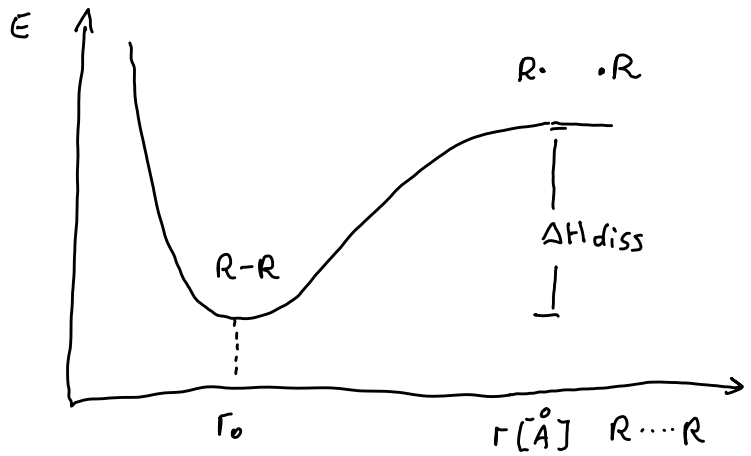
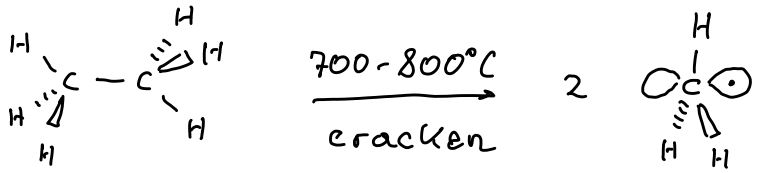
Chem 303

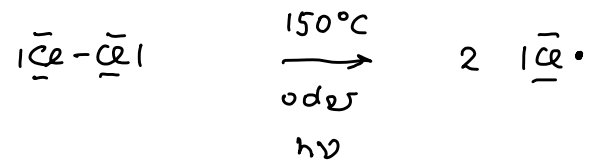
Radikalische Substitution

$R-R \longrightarrow R\cdot + \cdot R$ homolytischer Bindungsbruch

$R-R \longrightarrow R^{\oplus} + {}^{\ominus}R$







Bindungsdissoziationsenergien

X-X	ΔH diss $\left[\frac{kJ}{mol}\right]$	H-X	ΔH diss
F-F	155	H-F	566
Cl-Cl	239	H-Cl	438
Br-Br	190	H-Br	363
I-I	149	H-I	295
H_3C-CH_3	370		

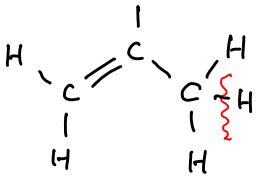
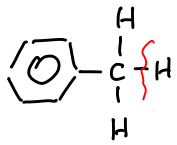
Licht $E = h \cdot \nu$

300 nm $\hat{=}$ 400 $\frac{kJ}{mol}$

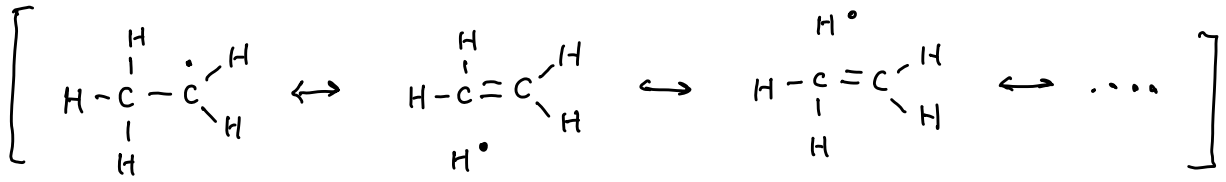
400 nm $\hat{=}$ 300

600 nm $\hat{=}$ 200

Stabilität von Radikalen

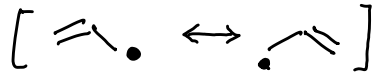
	ΔH_{diss} $\frac{kJ}{mol}$
$CH_3-H \rightarrow CH_3\cdot + H\cdot$	Methyl 435
$CH_3CH_2-H \rightarrow CH_3CH_2\cdot + H\cdot$	prim. 411
$(CH_3)_2CH-H \rightarrow (CH_3)_2\dot{C}H + H\cdot$	sec. 396
$(CH_3)_3C-H \rightarrow (CH_3)_3C\cdot + H\cdot$	tert. 385
	allyl 371
	benzyl 356

