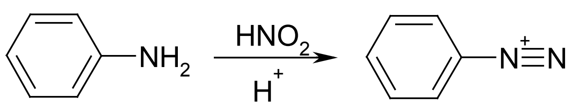


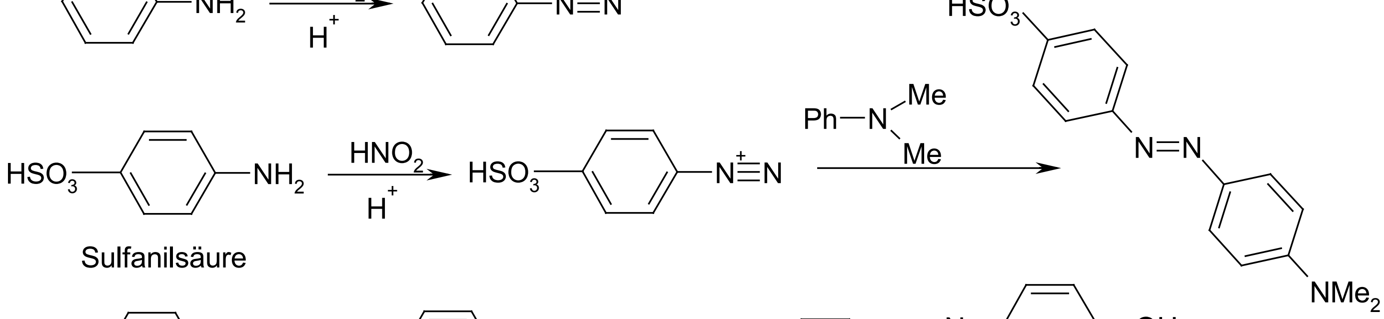


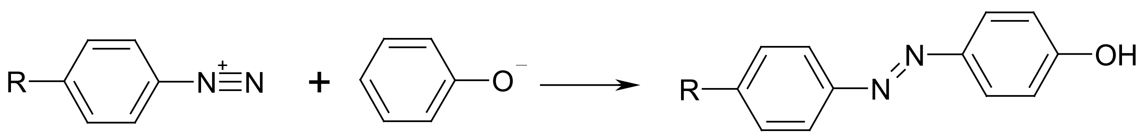
$N \equiv O^+$ Nitrosylkation weniger reaktiv

3.2.3 Azokupplung

R	NO_2	SO_3^-	H	CH_3	OCH_3
K(rel)	1360	13	1	0,4	0,1

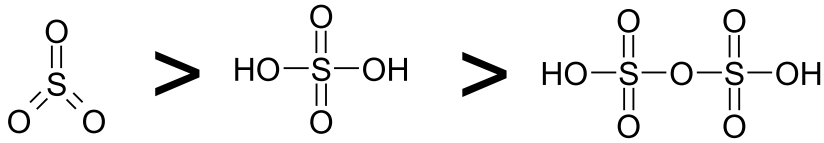


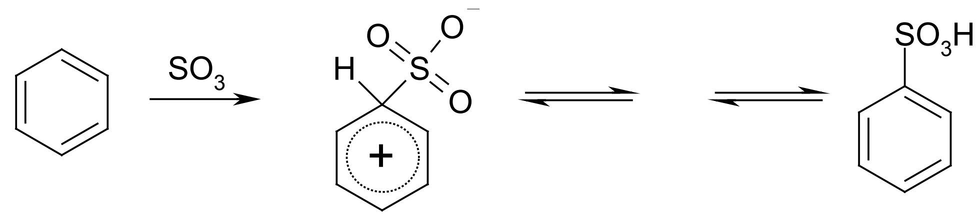


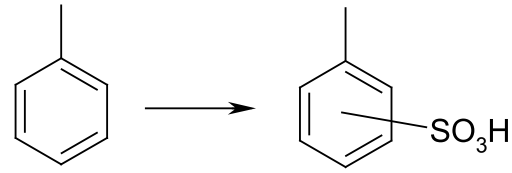


3.3 Elektrophiler Schwefel

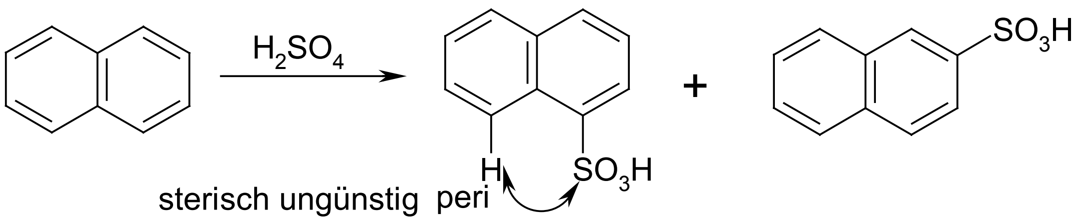
3.3.1 Sulfonierung







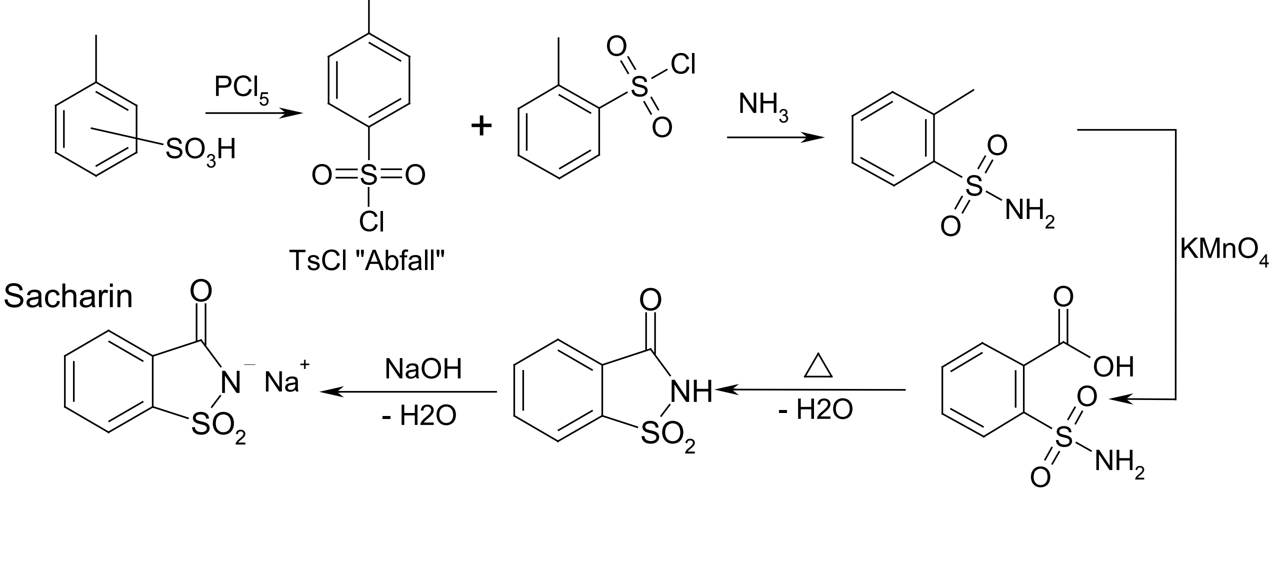
	o	m	p
0°C	43	4	53
100°C			>=90



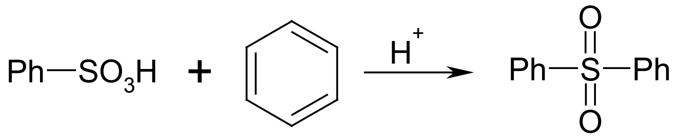
kinetische Kontrolle 80°C	96%	4%
thermodynamische Kontrolle 165°C	15%	85%

$$Ar{-}SO_3H \xrightarrow[H2O/\,H_2SO_4]{135°\text{-}200°C} Ar{-}H$$

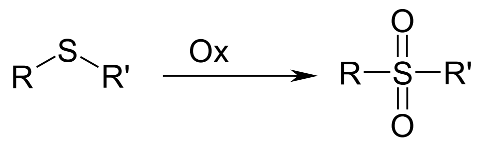
Sacharin

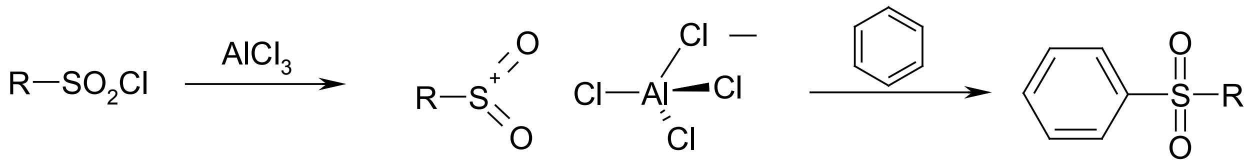


3.3.2 Sulfonylierung

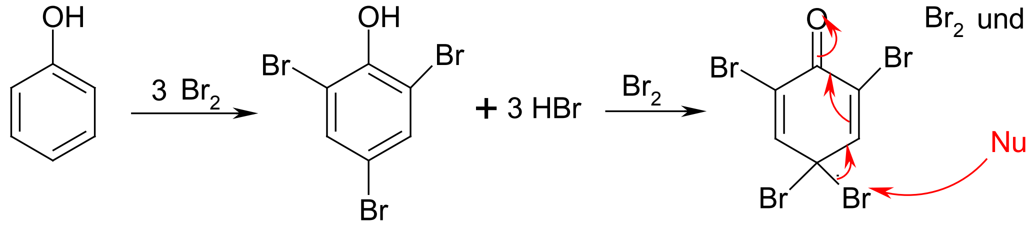


Oxidation von Thioethern



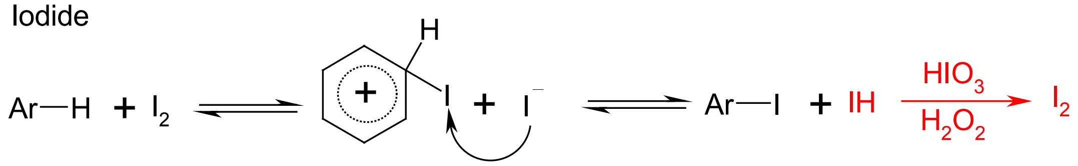


3.4 elektrophiles Halogen

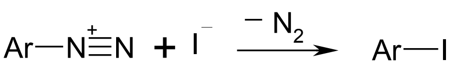


Br_2 und Cl_2 fast gleich

Iodide

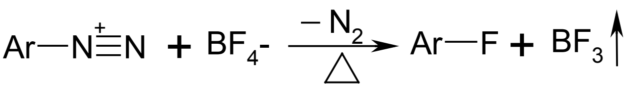


Rückreaktion bevorzugt

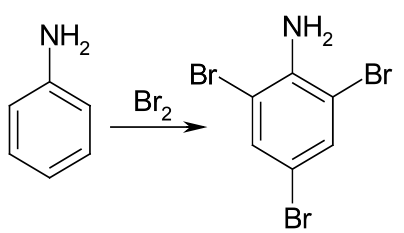


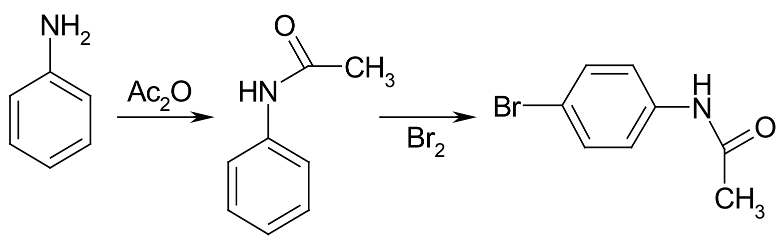
Schiemann-Reaktion

Wird wasserfrei durchgeführt



Schutzgruppen





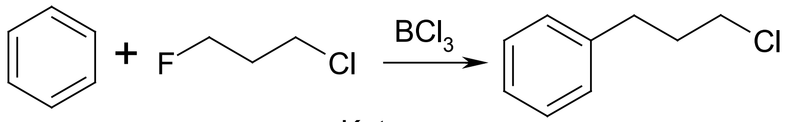
Katalysatoren: $AlCl_3$ (scharf) $Fe \xrightarrow{X_2} \overset{III}{Fe}X_3$ mild

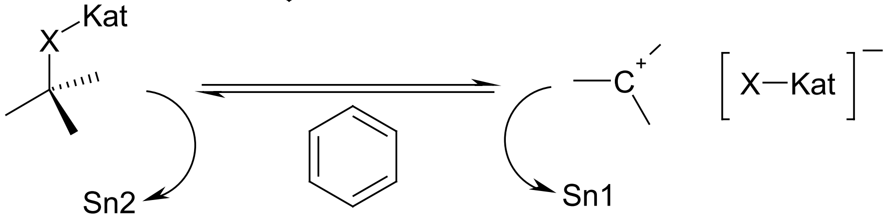
3.5 elektrophiler Kohlenstoff

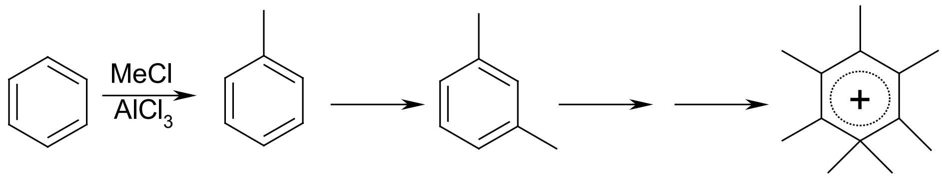
3.5.1 Friedel-Crafts-Alkylierung

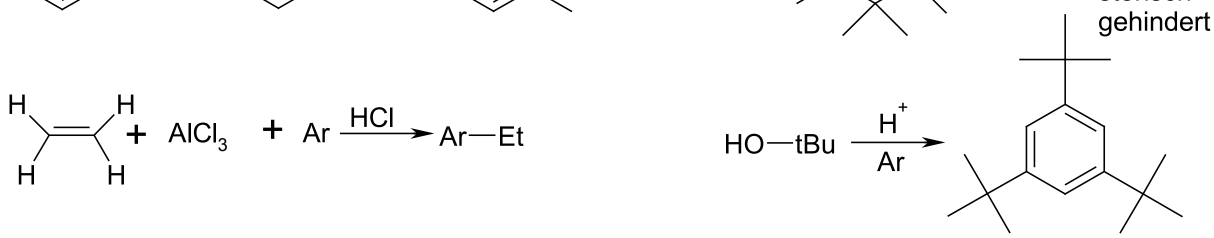
Katalysatoren: $AlBr_3 > AlCl_3 > FeCl_3 > SnCl_4 > BF_3 > TiCl_4 > ZnCl_2$

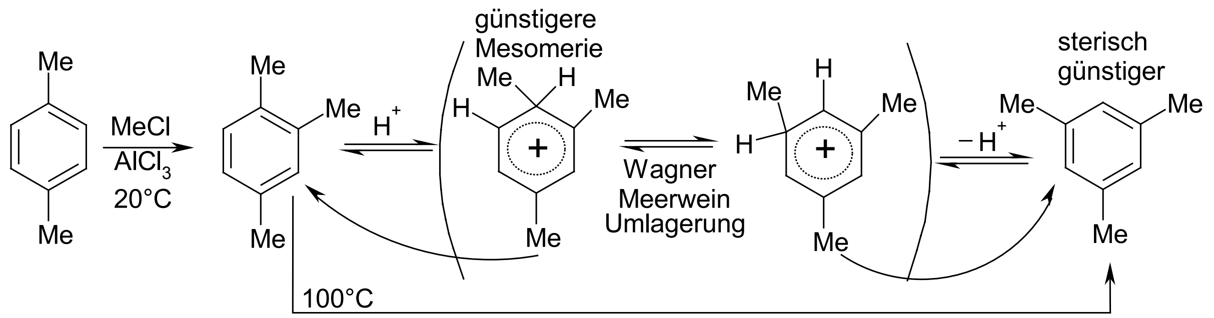
$Kat = BCl_3 : R-F > R-Cl > R-Br > R-I$

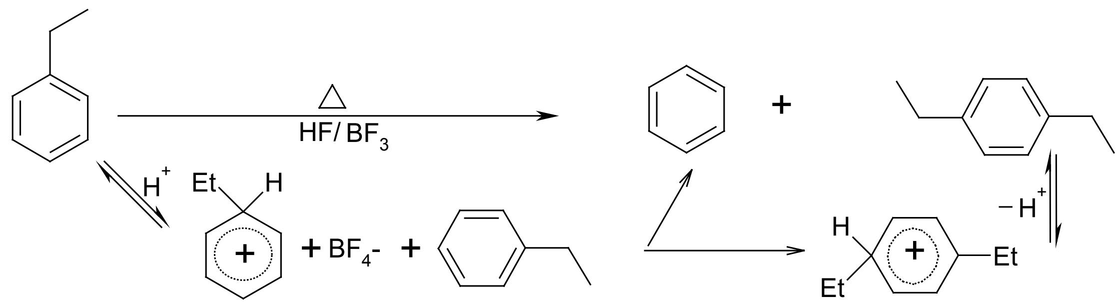


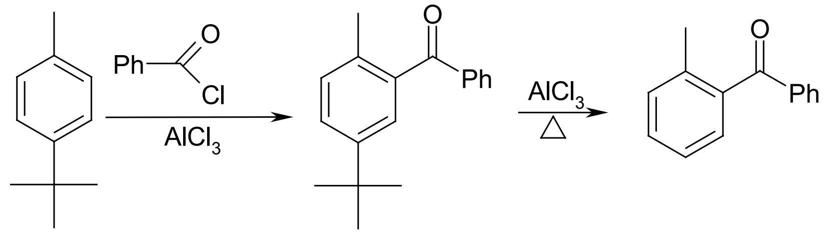


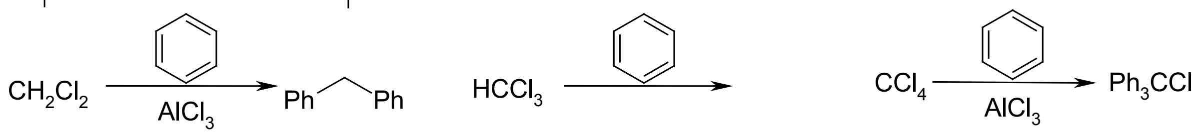


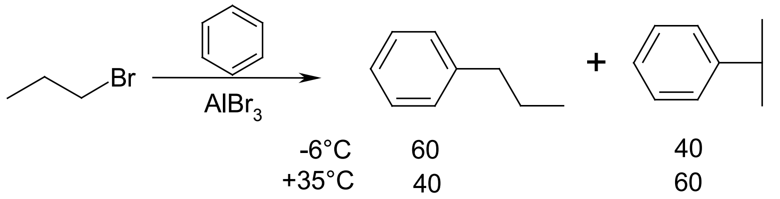




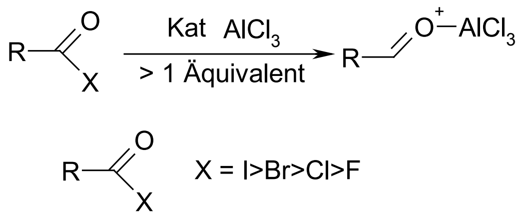


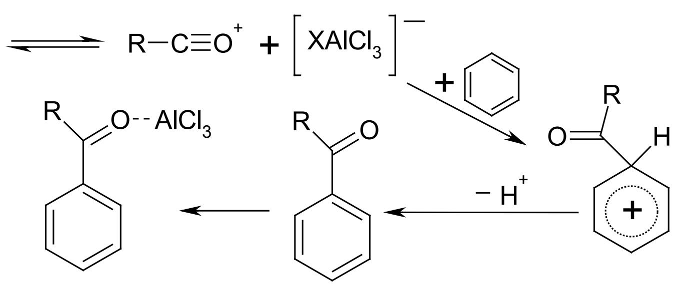




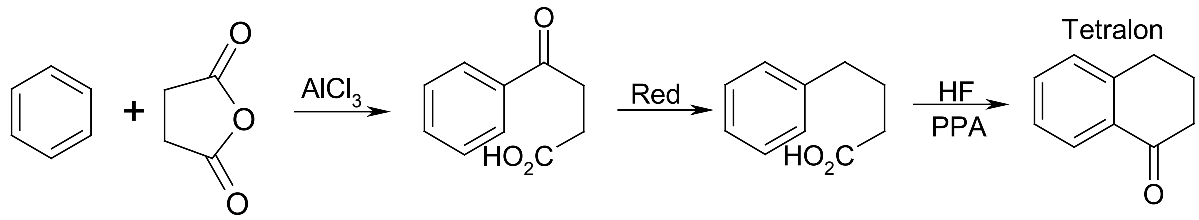


3.5.2 Friedel-Crafts-Acylierung





Kat	$SbCl_4$	$FeCl_3$	$AlCl_3$	$SnCl_4$
k(rel)	1300	570	1	0,03

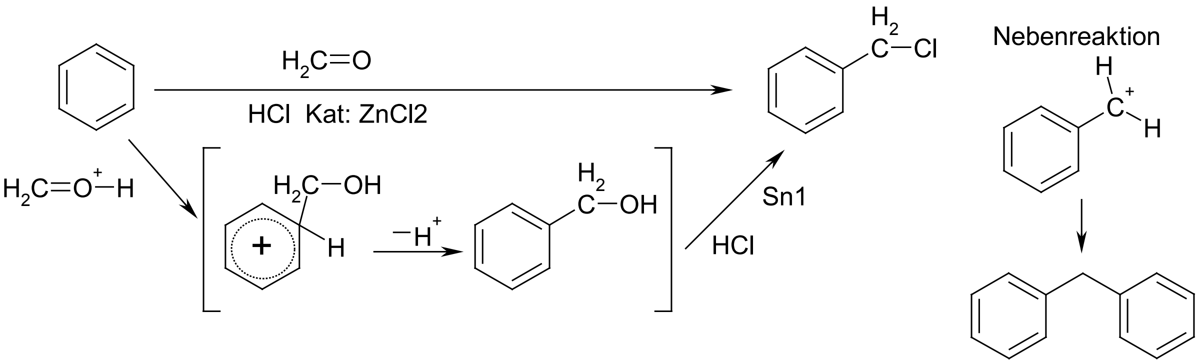


3.5.3 Wolff-Kishner-Reduktion

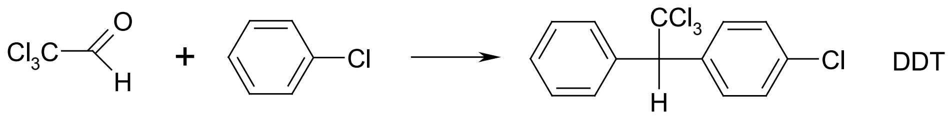
3.5.4 Clemmensen-Reduktion

weiter Möglichkeit (ohne Nahmen !?)

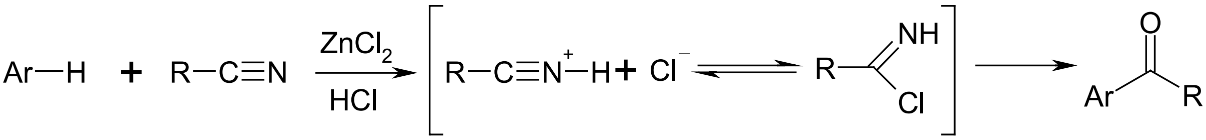
3.5.5 Chlormethylierung



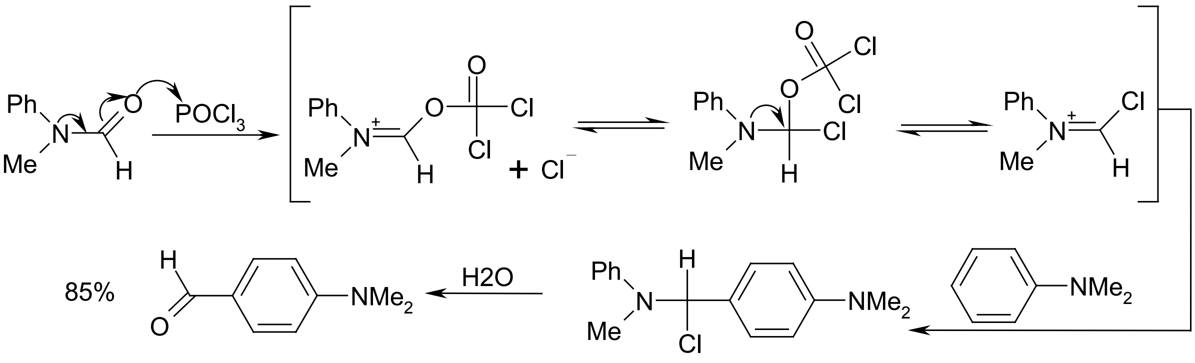
DDT Herstellung



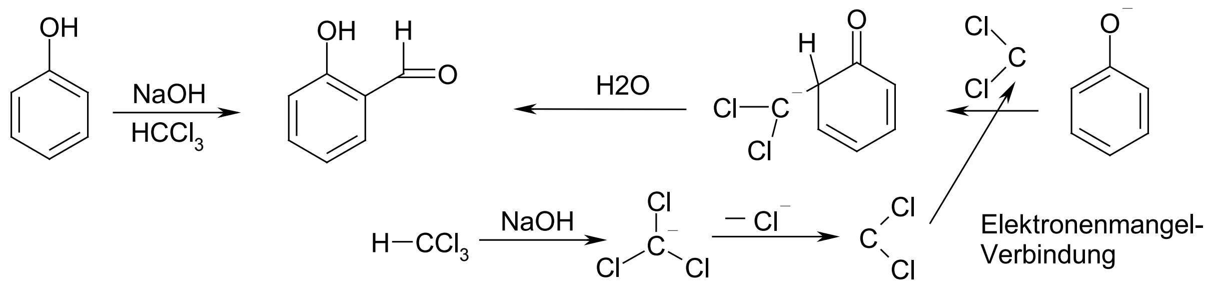
3.5.6 Gattermann-Hoesch-Reaktion



3.5.7 Vilsmeier-Haack-Reaktion

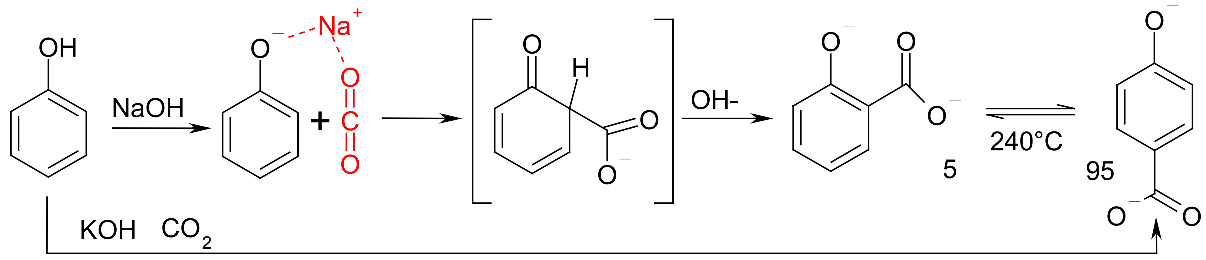


3.5.8 Reimer-Tiemann-Reaktion

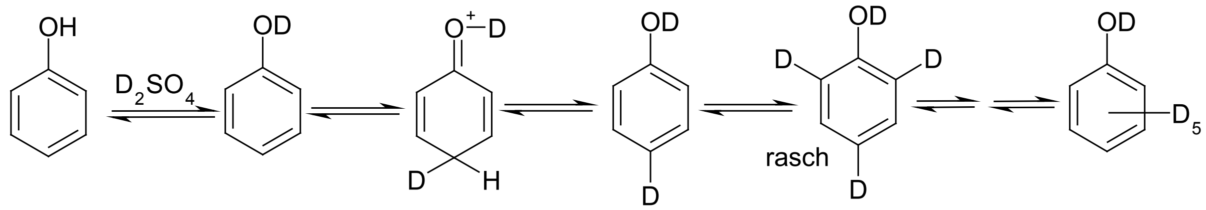


3.5.9 Kolbe-Schmitt-Reaktion

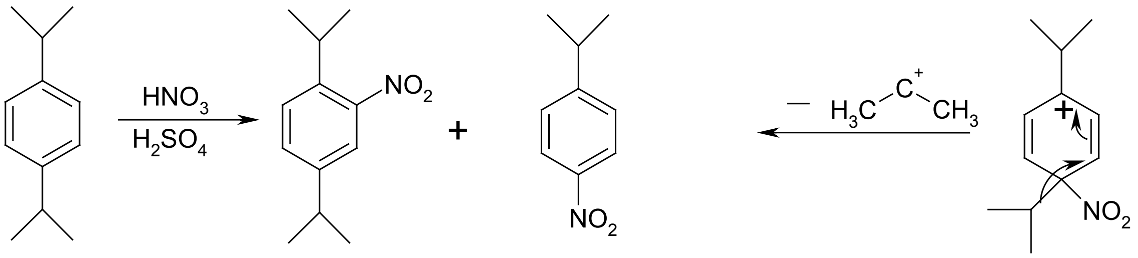
Synthese aromatischer Carbonsäuren, geht nur mit Phenolat-anion



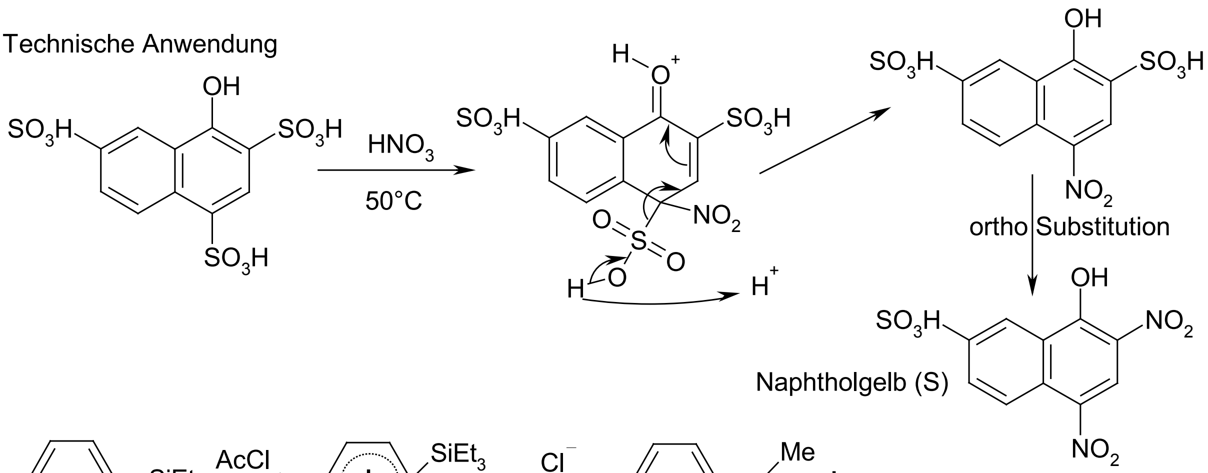
3.5.10 Deuterierung

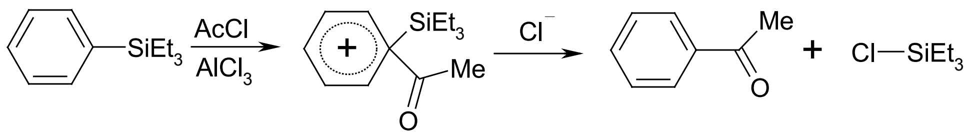


3.5.11 Ipso–Substitution

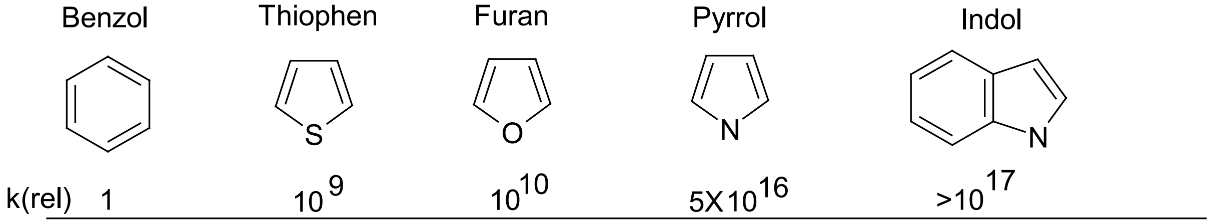


Technische Anwendung



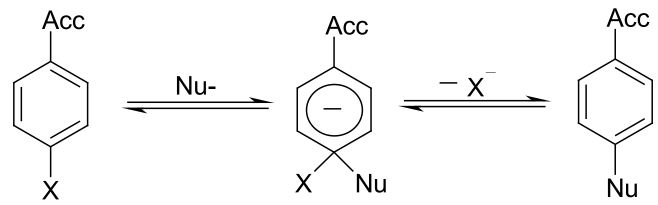


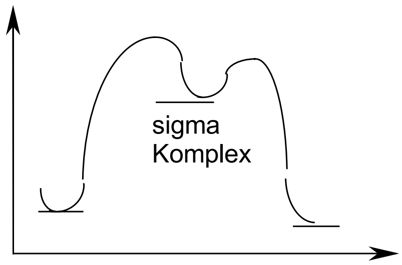
3.6 Reaktivität von Heteroaromaten



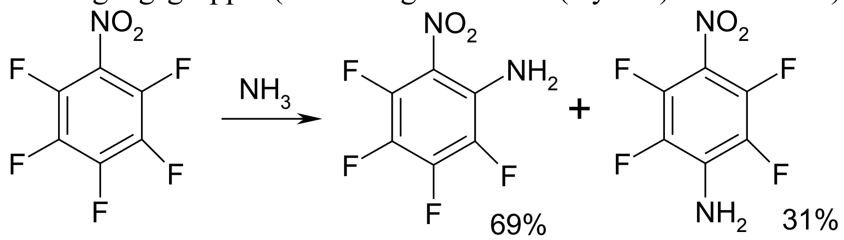
3.7 S_NAr: Additions-Eliminierungsmechanismus

3.7.1 Additions–Eliminierungsmechanismus

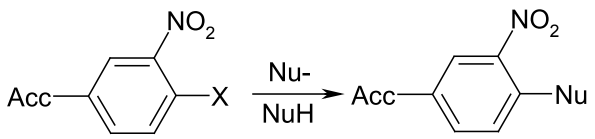


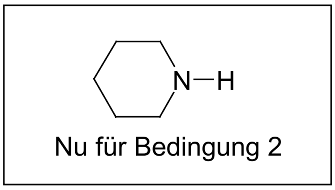


X= Abgangsgruppe (in der Regel nicht H^- (Hydrid) Wasserstoff)



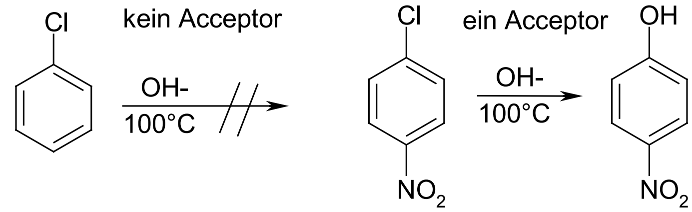
3.7.2 Die aktivierende Gruppe

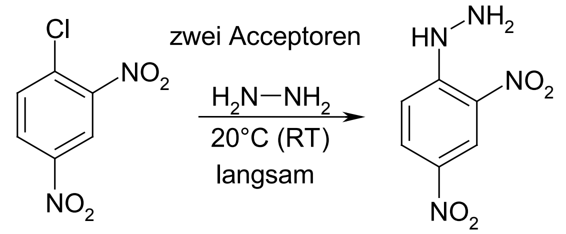


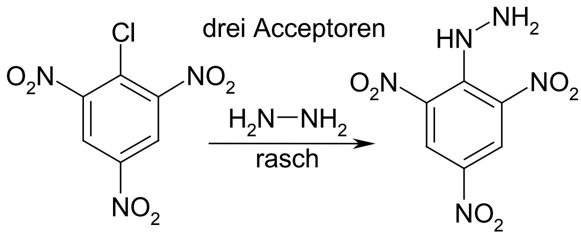


Acc	N_2^+	NO	NO_2	C ≡ N	Cl	H	Me	MeO	NH_2
k(rel)	$3{,}8*10^8$	$5*10^5$	$6*10^5$	$4*10^{-4}$	15	1	0,15	0,018	$1{,}2*10^{-4}$
Bedingung	1	1	1	1	1	1	2	2	2

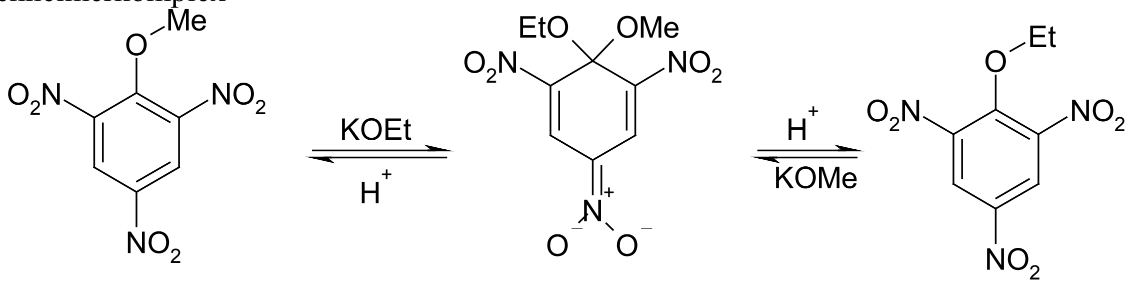
Bedingung 1: X= Cl Nu^- =MeO^- Bedingung 2: X=Br Nu= siehe oben







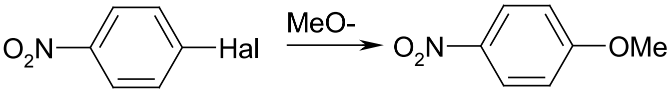
Meisenheimerkomplex



3.7.3 Die eintretende Gruppe

RG besser je besser das Nucleophil; Zeigt Sn2 Lösemitteleffekte (dipolar-aprotische gut)

3.7.4 Die austretende Gruppe



macht nukleophilen Angriff leichter, da es wenig sterische Hinderung erzeugt

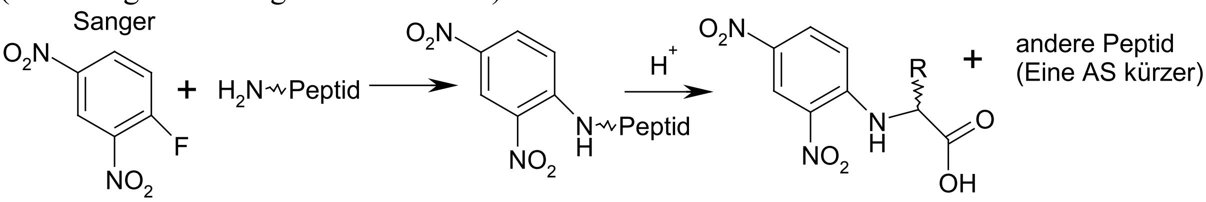
Hal	I	Br	Cl	F
k(rel)	0,36	0,79	1	312

(Fluor ist aber eigentlich sonst eine schlecht Abgangsgruppe)

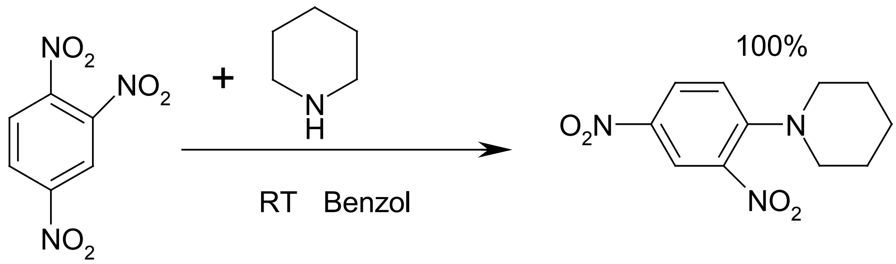
$F >> NO_2^- > OTs > Hal \approx SO_3H > N_3 > OR$

3.7.5 Sanger-Reagenz

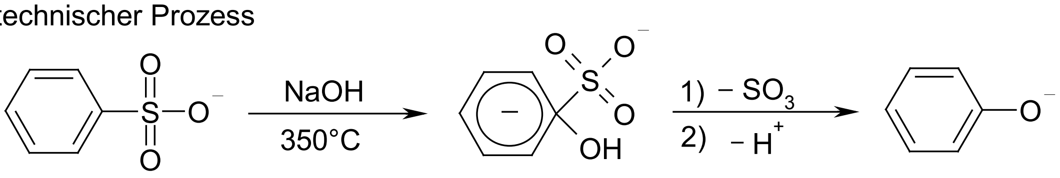
(Ermitlung endständiger Aminosäuren)



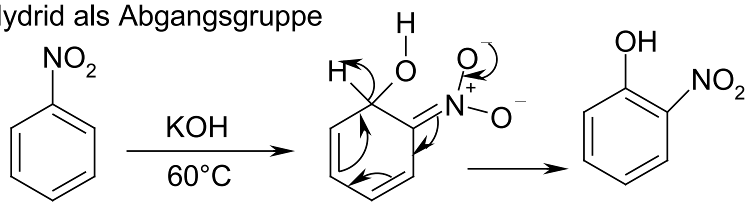
3.7.6 weitere Reaktionen:

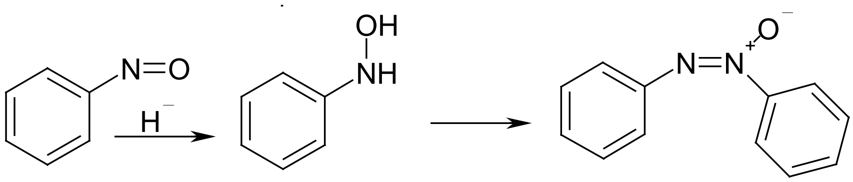


technischer Prozess

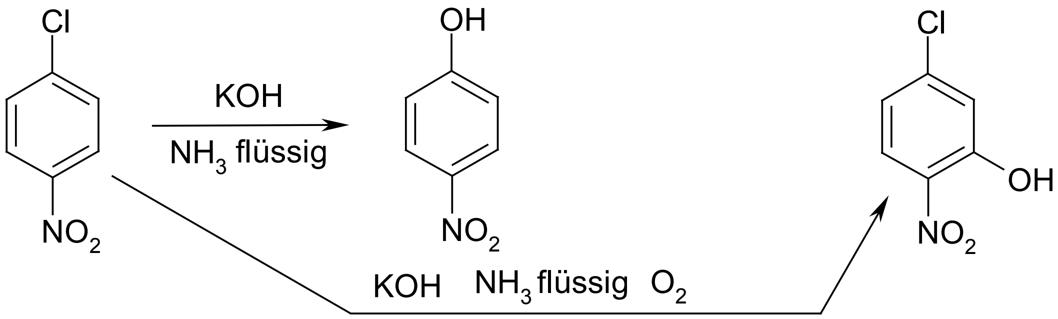


Hydrid als Abgangsgruppe

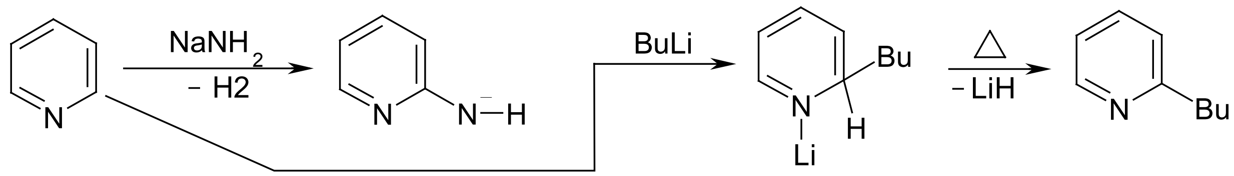


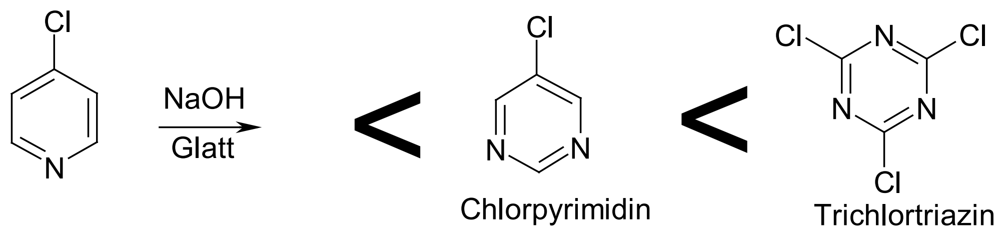


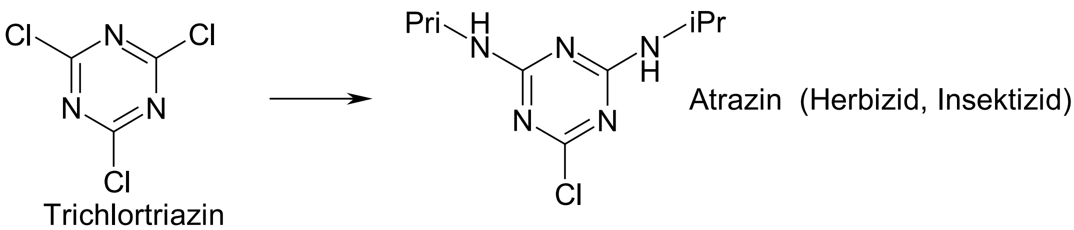
präpararív kaum nutzbar Ausnahme:



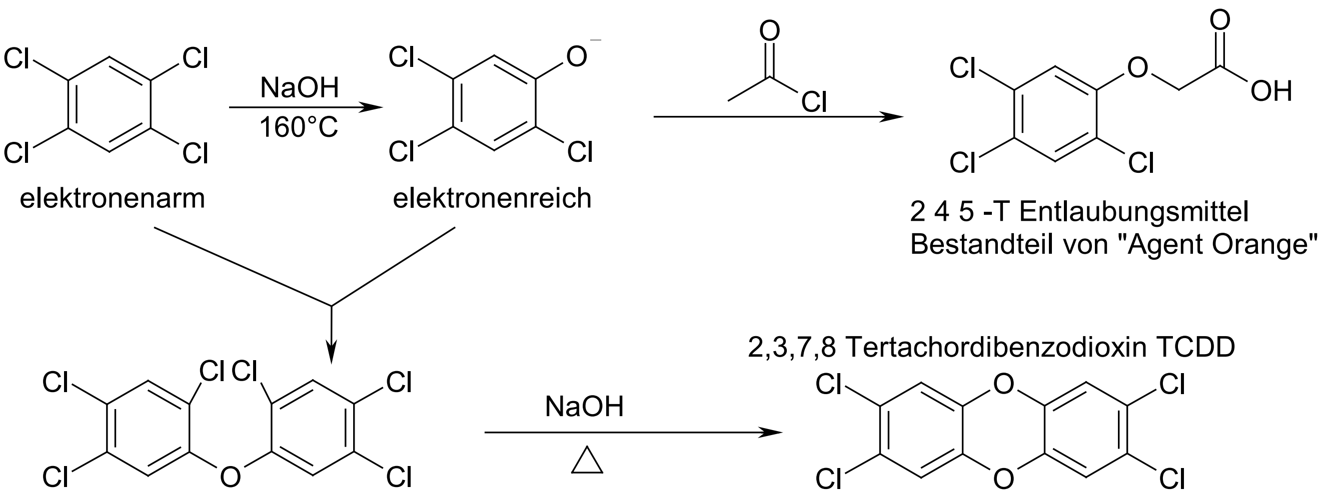
Merkregel: NO_2 am Ring ungefähr gleich N im Ring (Tschitschibain)

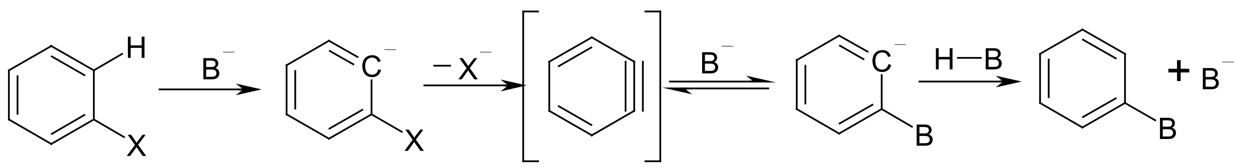




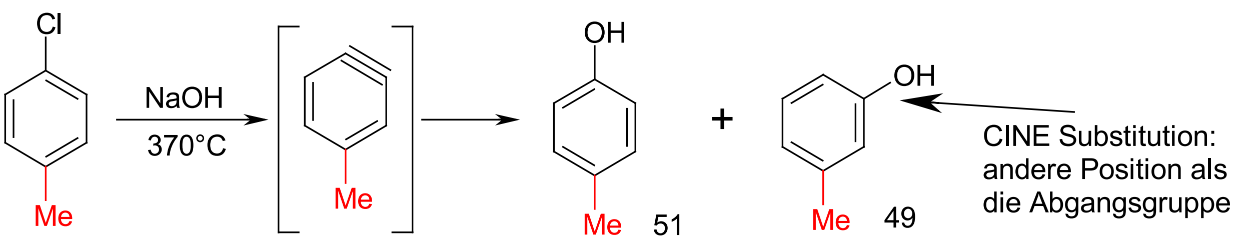


TCDD (umgangssprachlich Dioxin) und Verwandte:

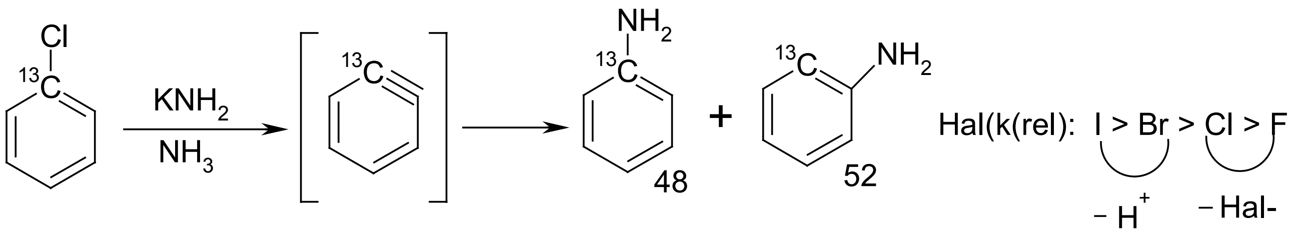


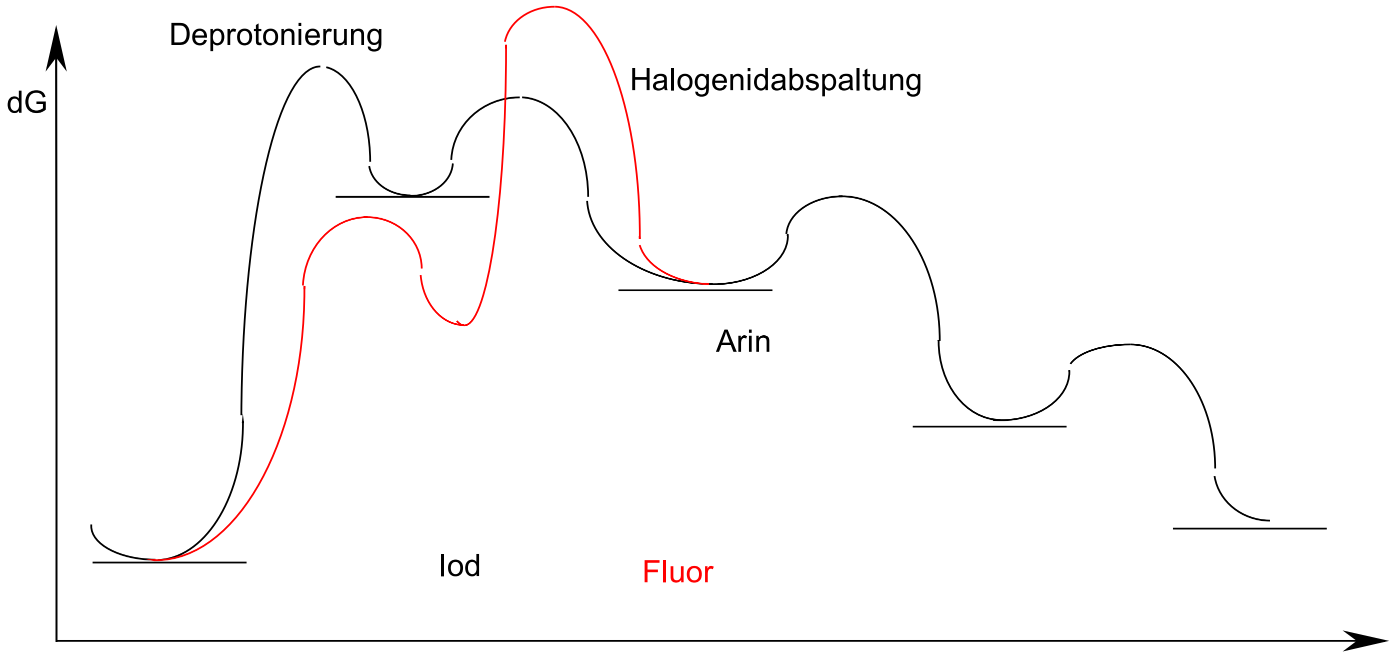


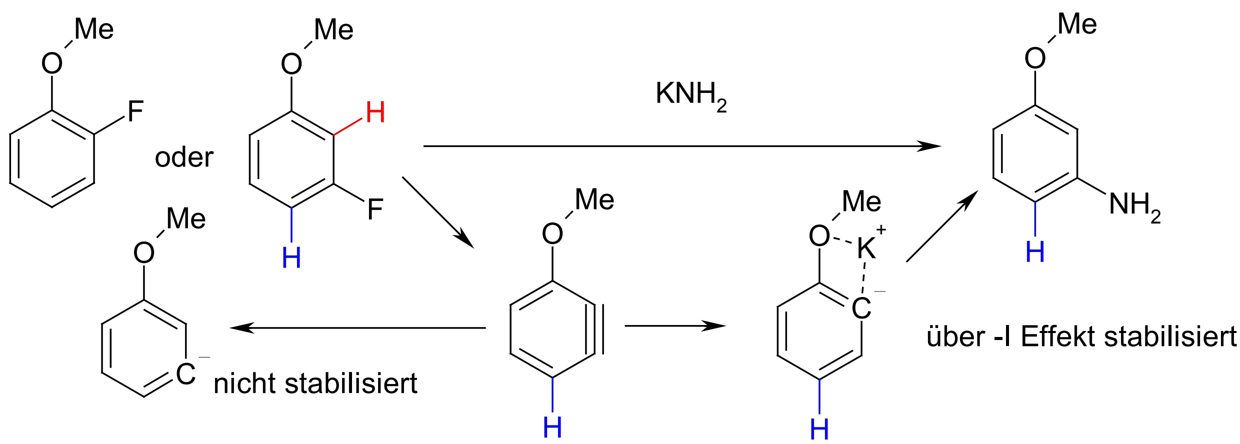
3.8 S_NAr: Eliminierungs-Additionsmechanismus



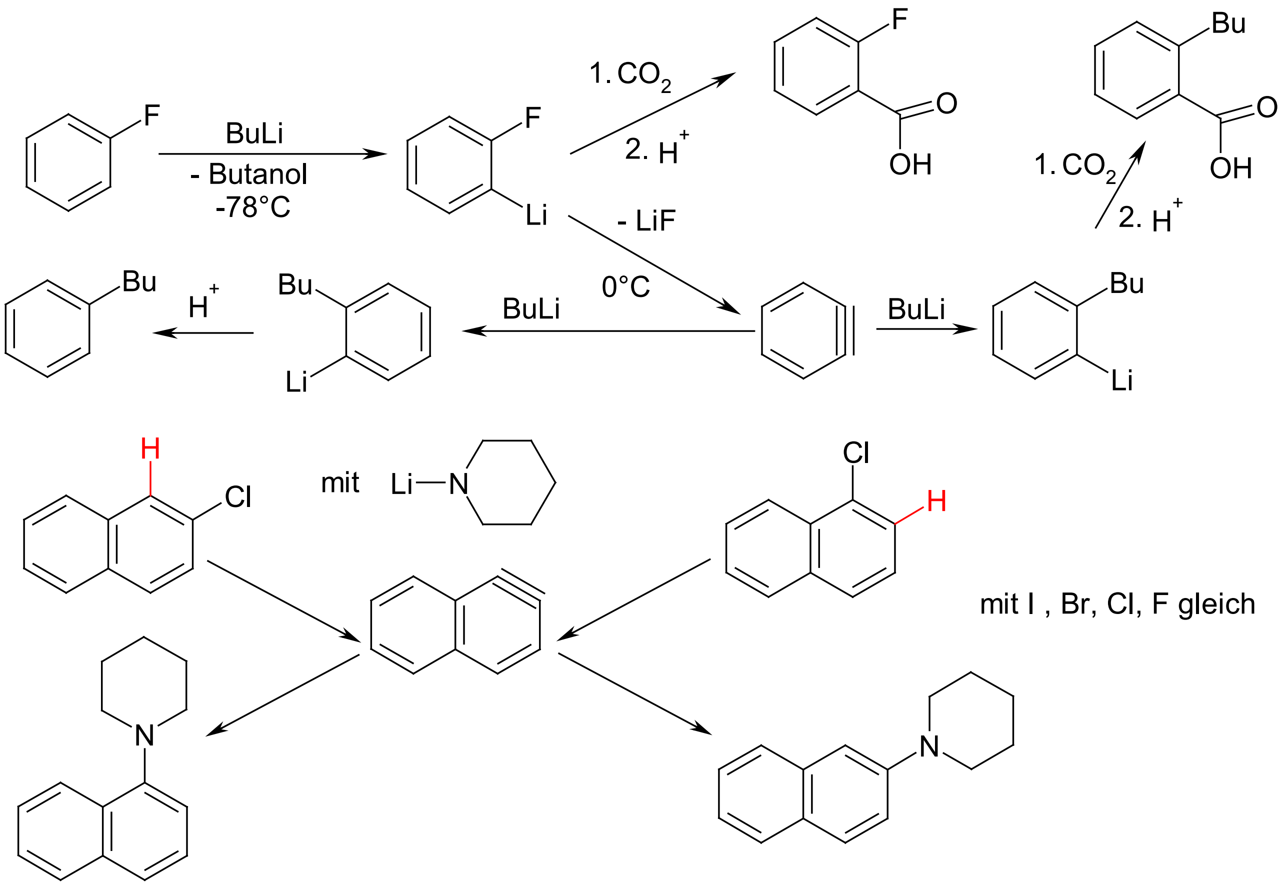
3.8.1 Roberts–Reaktion



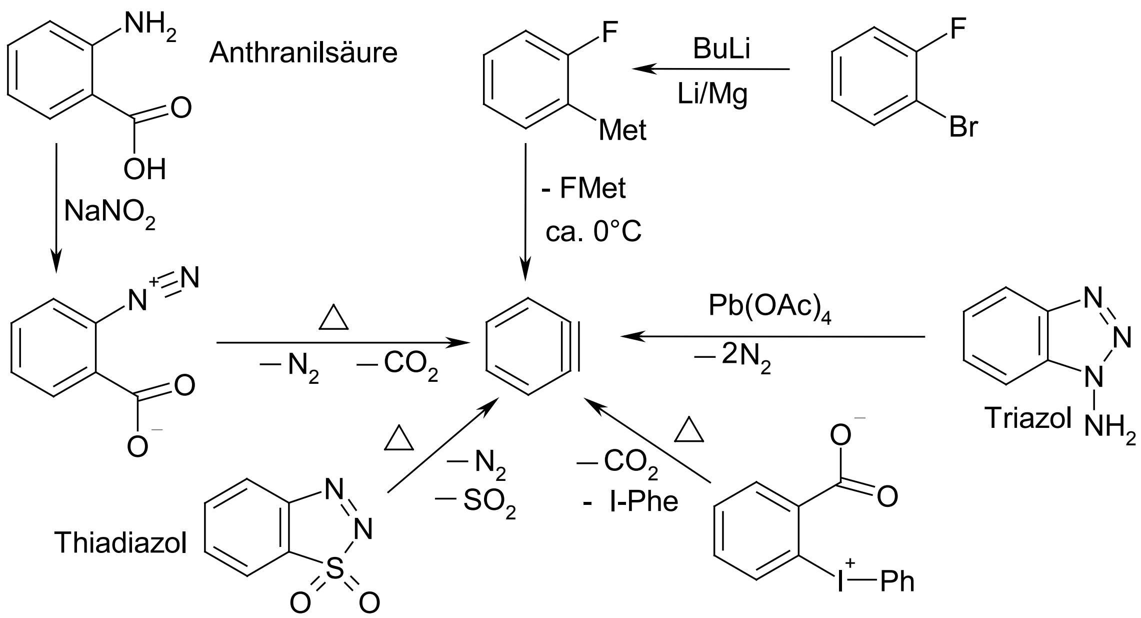




3.8.2 Nachweiß von Zwischenstufen

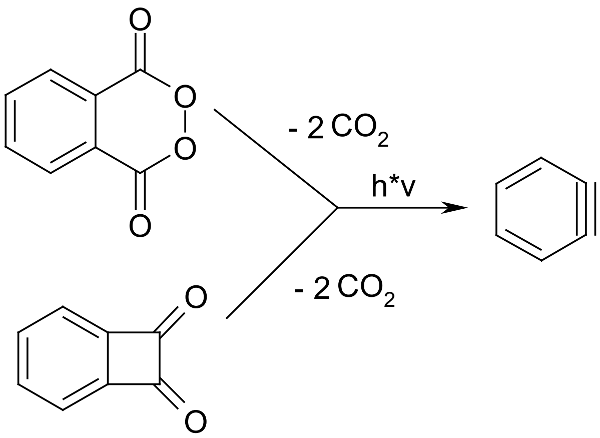


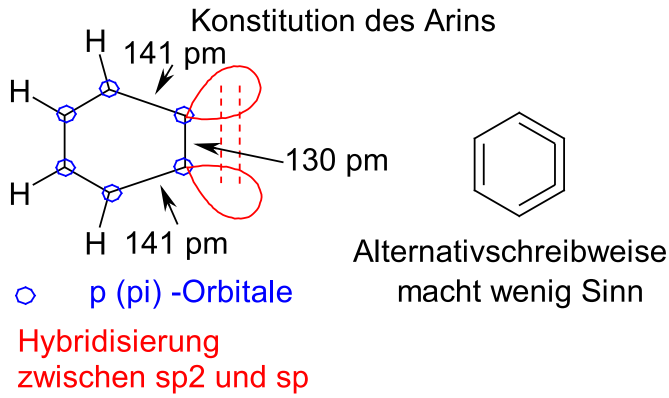
3.8.3 Zugangswege zum Arin:



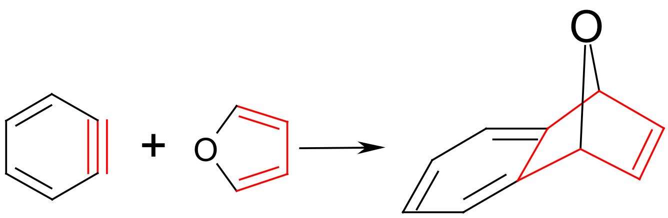
3.8.4 Isolierung des Arins: Chapmann

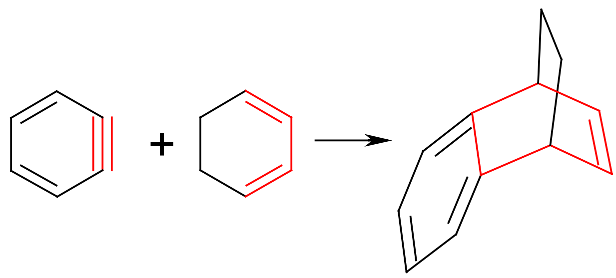
bei 8°K in einer Argonmatrix



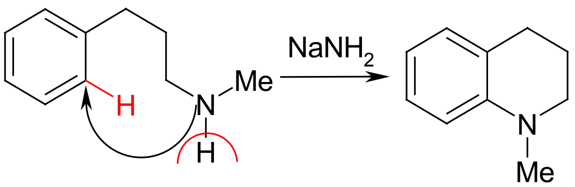


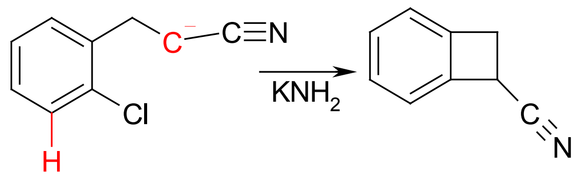
3.8.5 Diels - Alder mit Arin





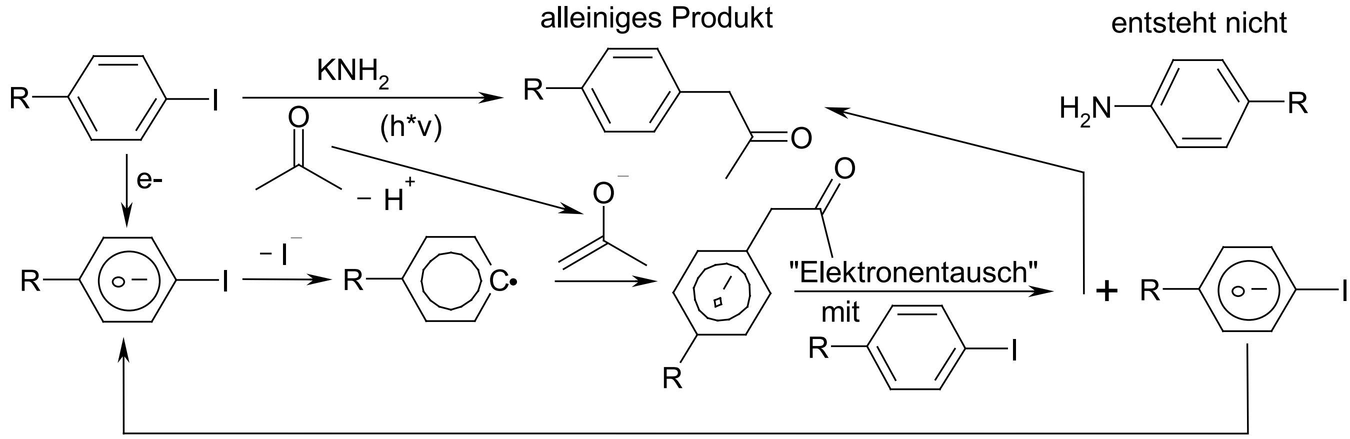
Intramolekulare Reaktionen



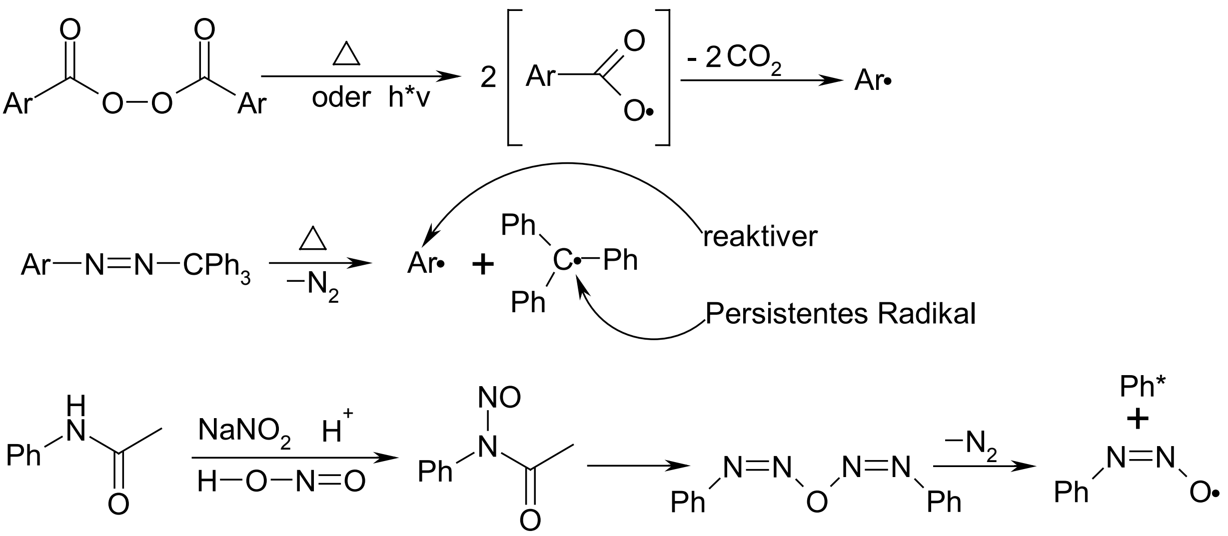


3.9 $S_{RN}Ar$: Nukleophile-Radikalische-Sub.

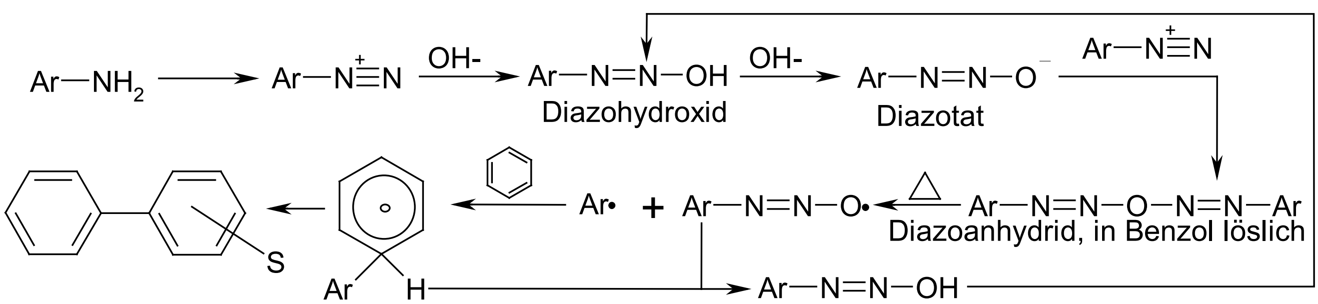
Funktioniert nach einem Radikalkettenmechanismus; wird auch Bunnet $S_{RN}1$ genannt



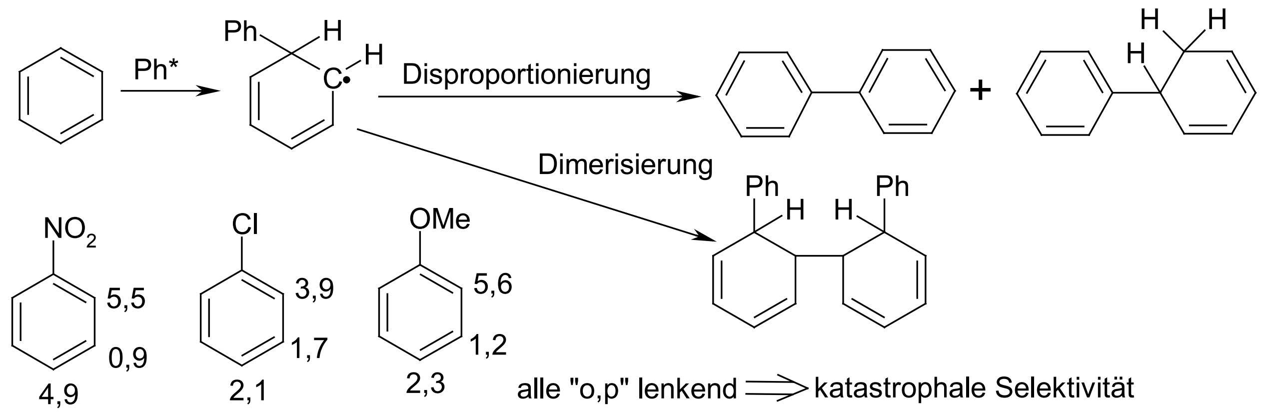
3.10 Radikalische aromatische Substitution S_RAr



3.10.1 <u>Gomberg-Bachmann-Reaktion</u>

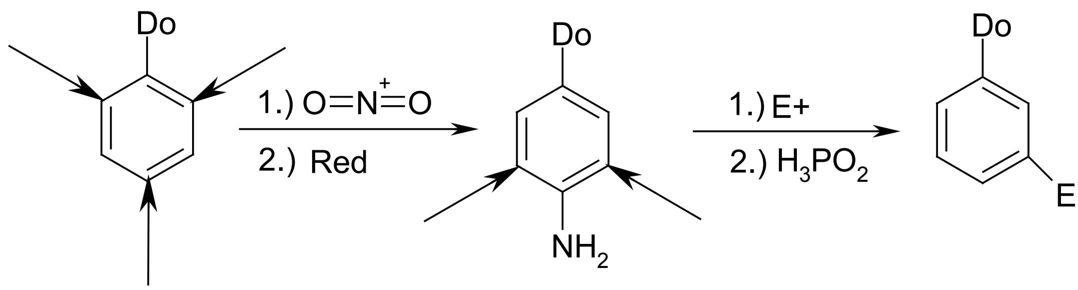


präparative Probleme: Selektivität ist schlecht

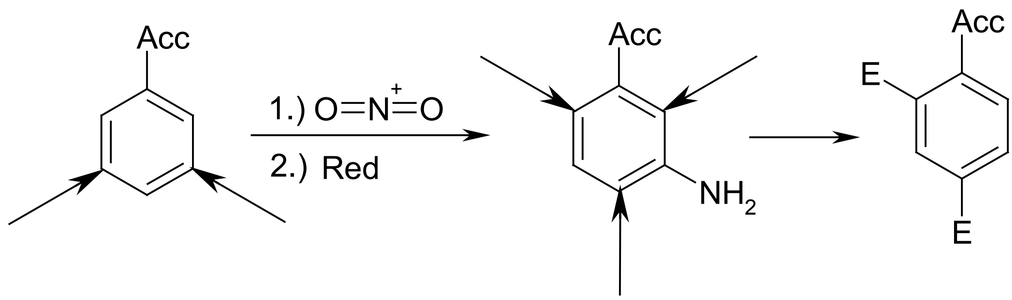


3.11 Zusammenfassung

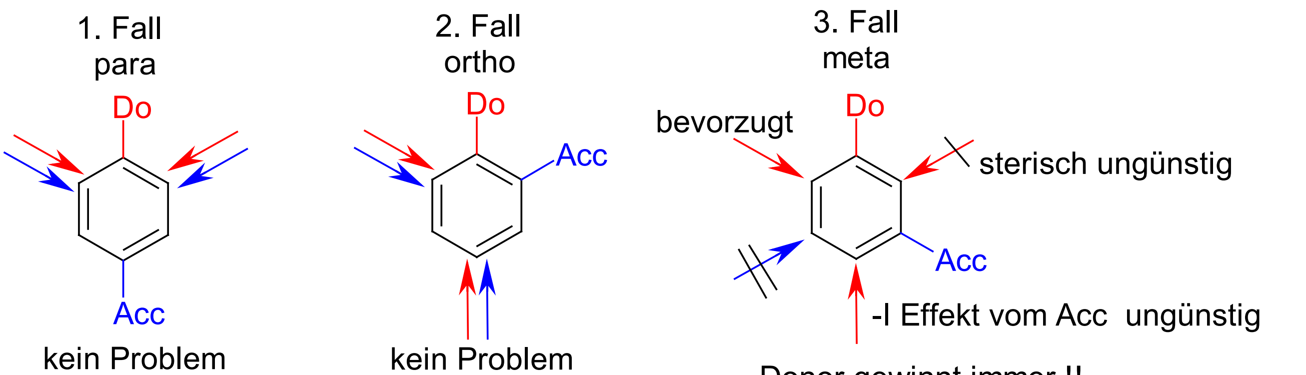
3.11.1 Meta -Substitutionstrategie



3.11.2 o,p Substitutionstrategie



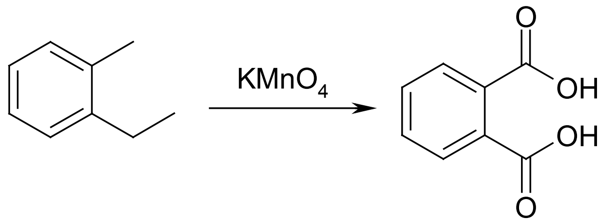
3.11.3 Donor Akzeptor Konkurrenz

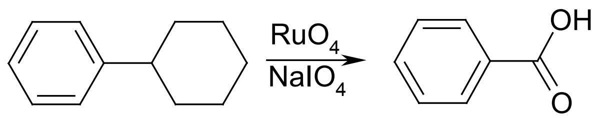


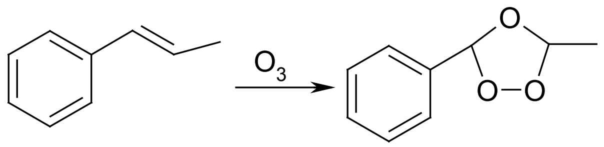
Donor gewinnt immer !!
k(rel): Beschleunigung versus Bremse

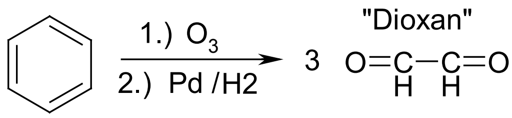
3.12 Oxidation und Reduktion

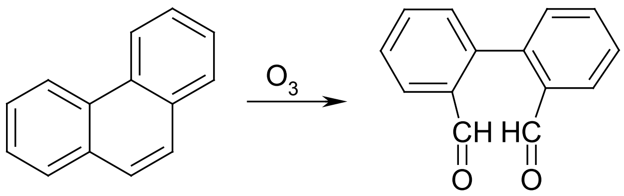
3.12.1 Oxidation



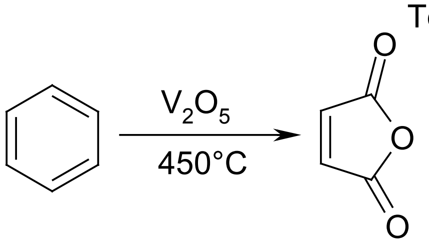


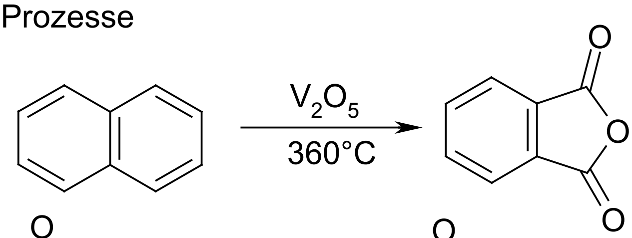


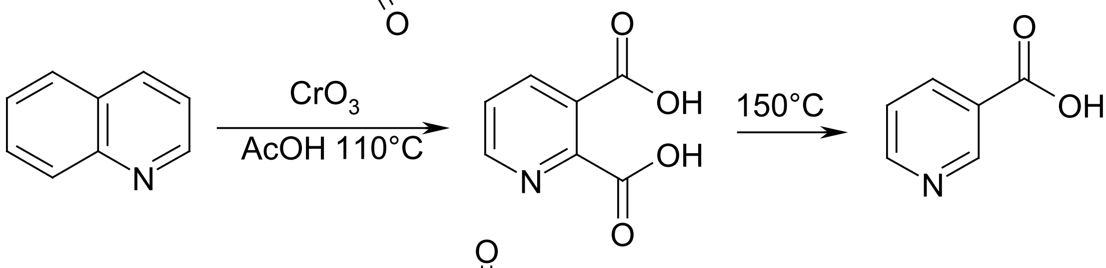


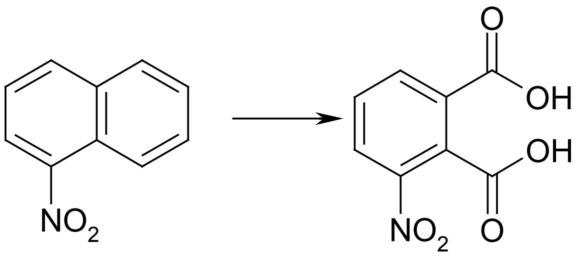


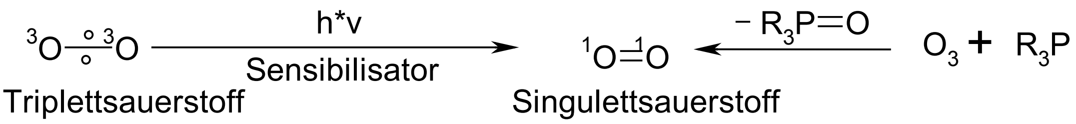
Technische Prozesse

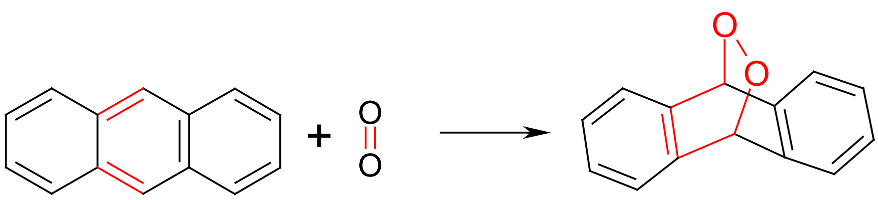






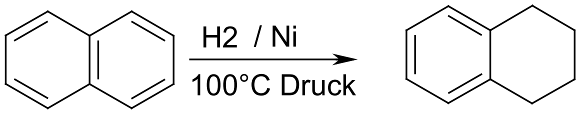




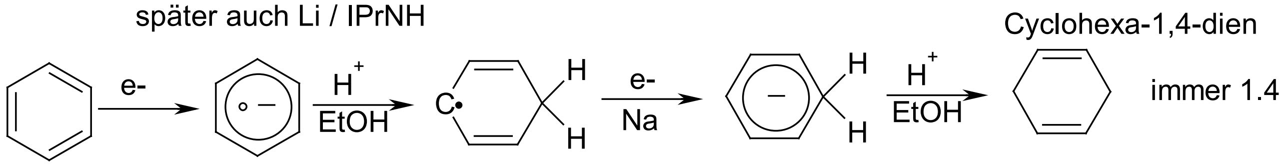


3.12.2 Reduktion

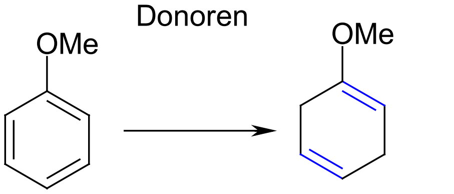
Birch-Reduktion



BIRCH Na/ NH_3flüssig + EtOH(Protonenspender)
später auch Li / IPrNH

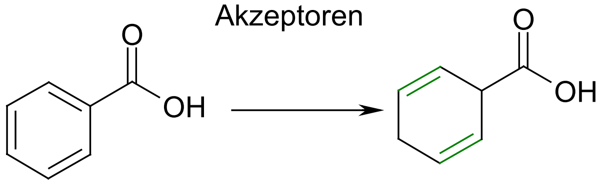


Donoren



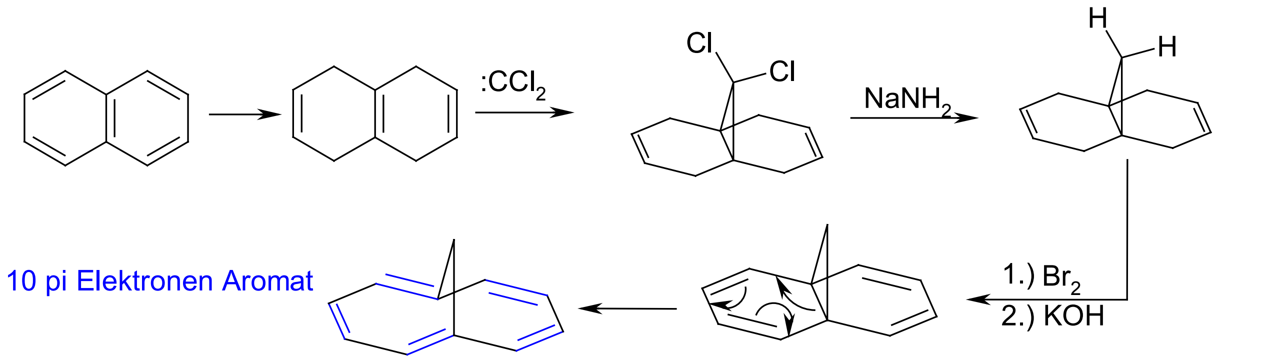
Donoren enden immer neben C=C Doppelbindung in Konjugation

Akzeptoren



Akzeptoren enden an nicht konjugierten Positionen

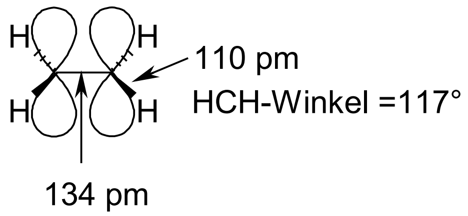
Carbene:



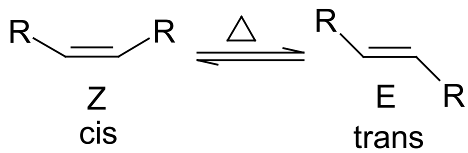
4 Alkene und Alkine

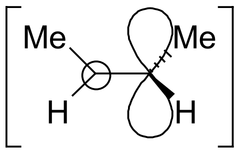
4.1 Alkene

4.1.1 Struktur und Isomerie



C=C	146 kcal/mol
C--C	83 kcal/mol
	63 kcal/mol



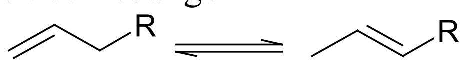


dH* = 62,4 kcal/mol für R=Me
sehr hoch, bei RT Stabil

R	Ph	CO2Et
dH*(kcal/mol)	43	28

Trans ist thermodynamisch stabiler als cis, wenn R mit C beginnt

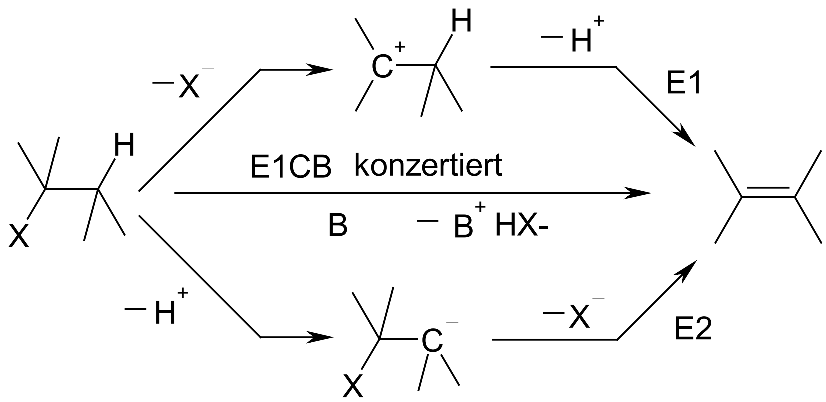
Verschiebungen



R ist Egal R=Me ΔH= -2,7 kcal/mol

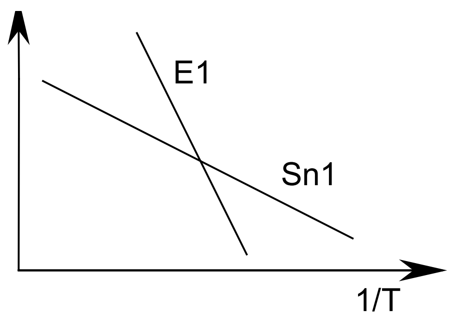
4.1.2 Darstellung durch trans-HX-Eliminierung

4.1.2.1 Mechanismen, Stereochemie, Orientierung



X= Hal, O^+H_2;OSO_2R;S^+R_2;N^+R_4;(OH^-)

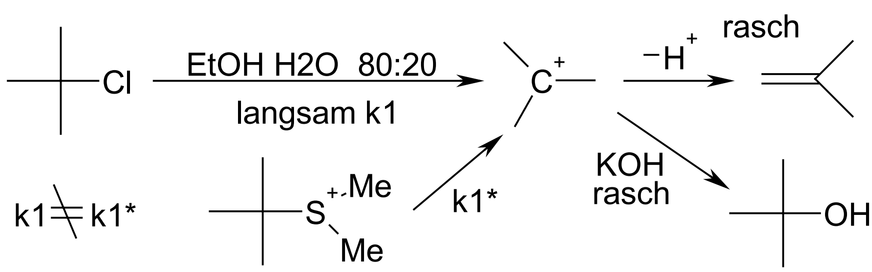
E1: RG=k_1[R-X]
Erster Schritt (Bildung des Carbeniumions) ist Geschwindigkeitsbestimmend



Arrhenius-Gleichung:

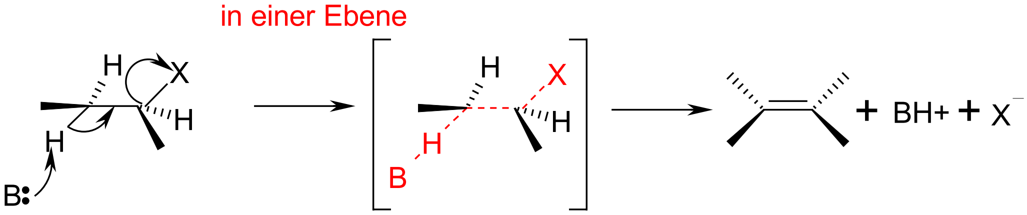
$$k = Ae^{\frac{-E_A}{RT}} \qquad \lg k = \lg\left(-\frac{E_A}{RT}\right)$$

Hohe Temperatur : E1
Tiefe Temperatur : S_{N1}



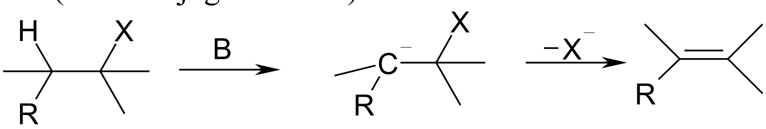
4.1.2.2 E2: Mechanismus

RG=k_1[R-X][B]

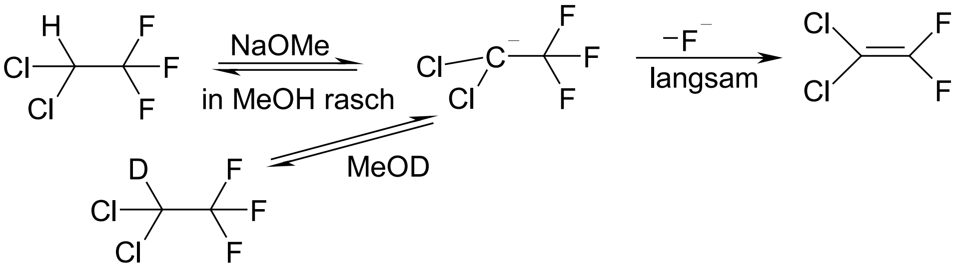


4.1.2.3 E1$_{CB}$: Mechanismus

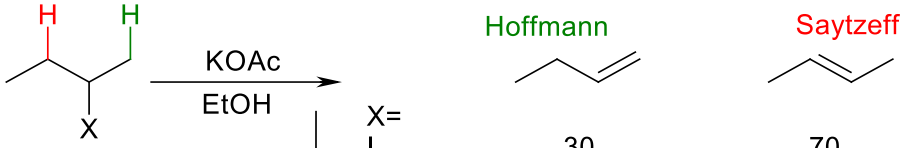
selten (CB= conjugierte Base)



R muß Carbanionen stabilisieren

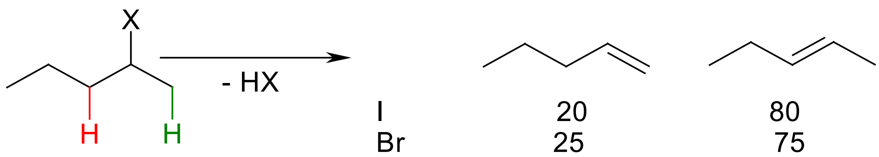


4.1.2.4 Orientierung nach HOFFMANN und SAYTZEFF



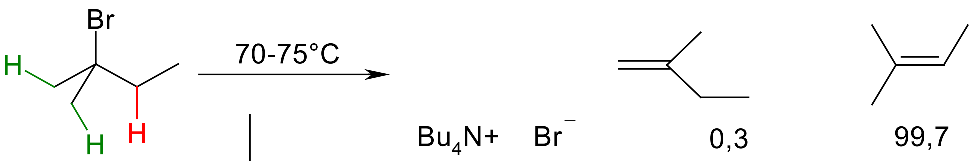
Zuhnahme der sterischen Hinderung ↓

X=	Hoffmann	Saytzeff
I	30	70
Br	31	69
OSO2R	48	52
Me2S+	87	13
Me3N+	98	2



X	Hoffmann	Saytzeff
I	20	80
Br	25	75
Cl	37	63
F	83	17

E1CB artig → (F)

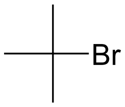
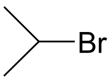
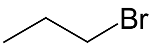


Basenstärke sterische Hinderung ↓

		Hoffmann	Saytzeff
Bu_4N^+	Br^-	0,3	99,7
K^+	O^-–Et	30	70
K^+	O^-–tBu	73	27
K^+	O^-–C(ET)$_3$	89	11

Sterische Hinderung und E1$_{CB}$ -artiger Mechanismus verschieben nach Hoffmann!

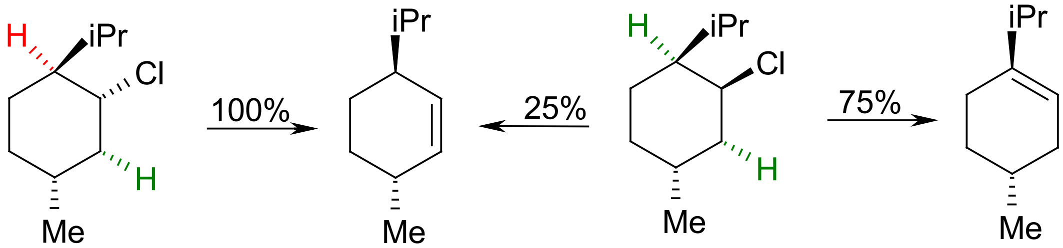
4.1.2.5 Eliminierung versus nukleophile Substitution

			% Elimination
tert		Bu_4N^+ Cl^-	96
		Na^+ $^-O{-}Et$	100
sec		Bu_4N^+ Cl^-	0
		Na^+ $^-O{-}Et$	75
prim		Bu_4N^+ Cl^-	0
		Na^+ $^-O{-}Et$	8,8

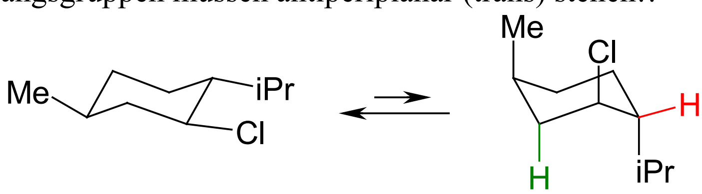
Substrateinfluß groß   starke Base → E2

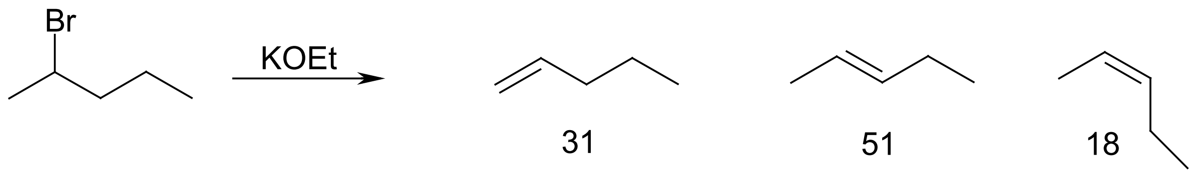
4.1.2.6 Stereochemie bei E2

like   unlike meso



Abgangsgruppen müssen antiperiplanar (trans) stehen!!

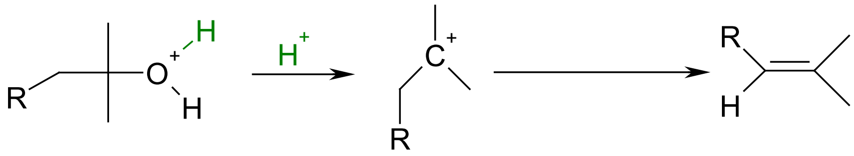




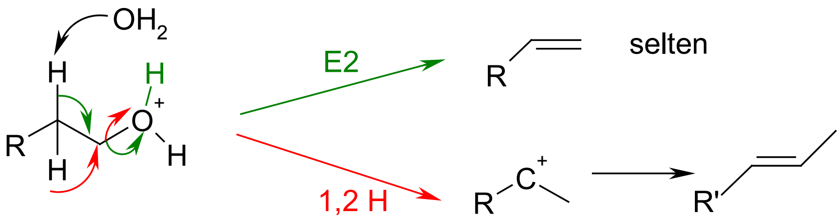
4.1.2.7 Dehydratisierung von Alkoholen

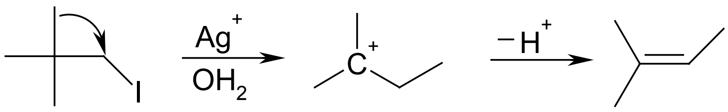
tert > sec >> prim S_N1 ähnlich

E1.................(E2)



stabilisiert über Hyperkonjugation

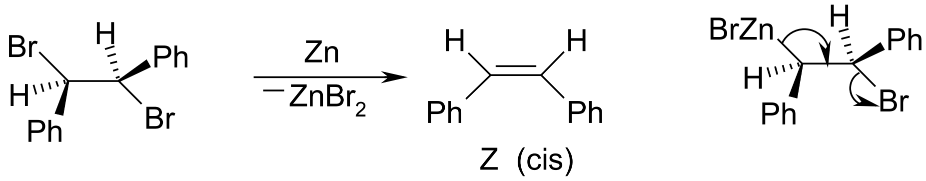




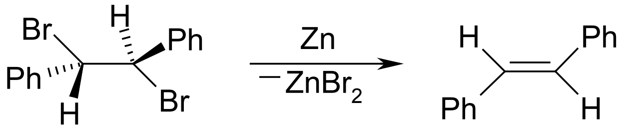
technisch

4.1.2.8 weitere trans-Eliminierungen

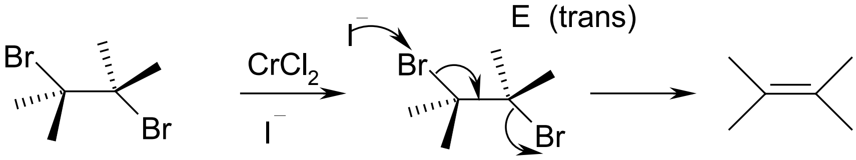
unlike



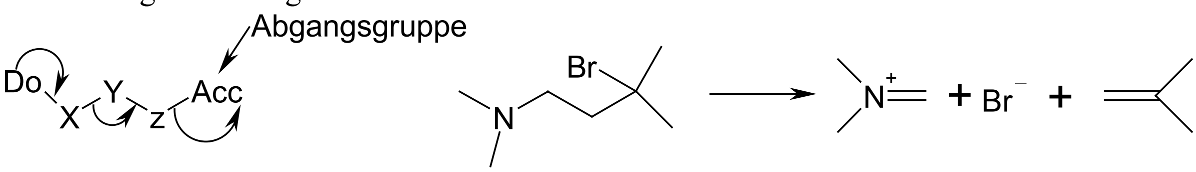
like

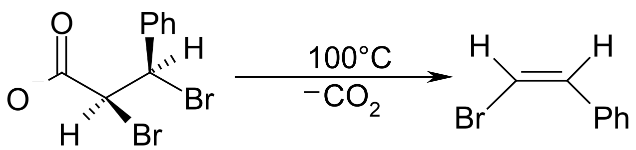


E (trans)

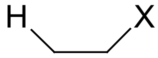


Grob – Fragmentierung

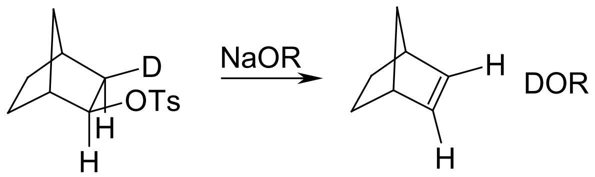




4.1.3 Darstellung durch cis-HX-Eliminierung

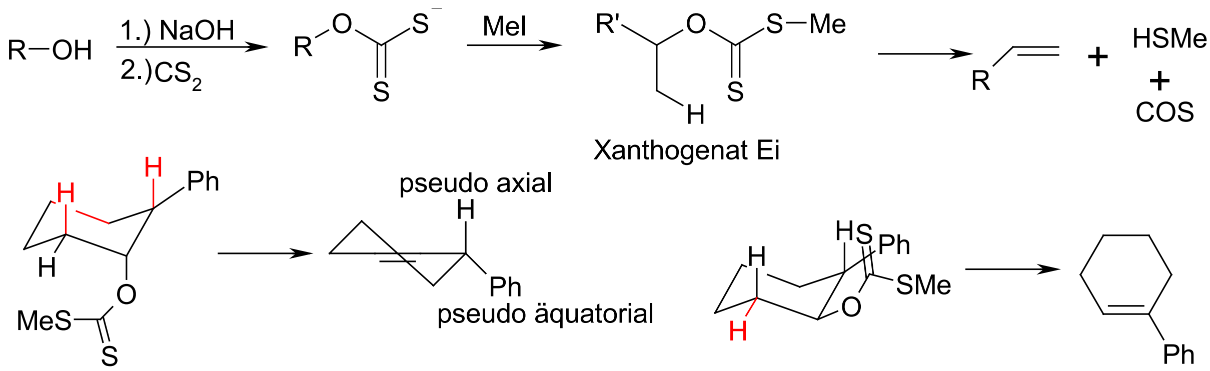


4.1.3.1 Geometrie lässt trans nicht zu:

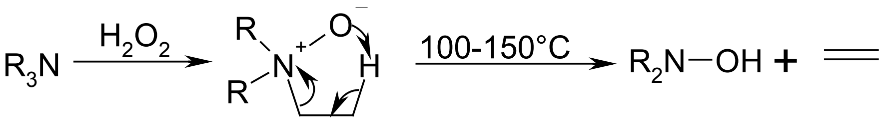


4.1.3.2 Chugaev-Reaktion

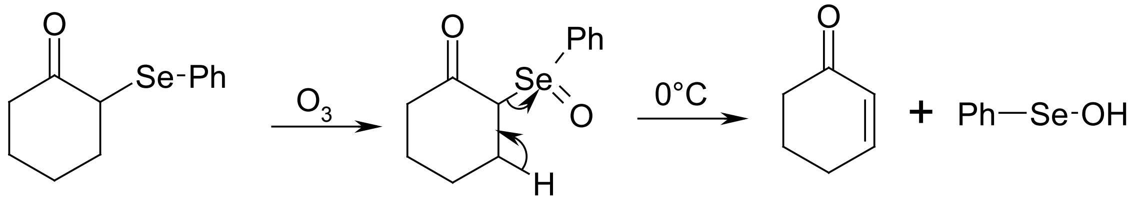
Pyrrolyse von Xanthogenaten



4.1.3.3 COPE Eliminierung

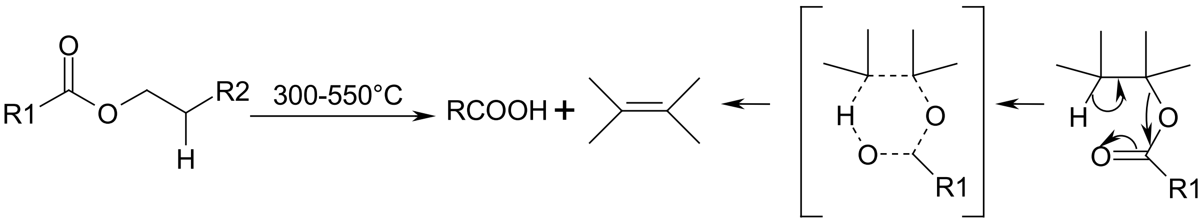


4.1.3.4 Selenoxid-Eliminierung



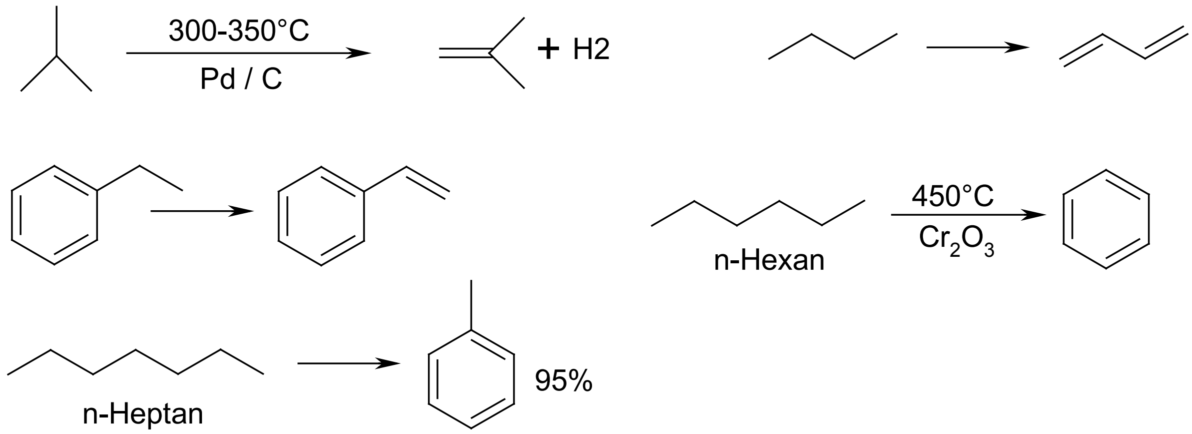
4.1.3.5 Esterpyrolyse

(FVP= Flash Vacuum Pyrolysis)

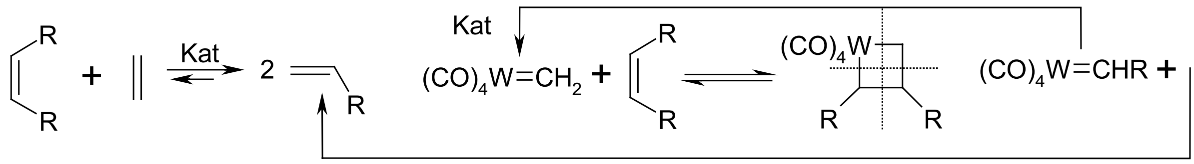


4.1.4 Alkan-Dehydrierung

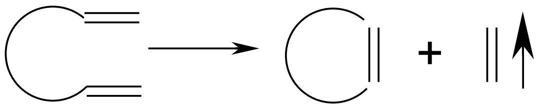
Diese Reaktionen sind eher von technischem Interesse



4.1.5 Alkenmetathese



Herstellung großer Ringe



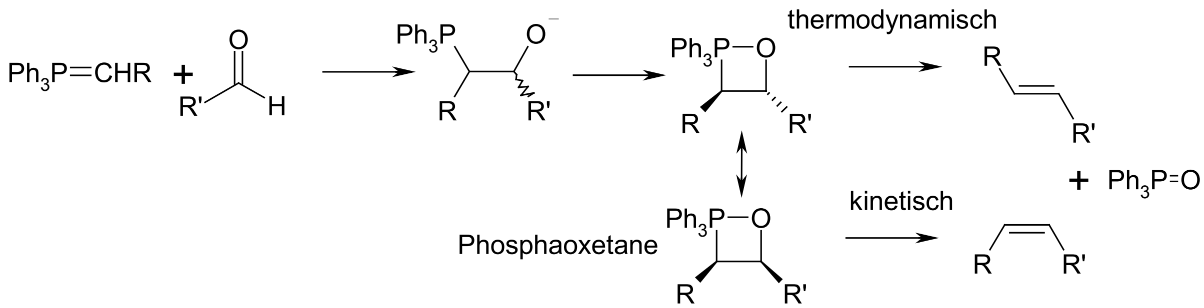
4.1.6 Wittig–Reaktion

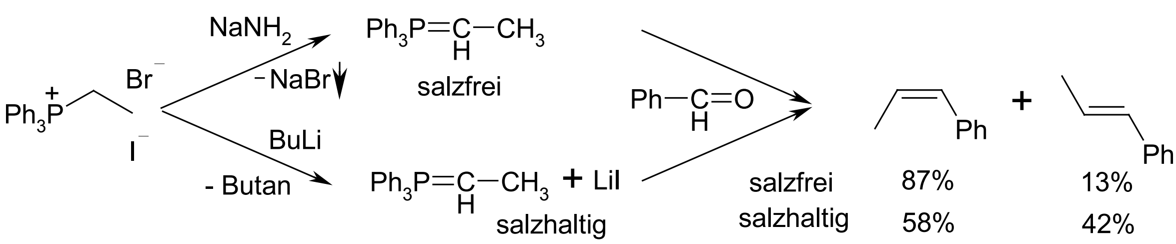
4.1.6.1 Herstellung von Phosphoryliden

$$Ph_3P| + X-CH_2-R \xrightarrow{S_N2} Ph_3P^+-CH_2-R + X^- \xrightarrow[NR_2^-]{RLi} Ph_3P-\overline{C}^-H-R \leftrightarrow Ph_3P=CH-R$$

Phosphorylide, Phophoran

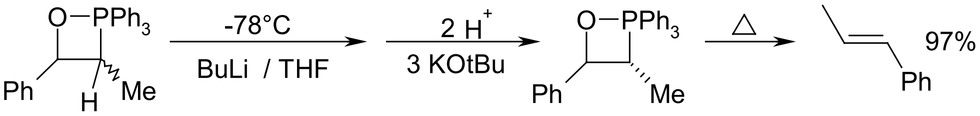
4.1.6.2 Reaktionsmechanismus



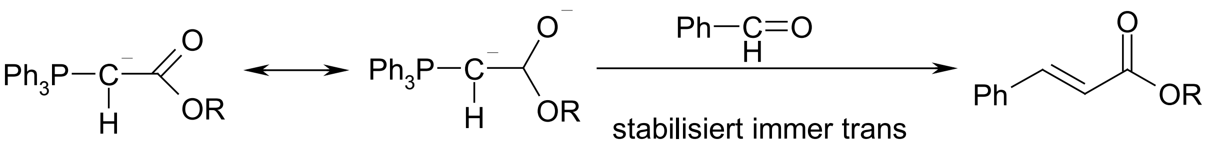


4.1.6.3 Schlosser Variante

Tiefe Temperatur, vorwiegend trans-Produkt

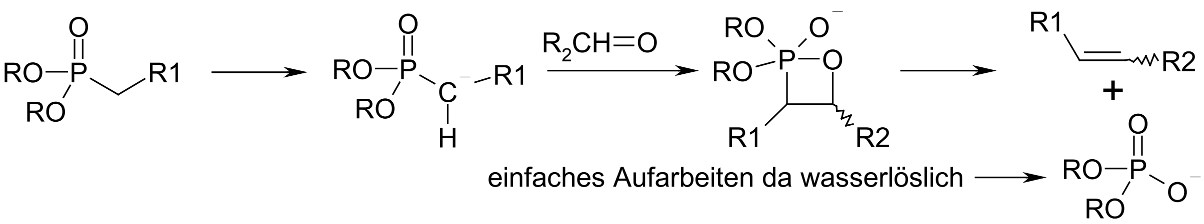


4.1.6.4 Stabilisierte Ylide

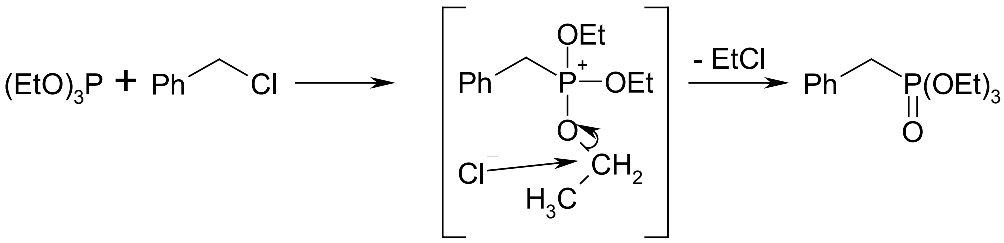


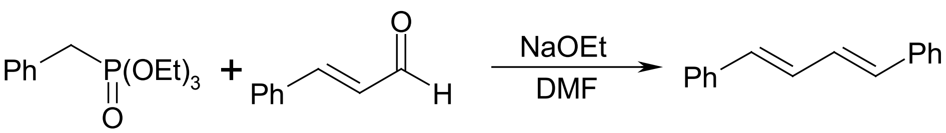
4.1.7 Horner-Wadsworth-Emmons-Reaktion

4.1.7.1 Mechanismus

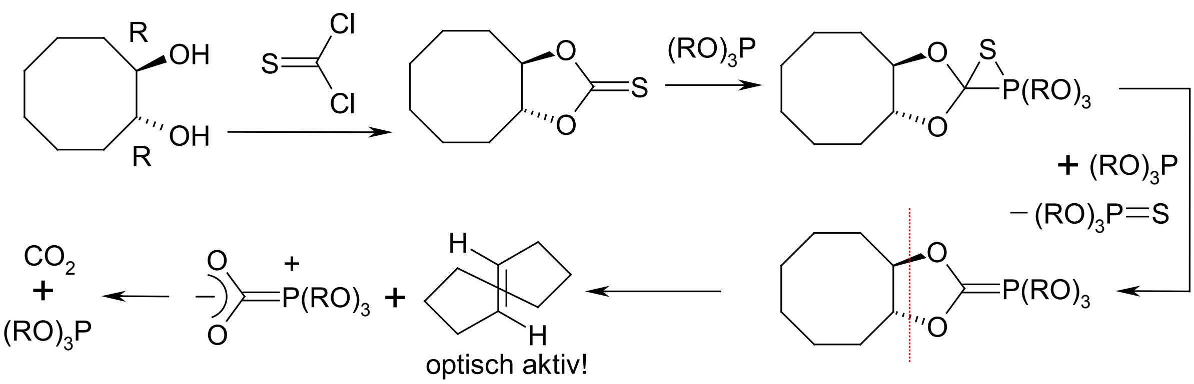


4.1.7.2 Arbuzov–Reaktion



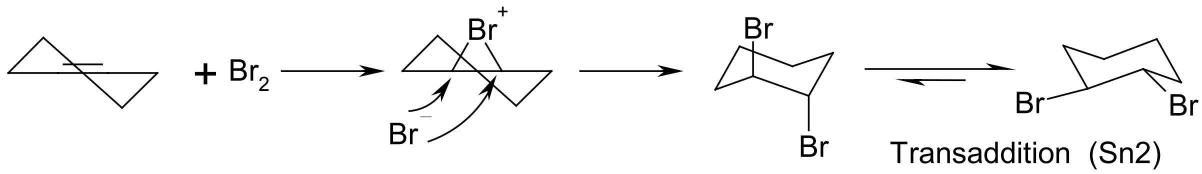


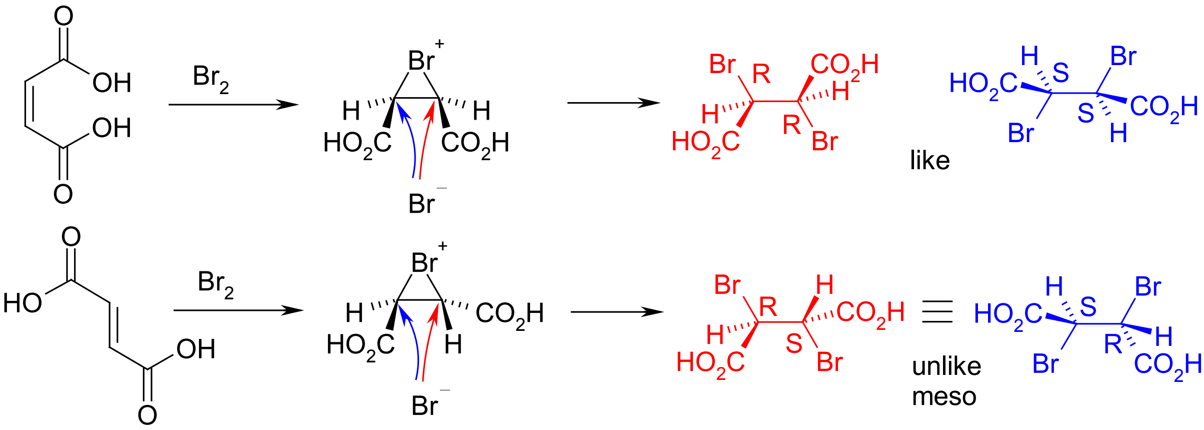
4.1.8 Corey-Winter-Synthese (Fragmentierung)



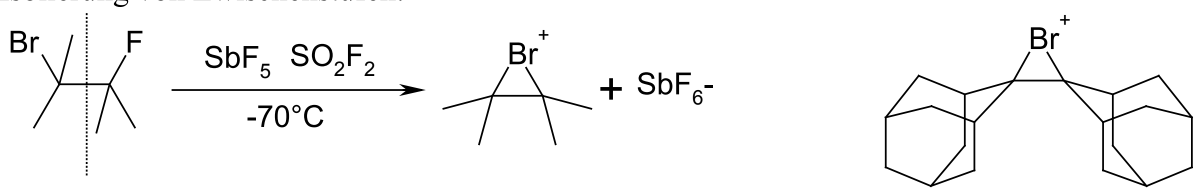
4.1.9 Reaktionen der Alkene

4.1.9.1 Halogenaddition





Isolierung von Zwischenstufen:



2 NMR Signale

1 NMR Signal

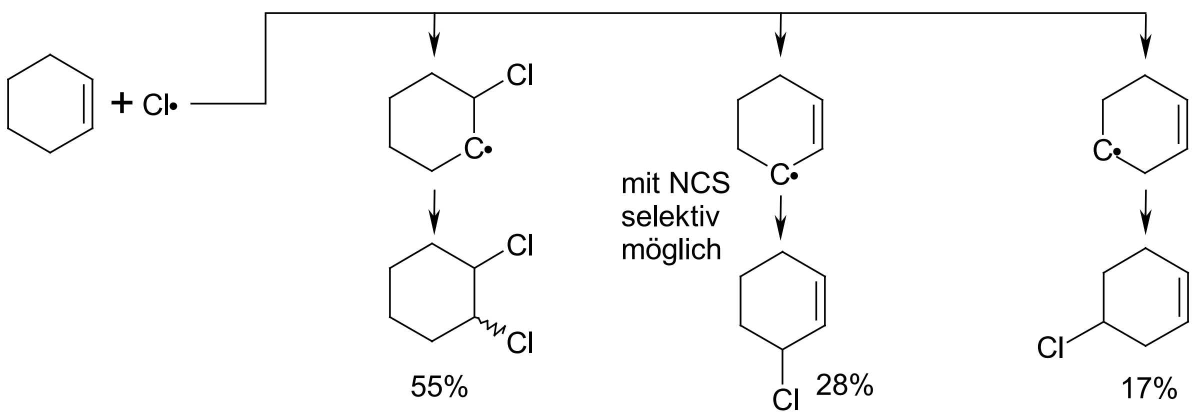
Adamantanreste

Radikalisch:

$$Br_2 \xrightarrow{h*\nu} 2Br\bullet$$

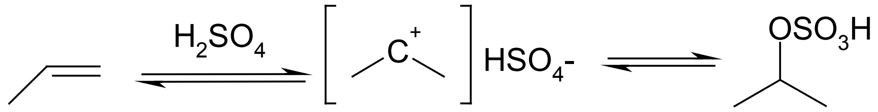
$$Br\bullet + H_2C = CH - R \rightarrow Br - CH_2 - \dot{C}H - R$$

$$Br - CH_2 - \dot{C}H - R + Br_2 \rightarrow Br - CH_2 - CHBr - R + Br\bullet$$

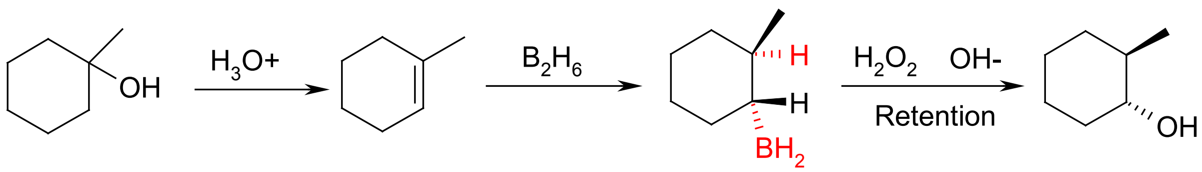


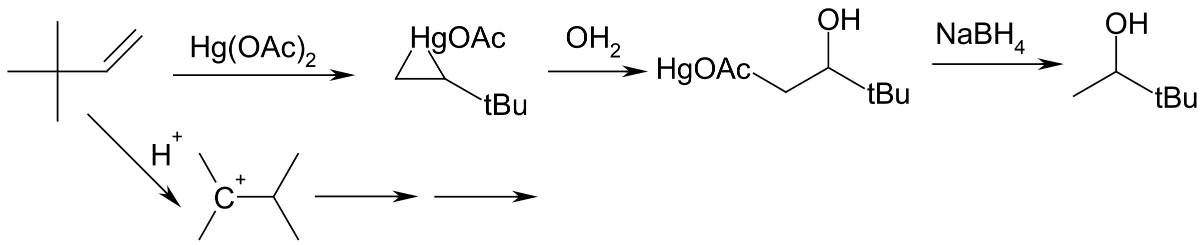
4.1.9.2 Addition von HX

Rückreaktion der Eliminierung
Ionisch: H-Hal $H\text{-}SO_4H$ H-OH (Rückreaktion von E1)
Regel von Markownikow: Es bildet sich das stabilere Carbeniumion
(auch: Der Wasserstoff geht ans wasserstoffreichere C-Atom, das Halogen ans wasserstoffärmere C-Atom)



4.1.9.3 Hydroborierung / Quecksilberreagenzien





4.1.9.4 Radikalische Addition von HX

anti-Markownikow !!!

$$R-CH=CH_2 \xrightarrow{Br\bullet} R-\dot{C}H-CH_2-Br \xrightarrow{HBr} R-CH_2-CH_2-Br+Br\bullet$$

Radikalstarter: Δ oder $h*\nu$

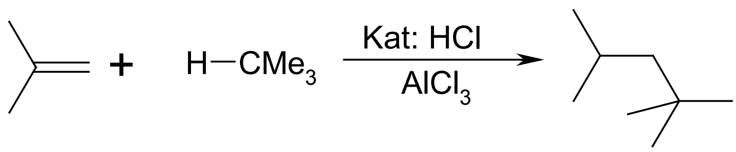
Start: $R\bullet + H-CCl_3 \rightarrow RH + \bullet CCl_3$

Kette:
$$R-CH=CH_2+\bullet CCl_3 \rightarrow R-\dot{C}H-CH_2-CCl_3$$
$$R-\dot{C}H-CH_2-CCl_3+H-CCl_3 \rightarrow R-CH_2-CH_2-CCl_3+\bullet CCl_3$$

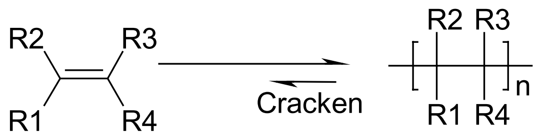
Mögliche Substanzen: $H-CCl_3; Cl-CCl_3; Br-CCl_3; H-SiCl_3; H-SR; H-SnBu_3$

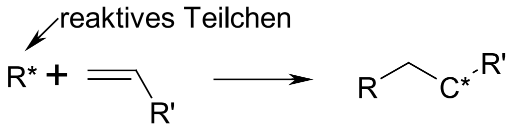
4.1.9.5 Ipatieff-Reaktion

Addition von R_3C-H an terminale Alkene



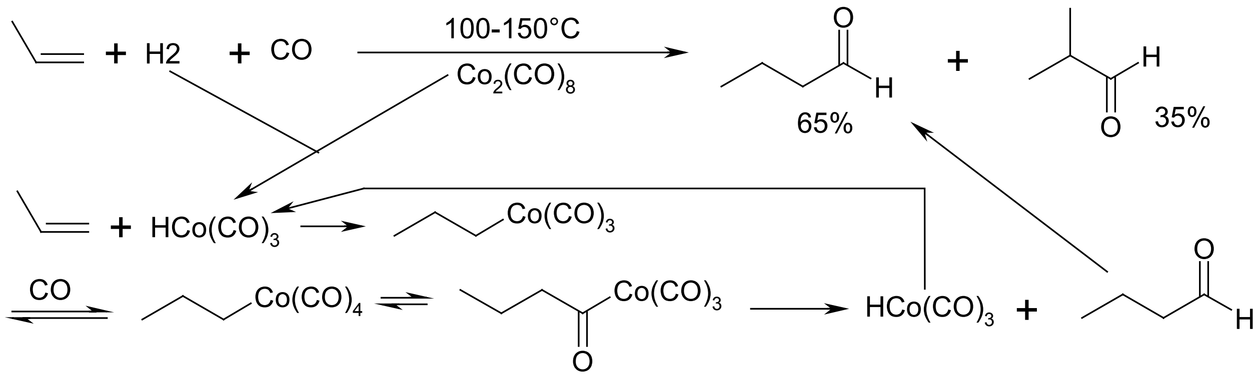
4.1.9.6 Polymerisation





Mechanismen: radikalisch anionisch kationisch

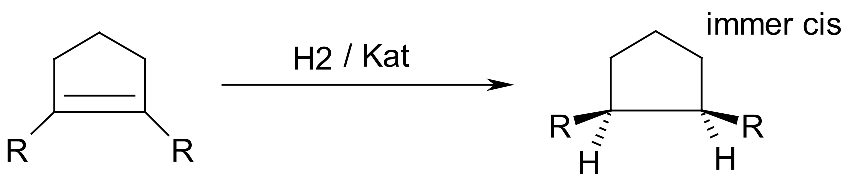
4.1.9.7 Oxosynthese



monosubstituierte C=C >disubstituierte C=C > trisubstituierte C=C

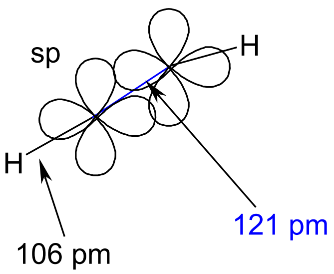
4.1.9.8 Katalytische Hydrierung

hoch stereospeziefische Reaktion



4.2 Alkine

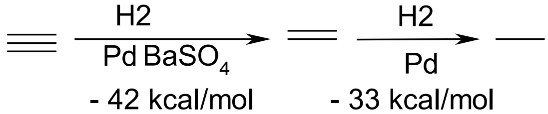
4.2.1 Eigenschaften

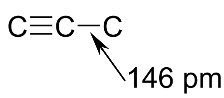


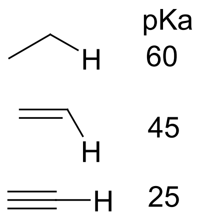
Bindungsenergie (kcal/mol)

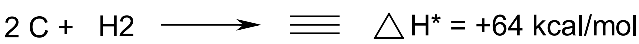
C–C	C=C	C≡C
83	146	200

△ = 54







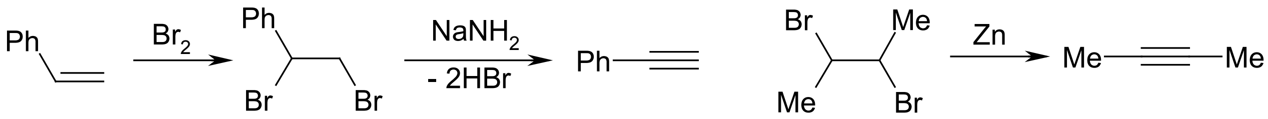


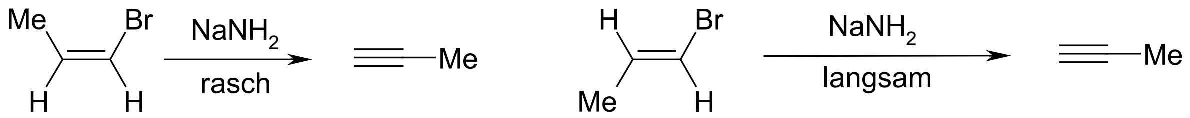
4.2.2 Herstellung

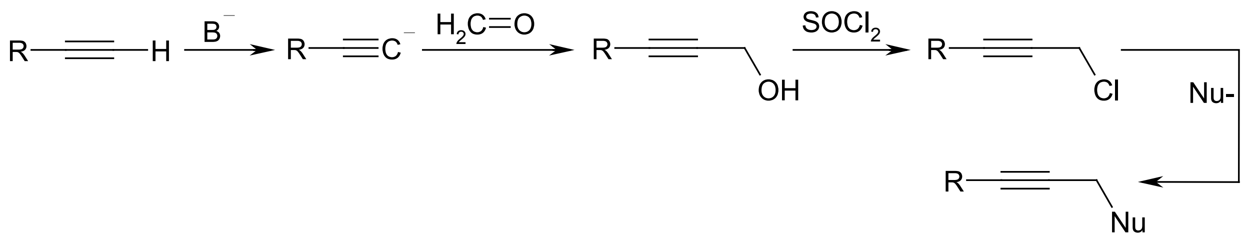
4.2.2.1 Herstellung von Ethin

alt: $CaC_2 \xrightarrow{H_2O} CaO + C_2H_2$ technisch: $6CH_4 + \frac{1}{2}O_2 \xrightarrow{2500°C} 2C_2H_2 + CO + 4H_2$

4.2.2.2 Laborsynthesen für Alkine

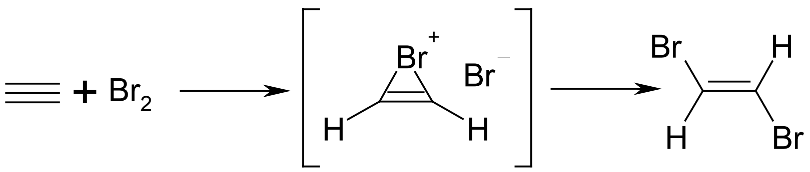






4.2.3 Reaktionen

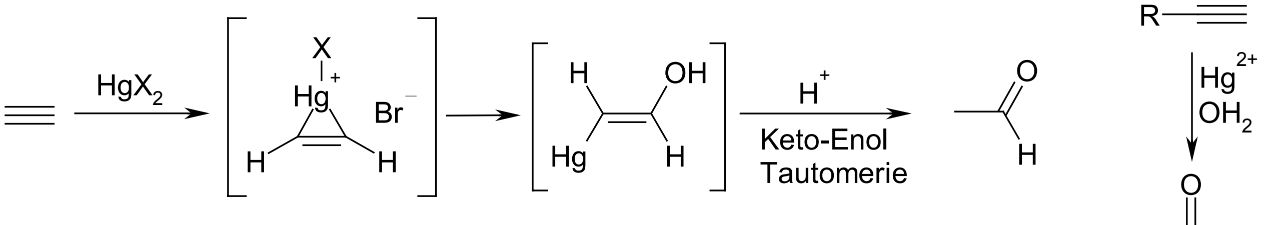
4.2.3.1 Elektrophile Addition



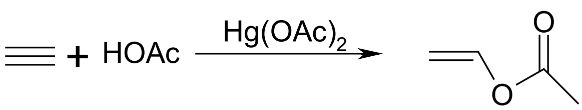
relativ instabil

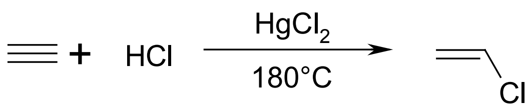
4.2.3.2 H-X Addition mit Hg^{2+}-Kat

Additionen von Wasser

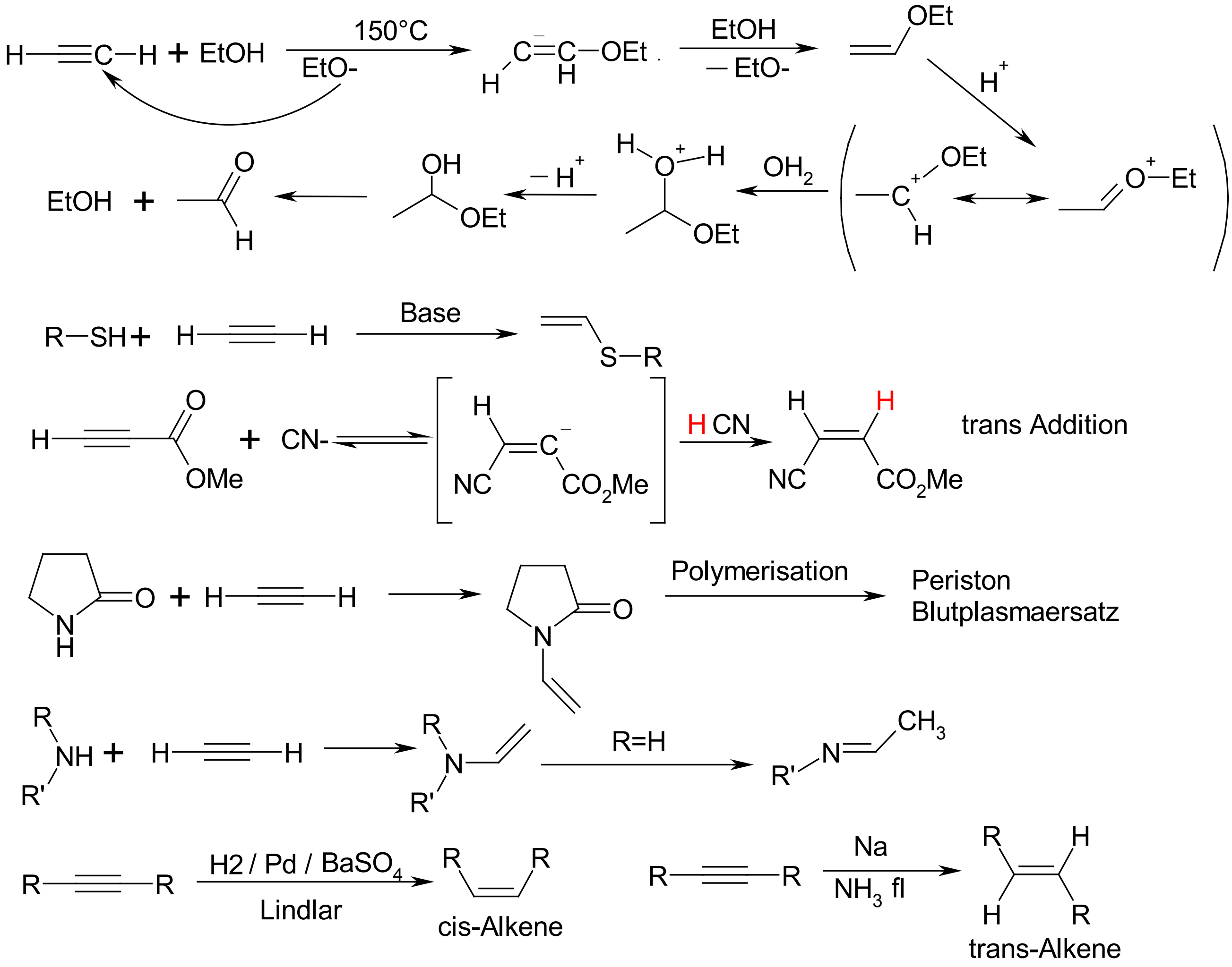


andere Additionen

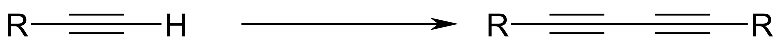




4.2.4 Nukleophile Addition

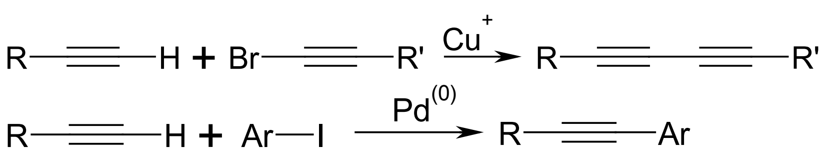


4.2.5 Oxidative Kupplung

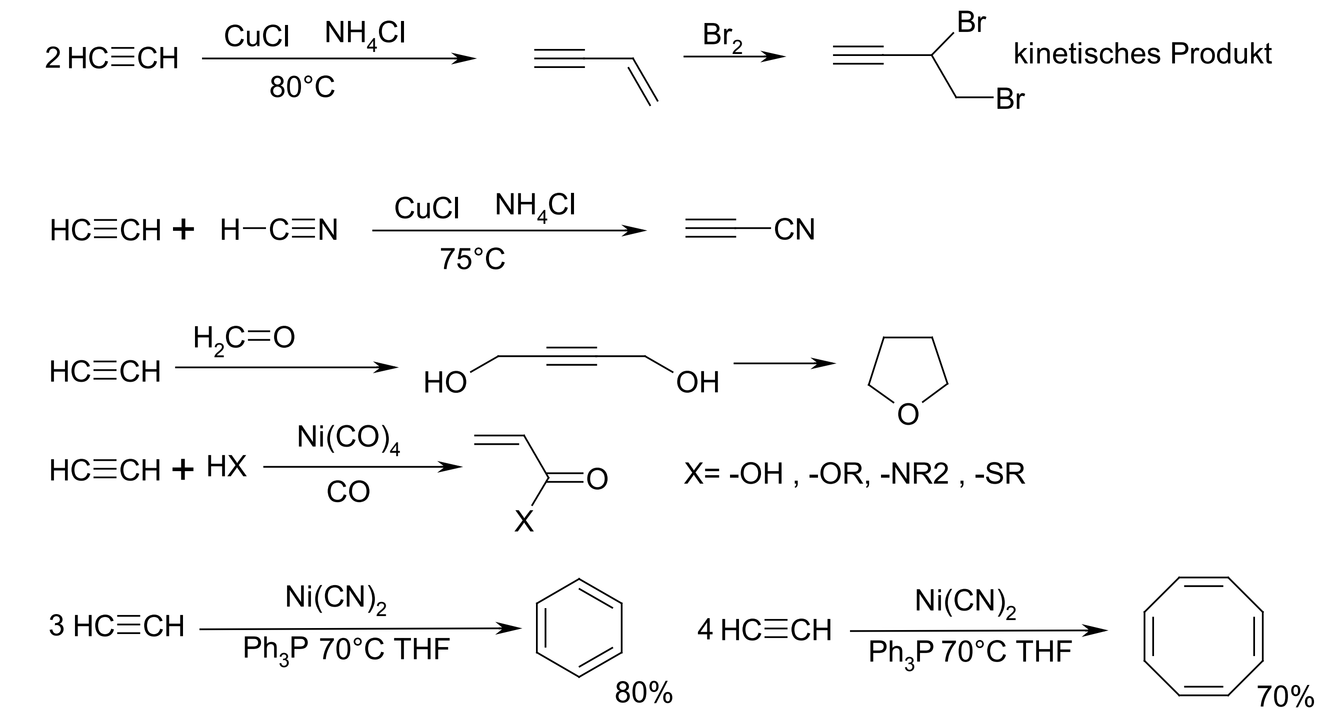


Eglington-Kupplung: $Cu(OAc)_2$ in Pyridin ($\overset{II}{Cu} \rightarrow \overset{I}{Cu}$)
Glaser-Kupplung: Cu(I)X NH_4^+ in NH_3 mit O_2