- Stabilisierung durch Hyperkonjugation, z.B. $CH_3-\dot{C}H_2$



"no-bond" Resonanzstrukturen

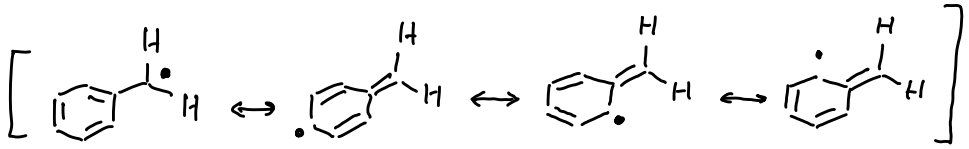
- stabilisierung durch Delokalisierung



Allyl-Radikal

nicht verwechseln → 

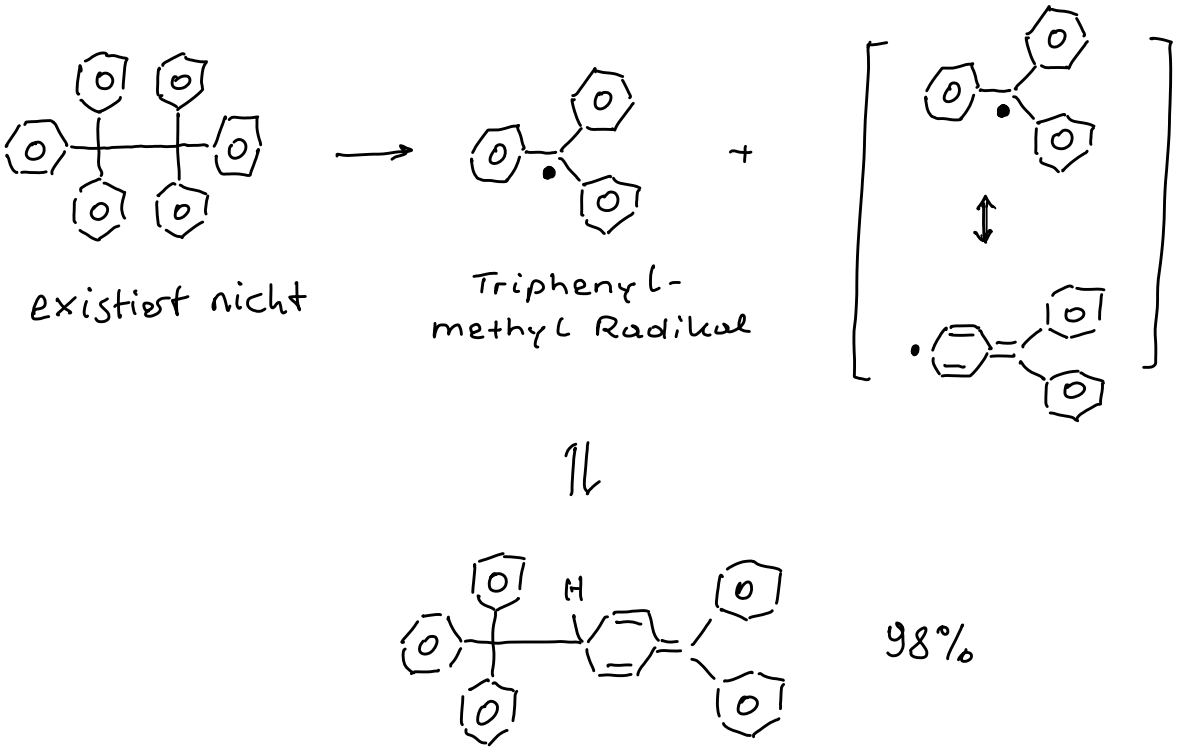
Vinyl-



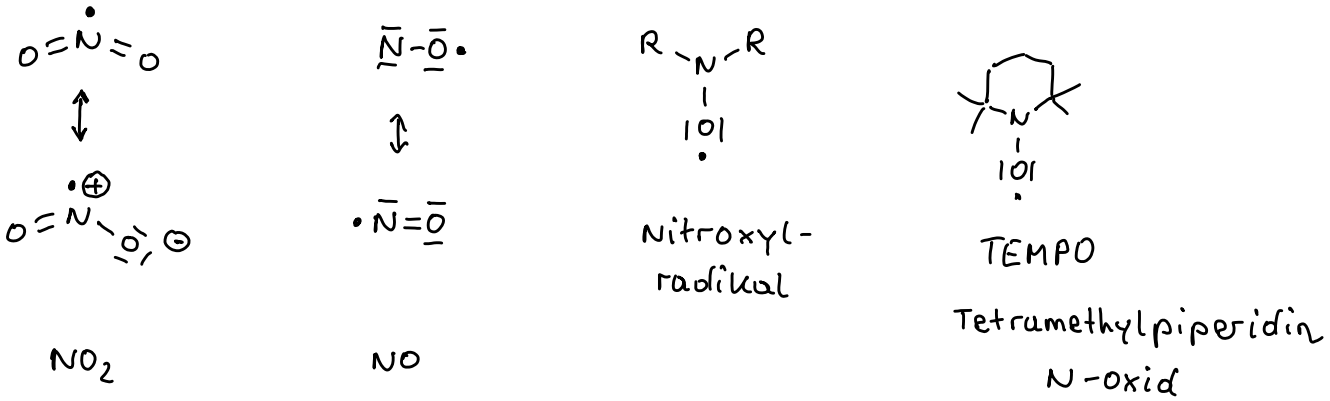
Benzyl-Radikal

Phenyl-

Moses Gomberg



Stabile Radikale



— Reaktionen von Radikalen

1. $R\cdot + R\cdot \longrightarrow R-R$ Rekombination

2. $CH_3-\dot{C}(CH_3)_2 + CH_3-\dot{C}(CH_3)_2$ Disproportionierung

$CH_3-CH(CH_3)_2 + CH_2=C(CH_3)_2$

3.  Zerfall

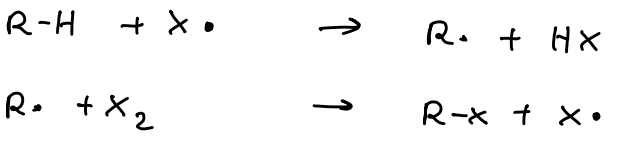
4.  Addition an Alkene

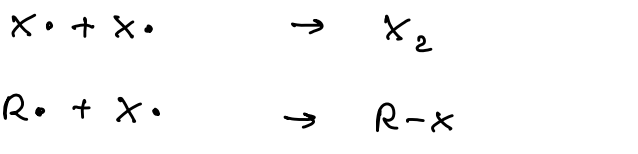
5. $R\text{-}H + X^{\bullet} \rightarrow R^{\bullet} + H\text{-}X$ Substitution

$R^{\bullet} + X\text{-}X \rightarrow R\text{-}X + X^{\bullet}$

Radikalische Substitution (Mechanismus)

 Kettenstart



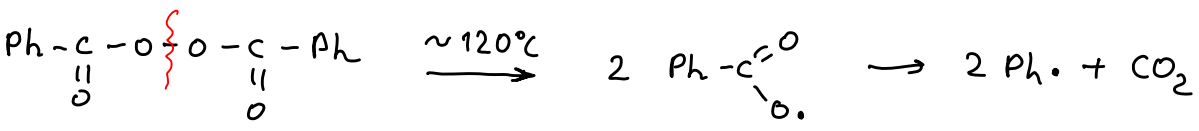


 Kettenabbruch

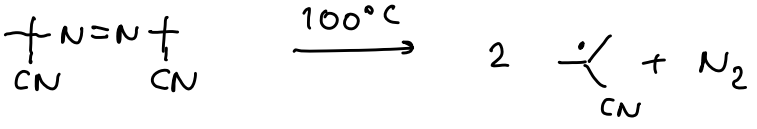
Disproportionierung

Kettenstart durch Initiator

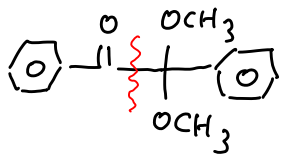
Benzoylperoxid



Azobisisobutyronitril AIBN



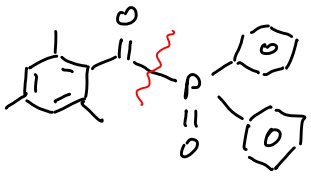
Lichtinduzierte Radikal Starter



DMPA

2,2-Dimethoxy-2-phenyl-acetophenon

uvicure (Ciba)



TPO

2,4,6-Trimethylbenzoyl diphenyl phosphinoxid

Luciridin BASF

Thermodynamik

	F	Cl	Br	I	$\Delta_R H^\circ \left[\frac{kJ}{mol}\right]$
$R-H + X\cdot \rightarrow R\cdot + HX$	-128	-1	69	136	
$R\cdot + X_2 \rightarrow R-X + X\cdot$	-302	-103	-100	-83	
$R-H + X_2 \rightarrow R-X + HX$	-430	-104	-31	+53	

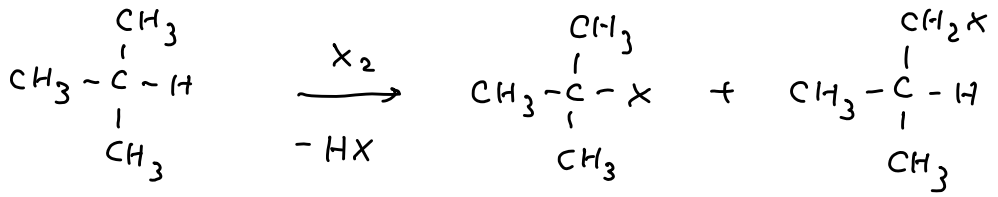
F_2 + RH exotherm (explosiv) 3Fluor.avi

Cl_2 reaktiv unselektiv

Br_2 reaktiv selektiv

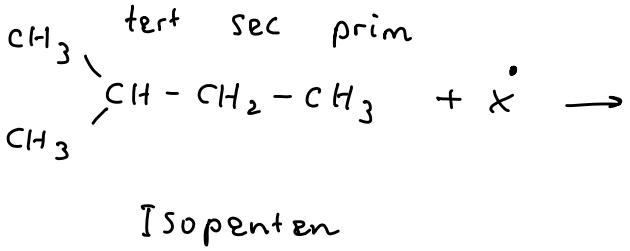
I unreaktiv

- Selektivität

z.B. 