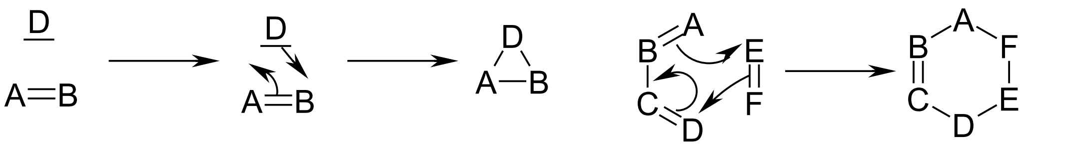
Cadiot-Choclkiewiez-Kupplung:



4.2.5.1 Technik des Ethins (Acetylen)



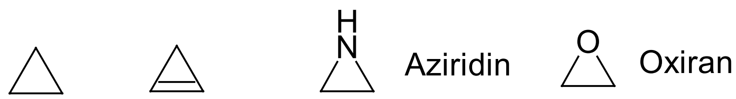
4.3 Cycloadditionen der Alkene und Alkine

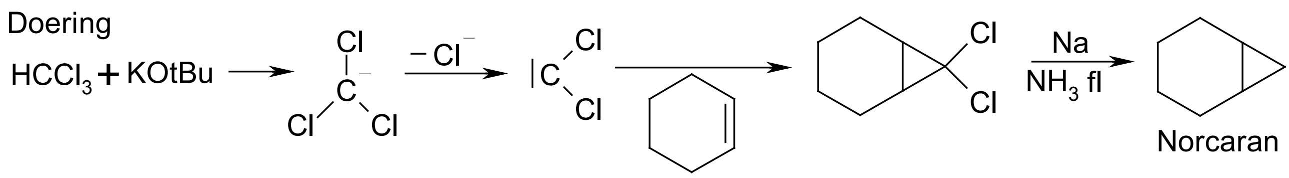


[2+1] Cycloaddition [4+2]Cycloaddition (Diels -Alder)

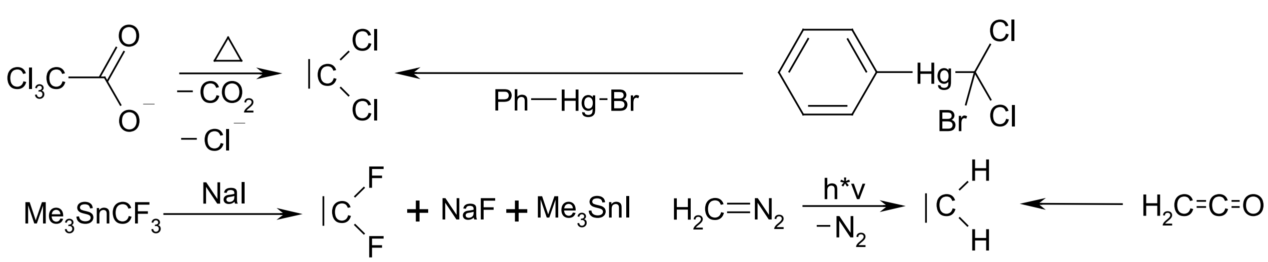
allgemein: [m+n]Cycloaddition m,n : Zahl der beteiligten Atome

4.3.1 [2+1]Cycloaddition

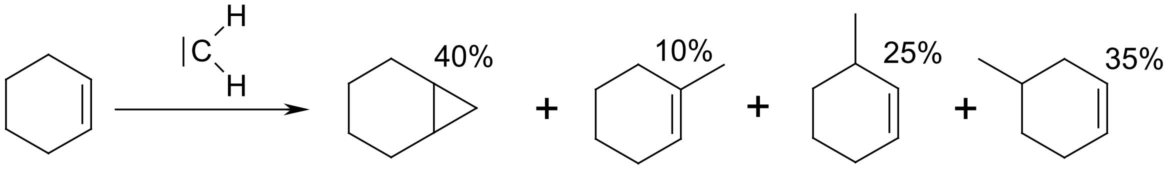


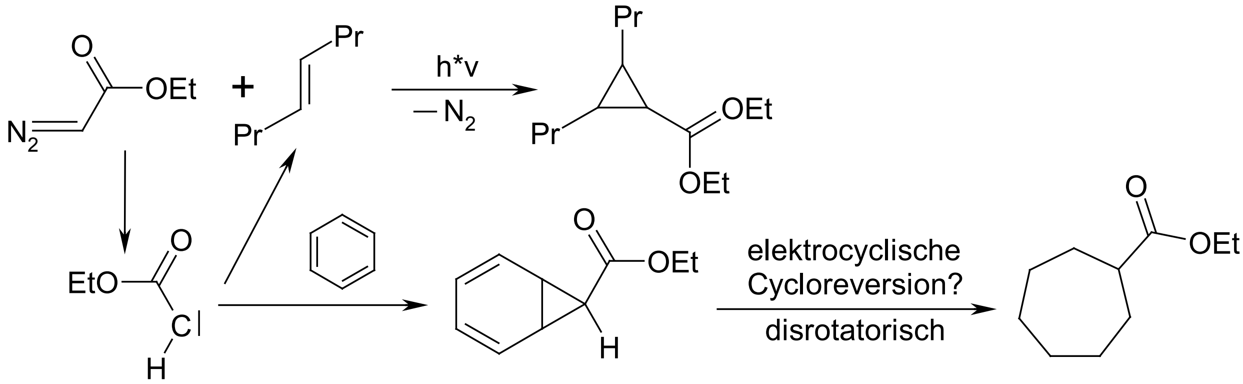


4.3.1.1 Zugangswege zu Carbenen

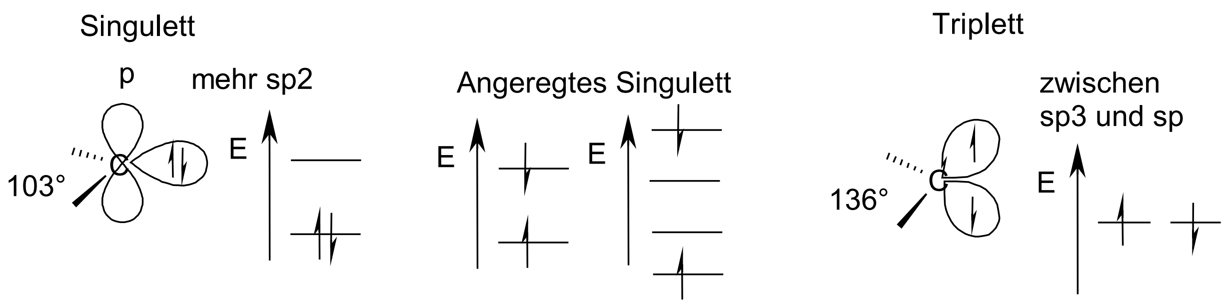


4.3.1.2 Reaktionen der Carbene



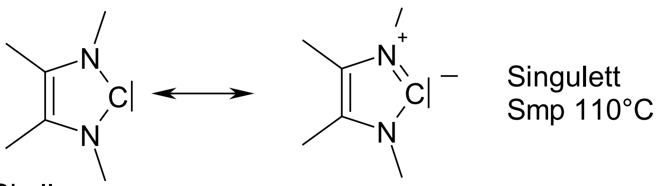


4.3.1.3 Singulett und Triplett Carbene

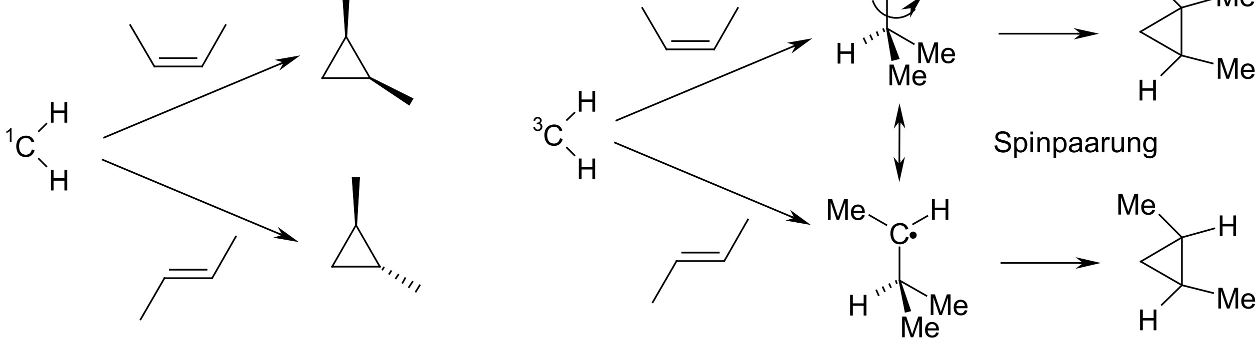


Zuerst entsteht immer Singulett, danach Änderung durch Substituenteneffekte:
Singulett: $|CCl_2$ $|CBr_2$ (stabilisieren leeres p-Orbital)
Triplett : $:CH_2$ $:C(CN)_2$ $:C(Ph)_2$ (Stabilisieren Radikale über Mesomerie)

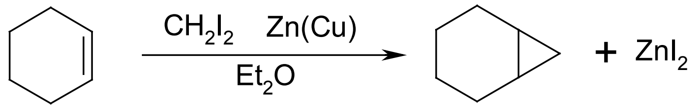
4.3.1.4 Stabile Carbene



Skell



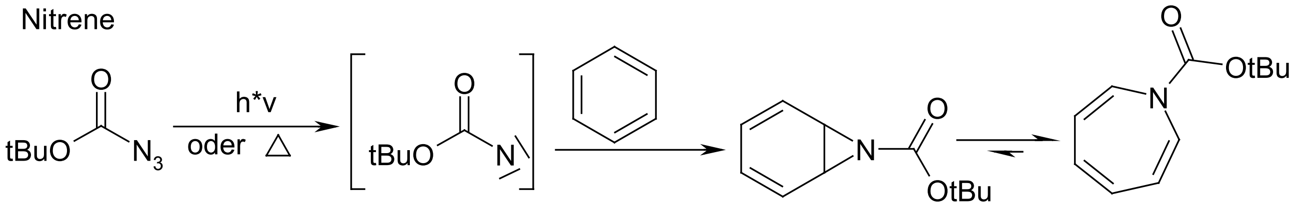
4.3.1.5 Carbenoide: Simmons-Smith-Reaktion

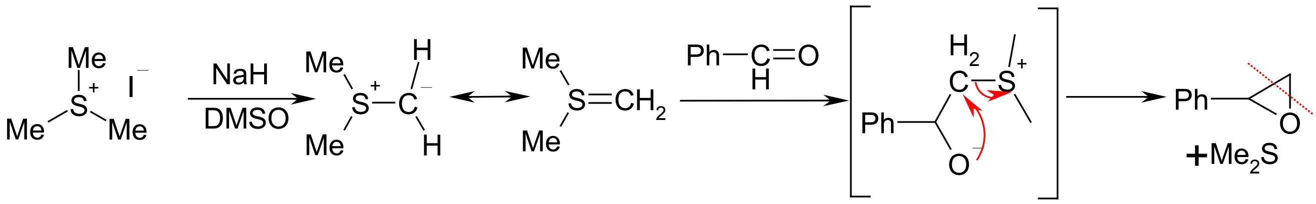


wahrscheinliche Zwischenstufe

I—C—Zn—I
H_2

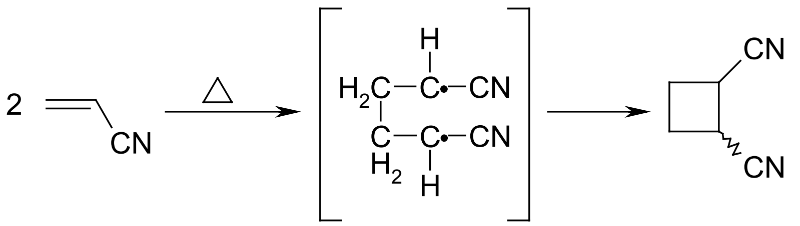
Nitrene

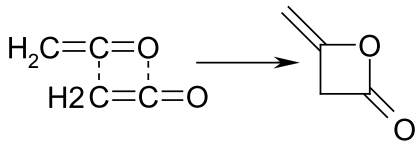


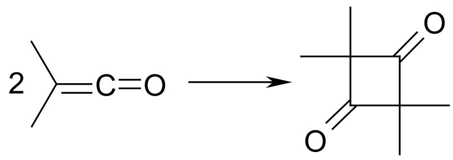


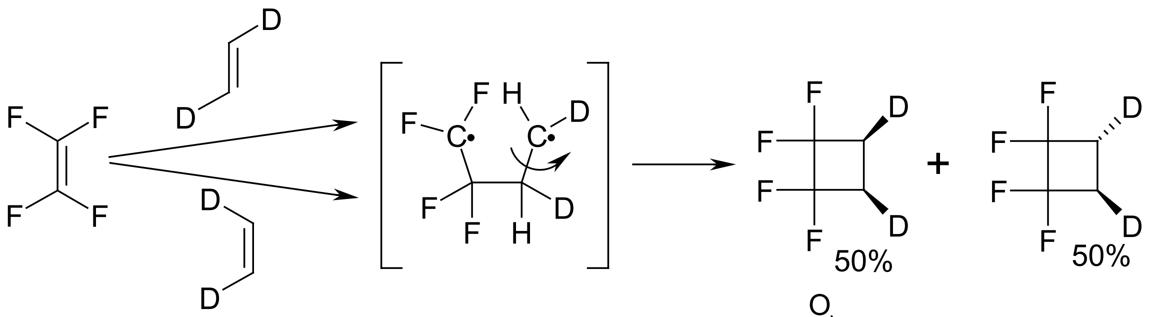
4.3.2 [2+2] Cycloaddition

prinzipiell nicht stereospezifisch (Ausnahmen)



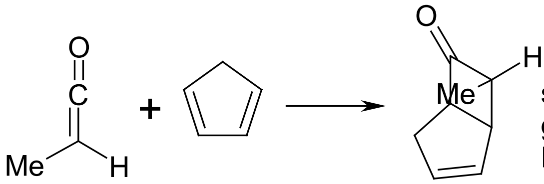




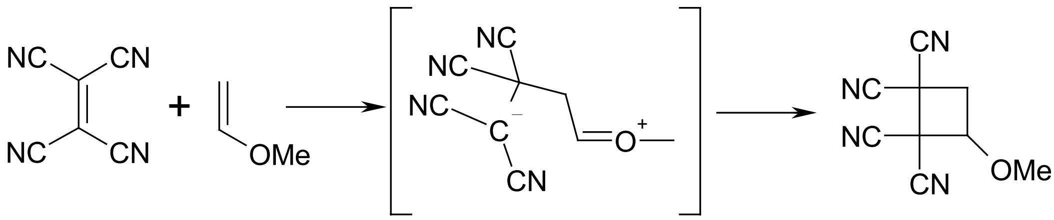


Ausnahme:

1. Keine Diels-Alder bei Ketenen
2. 2. stereospezifisch



sterisch mehr gehindertes Endo-Produkt

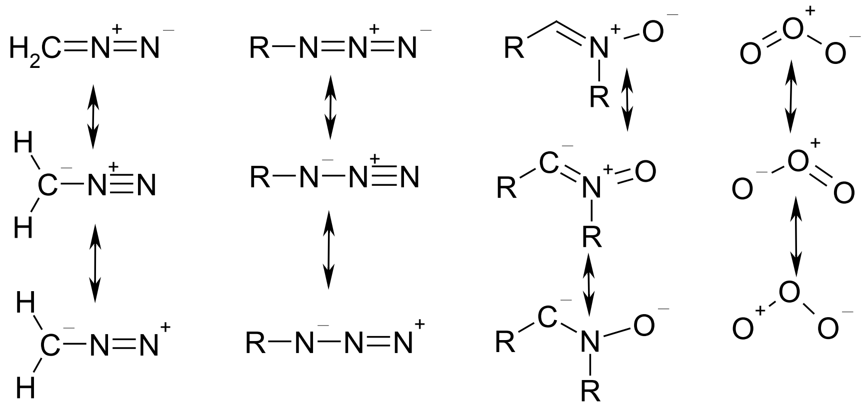


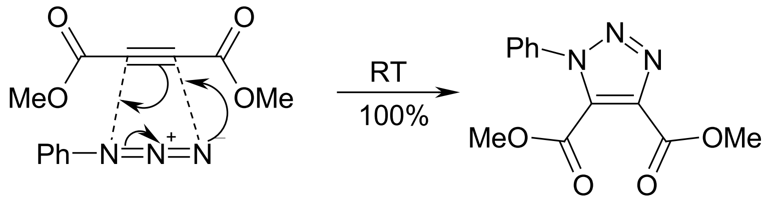
Zwitterion

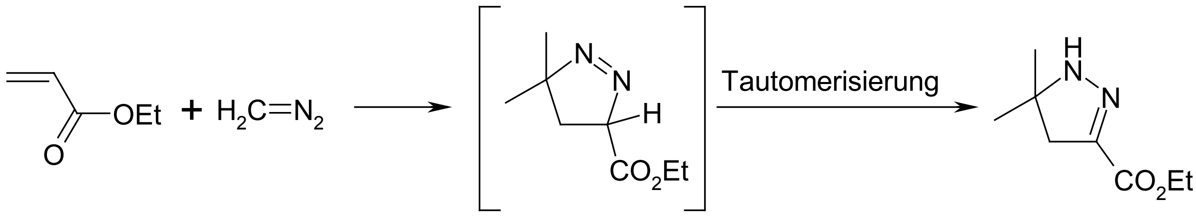
4.3.3 [3+2] Cycloaddition

1,3 dipolare Cycloaddition

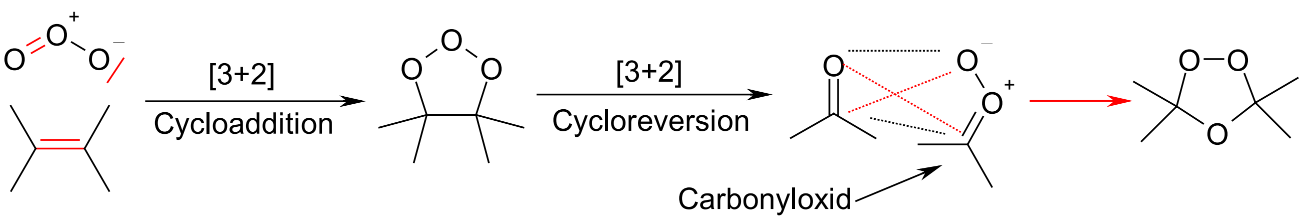
4.3.3.1 Beispiel für 1,3-Dipole



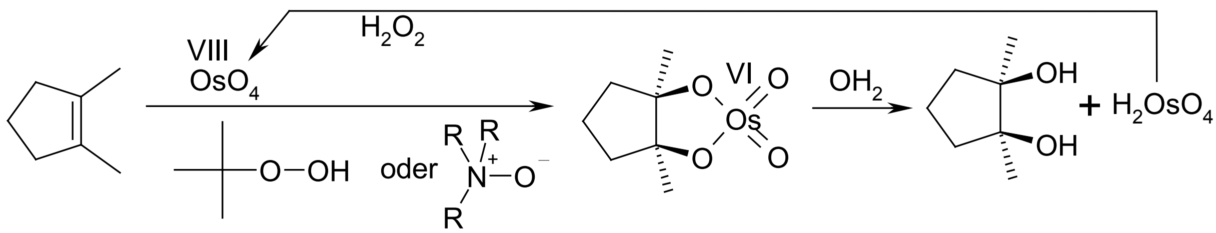


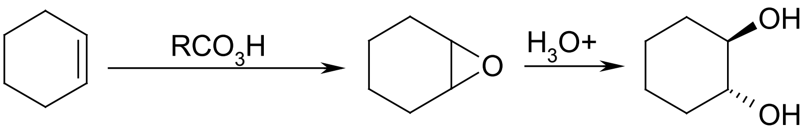


4.3.3.2 Ozonolyse

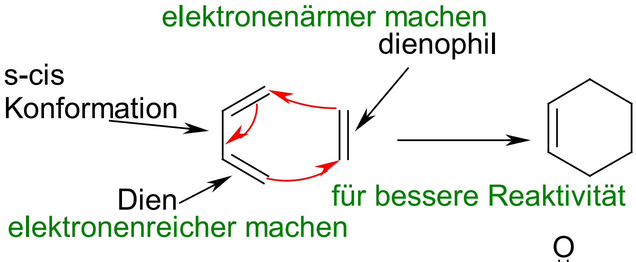


4.3.3.3 Weitere Reaktionen

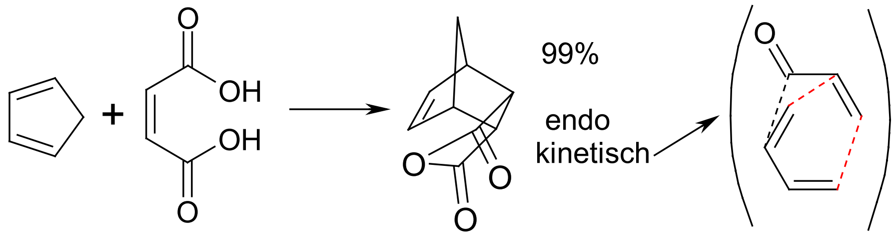


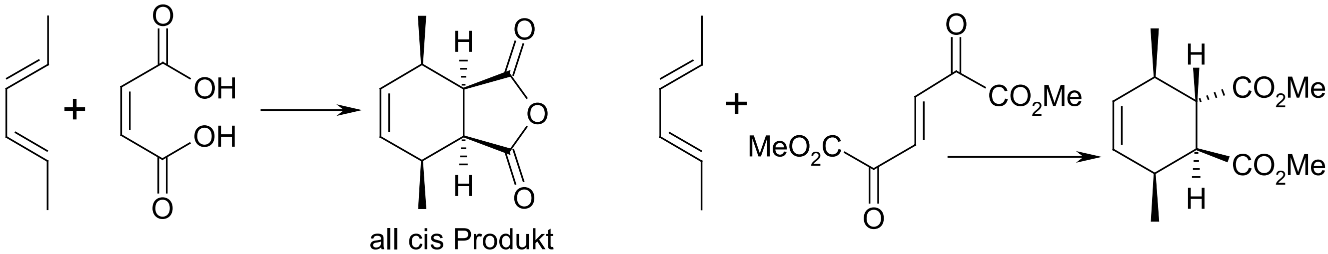


4.3.4 [4+2] Cycloaddition: Diels-Alder-Reaktion

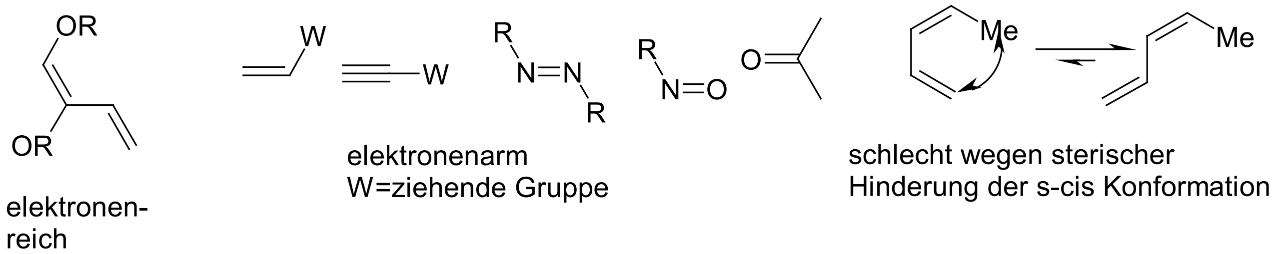


besonders gut, da s-cis Konformation eingefroren

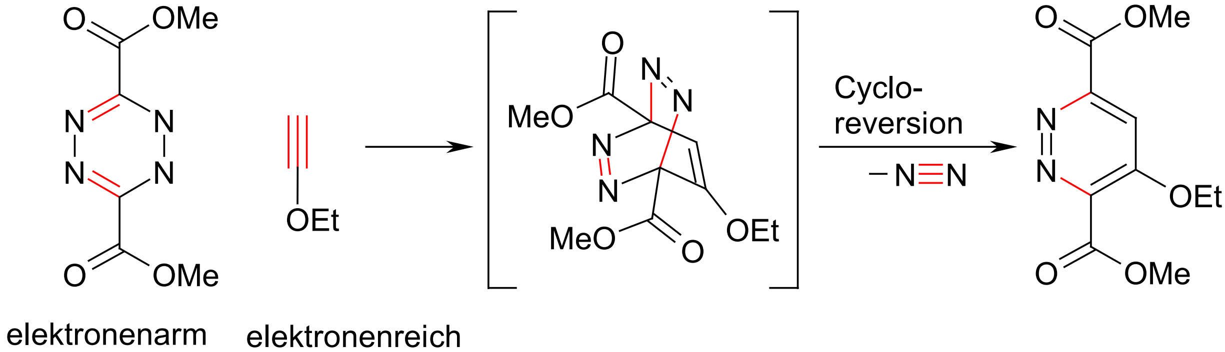




relative Stereochemie bleibt erhalten, bevorzugt wird das Endo-Produkt gebildet

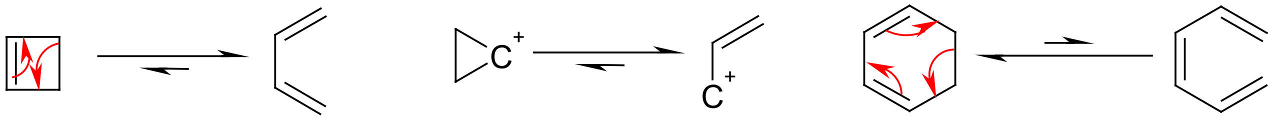


Reverse Diels-Alder (auch Diels -Alder mit inversem Elektronenbedarf):

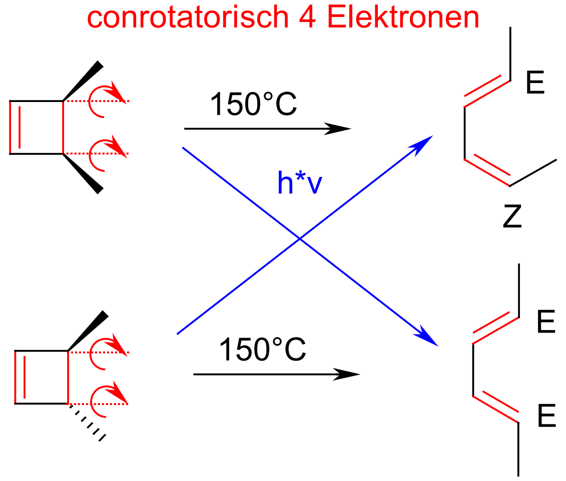


4.4 Woodward-Hoffmann-Regeln

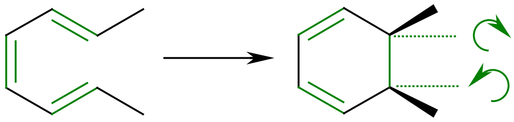
Prinzip der Erhaltung der Orbitalsymmetrie bei elektrocyclischen Reaktionen



conrotatorisch 4 Elektronen

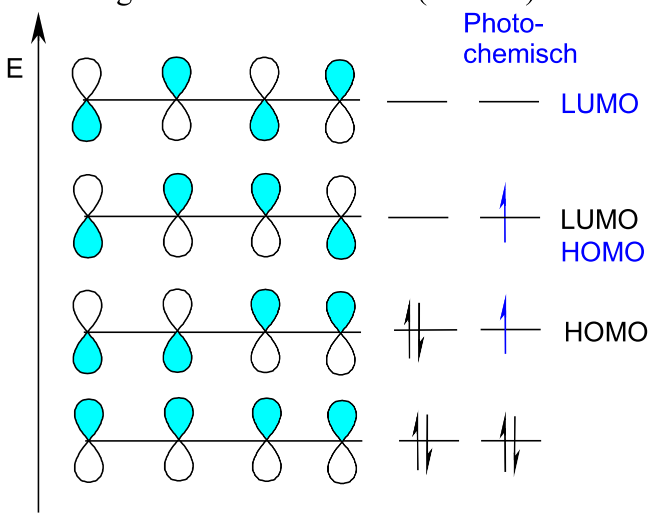


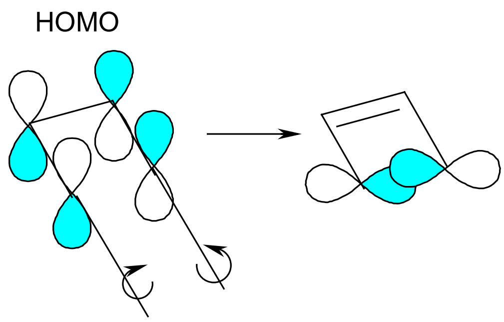
disrotatorisch 6 Elektronen

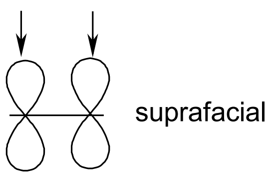


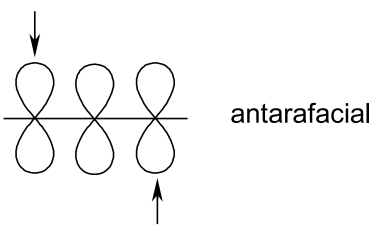
4n+2 Elektronen (Hückel-Aromat)	→ disrotatorisch
4n Elektronen(Hückel Anti-Aromat)	→ conrotatorisch

Erklärung: Grenzorbitaltheorie (FUKUI)

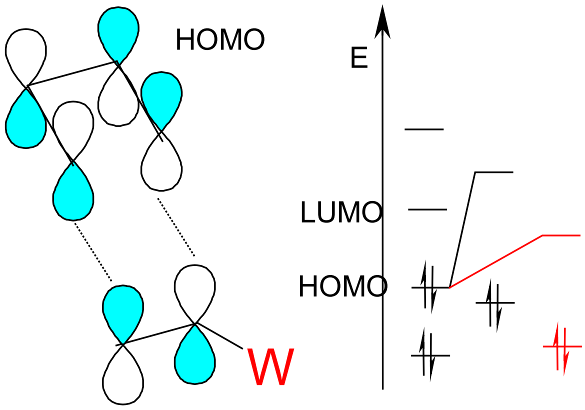




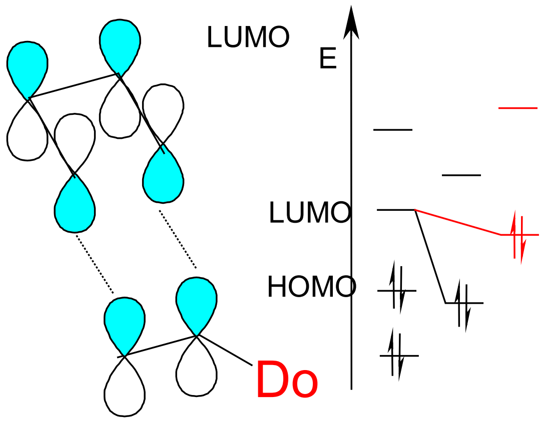




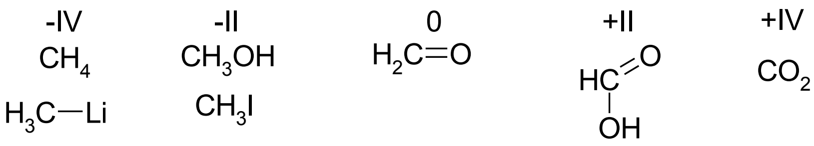
normale Diels-Alder

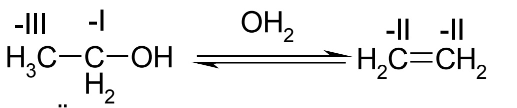


inverse Diels-Alder



5 Reduktion&Oxidation



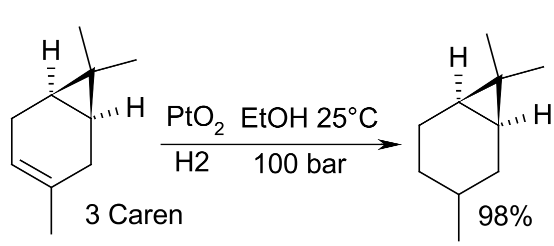


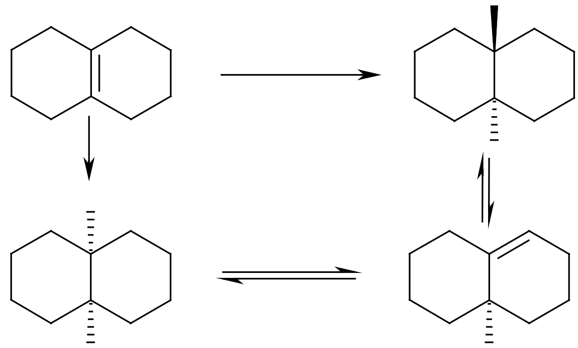
keine Änderung der Gesamtoxidationszahl

5.1 Reduktion

5.1.1 Reduktionsmittel

5.1.1.1 Katalytische Hydrierung

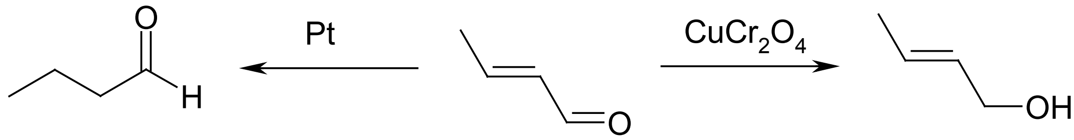




Katalysatoren: Platin, Palladium auf Trägern;

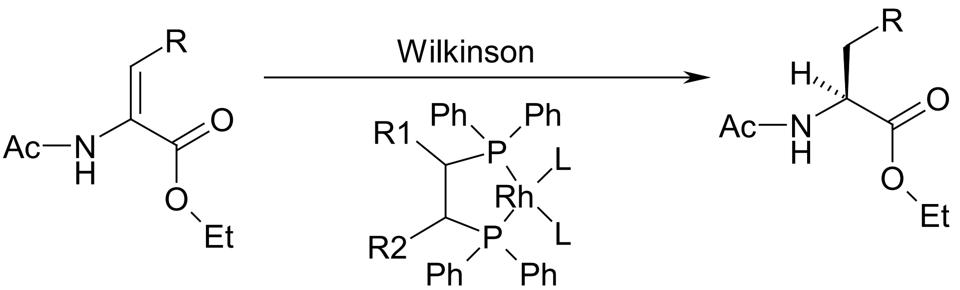
Ranney-Nickel: $NiAl + NaOH \rightarrow Ni + Al(OH)_4^-$

Kupferchromit: $CuO + Cr_2O_3 \rightarrow CuCr_2O_4$

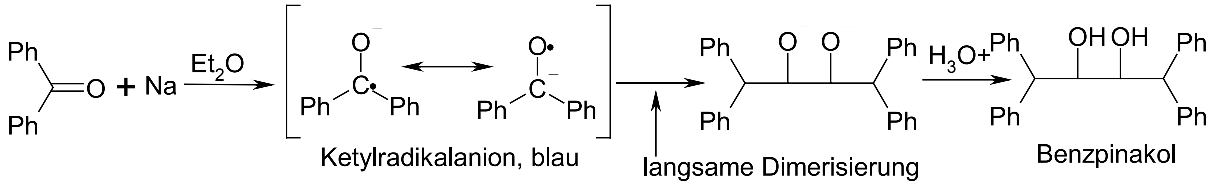


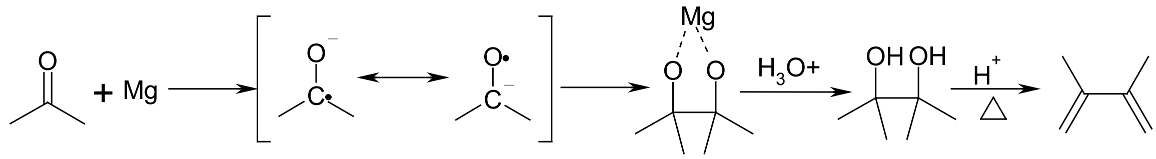
Homogene Katalyse: Katalyse in Lösung, nicht an Oberfläche

Wilkinson-Katalysator: $ClRh(PPh_3)_3$

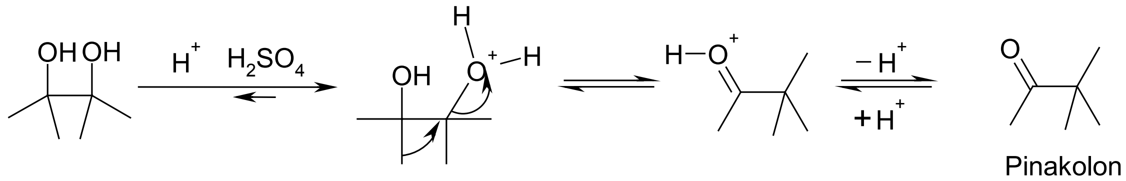


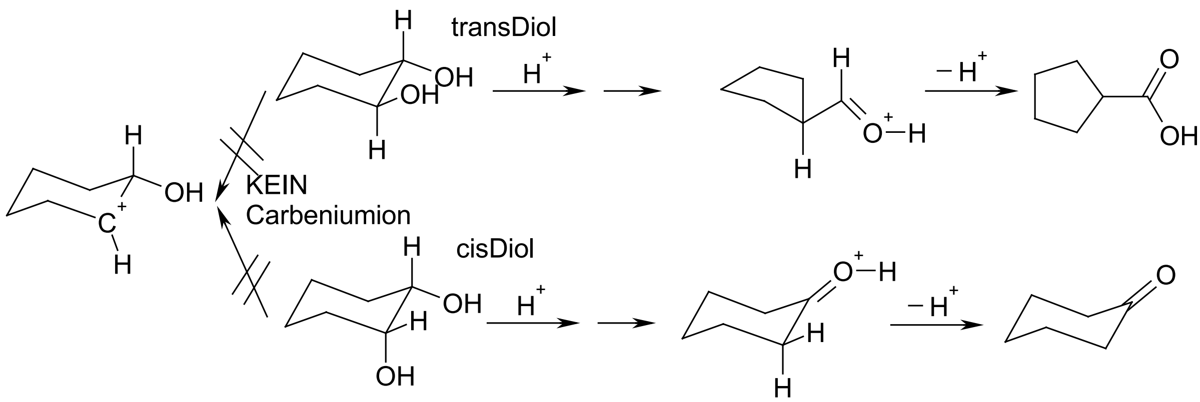
5.1.1.2 Reduktion mit Metallen



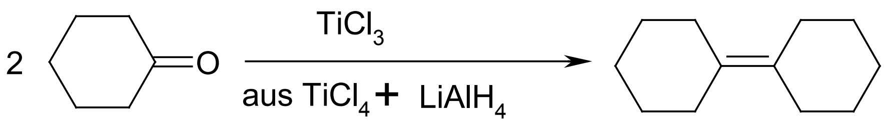


5.1.1.3 Pinakol-Umlagerung



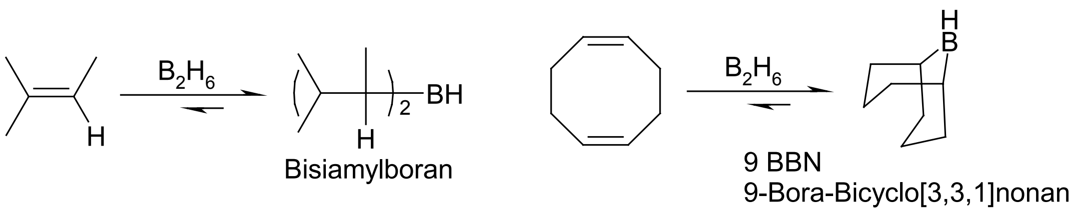


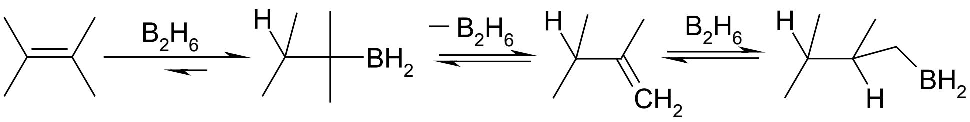
5.1.1.4 McMurrey-Reaktion

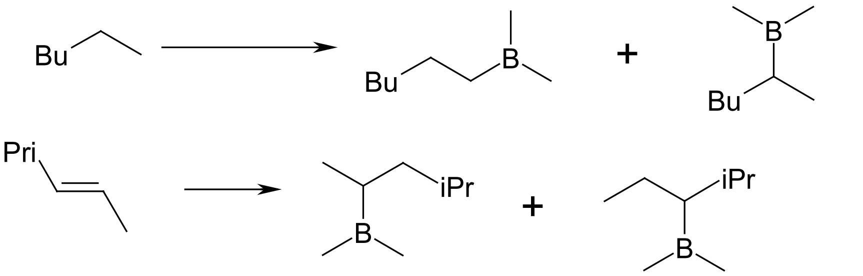


5.1.1.5 Reduktion mit Boranen

Diboran: B_2H_6 Synthese aus $2NaBH_4 + 4BF_3 \rightarrow 3NaBF_4 + 2B_2H_6$

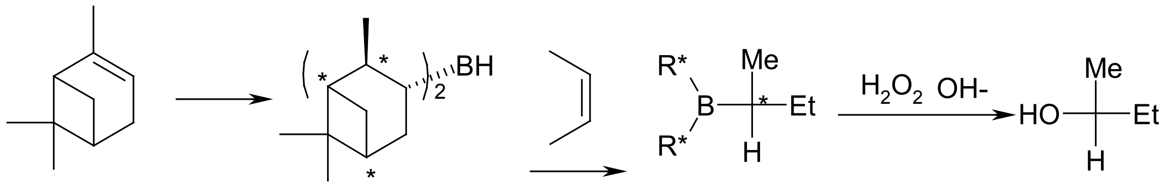






Diboran 94 : 6
Disiamyl 99 : 1
9BBN 99,9 : 0,1

Diboran 57 : 43
Disiamyl 97 : 3
9BBN 99,8 : 0,2



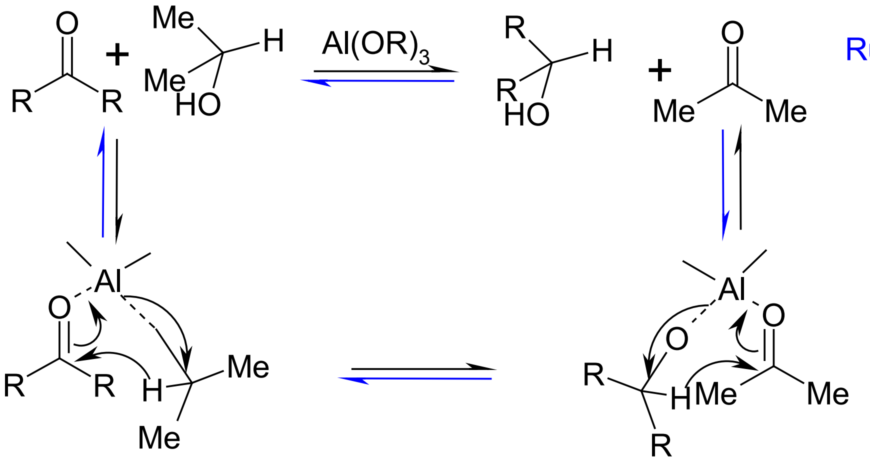
alpha Pinen

5.1.1.6 Anorganische Hydride

$LiAlH_4$ $NaBH_4$ (Nur Aldehyde und Ketone)

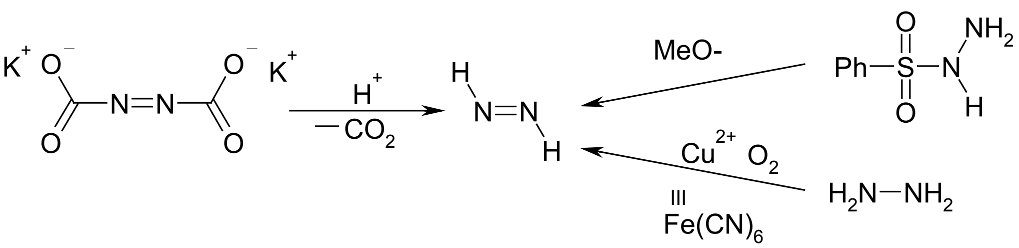
5.1.1.7 Organische Hydriddonatoren

Meerwein-Ponndorf-Verley-Reduktion
Die Rückreaktion ist als Oppenauer-Oxidation bekannt.



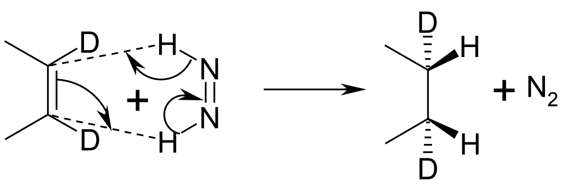
Rückreaktion: Oppenauer

5.1.1.8 Diimin



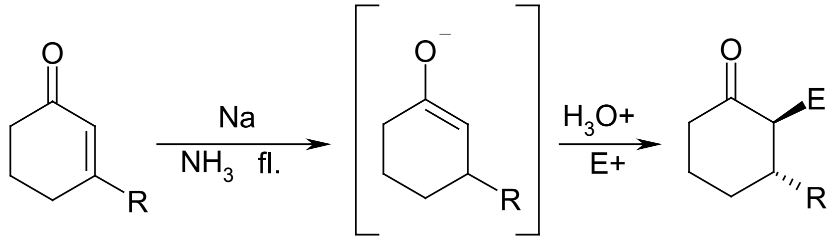
alles in sito

cis Anlagerung von Wasserstoff (konzertierte Endgruppenübertragung):

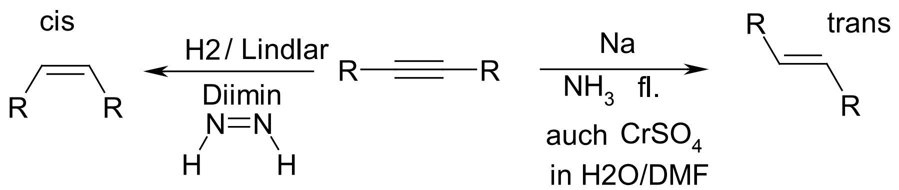


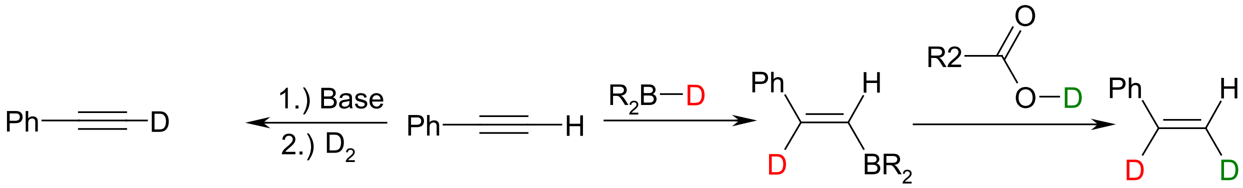
5.1.2 Reduktion funktioneller Gruppen

5.1.2.1 Alkene



5.1.2.2 Alkine

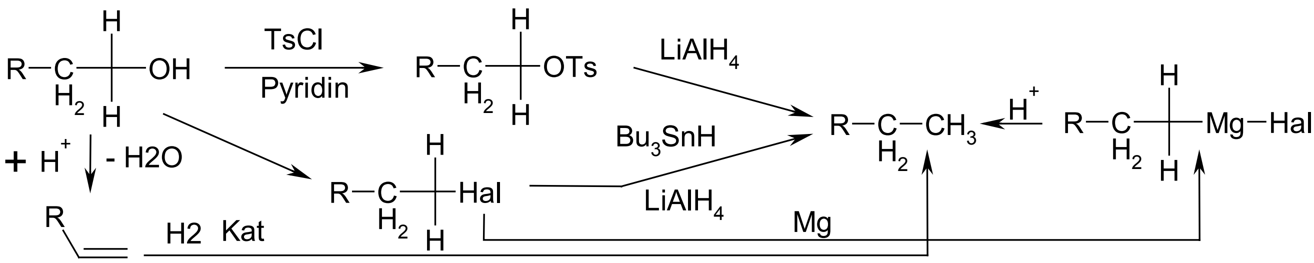




5.1.3 Aromaten

Birch-Reduktion

5.1.3.1 Halogenide, Alkohole, Ether, Phenole



nie R-OH direkt

radikalisch:

AIBN C_6H_6 im Rückfluss:

Start: $R\cdot + HSnBu_3 \rightarrow RH + \cdot SnBu_3$

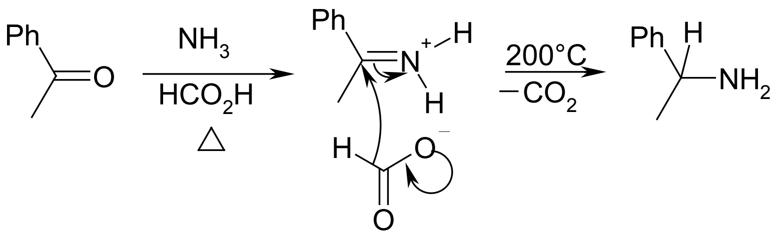
Kette: $R'{-}Br + \cdot SnBu_3 \rightarrow R'\cdot + BrSnBu_3$

$R'\cdot + HSnBu_3 \rightarrow RH + \cdot SnBu_3$

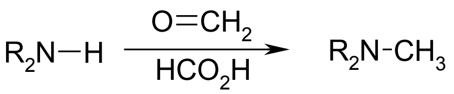
$I > Br > Cl$ F innert

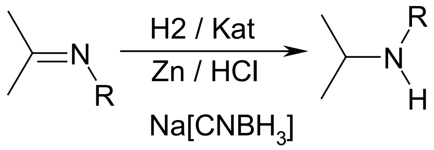
5.1.3.2 Aldehyde und Ketone

zu Alkoholen:($NaBH_4$)
Reduktive Aminierung (Leukert-Wallach-Reaktion)

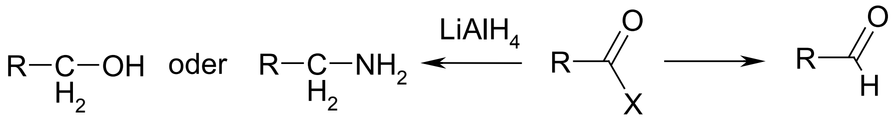


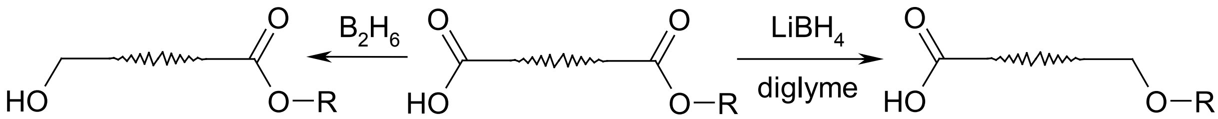
Eschweiler-Clarke



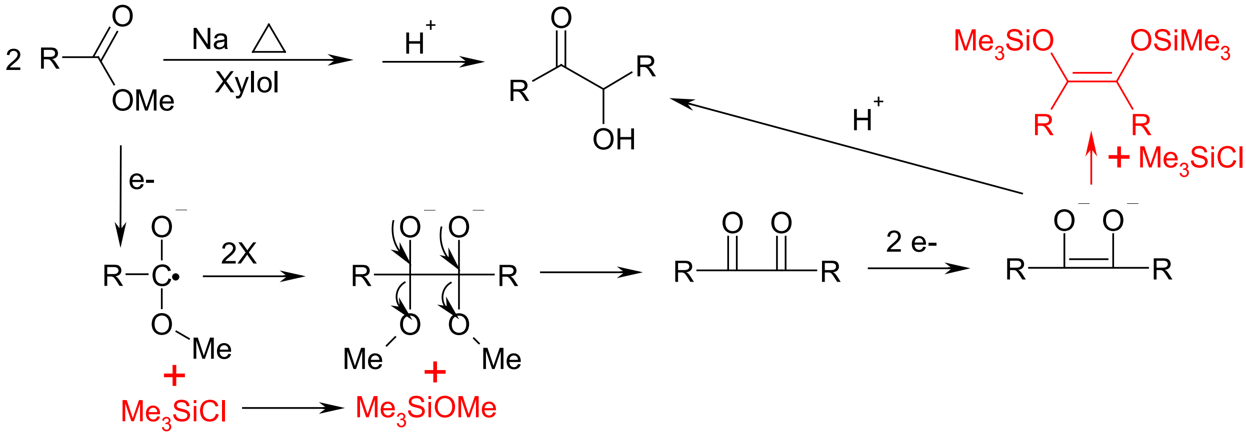


Reduktion zu Kohlenwasserstoffen: Wolf-Kishner-Reduktion, Clemensen –Reduktion, etc.





5.1.3.3 Carbonsäuren und Derivate

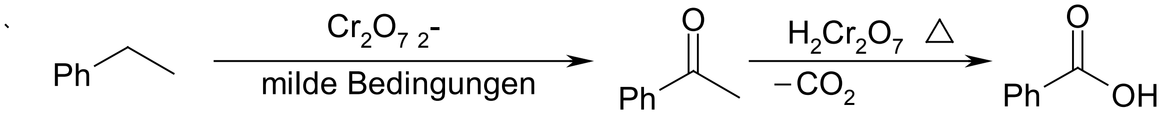


5.1.3.4 Acyloin-Kondensation

5.2 Oxidation

5.2.1 Alkane

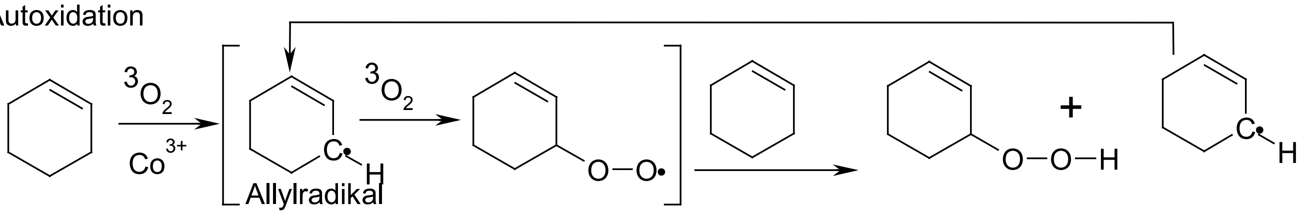
Chromsäure und Kaliumpermanganat



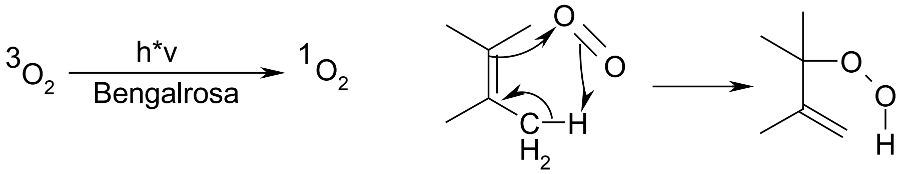
5.2.2 Alkene

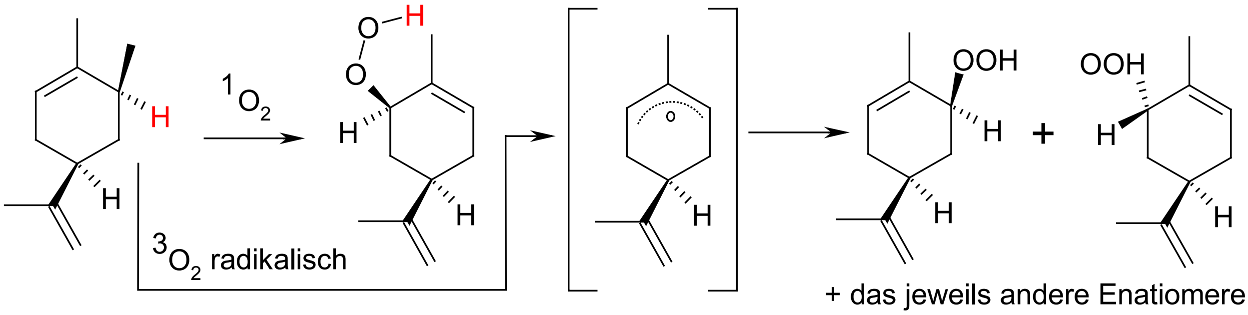
5.2.2.1 Autoxidation, Singulett-Sauerstoff

Autoxidation

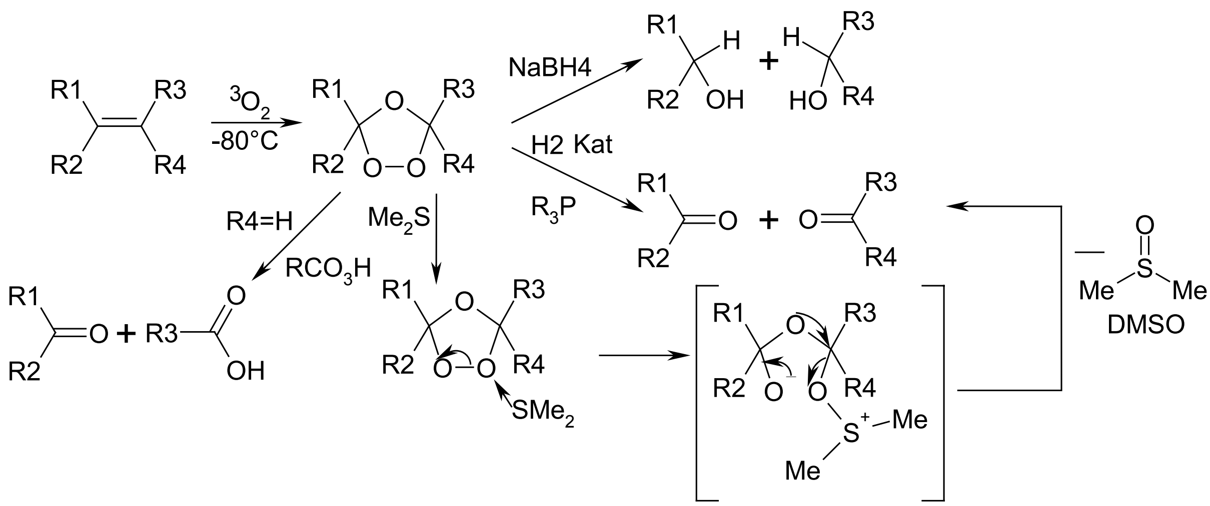


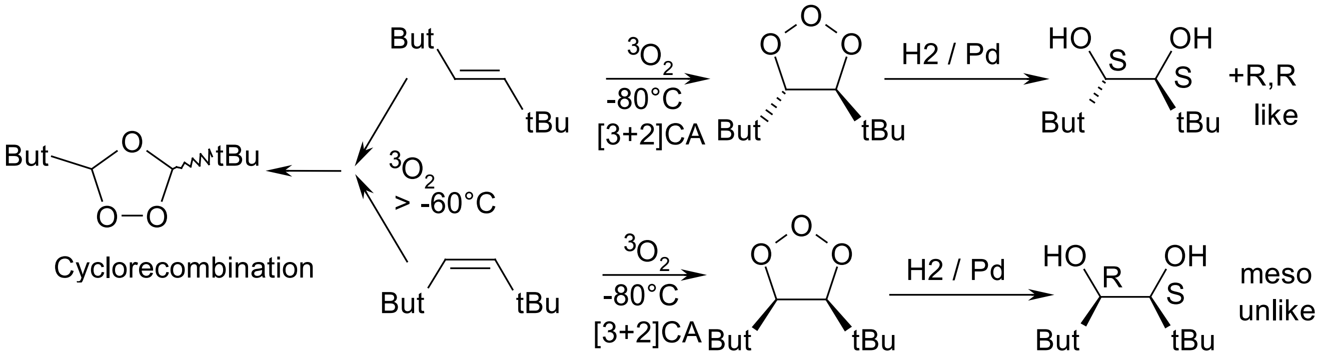
Sigulett-Sauerstoff



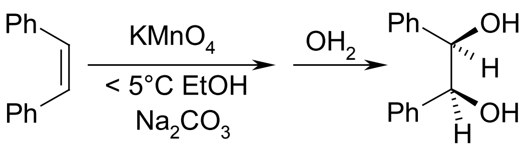


5.2.2.2 Ozonolyse

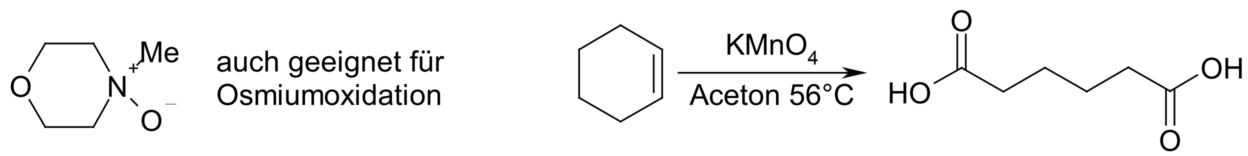




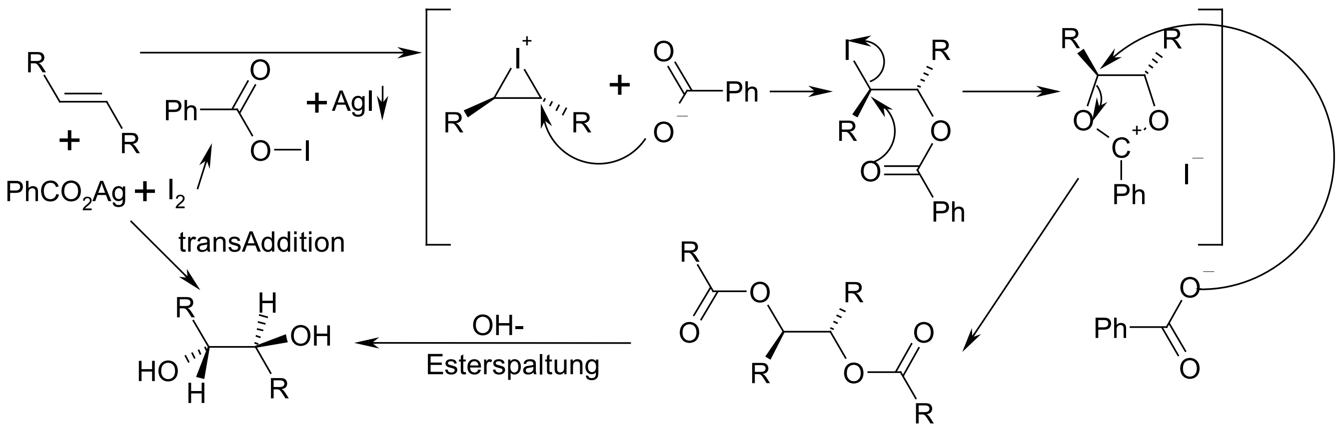
5.2.2.3 Diole (Glycol)



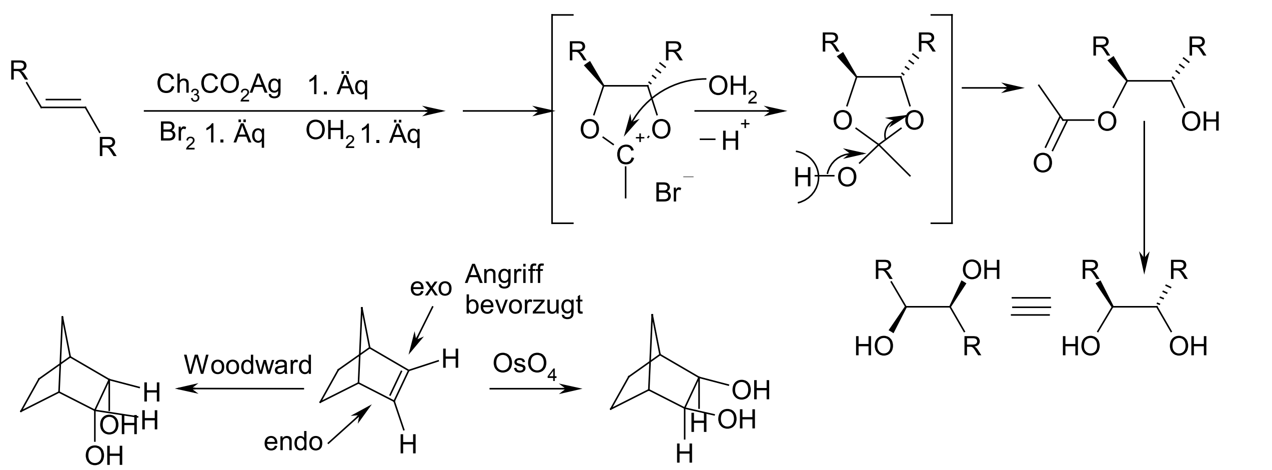
auch OsO_4 mit H_2O_2 oder tBu-O-O-H in OH^-



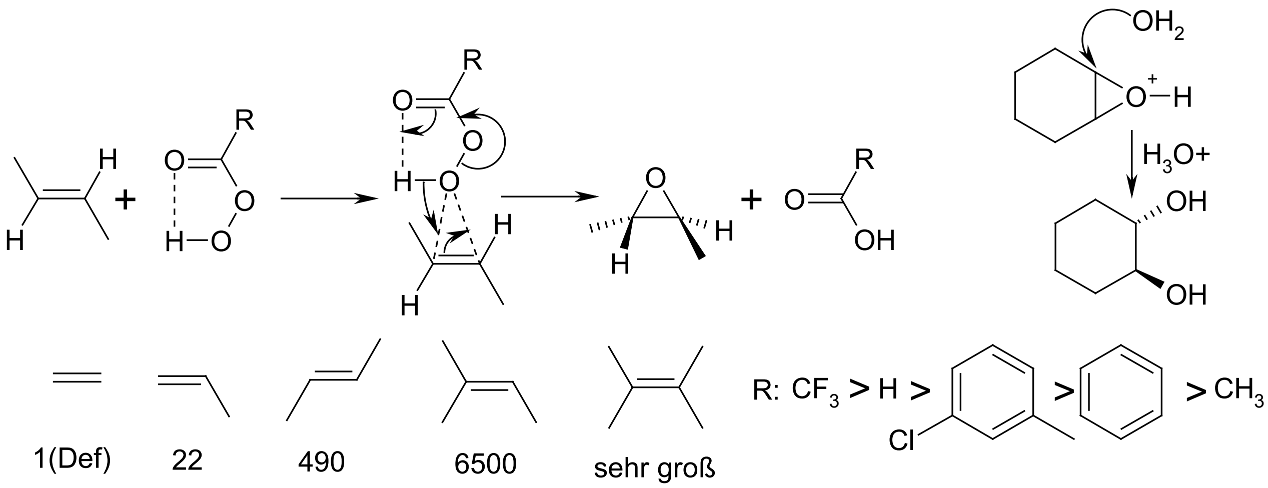
Prevost-Reaktion:



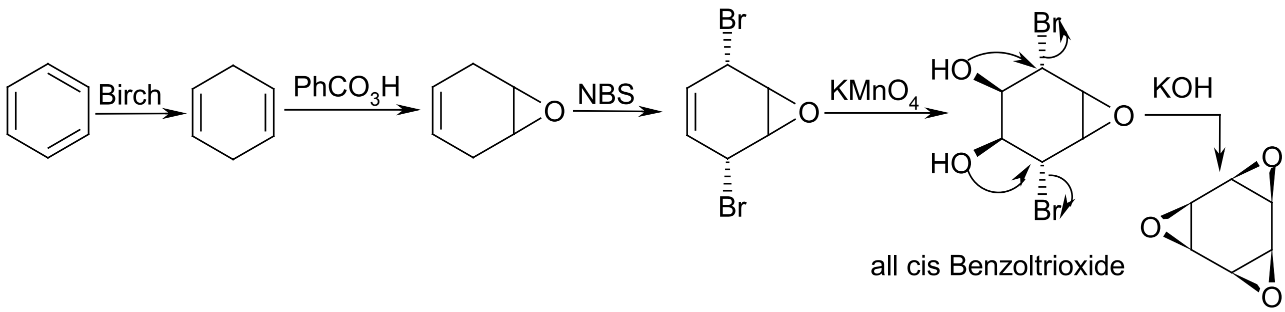
Woodward syn-Hydroxylierung



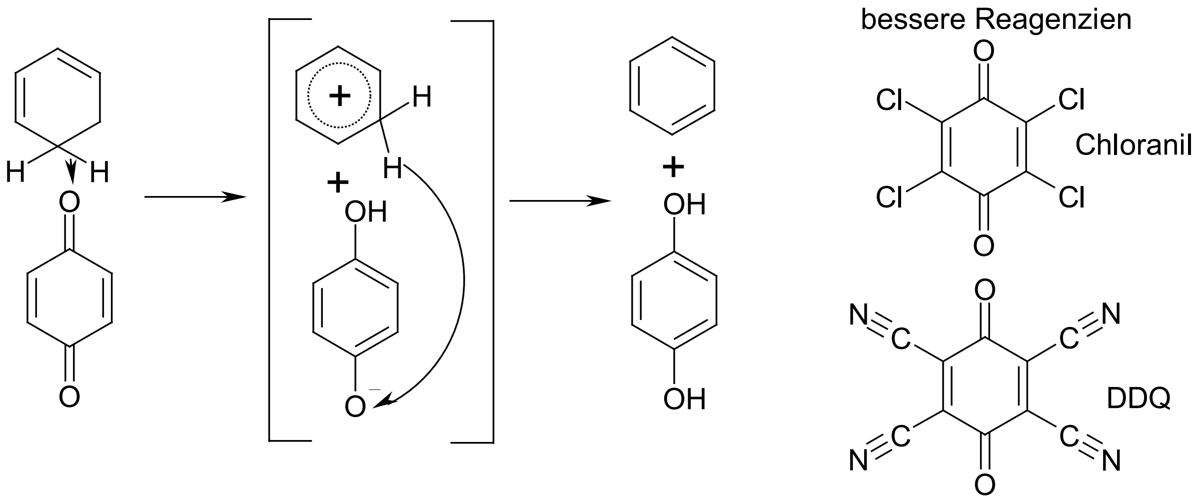
5.2.2.4 Epoxide



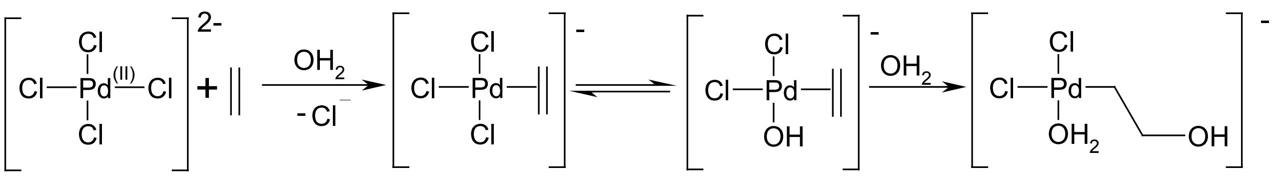
Prinzbach-Reaktion

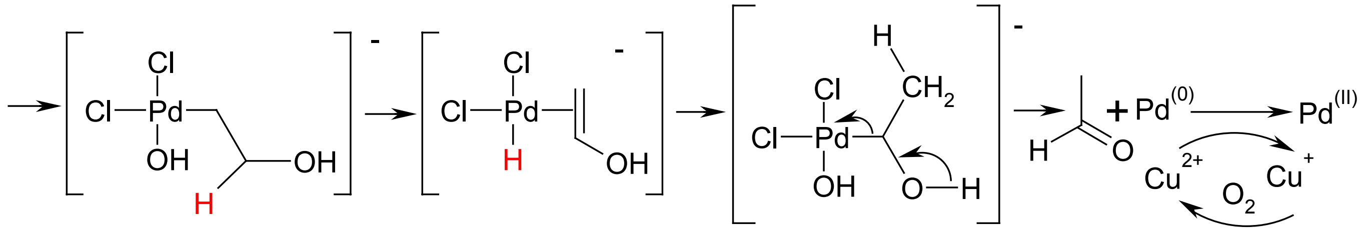


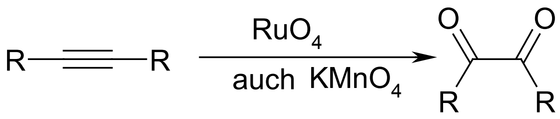
5.2.2.5 Dehydrierung mit Chinonen



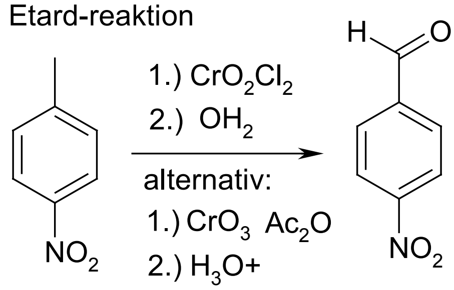
5.2.2.6 Oxidation mit Pd-Salzen (Wacker-Prozess)





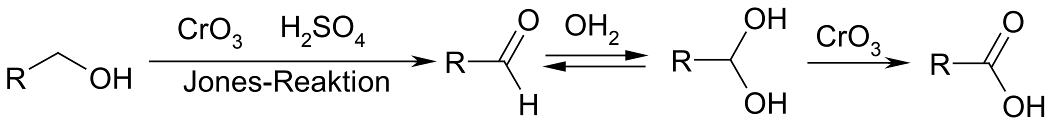


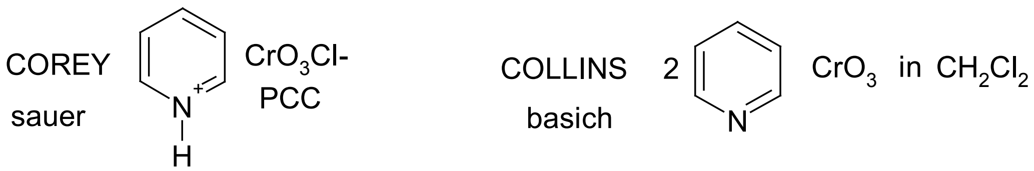
Etard-reaktion



5.2.3 Alkine

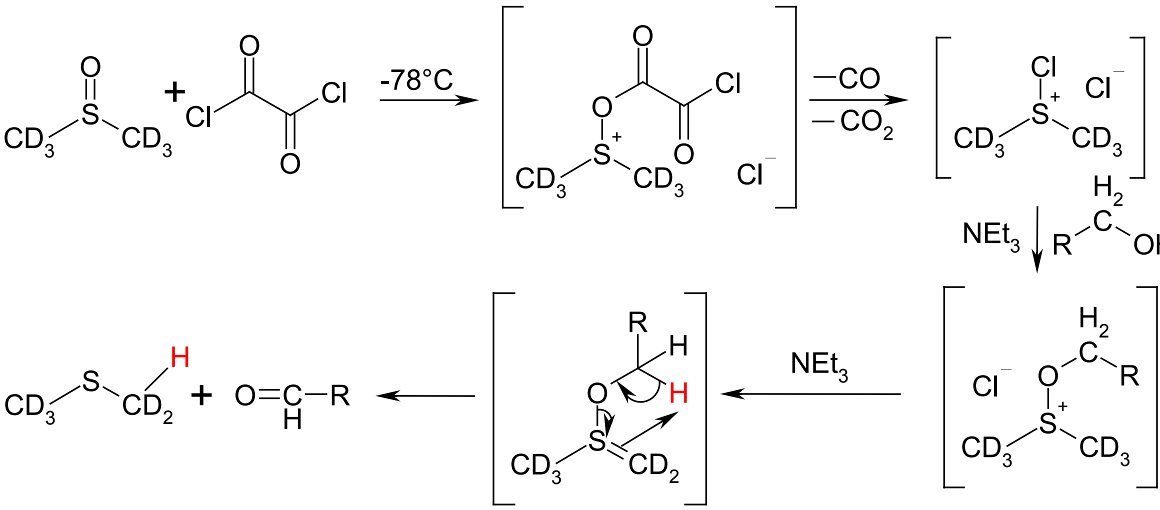
5.2.4 Alkohole



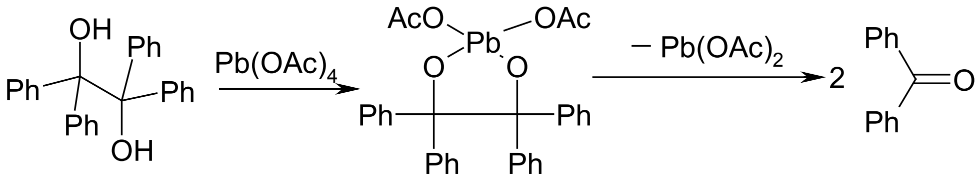


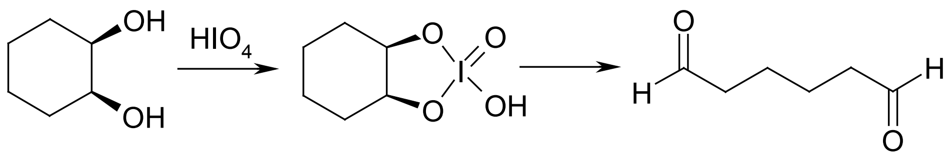
5.2.4.1 Chromsäure

5.2.4.2 Swern-Oxidation



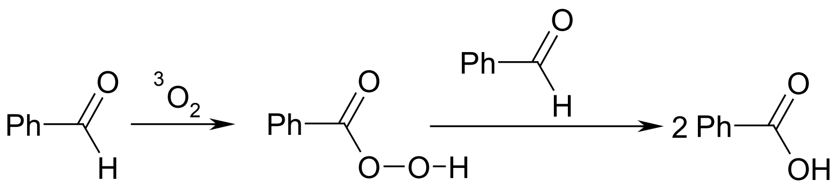
5.2.4.3 Glykolspaltung



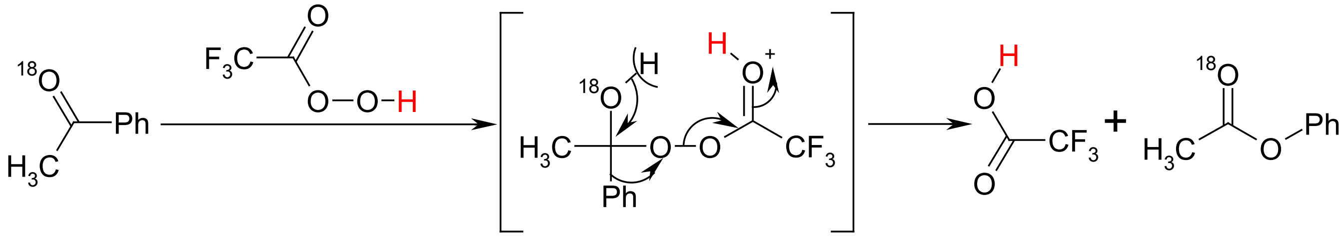


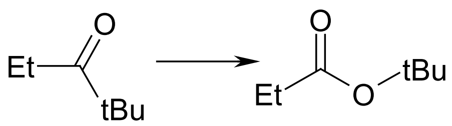
5.2.5 Aldehyde

Autoxidation



5.2.6 BAYER-VILLIGER-Oxidation





Wanderungstendenz
tert > H, Ph > sec > prim > Me

6 Carbonylverbindungen

6.1 Darstellung der Aldehyde und Ketone

6.1.1 Oxidation

$$R-CH=CH-CH_2-OH \xrightarrow[\text{Aceton;RT}]{MnO_2} R-CH=CH-CH=O$$

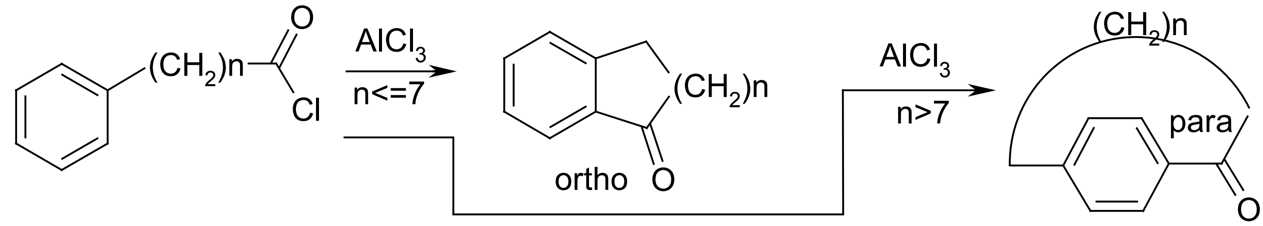
6.1.2 Reduktion

Rosenmund-Reaktion abgeschwächtes $LiAlH_4$

6.1.3 Aromatische Aldehyde und Ketone

6.1.3.1 Friedel-Crafts-Alkylierung

Intramolekulare Variante:

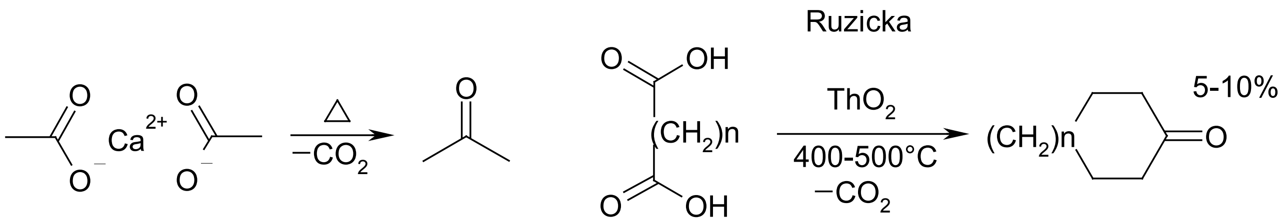


6.1.3.2 Hydrolyse geminaler Dihalogenide

$$Ar-CH_3 \xrightarrow[Cl_2]{h*\nu} Ar-CHCl_2 \xrightarrow[\vee OH^-]{H_3O^+} Ar-CH=O$$

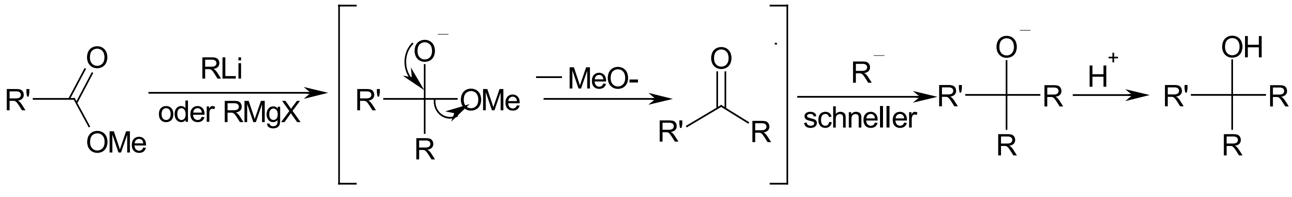
6.1.4 Thermische Decarboxylierung von Carbonsäuresalzen

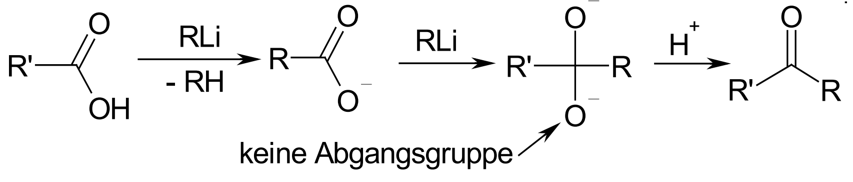
Ruzicka-Synthese:Wird wegen des ThO_2 kaum angewandt.