X	tert	prim
Br	98%	2%
Cl	65%	35%

statistischer Faktor 1 : 9



Isopenten

X	prim	sek	tert.
F·	1	1.2	1,4
Cl·	1	3,9	5,1
Br·	1	32	1600

electrophile Radikale, (electronisch kontrollierte Reaktivität)

HO·, Cl·, F·

z.B. Butyronitril + Cl· :

electronenarm

prim sec sec

electronenarm — electronenziehender Subst.

$H_3C - CH_2 - CH_2 - C\equiv N$

1 3,3 0 rel. Reaktivität

30.10.2013

Wiederholung

Homolyse, Heterolyse

Bindungsdissoziationsenergien

Stabilität von Radikalen, stabile Radikale

Reaktionen von Radikalen

- Rekombination
- Disproportionierung
- Zerfall, Fragmentierung
- Addition an Alkene
- Substitution (Radikal-Kettenfortpflanzung)

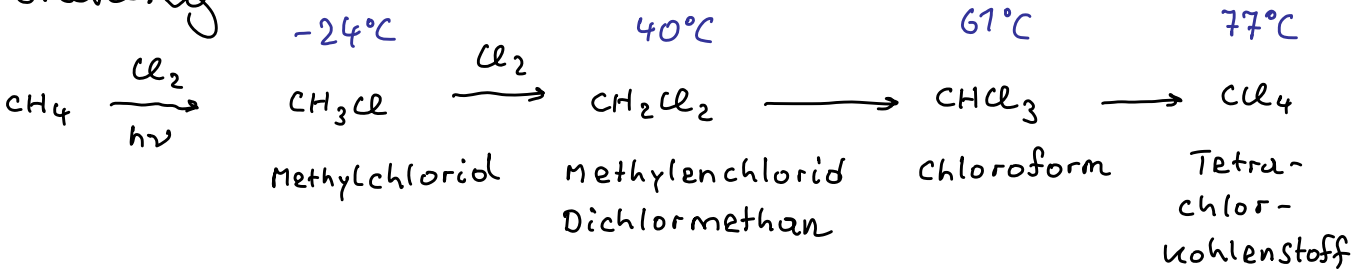
Mechanismus der rad. Subst.

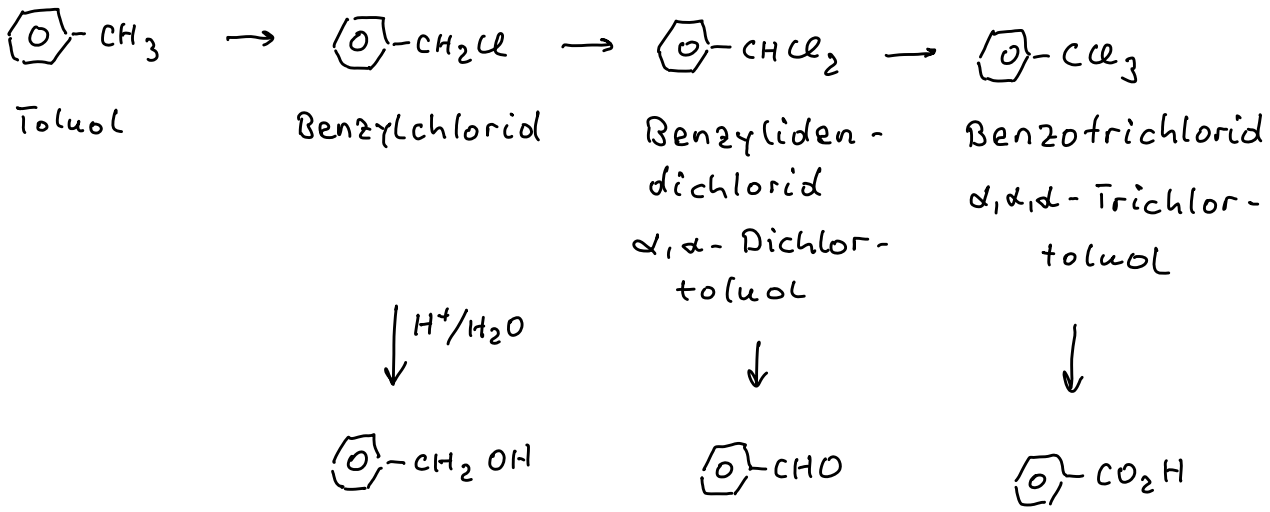
- Start, Fortpflanzung, Abbruch
- Thermodynamik

- Selektivität

Beispiele

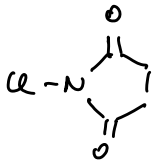
- Chlorierung





andere Chlorierungsmittel:

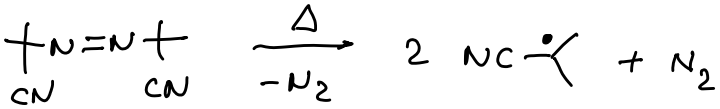
SO_2Cl_2 Sulfurylchlorid ($SOCl_2$ Thionylchlorid)



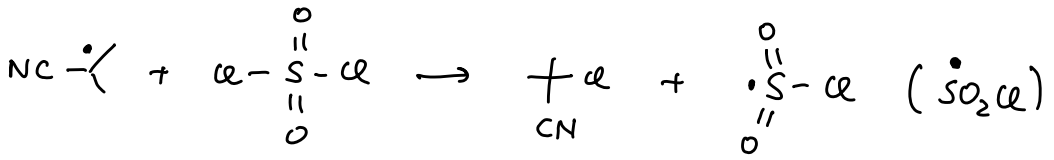
N-Chlorsuccinimid

PCl_5 Phosphorpentachlorid

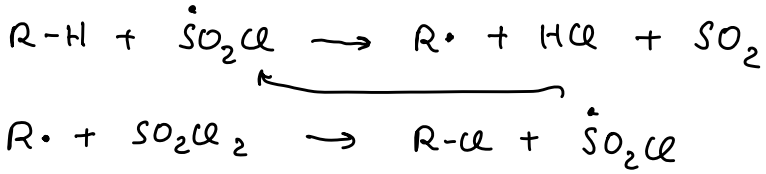
Radikalische Chlorierung mit SO_2Cl_2

Start: 

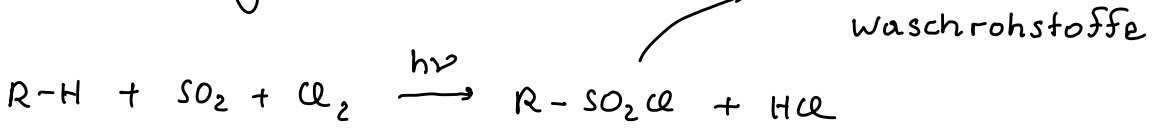
AIBN



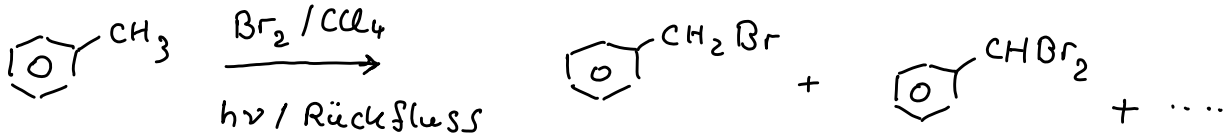
Kette:



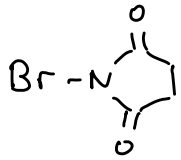
Sulfochlorierung:



- Bromierung

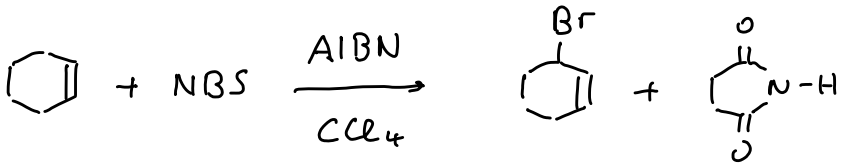


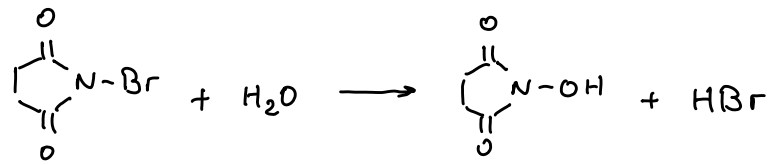
andere Bromierungsmittel

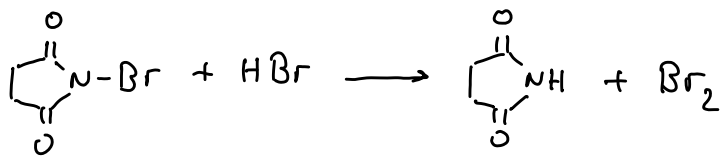


N-Bromsuccinimid NBS

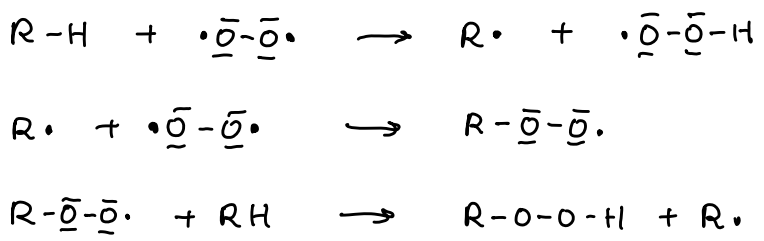
Bsp. allylische Bromierung

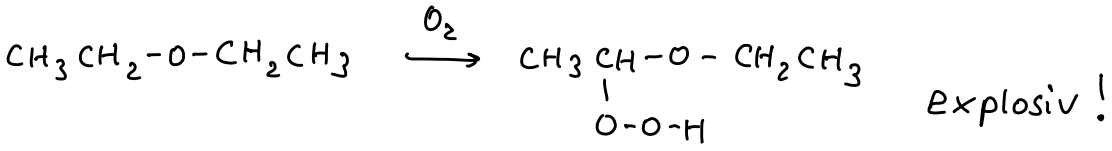


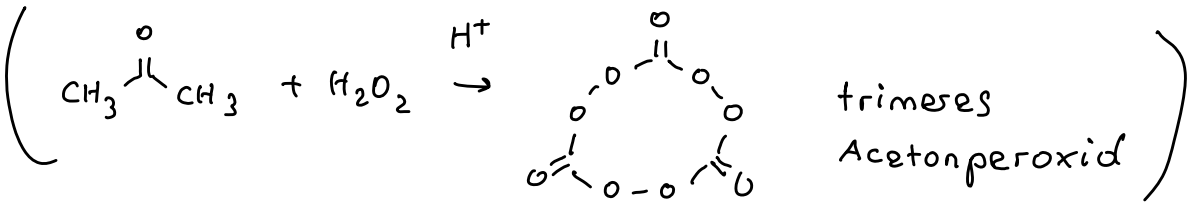


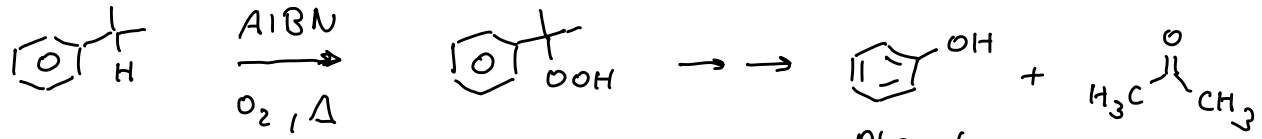


Peroxygenierung



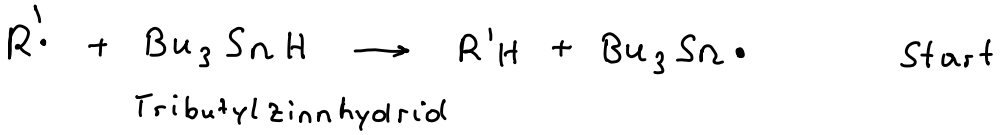


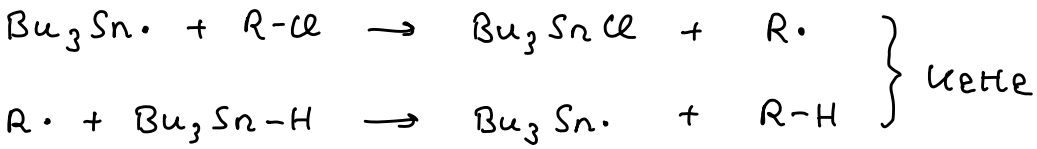




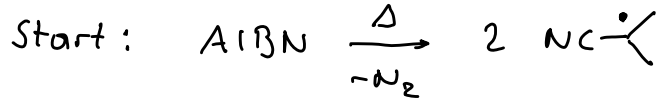
Hock'sche Phenolsynthese

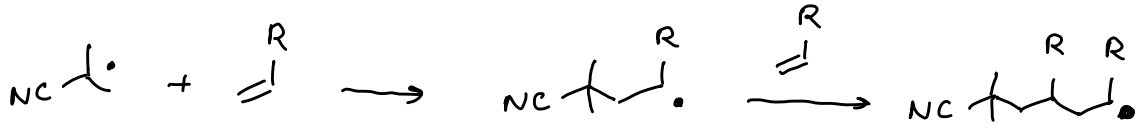
– radikalische Reduktion



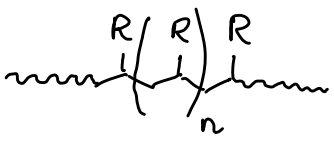


- radikalische Polymerisation

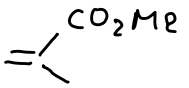
Start: AIBN $\xrightarrow[-N_2]{\Delta}$ 2 



R = H	(Ethylen)	→	PE
Cl	(Vinylchlorid)	→	PVC
CH_3	(Propylen)	→	PP
Ph	(Styrol)	→	PS