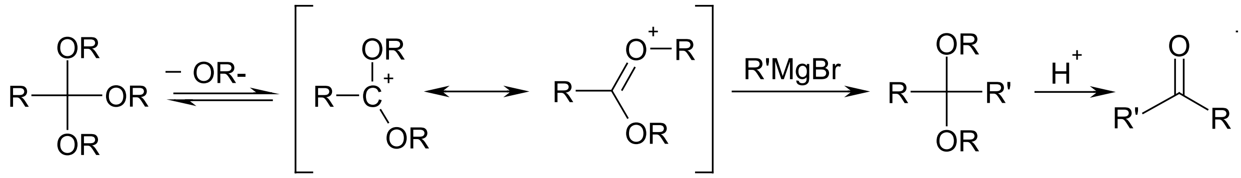
6.1.5 Metallorganische Synthesen

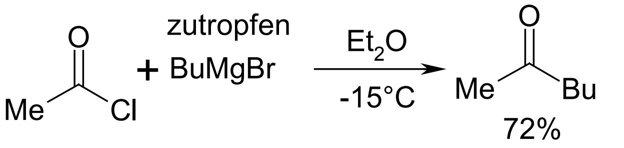
6.1.5.1 Organolithiumverbindungen

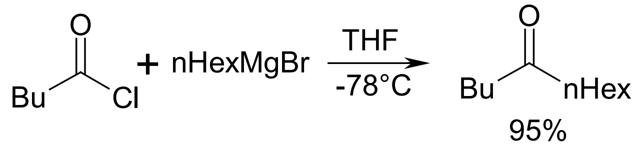




6.1.5.2 Grignard-Reagenzien

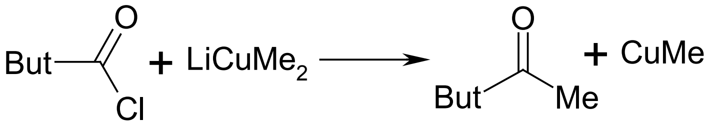


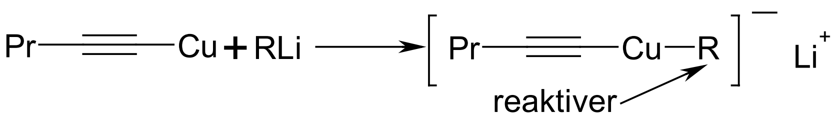




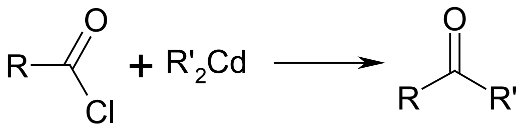
6.1.5.3 Organocuprate

$$2\mathrm{RLi} + \overset{\mathrm{I}}{\mathrm{Cu}}\,\mathrm{I} \rightarrow [\mathrm{R}-\mathrm{Cu}-\mathrm{R}]^{-}\,\mathrm{Li}^{+}$$

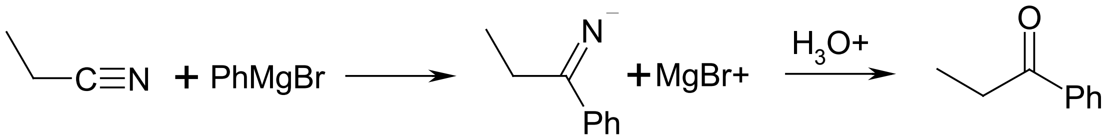




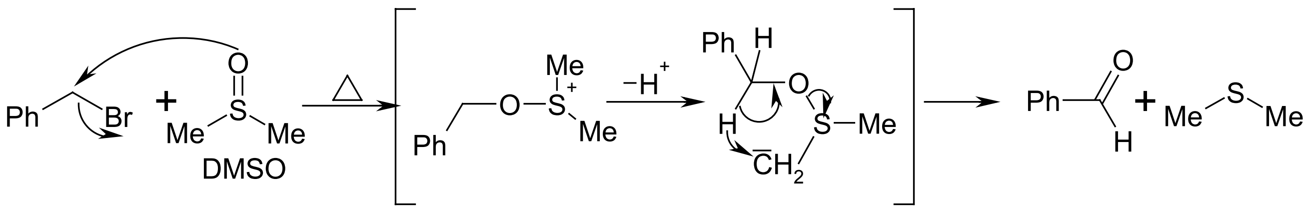
6.1.5.4 Organocadmium



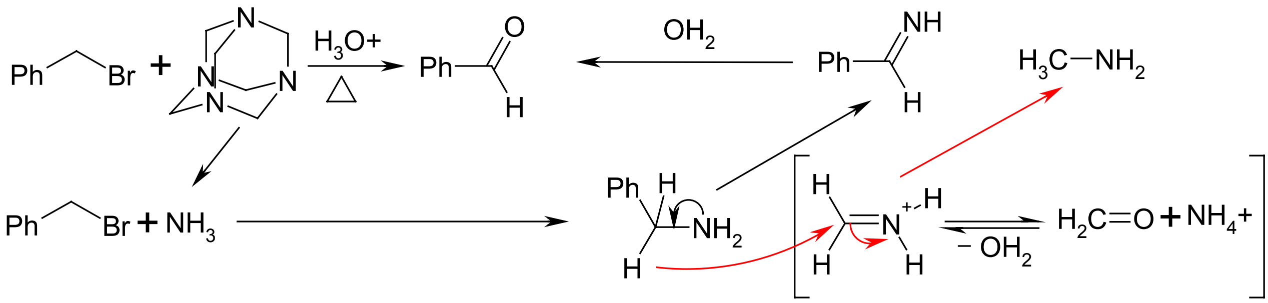
6.1.5.5 Nitrile + Grignard



6.1.6 Kornblum-Oxidation

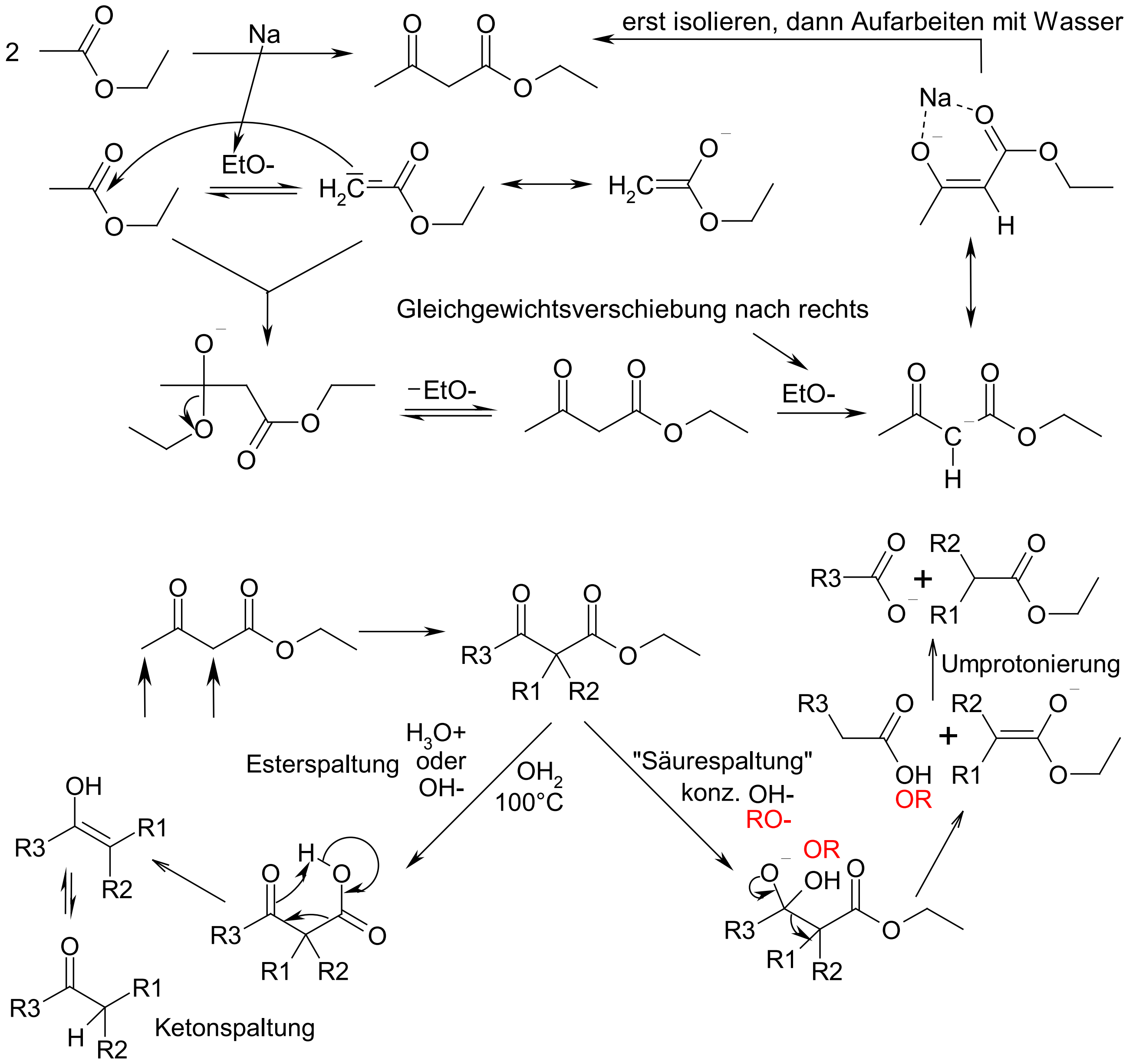


6.1.7 Sommelet-Reaktion

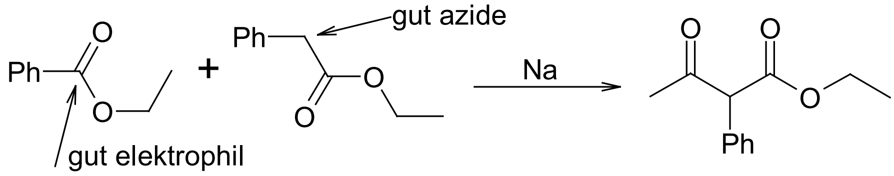


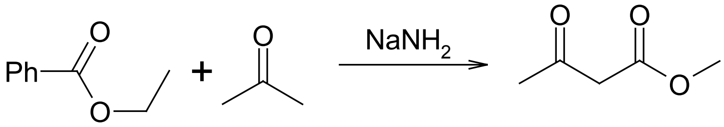
6.1.8 Esterkondensation (Claisen-Kondensation)

6.1.8.1 Mechanismus

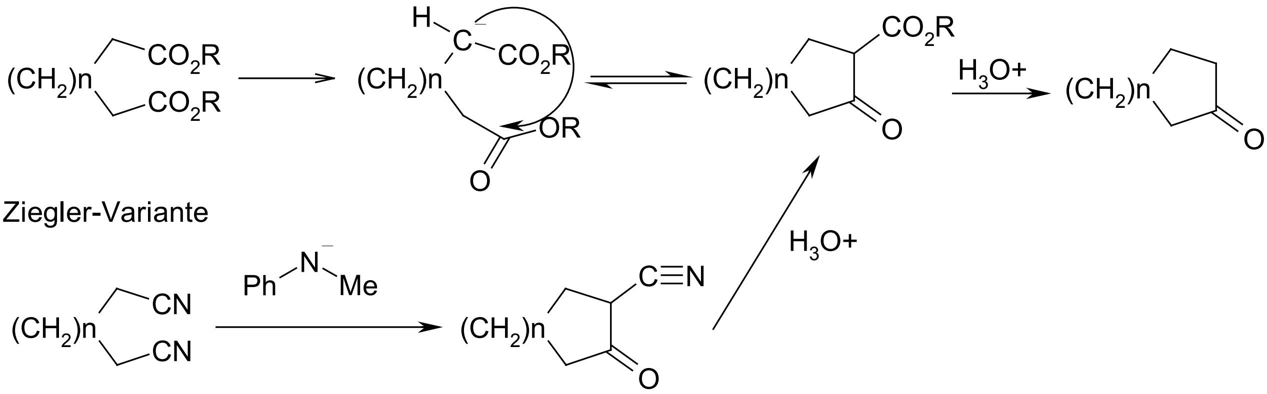


6.1.8.2 Verschiedene Ester



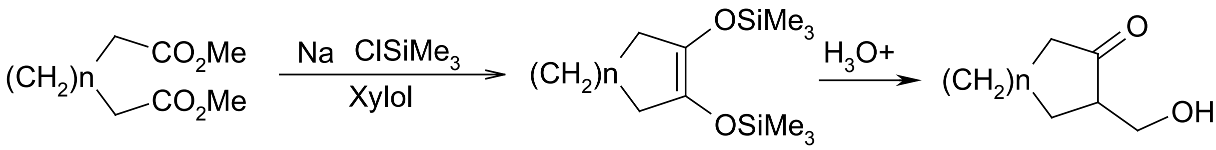


6.1.8.3 Dieckmann-Variante(Intramolekular)



6.1.9 Acyloin-Kondensation

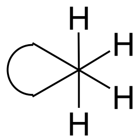
(siehe auch Redox!)



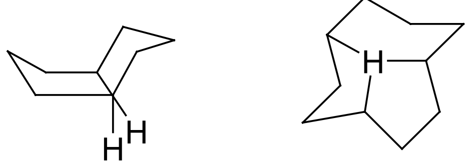
Ringbildungstendenz

1. Bayer-Spannung: ideal = 109,5° Tetraederwinkel
   Cyclopropan 60° Cyclobutan 90° 5,6,7-Ringe fast ideal

2. Pitzer-Spannung, Konformative Spannung
   5,6,7-Ringe fast ideal



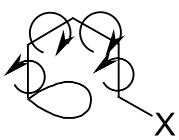
3. Transannulare Wechselwikung
   (treten von 8 bis 12 auf)



4. Entropie
   Dreiringe

3 Hauptkonfigurationen je Bindung
→1/9 nur nutzbar (1 von 9)
→Dreiringe bilden sich leichter

Vierringe

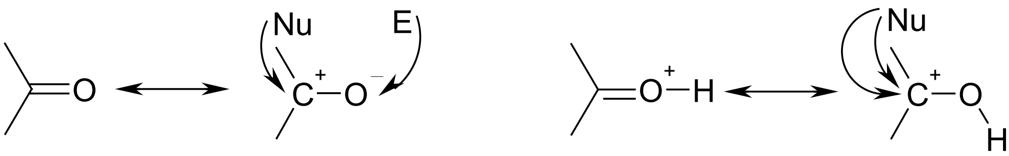


1/81 statistisch
energetisch noch
ungünstiger

6.2 Bindungzustand

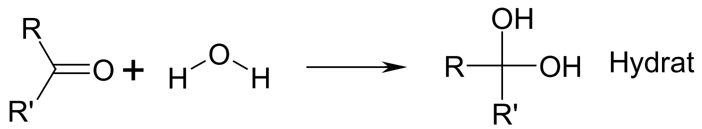
C-C : 83 C=C : 146 →π = 63

C-O : 86 C=O : 175 →π = 89 C=O meist(nicht immer) günstiger

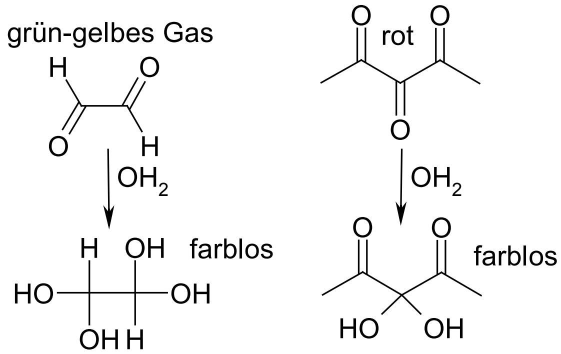


6.3 Reaktionen

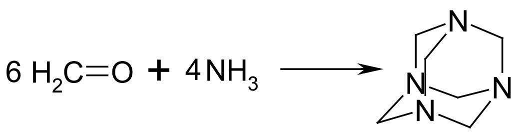
6.3.1 Nucleophile Addition von H-X

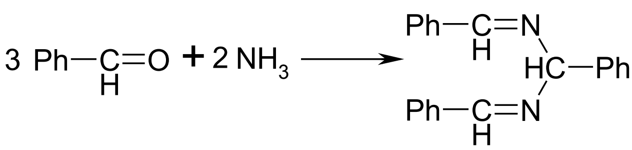


R	R'	%Hydrat
H	H	>98
H	Me	64
H	Et	57
Me	Me	<1
H	CCl_3	100
Me	CH_2Br	57

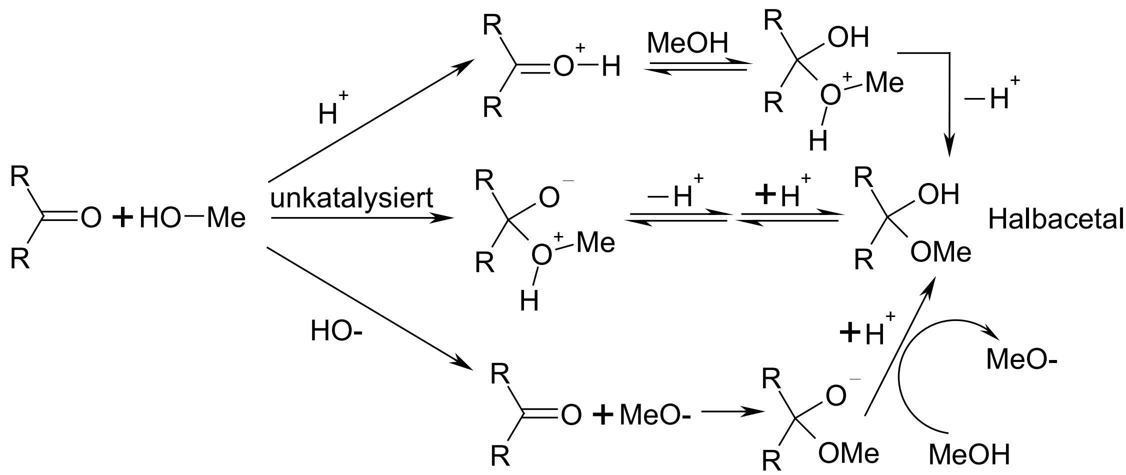


6.3.2 Addition von Ammoniak

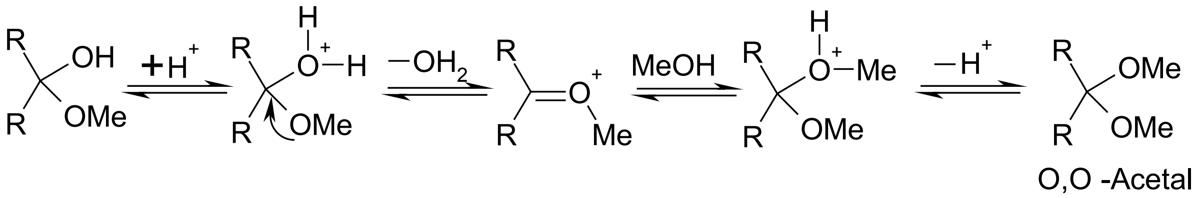


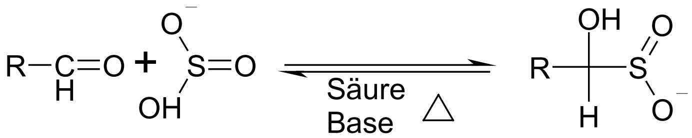


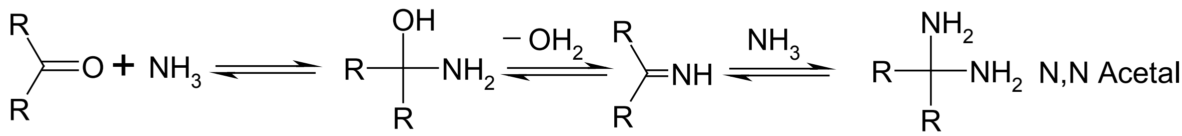
6.3.3 Addition von Alkoholen



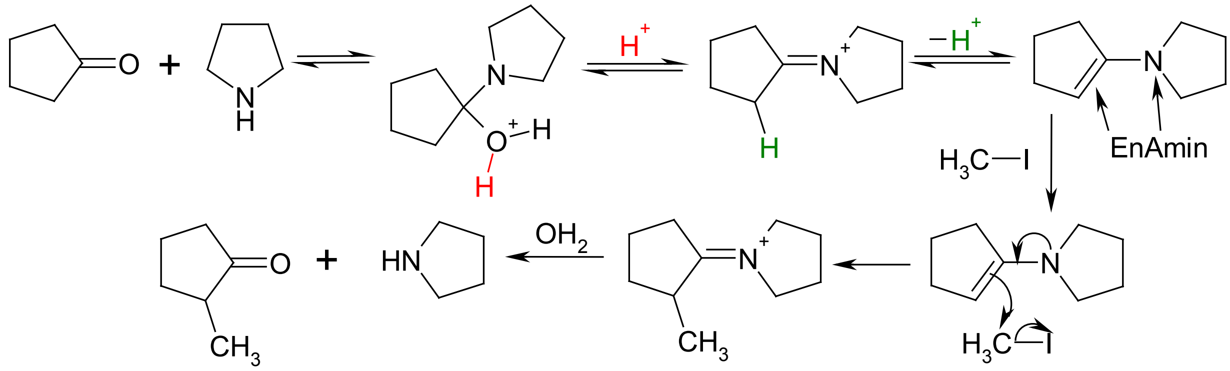
Weiterreaktion ist säurekatalysiert:

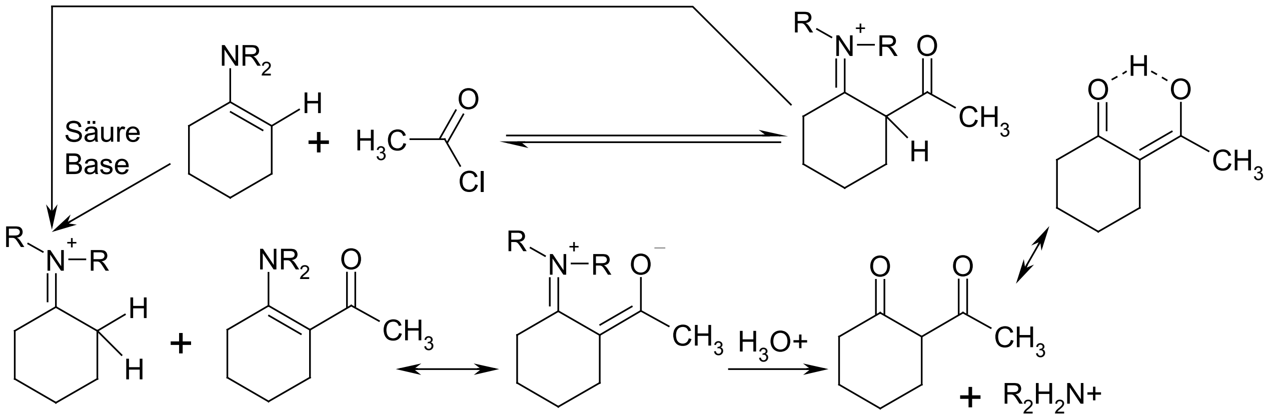


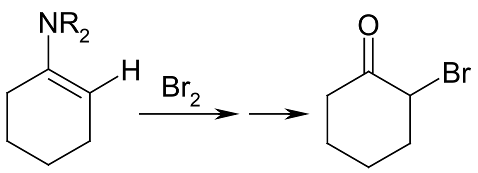


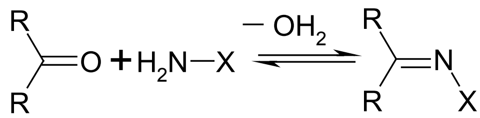


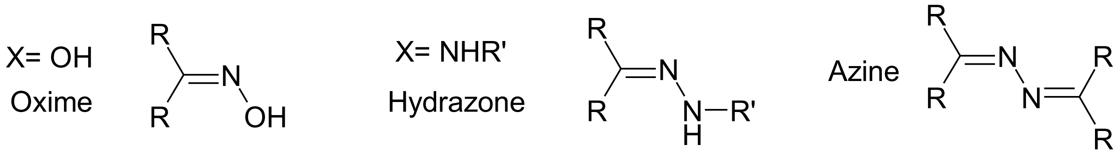
6.3.4 Enamine





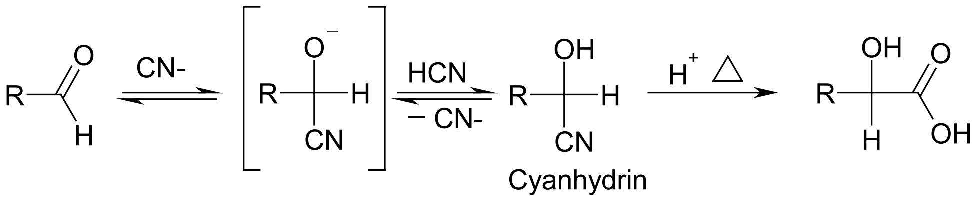


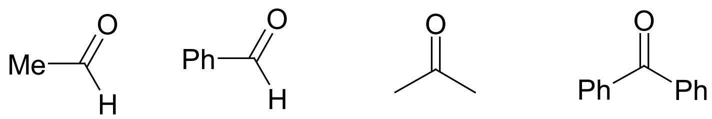




6.3.5 Addition von C-H aciden Verbindungen

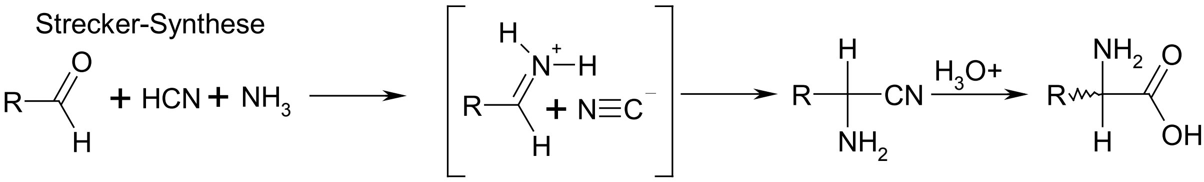
6.3.5.1 Cyanid und Strecker-Synthese



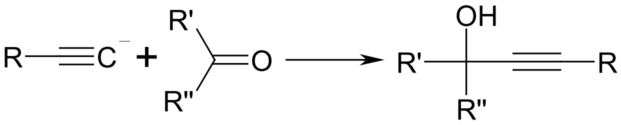


% Cyanhydrin 94 84 34 0

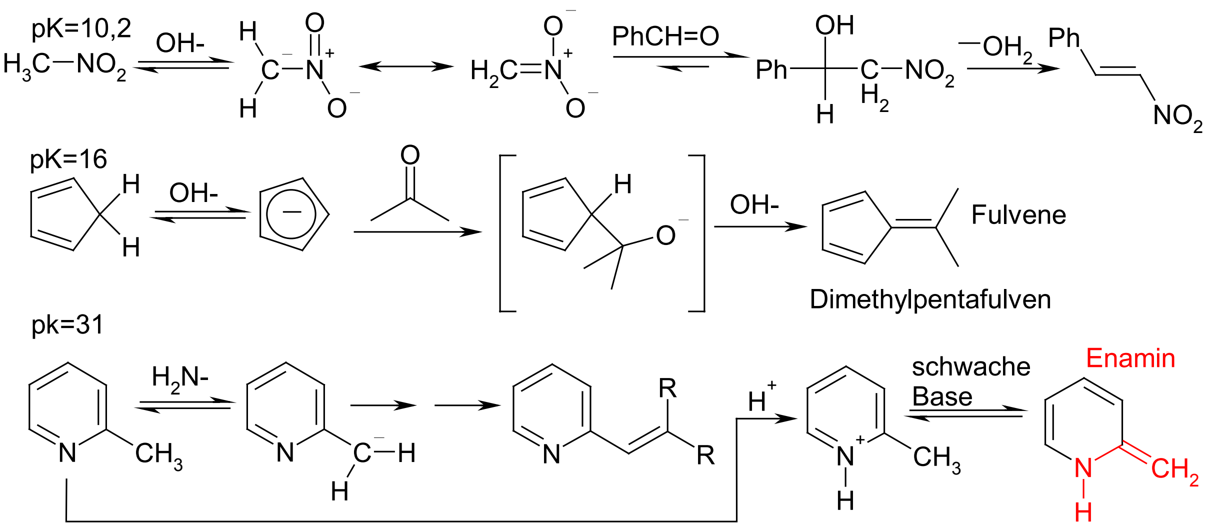
Strecker-Synthese



6.3.5.2 Ethine

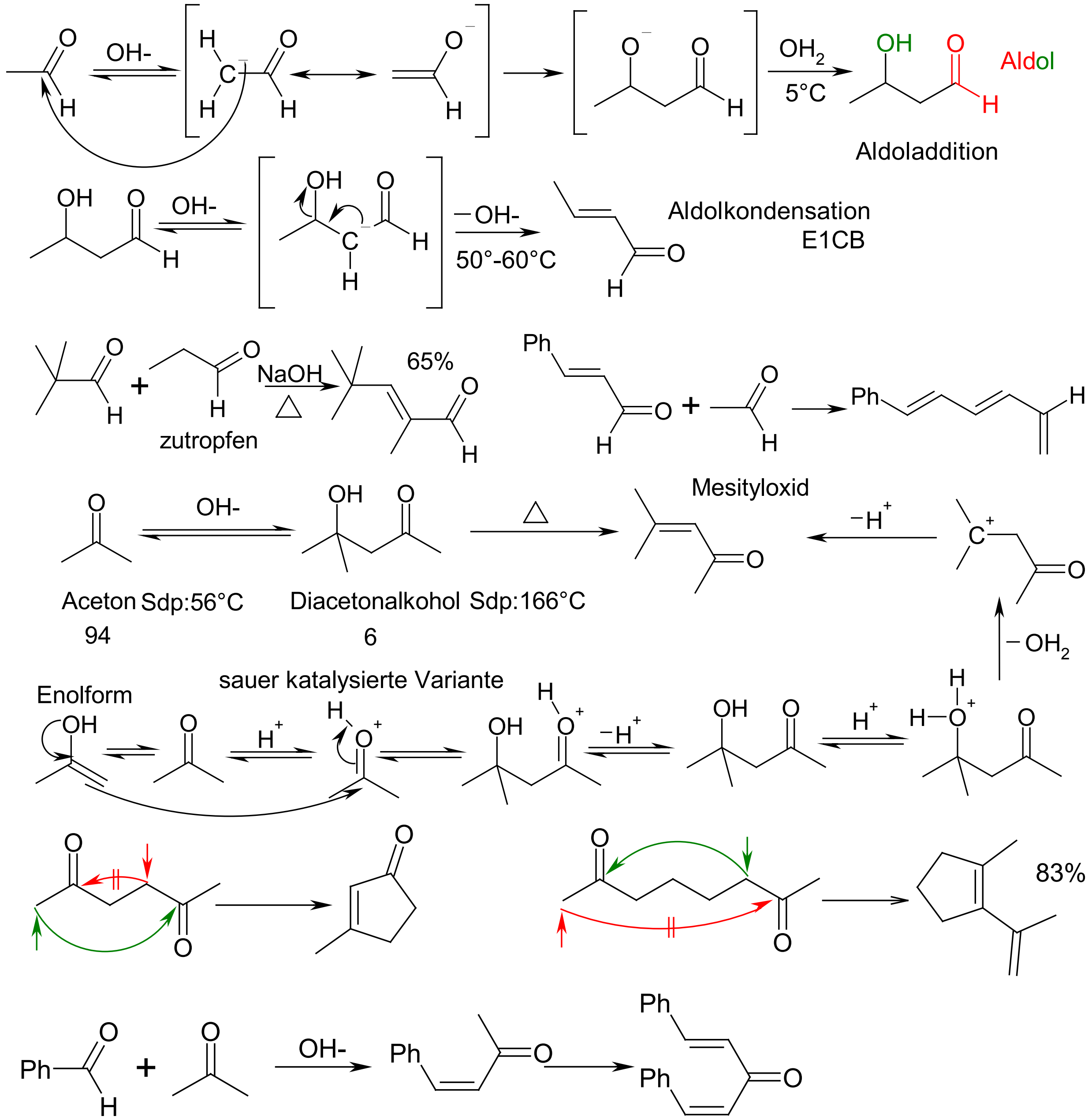


6.3.5.3 Nitroalkane

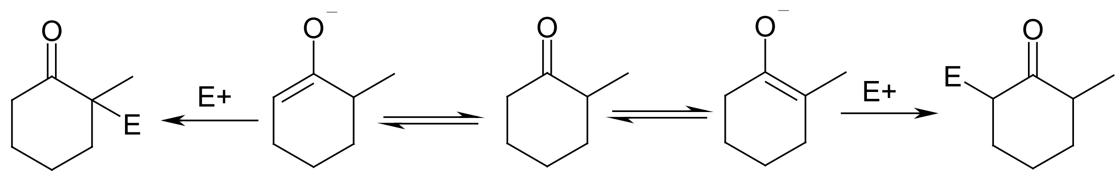


6.3.6 Addition von Enolaten an Aldehyde und Ketone

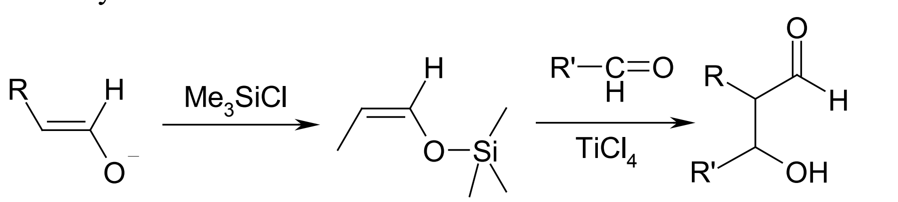
6.3.6.1 Aldoladdition, Aldolkondensation



Gleichgewichtsprobleme

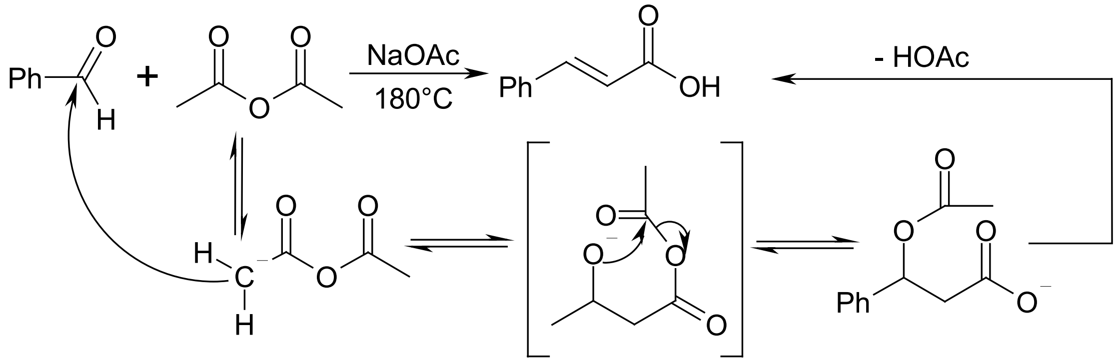


Mukaiyama-Variante

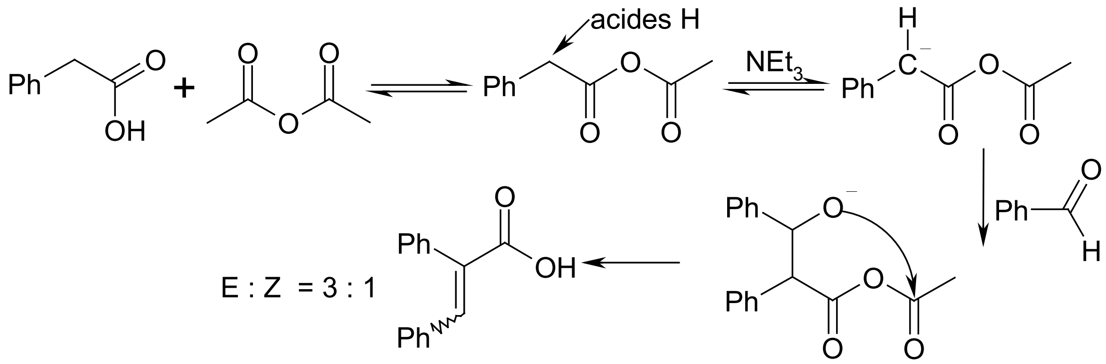


6.3.6.2 Perkin-Synthese

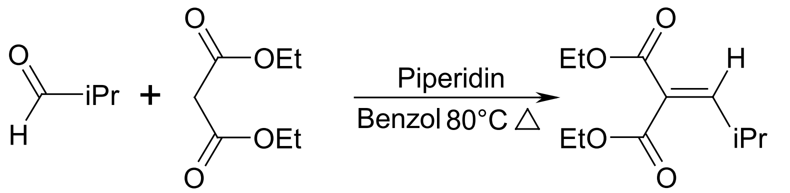
historisch:



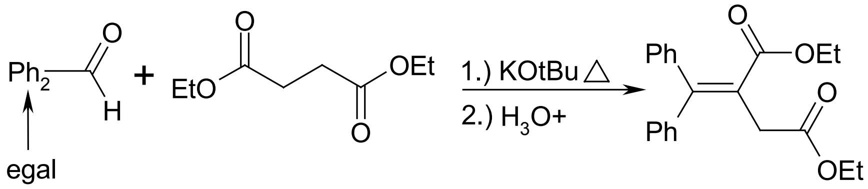
modern



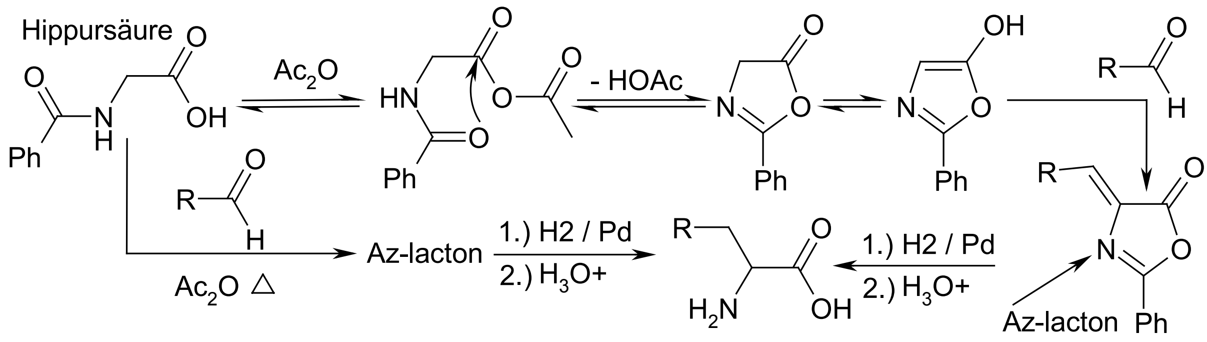
6.3.6.3 Knoevenagel-Kondensation



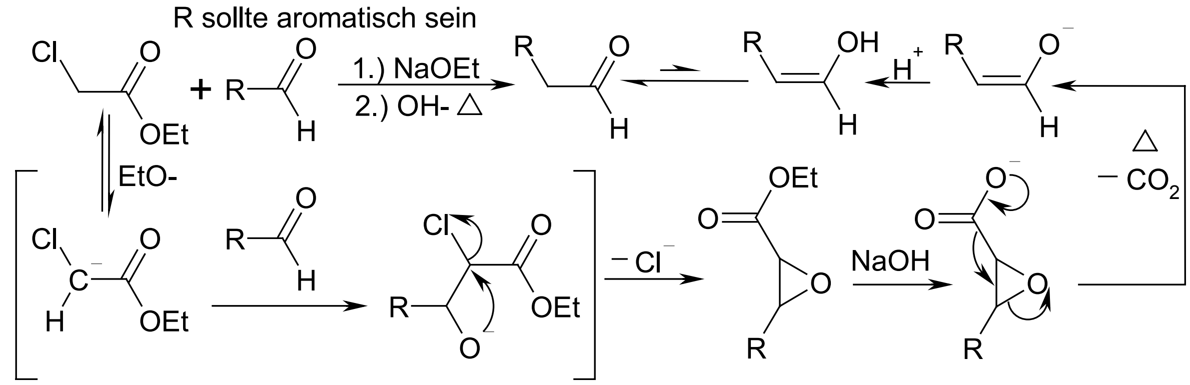
6.3.6.4 Stobbe-Kondensation



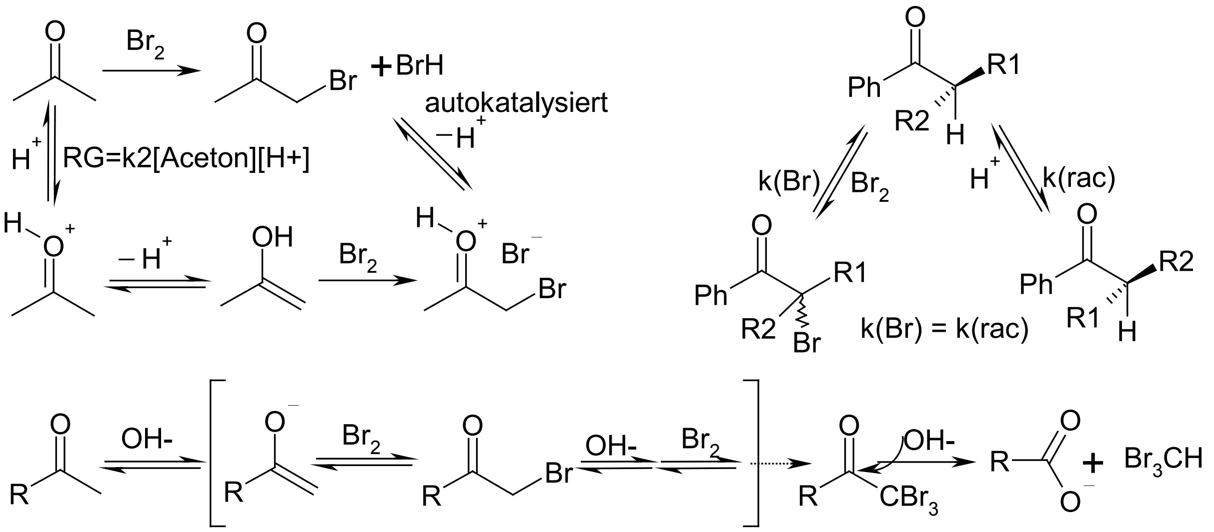
6.3.6.5 Erlenmeyer-Azlacton-Synthese



6.3.6.6 Darzens-Glycinester-Synthese

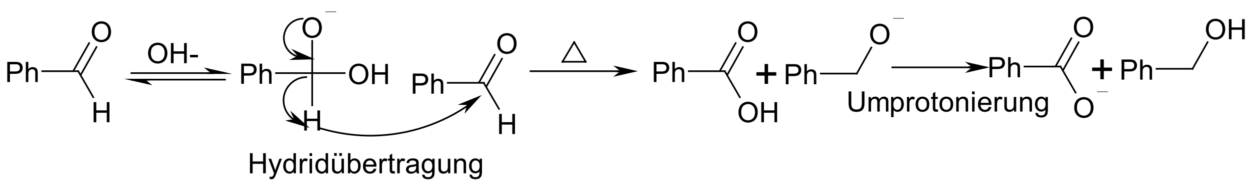


6.3.7 α-Halogenierung von Aldehyden und Ketonen



6.3.8 Redoxreaktionen

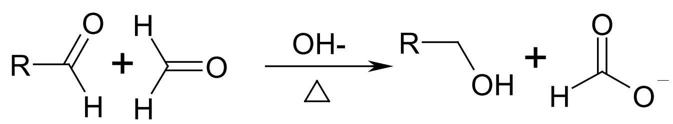
6.3.8.1 Cannizzaro-Reaktion (Dispropotionierung)



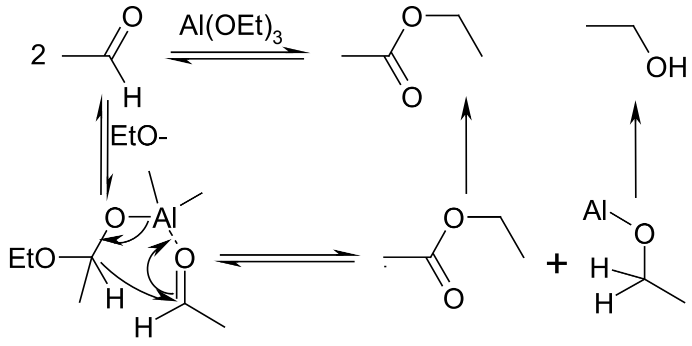
es darf kein α-Proton vorhanden sei, sonst kommt es zu Nebenreaktionen (Aldol...) Daher meist nur Aryl und tertiäre Reste.

gemischte Cannizzaro:

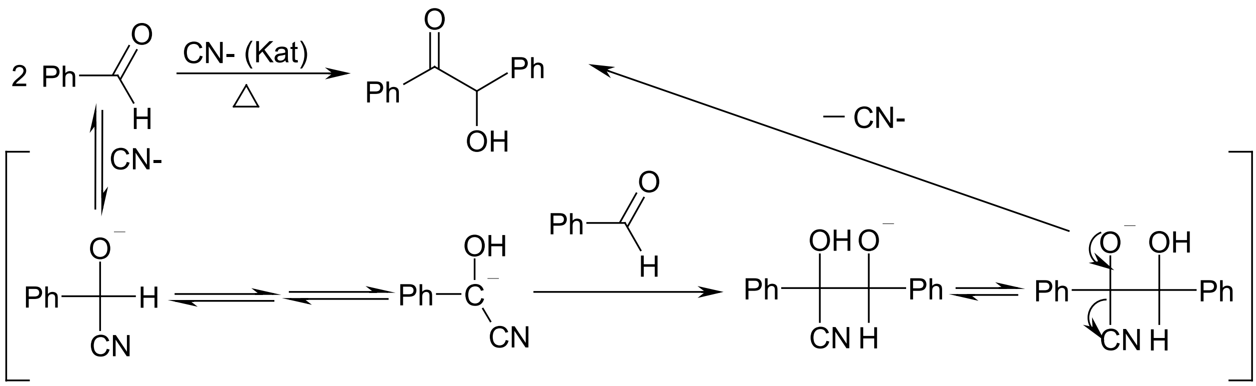
R beliebig



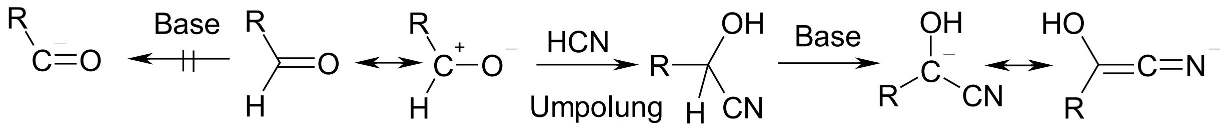
6.3.8.2 Tischtschenko-Reaktion (Intramolekulare-Variante)