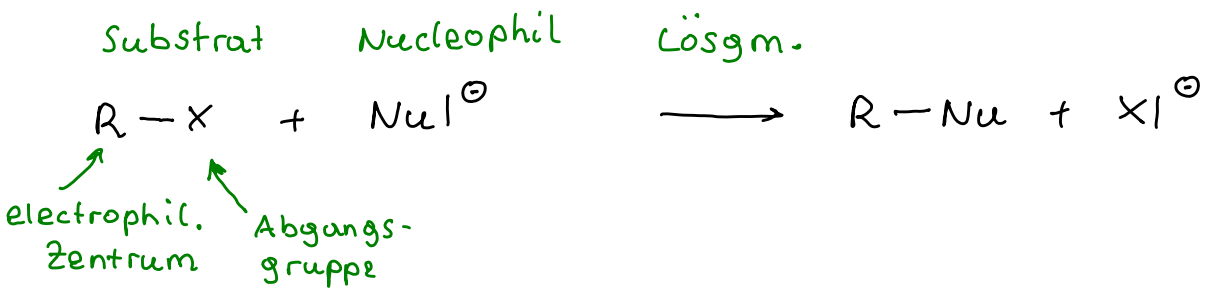
$n > 10^5$

 → PMMA (Plexiglas)

Abbruch: Rekombination oder Disproportionierung

Nucleophile Substitution D2

Allgemeines:



6 Parameter:

Substrat: Electrophilie
Sterik
Abgangsgruppe (Nucleofugie)

Nucleophil: Nucleophilie
Sterik

Lösungm. Polarität

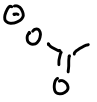
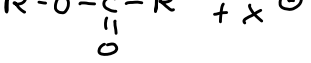
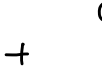
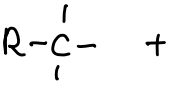
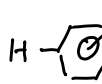
Mechanismen:

- S_N1
- S_N2
- S_N1 / S_N2
- S_Ni
- Nachbargruppeneffekte

Nucleophile
LSgm.
Nebenreakt.

---

synth. wichtige Beispiele (ohne Mechanismus)

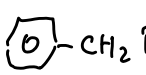
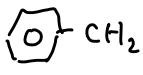
Substrat		Nucleophil		Produkt	
R-OH	+	HX	→	R-X + H_2O	
	+	R'OH	→	R-O-R' + H_2O	
R-X	+	$OH^{\ominus}$	→	R-OH + $X^{\ominus}$	Hydrolyse zum Alkohol
	+	$^{\ominus}OR'$	→	R-OR' + $X^{\ominus}$	Williamson Ether Synth.
	+		→		Estersynthese
	+	$^{\ominus}SH$	→	R-SH	Thiol, Mercaptam
	+	$H-\bar{N}<$	→	$R-N<$ + HX	Alkylierung von Aminen
	+	NR'_3	→	$R-\overset{\oplus}{N}R_3$	Quaternisierung
	+	$CN^{\ominus}$	→	R-C≡N	Nitril
			→	R-N=C	Isonitril
	+	$NO_2^{\ominus}$	→	$R-NO_2$	Nitroverbindung
			→	R-ONO	Salpetrige Säure ester, Nitrit
	+	$X'^{\ominus}$	→	R-X' + $X^{\ominus}$	Finkelstein Halogenaustausch
	+		→		Alkylierung C-H acider Verb.
			→		Friedel-Crafts

Allgemeines

- $Yl + R\text{-}X \rightarrow Y\text{-}R + Xl$

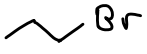
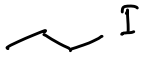
  Nucleophil neutral — Substrat neutral

  z.B.

  $H_2O +$  $\rightarrow$  $+ HBr$

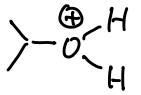
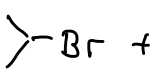
- $Yl^{\ominus} + R\text{-}X \rightarrow Y\text{-}R + Xl^{\ominus}$

  Anion Nucl. — neutral

  $I^{\ominus} +$  $\rightarrow$  $+ Br^{\ominus}$

- $Yl^{\ominus} + R\text{-}X^{\oplus} \rightarrow Y\text{-}R + X$

  z.B.

  $Br^{\ominus} +$  $\rightarrow$  $+ H_2O$

4.11.2013

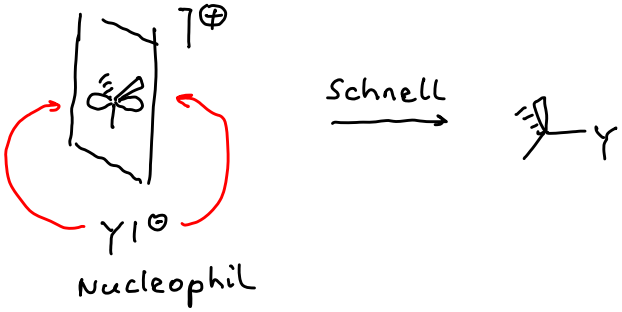
Mechanismen

- S_N1 

  langsam

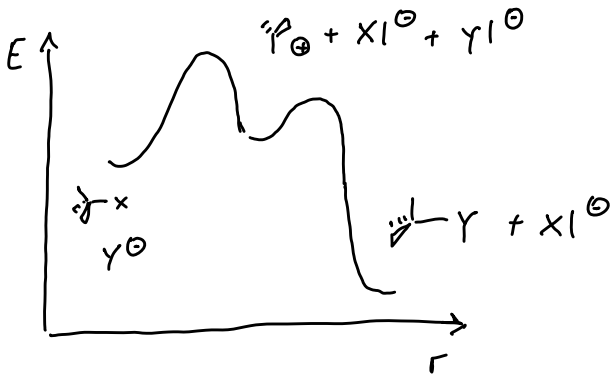
  $+ Xl^{\ominus}$

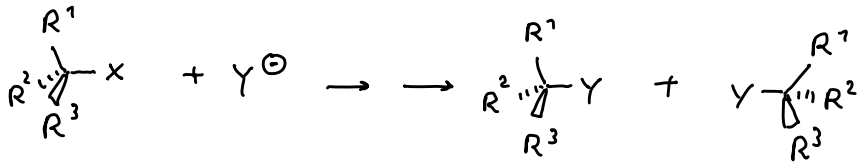
  Abgangsgruppe

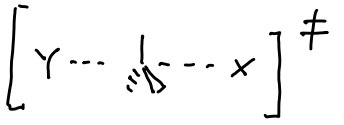


Reaktionsgeschw.

$$-\frac{d[RX]}{dt} = k_1 [RX] \qquad 1.\ Ordnung$$

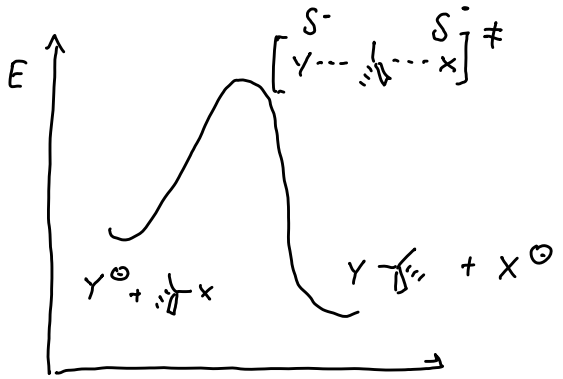




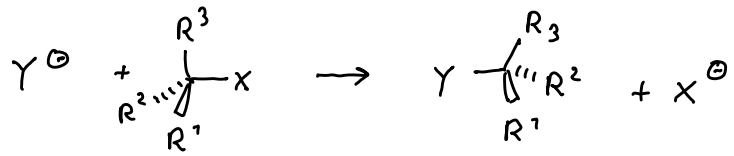
S_N2 : $Y1^{\ominus}$ +  → 

Reaktionsgeschw.

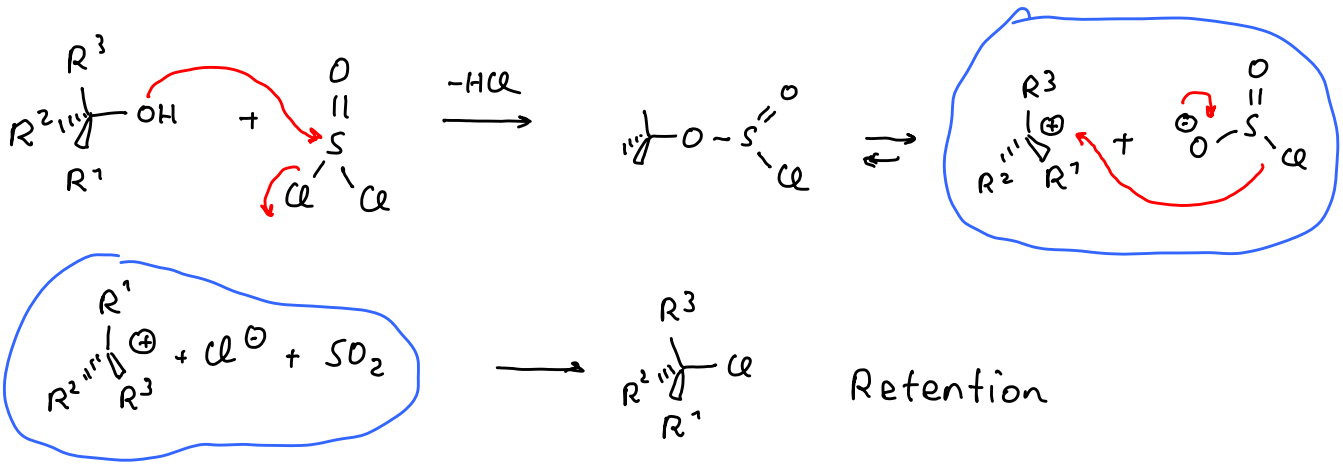
$$-\frac{d[RX]}{dt} = k\,[RX]\,[Y^{\ominus}] \qquad 2.\ Ordnung$$



Stereochemie:

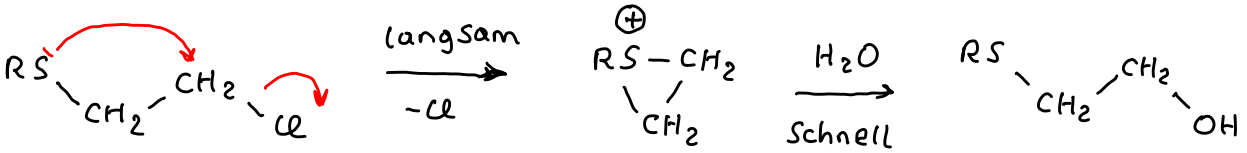


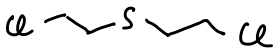
S_Ni: innere Substitution



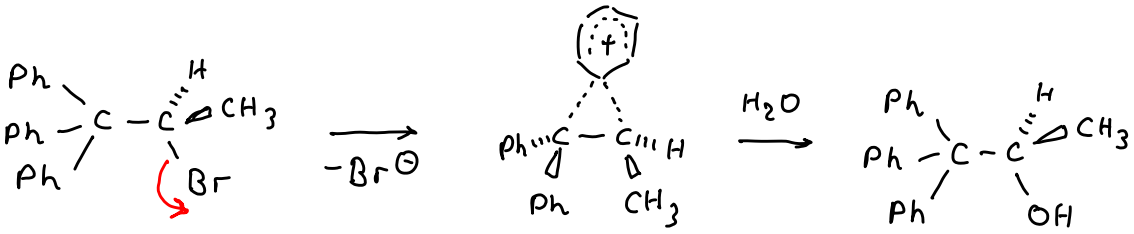
Nachbargruppeneffekte:

Beispiel:





Senfgas, Gelbkreuz, S-LOST



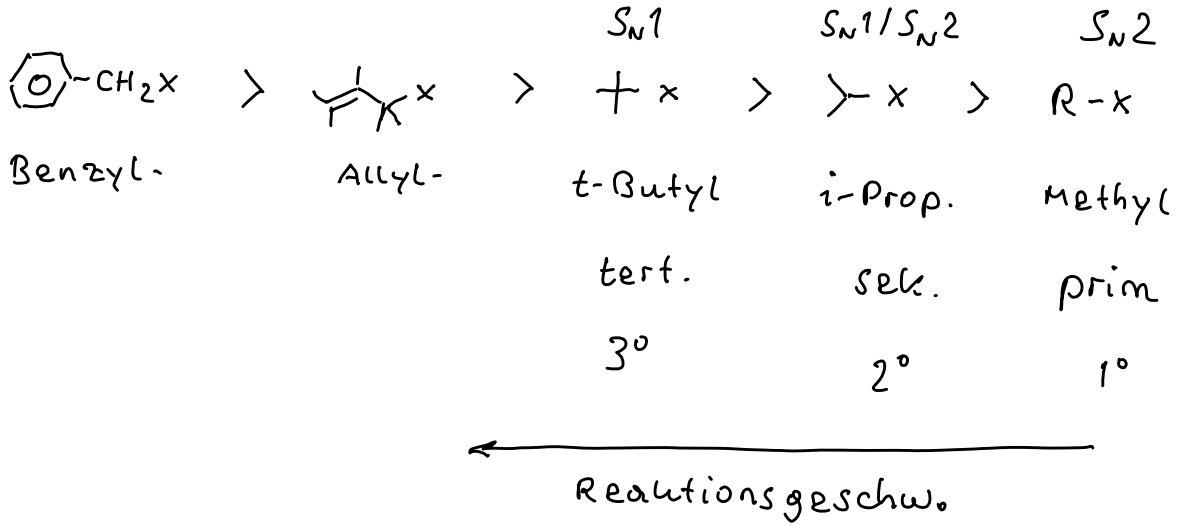
Phenoniumion

Einflüsse auf Mechanismus und Reaktivität

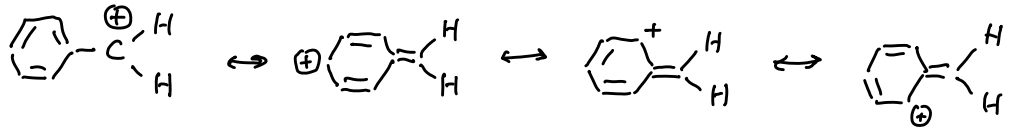
1. Substrat — Stab. der Ladung, Abgangsgruppe, sterischer Effekt
2. Nucleophil
3. Lösgm.