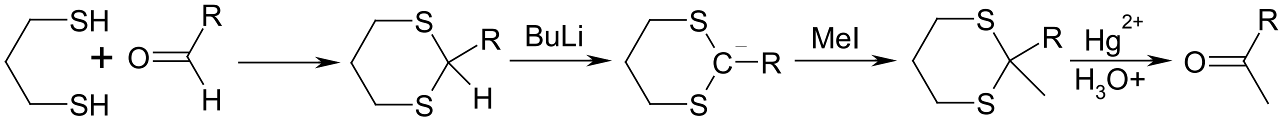


6.3.8.3 Benzoin-Kondensation

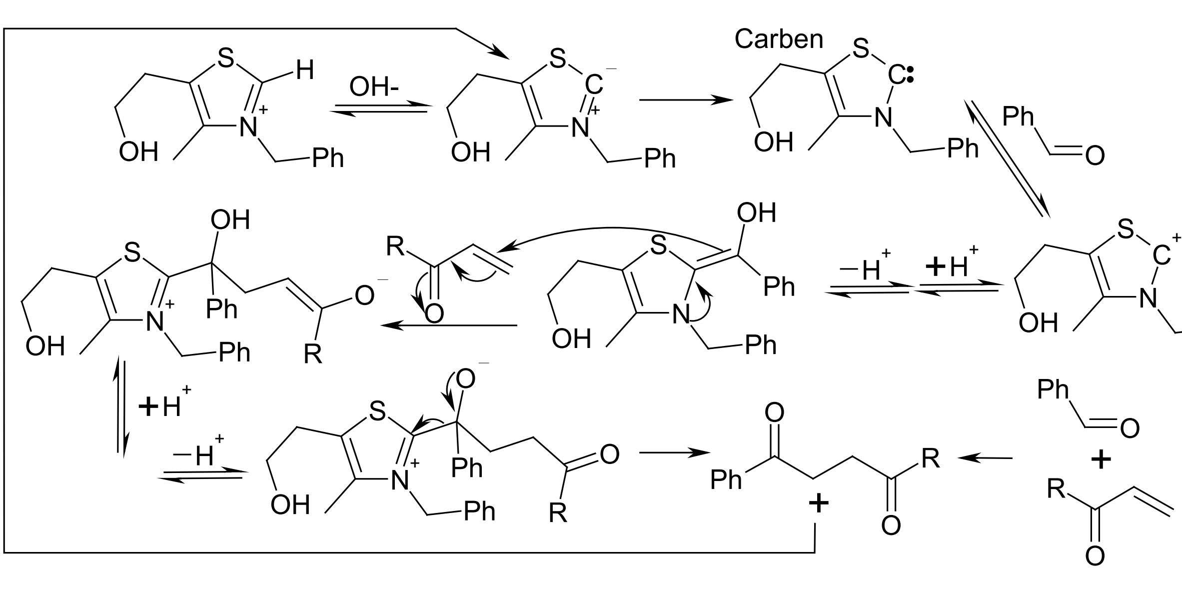


allgemein

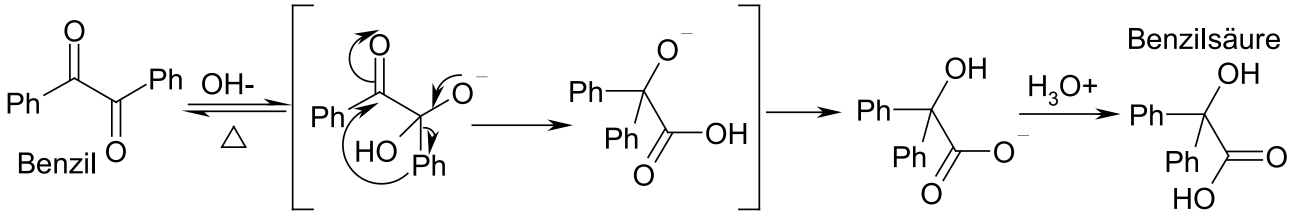




Laborvariante für Vitamin B1=Thiamin Synthese



6.3.8.4 Benzilsäure-Umlagerung



6.3.9 Reaktionen mit metallorganischen Verbindungen

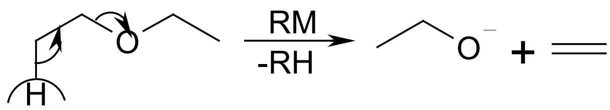
6.3.9.1 Allgemeines

$R-M \rightleftharpoons R^{-}\ M^{+}$ je elektropostiver M, desto reaktiver

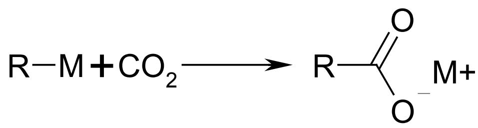
K >Na >Li >Mg >Zn>Cd >Sn >Hg

EN 0,8 0,9 1,0 1,2 1,4 1,7 1,72 1,9

EN <= 1.0 Etherspaltung



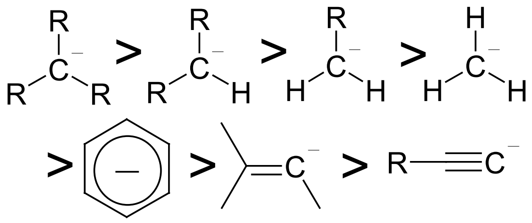
EN <= 1,5 Reaktion mit CO_2



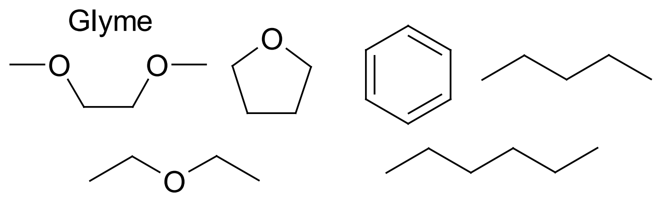
EN <= 1.7 Reaktion mit H_2O

$R-M+H_2O \rightarrow R-H+M^{+}+OH^{-}$ Sn und Hg sind Wasserstabil

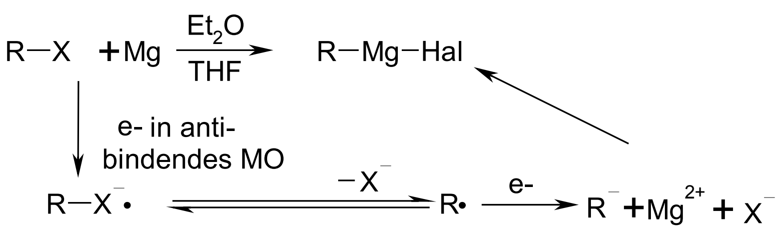
Reaktivität von R



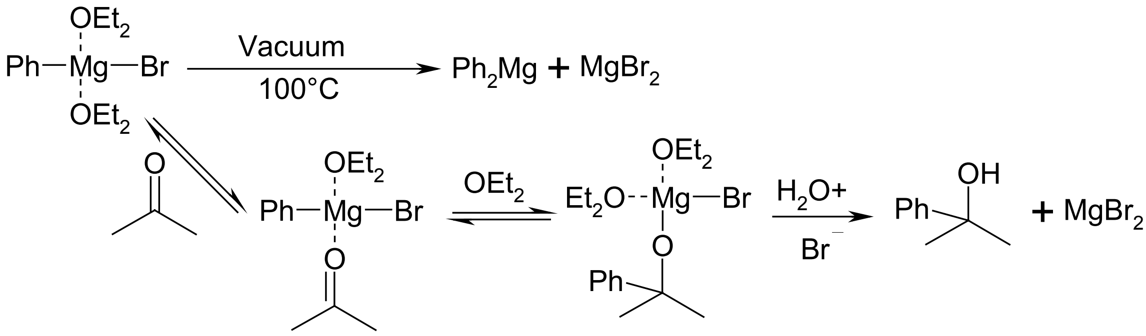
Lösemittel eingeschränkt



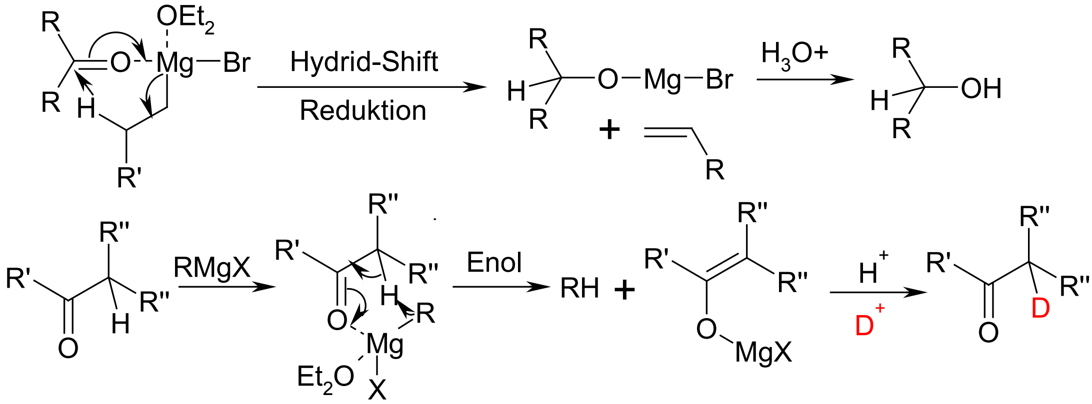
6.3.9.2 Grignard-Verbindungen

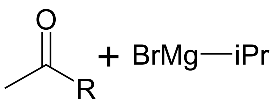


Schlenk-Gleichgewicht $2\ R-Mg-Cl \rightleftharpoons R_2Mg + MgCl_2$

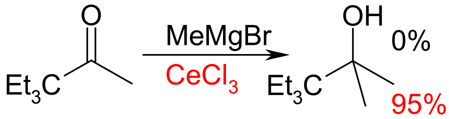


Nebenreaktionen

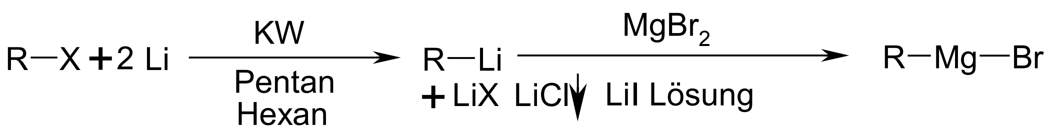


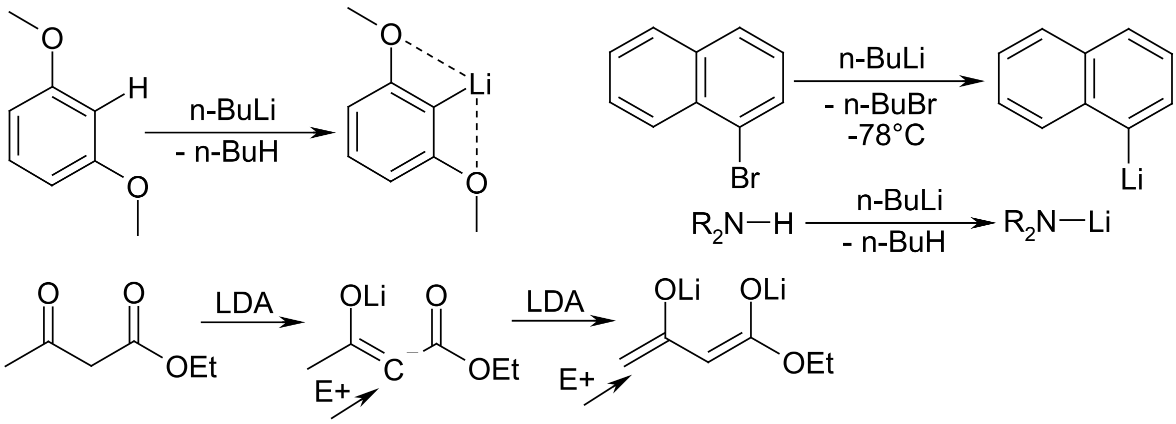


R	Add	Red	Enol
Me	61	4	35
tBu	5	17	78



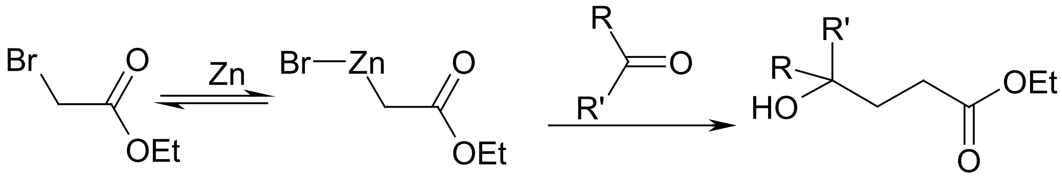
6.3.9.3 Lithiumorganische Verbindungen



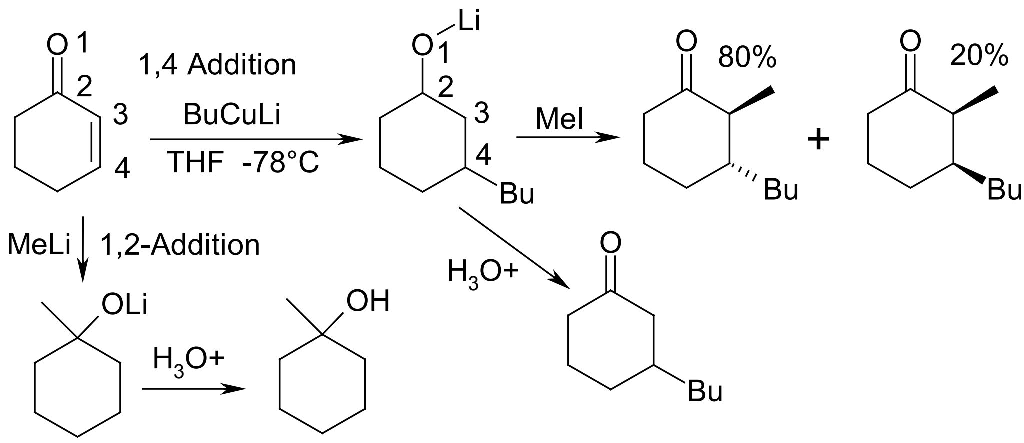


6.3.9.4 Zinkorganische Verbindungen

Reformatsky-Reaktion

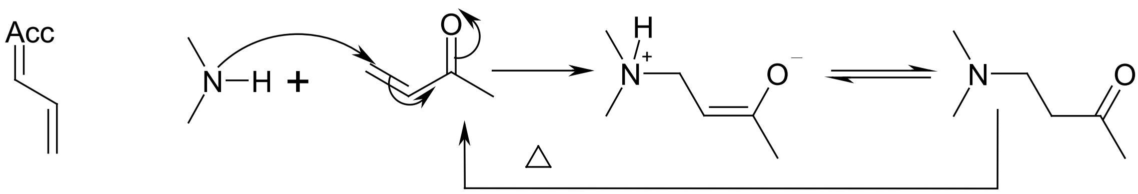


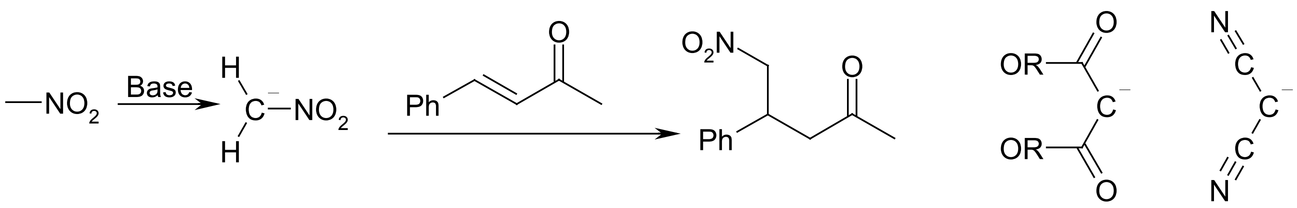
6.3.9.5 Kupferorganische Verbindungen (Organocuprate)



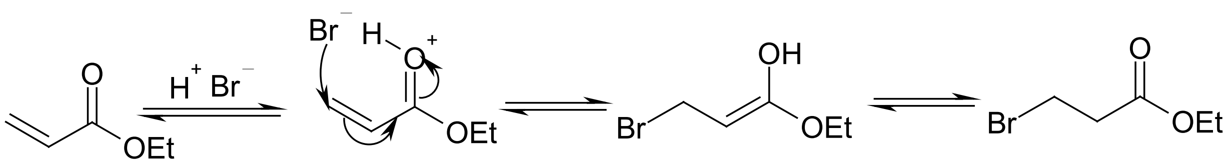
6.3.10 Addition an Michael-Systeme

6.3.10.1 Mechanismus der Michael-Addition

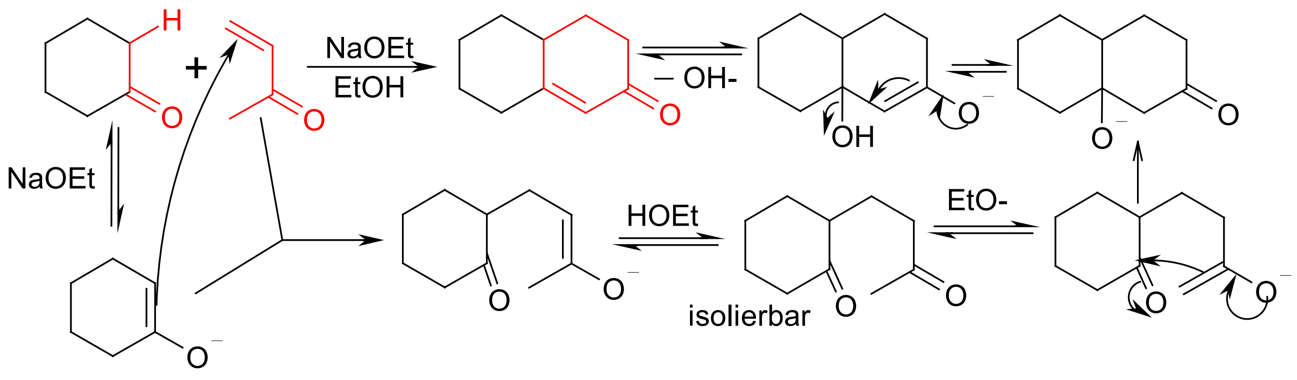




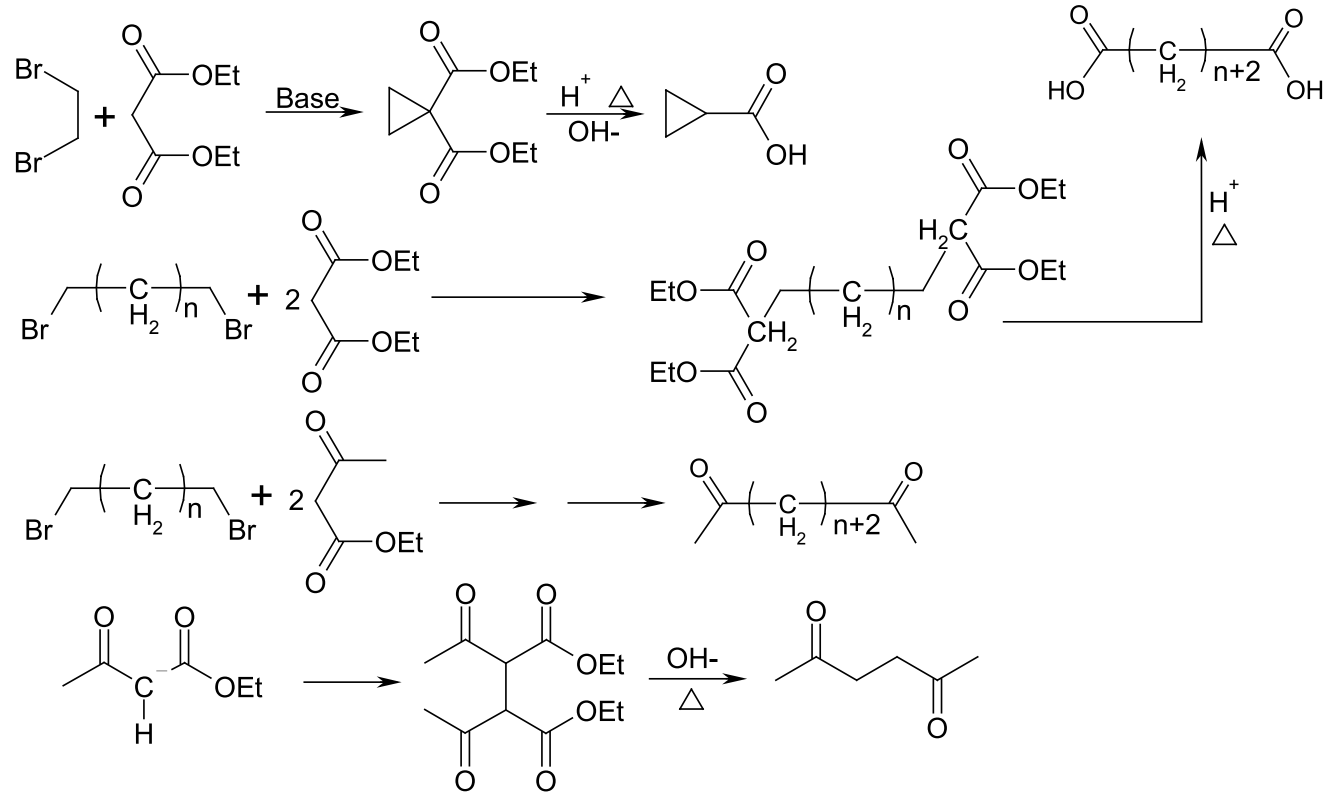
6.3.10.2 sauer katalysiert



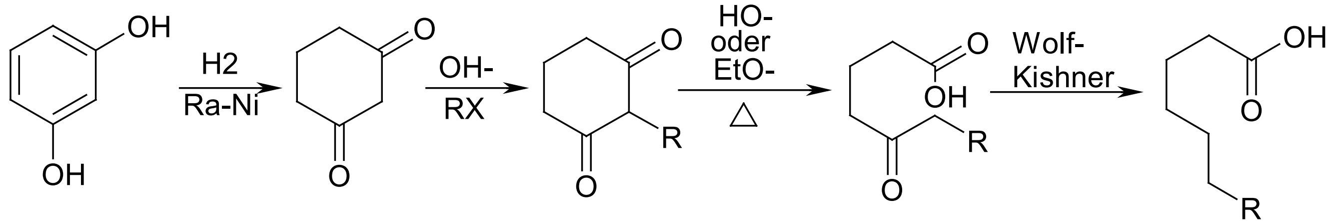
6.3.10.3 Robinson –Anellierung



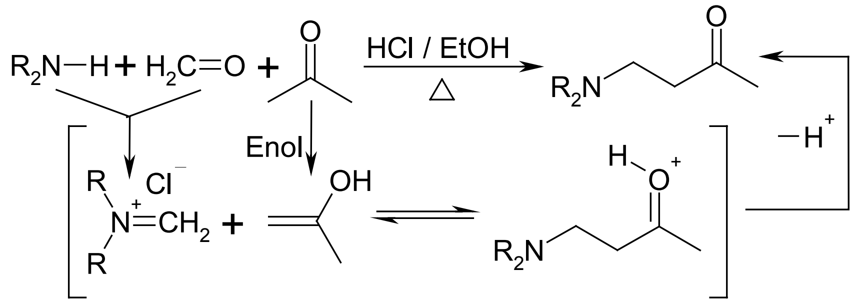
6.3.11 Alkylierung und Acylierung

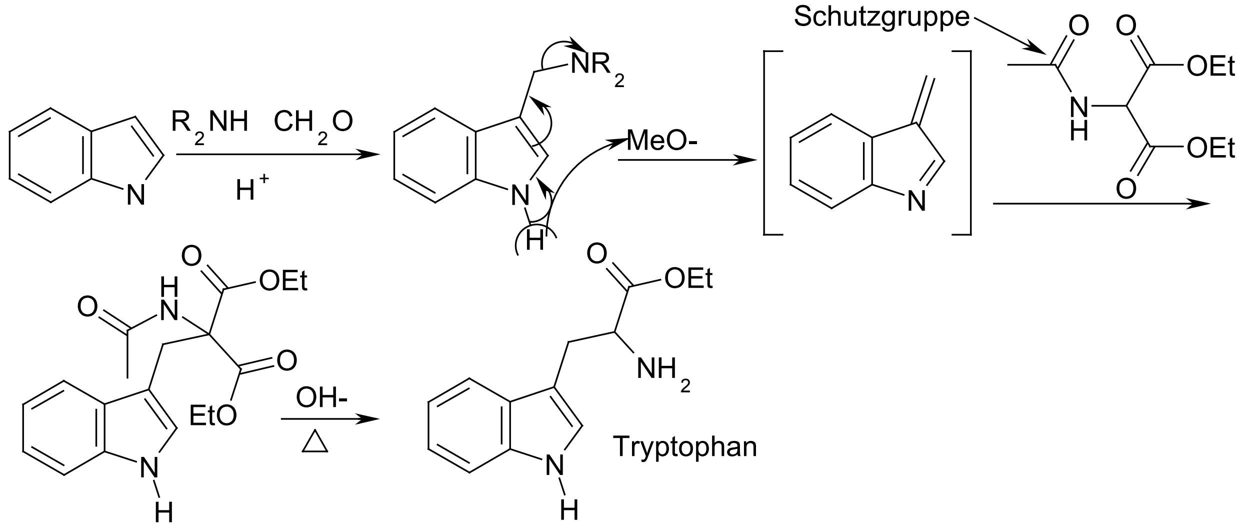


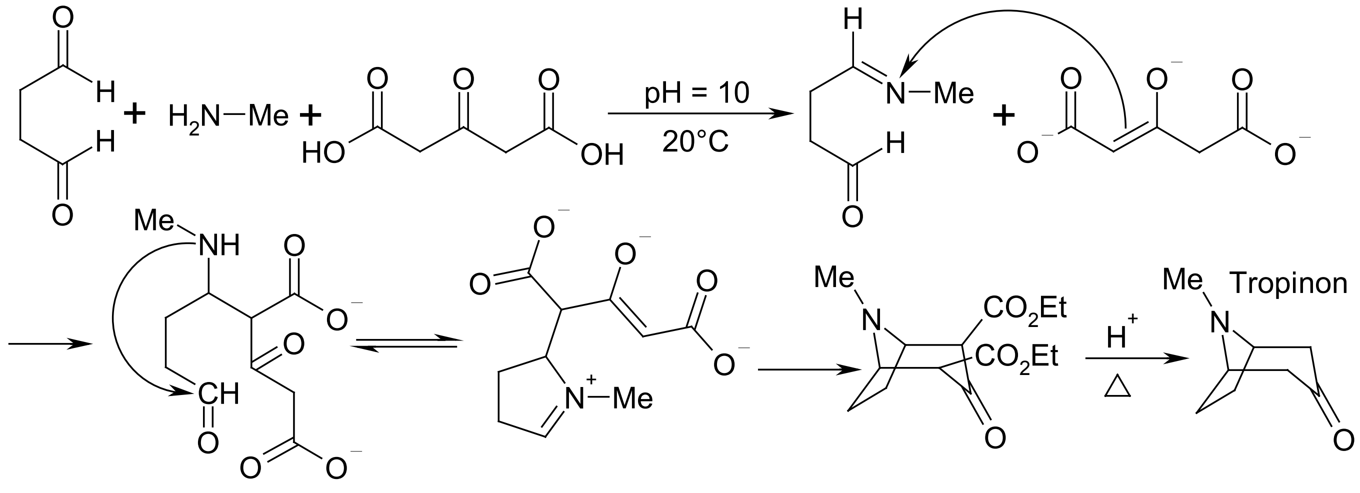
Stetter-Reaktion



6.3.12 Mannich-Reaktion

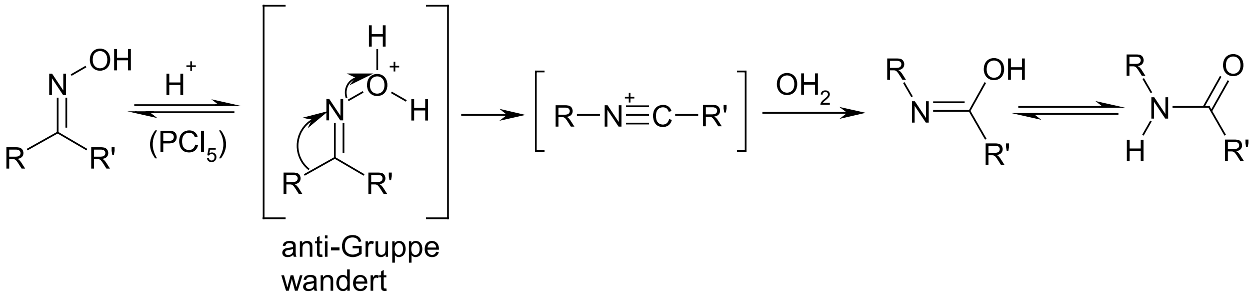




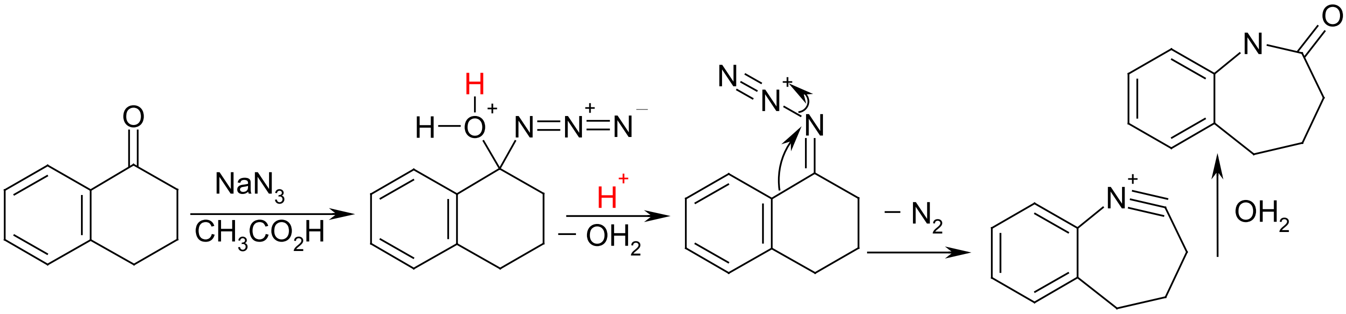


6.4 Umlagerungs-Reaktionen

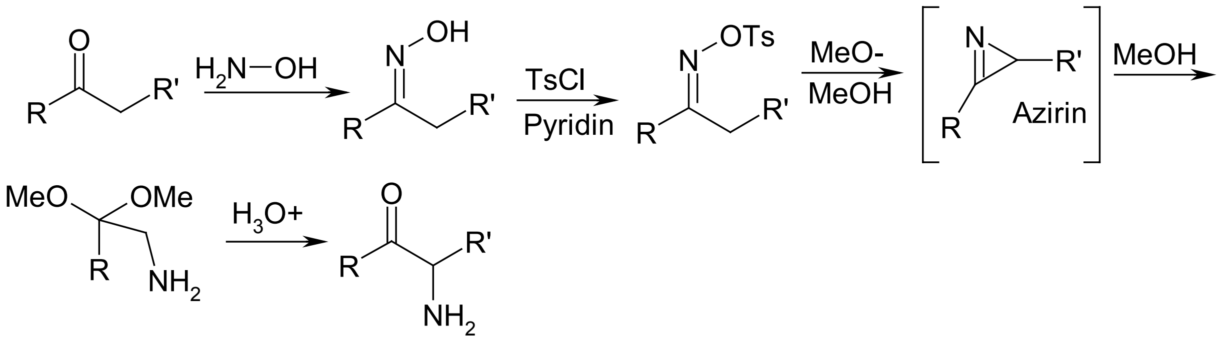
6.4.1 Beckmann-Umlagerung



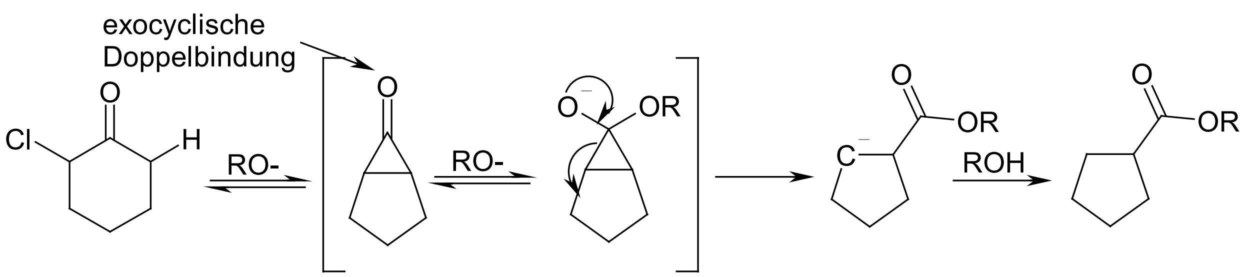
6.4.2 Schmidt-Abbau



6.4.3 Neber-Umlagerung

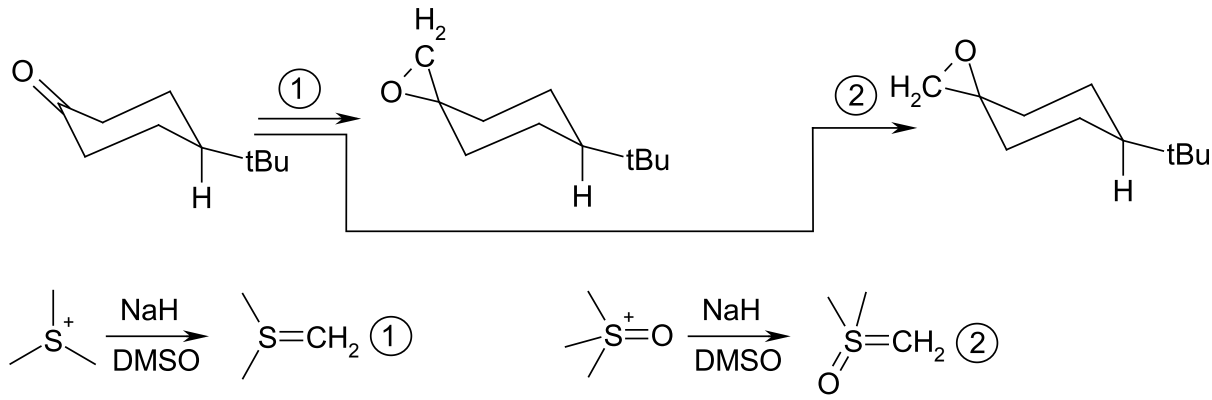


6.4.4 Favorskii-Umlagerung

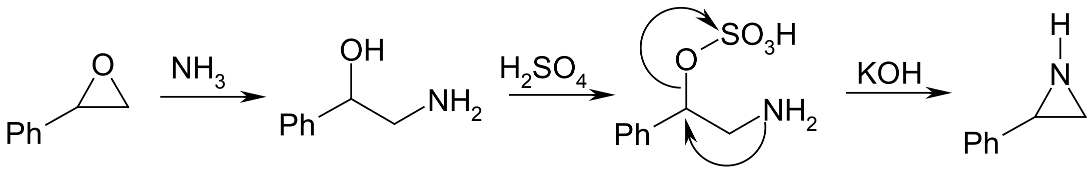


6.5 Synthesen von Heterocyclen

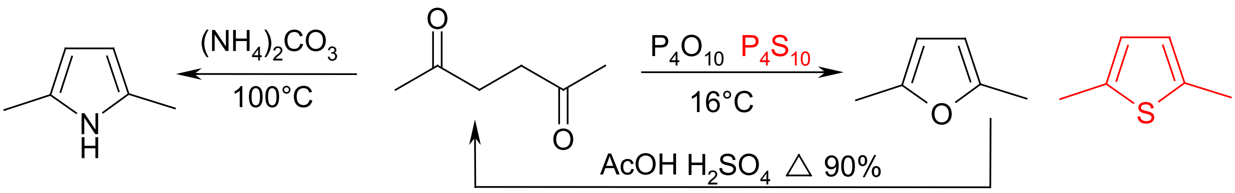
6.5.1 Oxirane



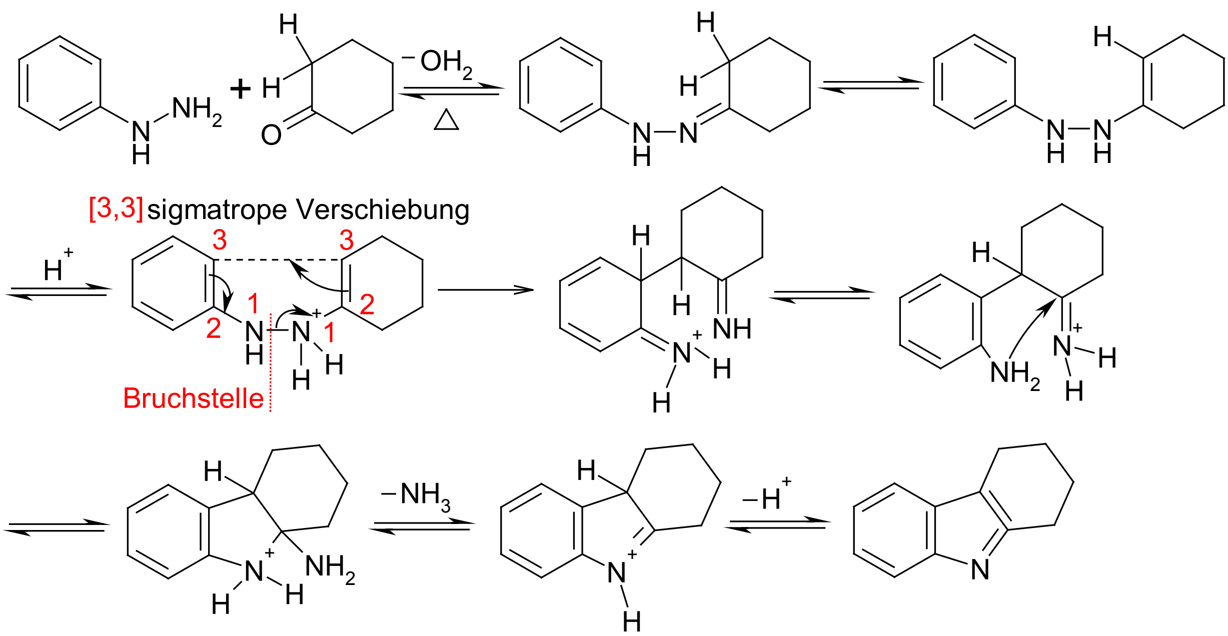
6.5.2 Aziridine



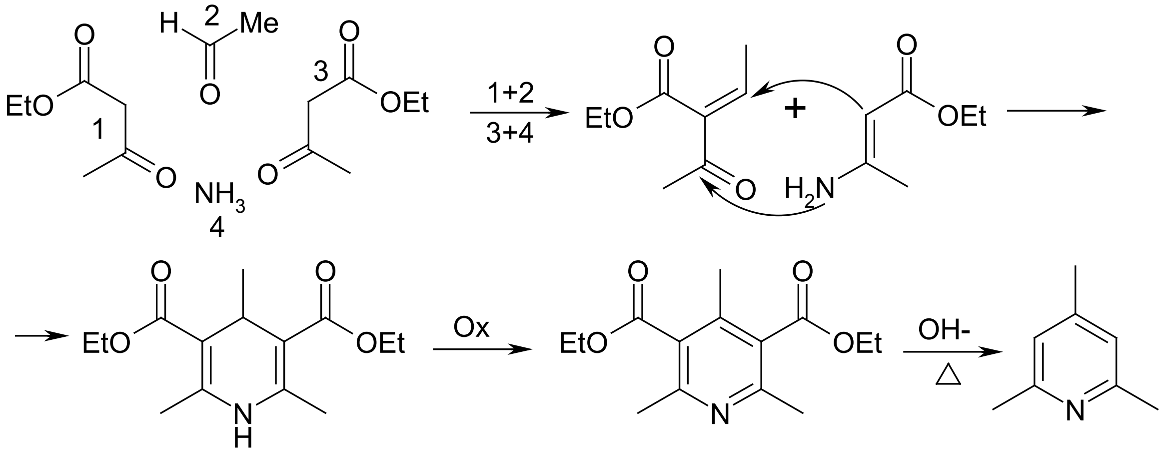
6.5.3 Paal-Knorr-Pyrrol-Synthese



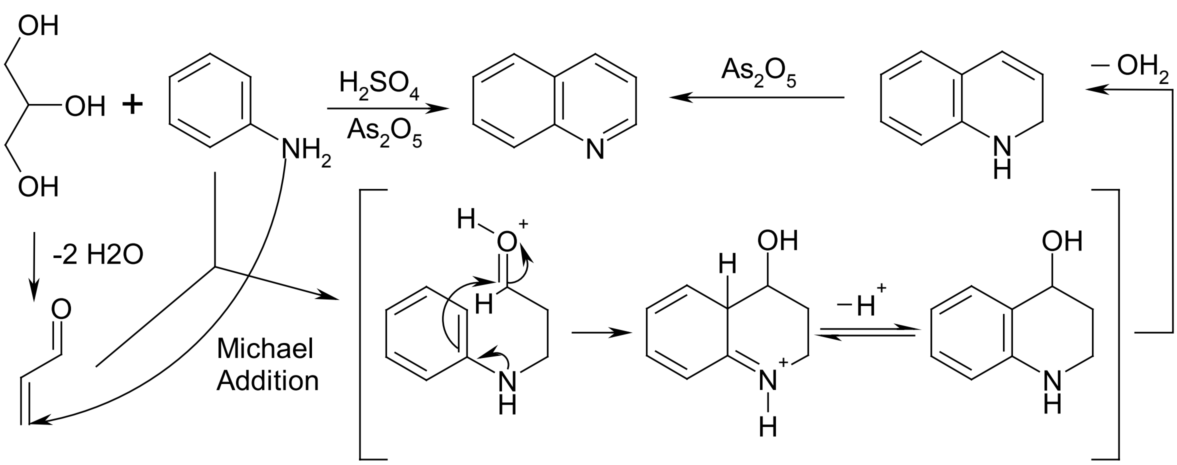
6.5.4 Fischer-Indol-Synthese

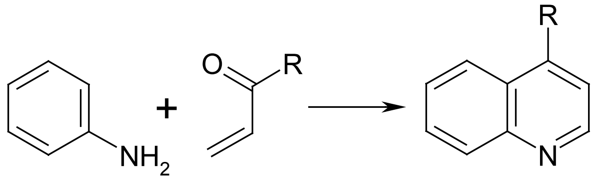


6.5.5 Hantzsch-Pyridin-Synthese



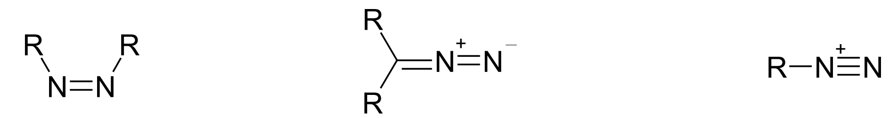
6.5.6 Skaup-Chinolin-Synthese





7 Diazoverbindungen

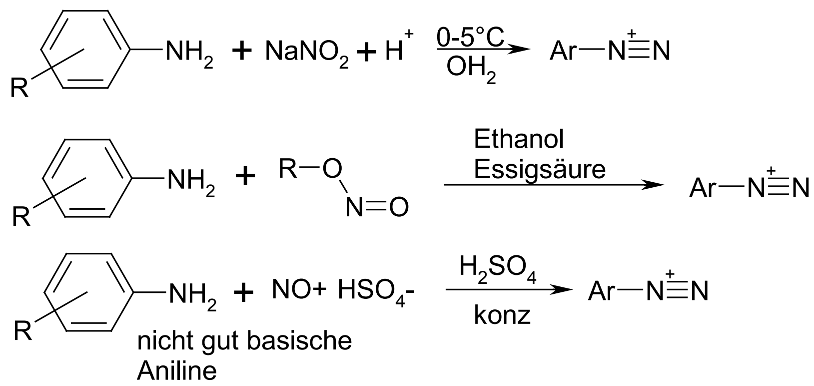
7.1 Nomenklatur

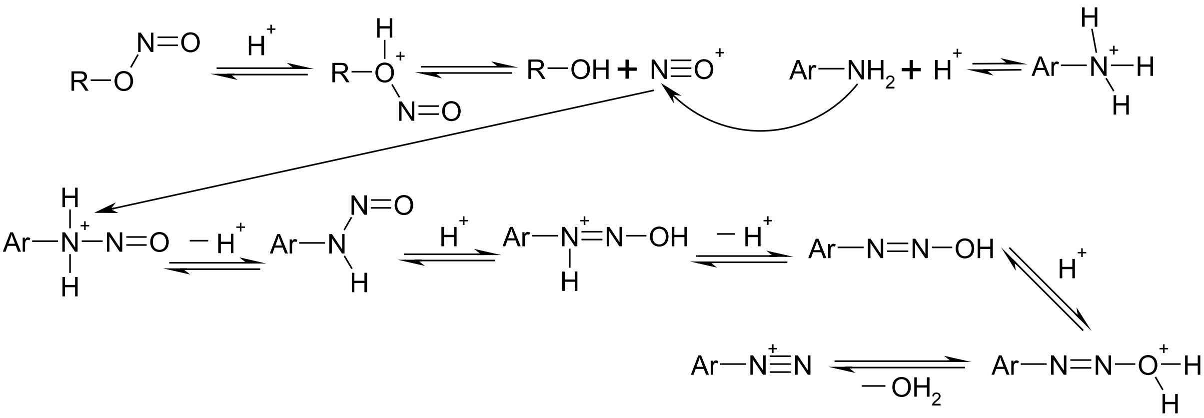


Azo-Verbindungen Diazo-Verbindungen Diazoniumsalze

7.2 Aromatische Diazoniumverbindungen

7.2.1 Darstellung

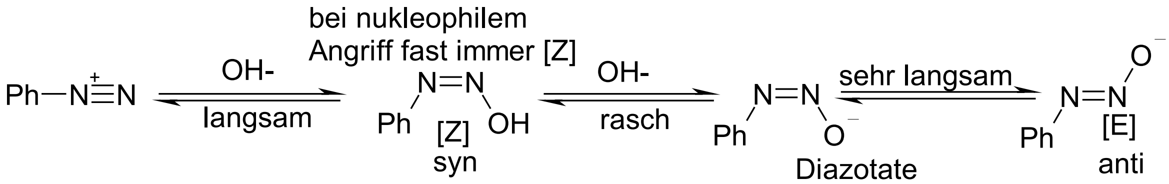


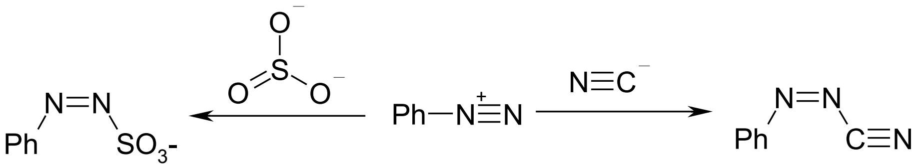


Gegenionen $Cl^-; HSO_4^-; BF_4^-; ClO_4^-$

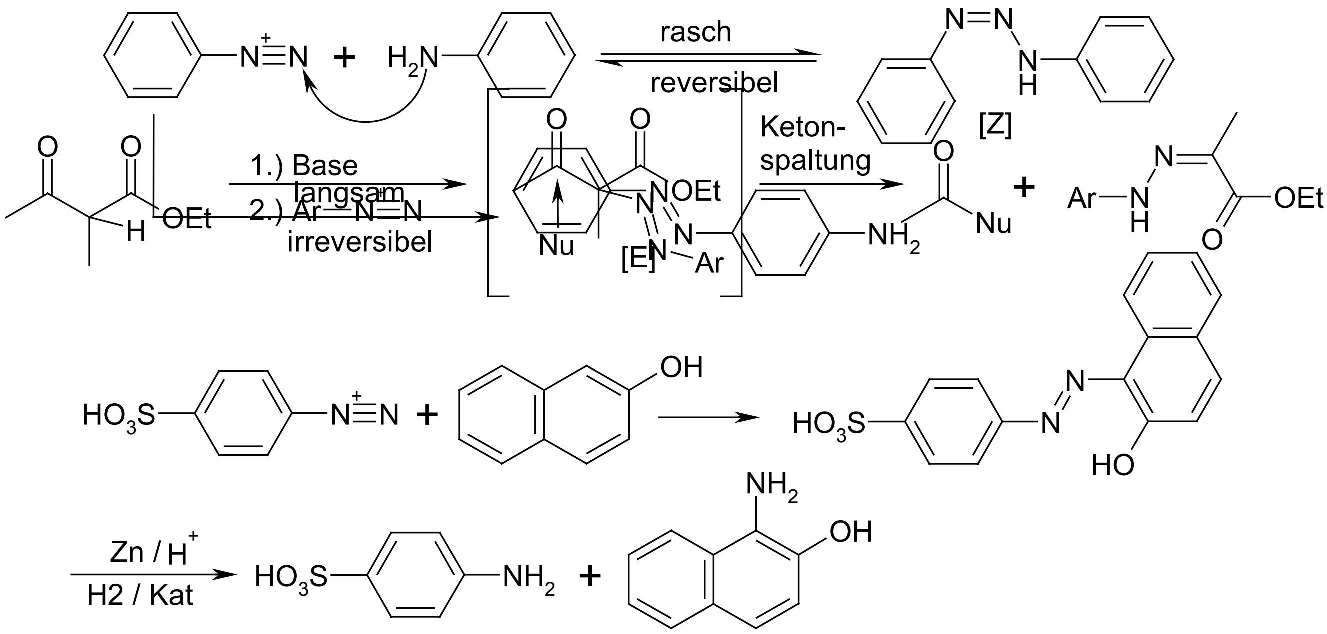
7.2.2 Reaktionen ohne Stickstoff-Eliminierung

7.2.2.1 Diazotate, Diazocyanide, Diazosulfite



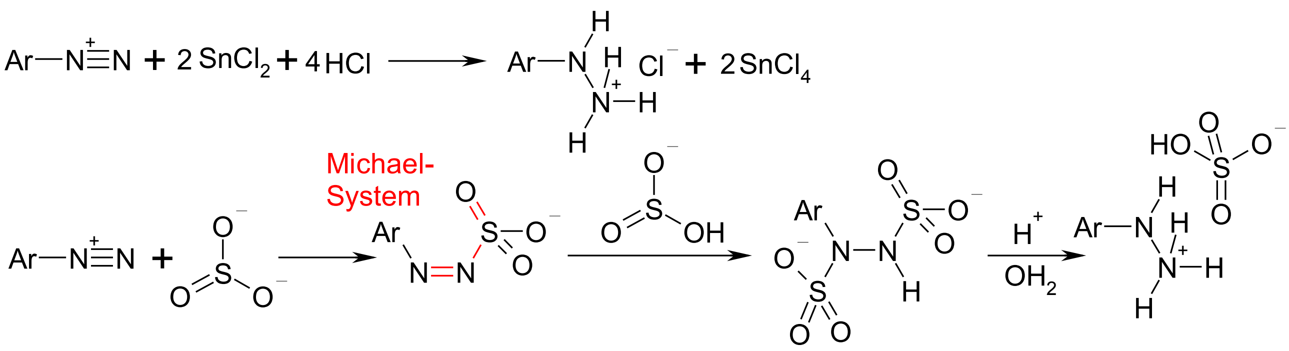


7.2.2.2 Azokupplung



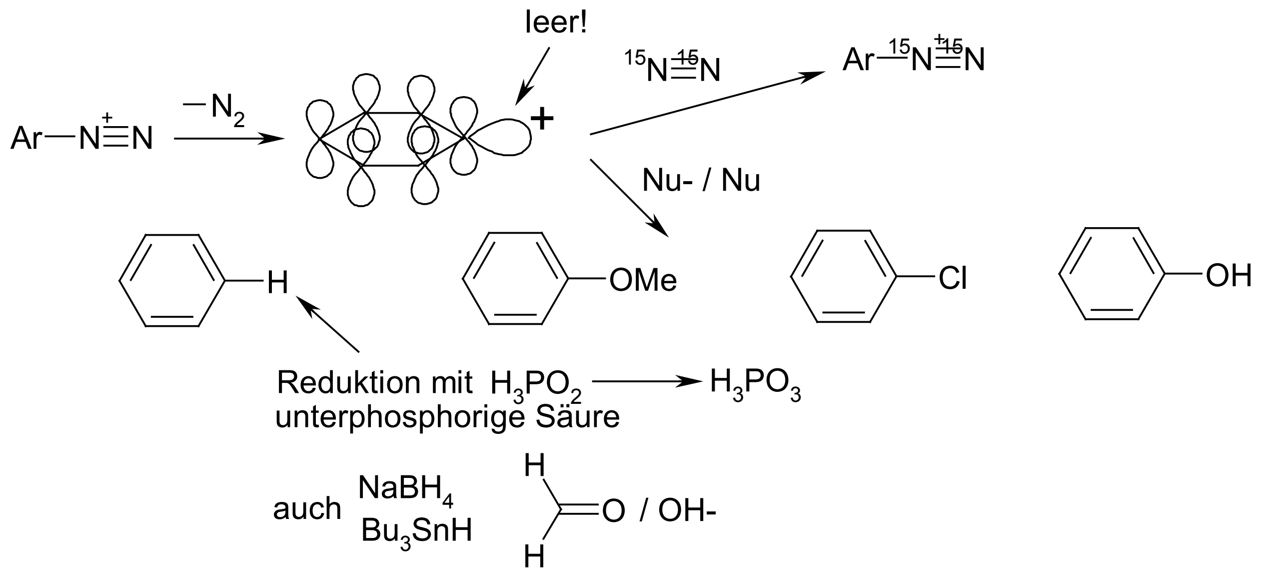
7.2.2.3 Japp-Klingemann-Reaktion

7.2.2.4 Reduktion zu Arylhydrazinen



7.2.3 Reaktionen unter Stickstoff-Eliminierung

7.2.3.1 Phenolverkochung



7.2.3.2 Radikalische Arylierung,

siehe: Gomberg-Bachmann-Reaktion 3.10.1 auf S 51

7.2.3.3 Reduktive Desaminierung:

Siehe: Reduktive Desaminierung

7.2.3.4 Sandmeyer-Reaktion

$$Ar - N_2^+X^- + CuY \xrightarrow{-N_2} Ar - Y + CuX$$

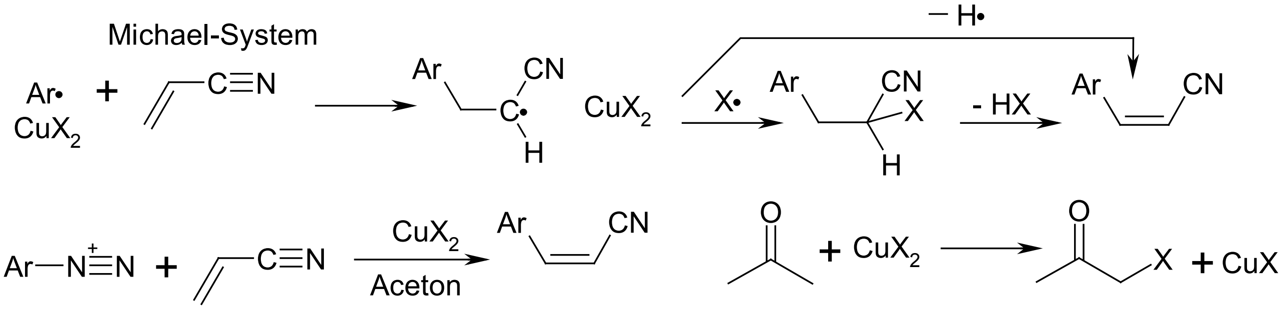
$$X^- : HSO_4^-; X^- = Y^- \qquad Y^- = Cl^-; Br^-; CN^-; NO_2^-$$

$$Ar - N_2^+X^- \xrightarrow{CuX} Ar - N_2^+[\overset{I}{Cu}X_2]^- \xrightarrow{e^-} Ar - N_2^\bullet + \overset{II}{Cu}X_2$$

$$\xrightarrow{-N_2} Ar\cdot + CuX_2 \xrightarrow{Sn} Ar - X\cdot^- + CuX^+ \rightarrow Ar - X + CuX$$

7.2.3.5 Meerwein-Arylierung

$$Ar - N_2^+X^- \xrightarrow{CuX} Ar - N_2^+[\overset{I}{Cu}X_2]^- \xrightarrow{e^-} Ar - N_2^\bullet + \overset{II}{Cu}X_2 \xrightarrow{-N_2} Ar\cdot + CuX_2$$



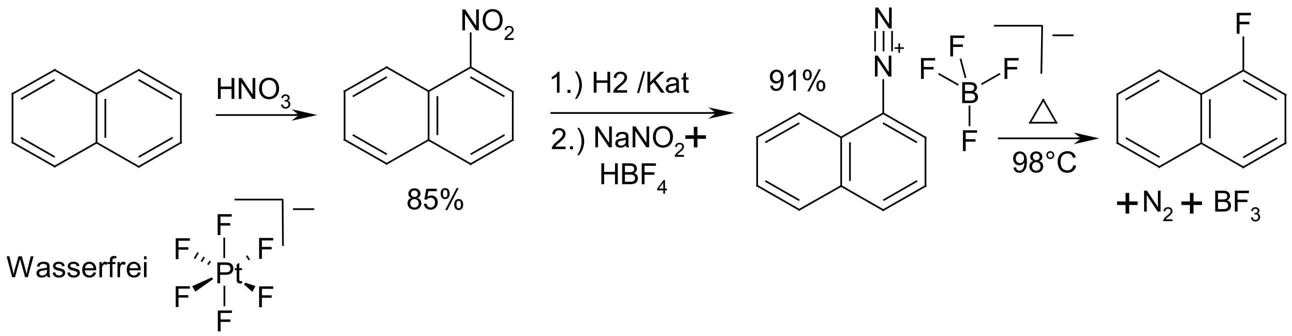
7.2.3.6 weitere Ar-X Synthesen

$$Ar-N_2^+ \xrightarrow[\Delta]{H_2O} Ar-OH$$

$$Ar-N_2^+X^- \xrightarrow{H_2O} Ar-X$$

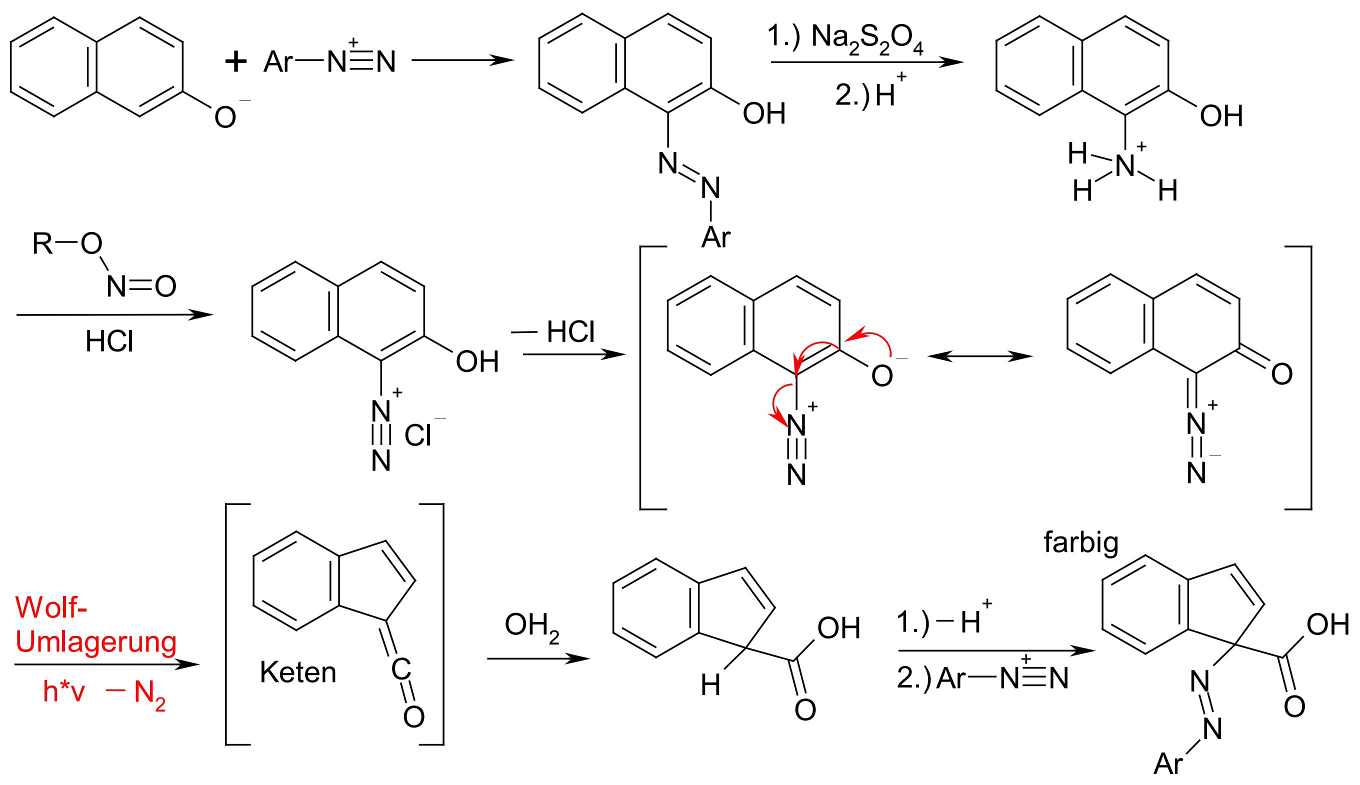
letzteres geht nur für sehr gute Nukleophile $X^-: I^-; I_3^-; R-S^-; SCN^-; N_3^-$

7.2.3.7 Schiemann-Reaktion



7.2.3.8 Süß-Reaktion (mit Wolf-Umlagerung)

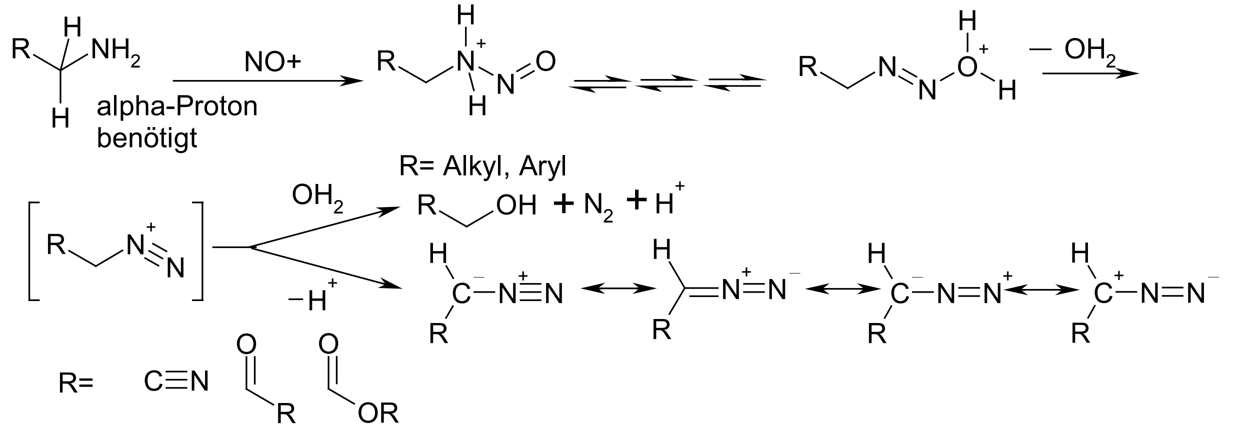
Technisch als Diazotypie (chemischer Kopierer)



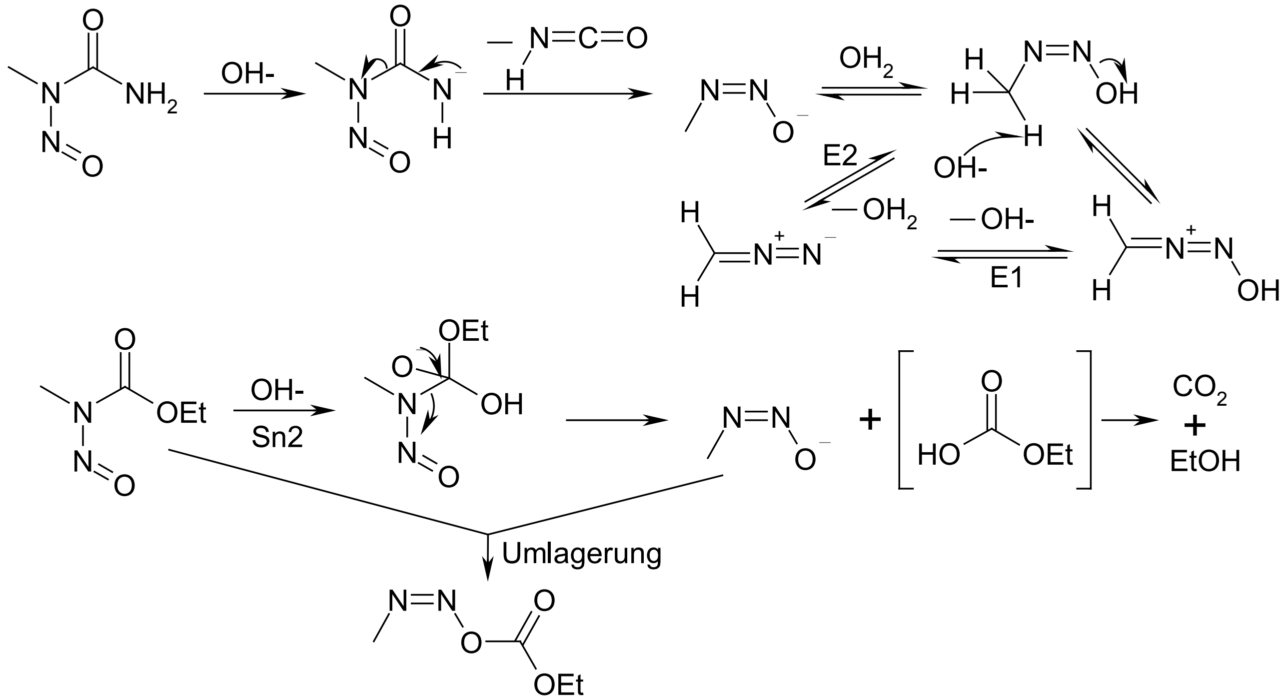
7.3 Aliphatische Diazoverbindungen

7.3.1 Darstellung

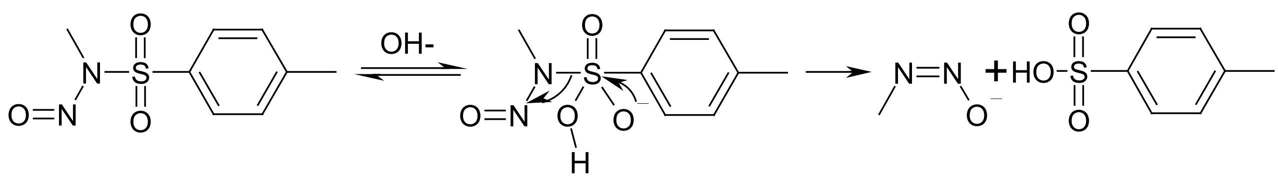
7.3.1.1 Diazotierung aliphatischer Amine



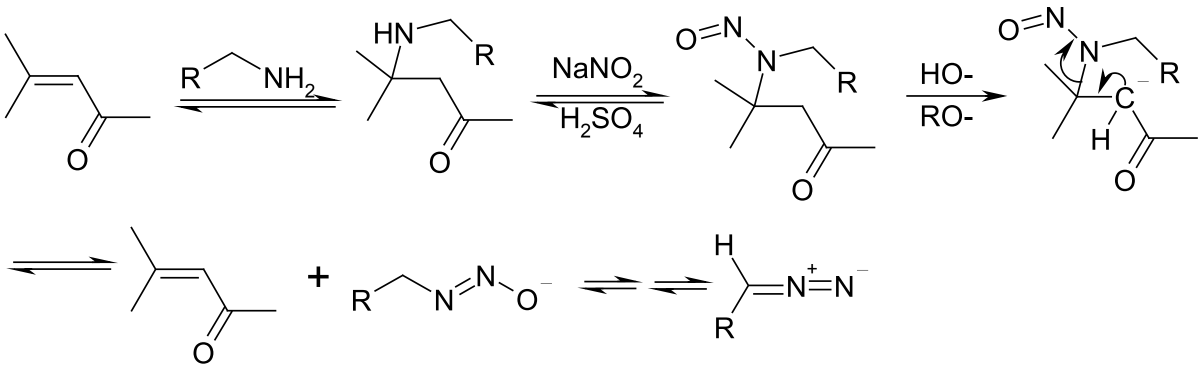
7.3.1.2 Spaltung von N-Nitroso-N-acyl-alkylaminen



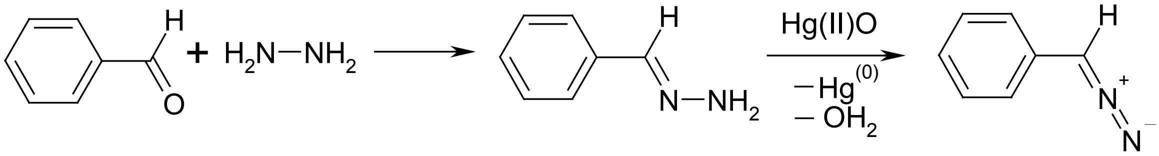
Diazald



7.3.1.3 aus Mesityloxid

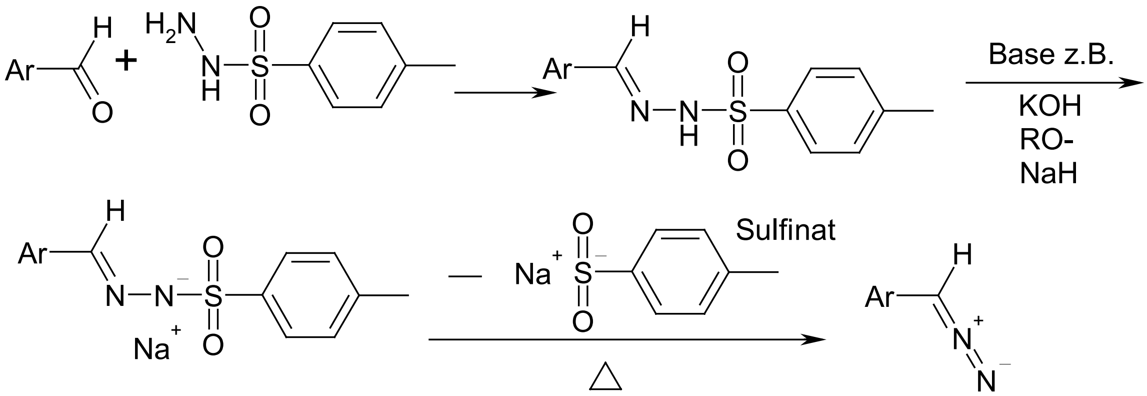


7.3.1.4 Dehydrierung von Hydrazonen

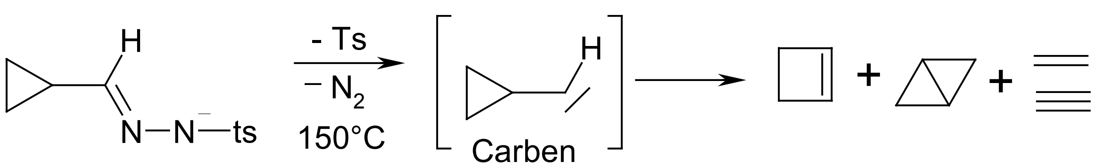


andere Oxidationsmittel: MnO_2 $Pb(OAc)_4$ Ag_2O

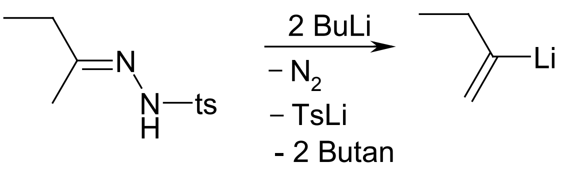
7.3.1.5 Bamford-Stevens-Verfahren



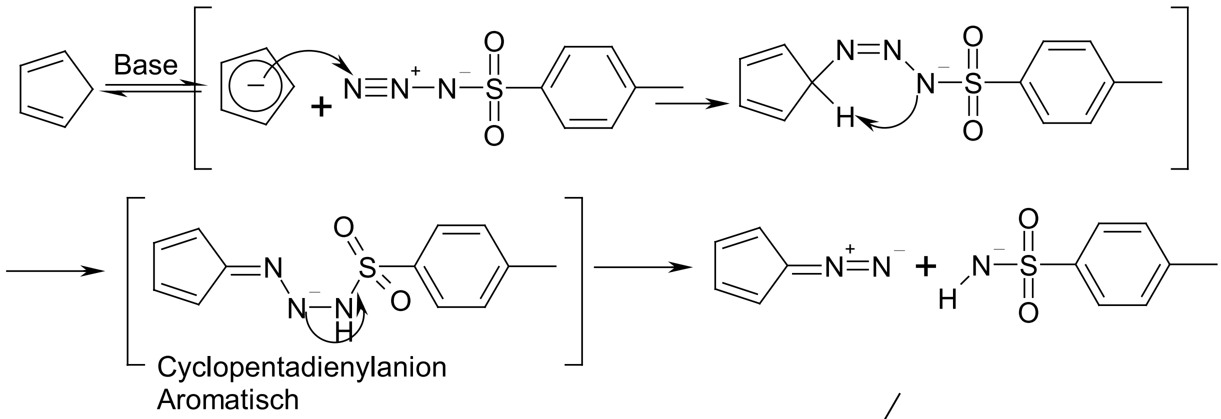
Ist auch mit alkylsubstituierten Aldehyden möglich, aber Nebenreaktionen:



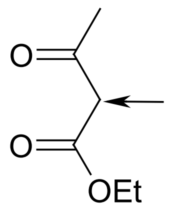
7.3.1.6 Shapiro-Reaktion



7.3.2 Diazogruppen-Übertragung

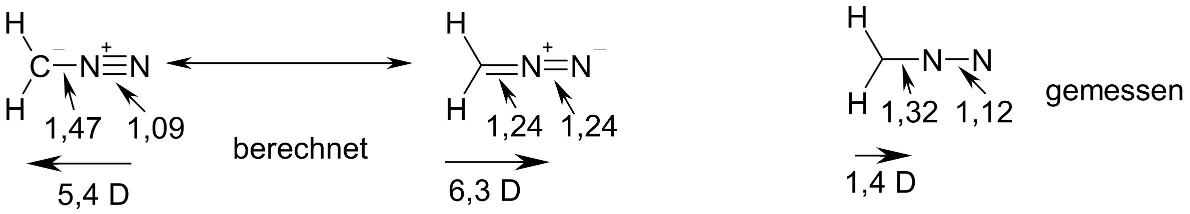


Geht mit allem, was Knoevenagel macht; also auch mit

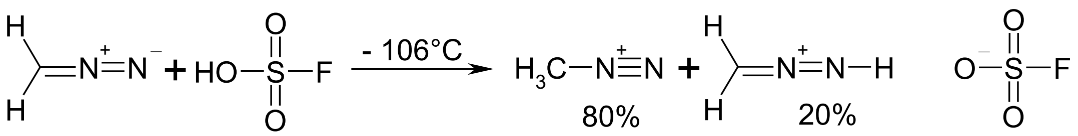


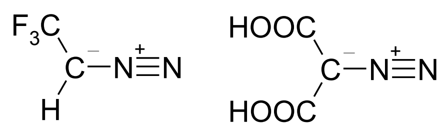
etc

7.3.3 Struktur



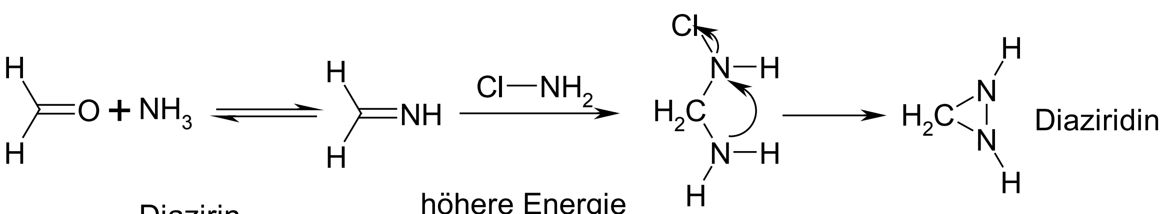
7.3.3.1 Wo ist die negative Ladung

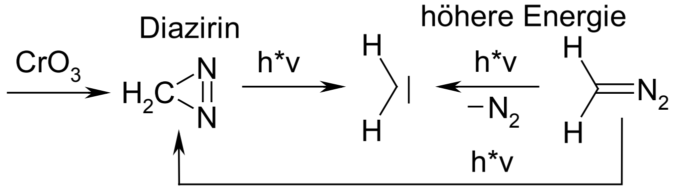




gegen verdünte Säuren stabil

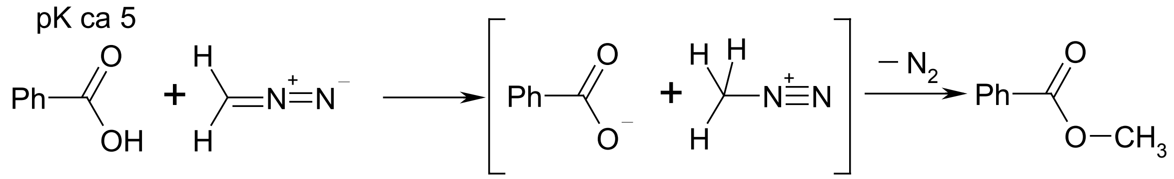
7.3.3.2 Schmitz

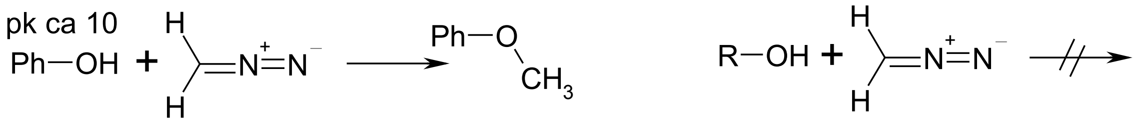




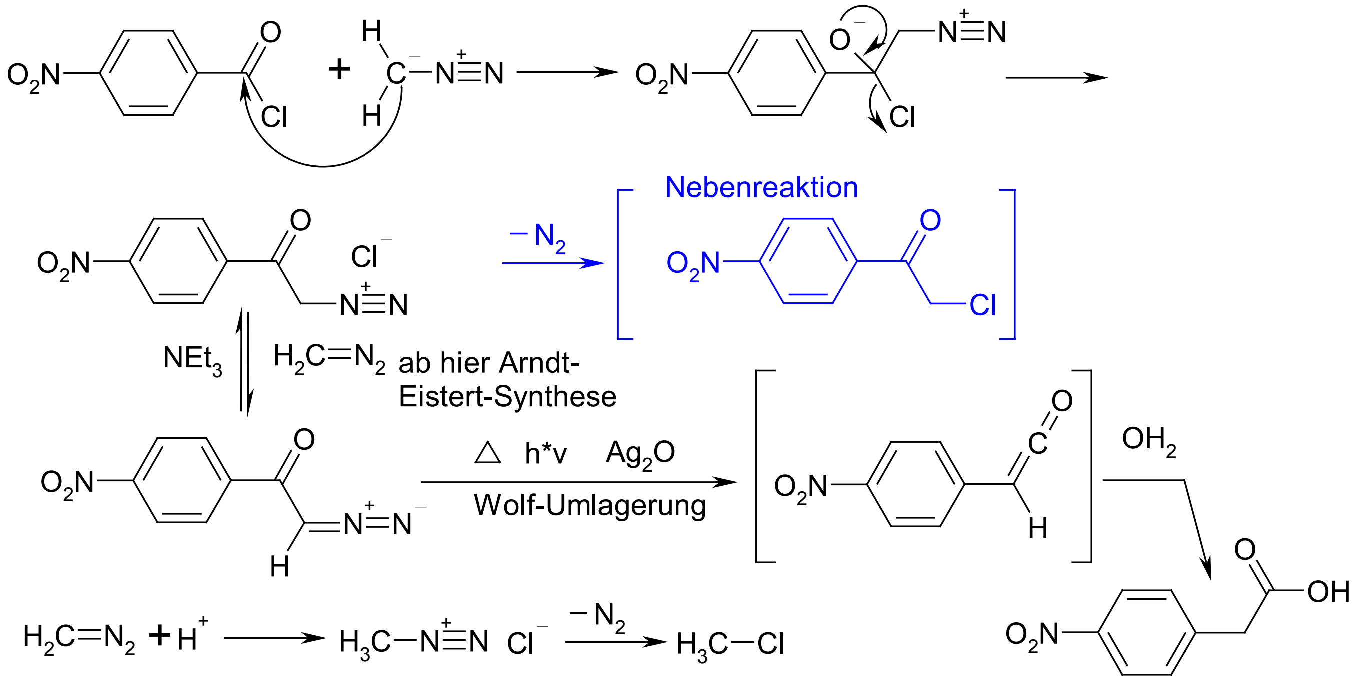
7.3.4 Reaktionen

7.3.4.1 Mit aciden Verbindungen

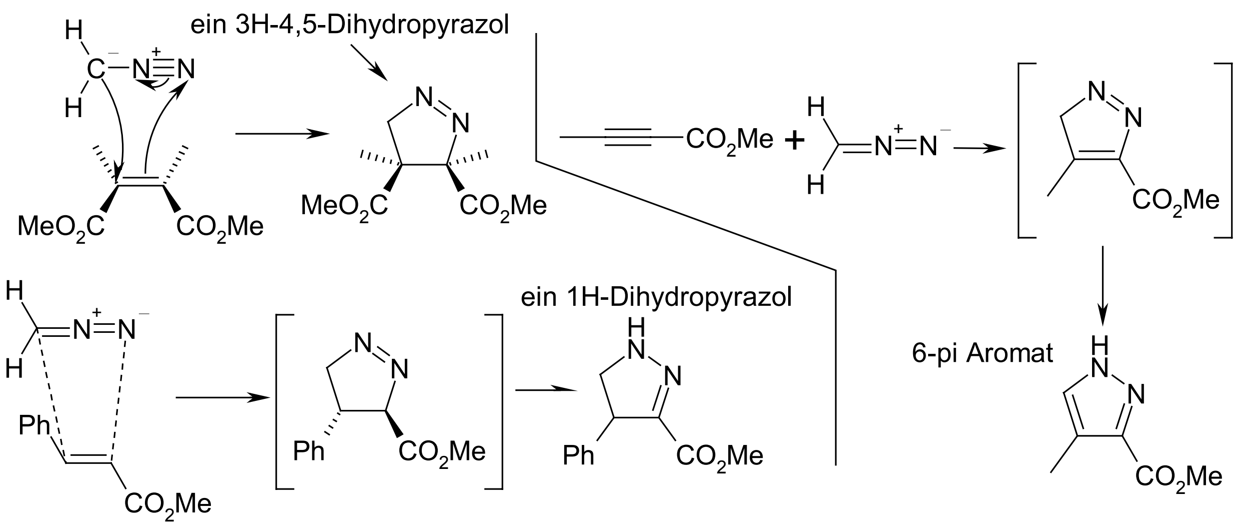




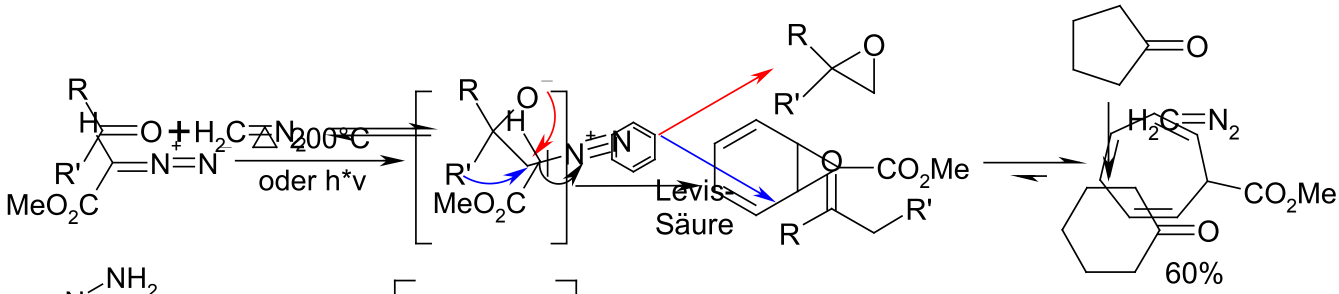
7.3.4.2 Mit Carbonsäurechloriden, Arndt-Eistert-Reaktion

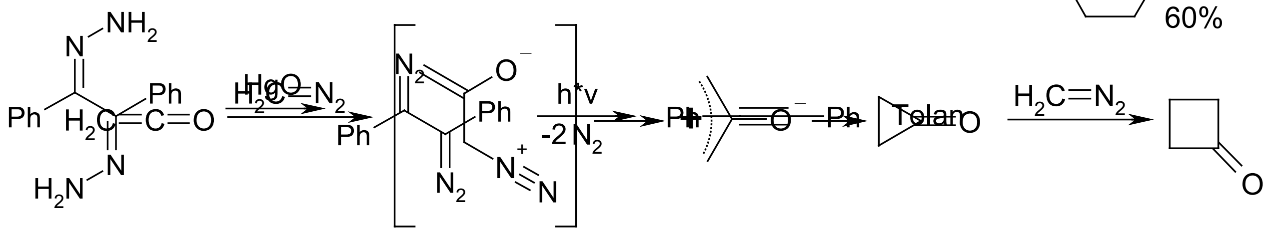


7.3.4.3 [3+2] Cycloaddition (1,3 dipolare Cycloaddition)



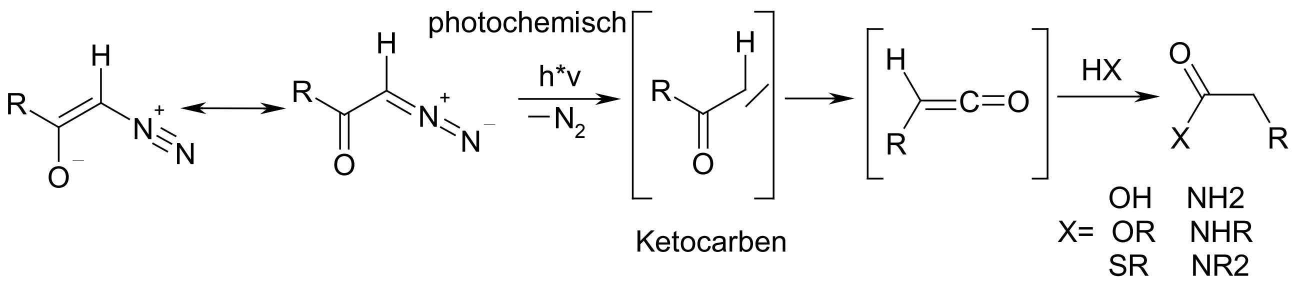
7.3.4.4 Mit Aldehyden und Ketonen

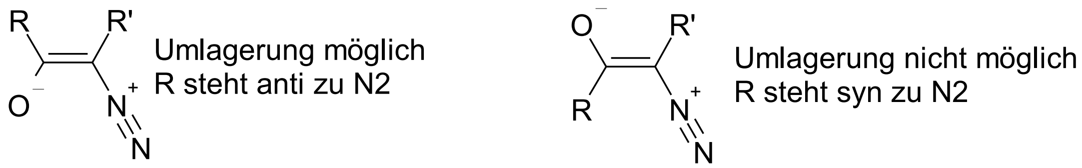




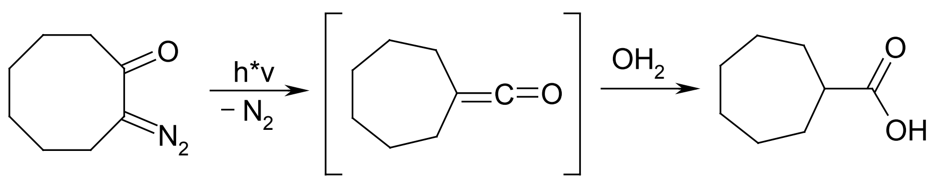
7.3.4.5 Thermolyse, Photolyse (Carbene, Ketocarbene)

7.3.4.6 Wolff-Umlagerung

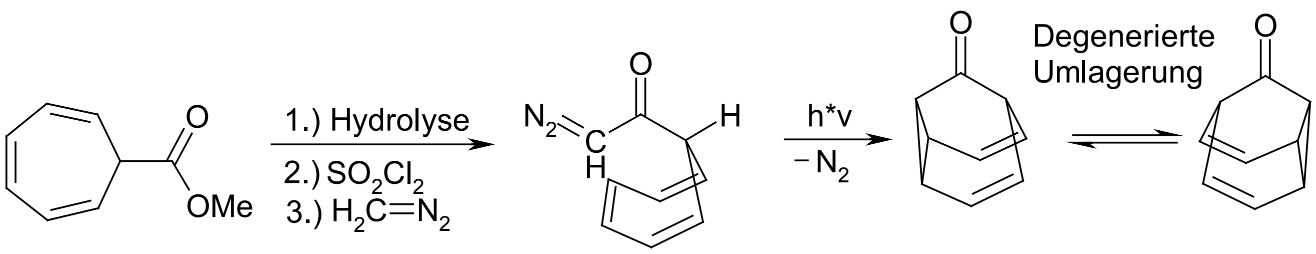




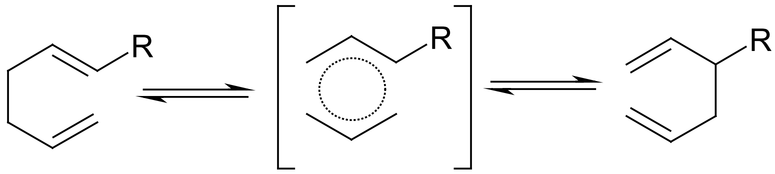
Ringverengung durch Wolf-Umlagerung



Barbaralon



Cope-Umlagerung



Namensreaktionsverzeichnis

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