Substrat (Substituenteneffekte)

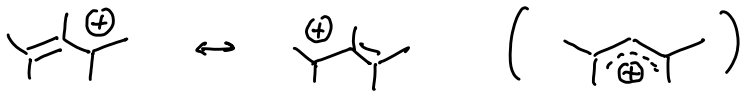
Stabilisierung des Kations bei S_N1



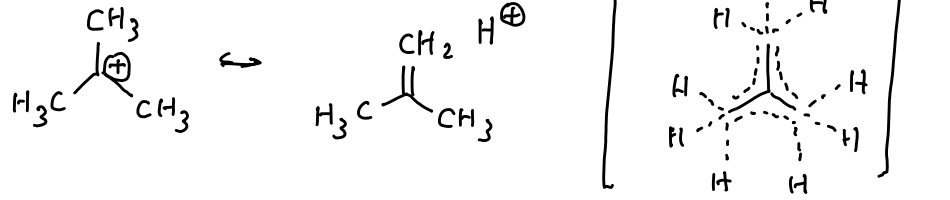
Benzyl:



Allyl:

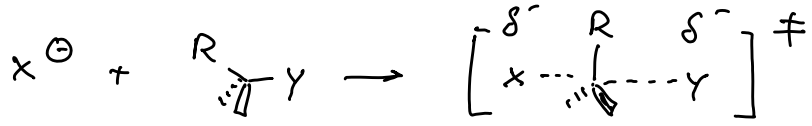


t-Butyl-kat.



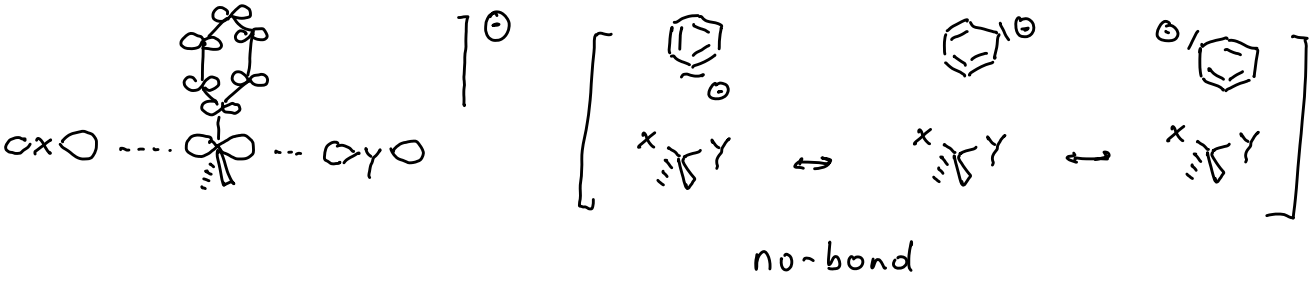
Hyperkonjugation

Stabilisierung der neg. Ladung im Üz der S_N2 Reaktion



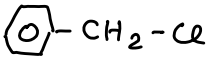
Übergangszustand

— Delokalisierung durch Benzyl- oder Allyl-Subst.



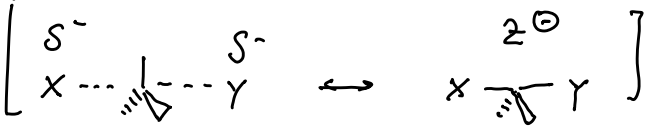
no-bond

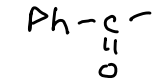
$$R\text{-}Cl + I^{\ominus} \xrightarrow{\text{Aceton}} R\text{-}I + Cl^{\ominus}$$

	$CH_3CH_2CH_2Cl$	$CH_2=CH-CH_2-Cl$	
k_{rel}	1	90	250

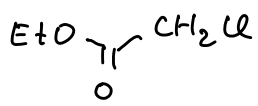
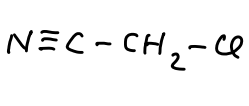
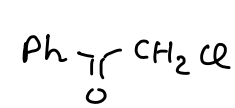
$\Rightarrow$ Benzyl-, Allyl beschleunigen S_N1 und S_N2

— elektronenziehende Subst. (beschl. nur S_N2)



Z = -CN,  , 

$$R\text{-}Cl + I^{\ominus} \xrightarrow{\text{Aceton}} R\text{-}I + Cl^{-}$$

R =   

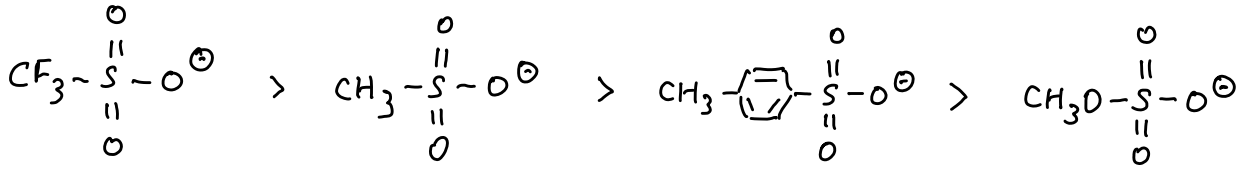
1600	28000	32 000
Chloressigsäureester	Chloracetonitril	Chloracetophenon

Abgangsgruppen

- Reaktivität korreliert mit pK_S der konjugierten Säure

$$I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$$

- große mesomeriestab. Anionen sind gute Abgangsgr.



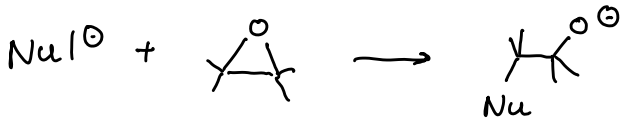
Triflat — Tf

Mesylat — Ms

Tosylat — Ts (Tos)

Sulfat

- "innere" Abgangsgruppen



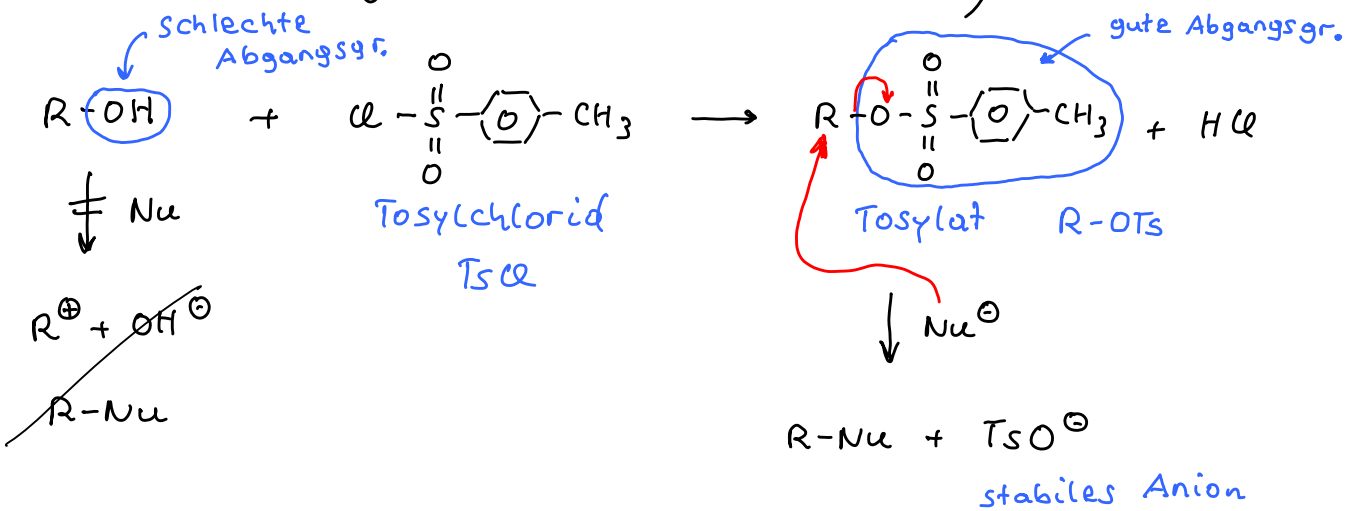
Abbau der Ringspannung

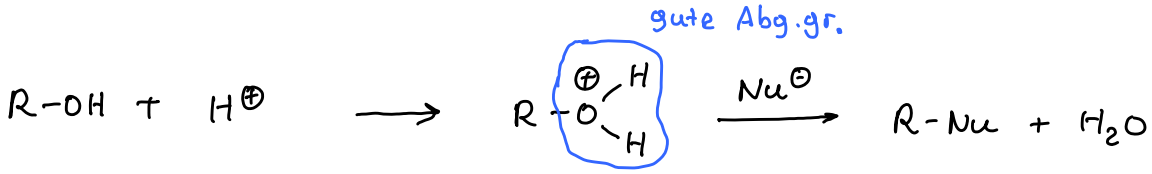
- "besondere" Abgangsgruppe

Diazonium-ion

immer S_N1

Anwendungen (aktivieren von -OH)

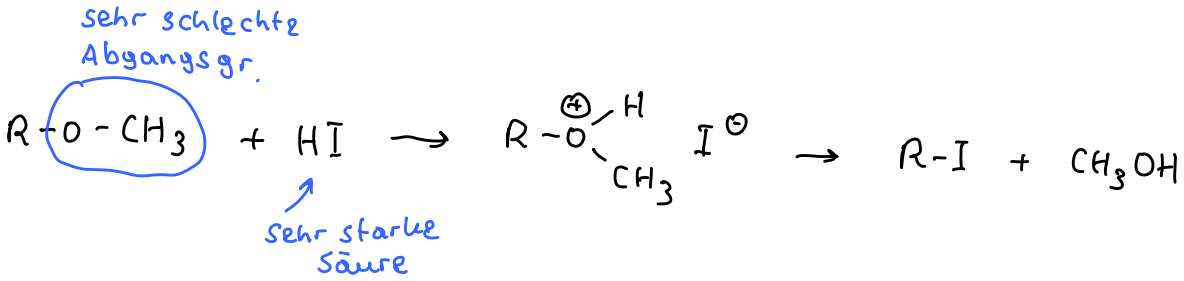




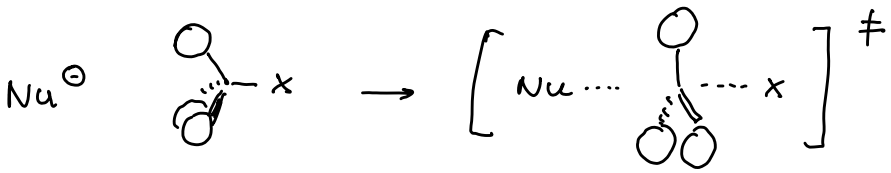
z.B.

$CH_3OH + KBr \not\rightarrow$

$CH_3OH + HBr \longrightarrow CH_3Br + H_2O$



- Sterische Einflüsse



- Bsp. S_N2 (prim. Alkylbromide)
  Subst. am β-C-Atom

$$R\text{-}CH_2\text{-}Br + {}^{\ominus}OCH_3 \longrightarrow R\text{-}CH_2\text{-}OCH_3 + Br^{\ominus}$$

R	H	CH_3	CH_3CH_2	$(CH_3)_2CH$
k_{rel}	122	13	5	1

- Bsp. Wechsel des Mechanismus
  Subst. am α-C-Atom

$$R\text{-}Br + OH^{\ominus} \longrightarrow R\text{-}OH + Br^{\ominus}$$

R	CH_3	CH_3CH_2	$CH_3(CH_3)CH$	$CH_3-C(CH_3)_3$
k_{rel}	21,4	1,7	0,29	1010
Mech.	S_N2	S_N2	S_N2 (S_N1)	S_N1

Wiederholung

6.11.2013

$$R\text{-}X + Nu^{\ominus} \rightarrow R\text{-}Nu + X^{\ominus}$$

Mechanismen

S_N1, S_N2, S_Ni, Nachbargruppeneffekte

Stereochemie

Reaktivität

Substrat

- Stab. der Zwischenstufe (Kation S_N1)
- stab. des Übergangszustandes (neg. Partialladung, S_N2)
- Abgangsgruppen
- Sterik

Nucleophil

Lösungsmittel

wichtige synth. Beispiele

Nucleophile u. Lösungsm.

S_N1: Geschw. abhängig von Lsgm.polarität

Bsp.: t-BuCl $\xrightarrow{Solv.}$ $(t\text{-}Bu^+)_{solv.} + (Cl^-)_{solv.}$

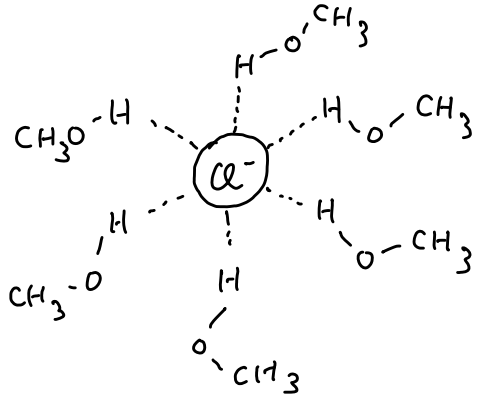
Solv.	EtOH	MeOH	HCOOH	H_2O
k_{rel}	1	9	12 200	335 000

S_N2: Geschw. abhängig von:

Nucleophil
- Basizität
- Polarisierbarkeit (hart/weich)
- geladen, ungeladen
- sterischer Anspruch

Lösungsmittel
- Polarität
- protisch / aprotisch

Nucleophilie in protischen Lsgm., z.B. CH_3OH:



Solvatisierung von Cl^- durch H-Brücken
⇒ Reduktion der Nucleophilie

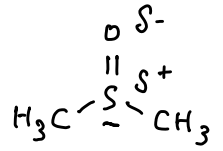
weich — wenig solv. — hart — stark solv

$$N_3^\ominus > I^\ominus > CN^\ominus > Br^\ominus > Cl^\ominus > F^\ominus$$

polarisierbar — weniger polarisierbar

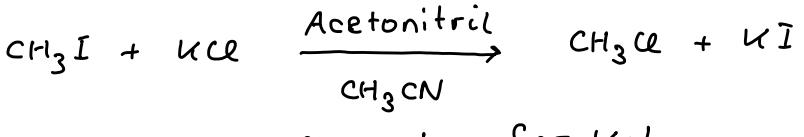
$$PhSe^\ominus > PhS^\ominus > PhO^\ominus$$

Nucleophilie in dipolar aprotischen Lsgm. z.B. DMSO

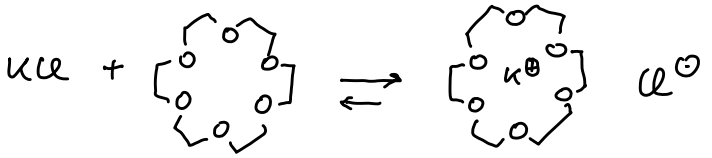


$$CN^\ominus > N_3^\ominus > Cl^\ominus > Br^\ominus > I^\ominus$$

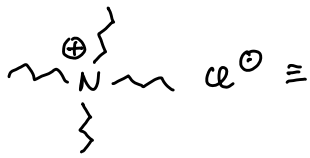
z.B. Finkelstein



Phasentransfer-Kat.



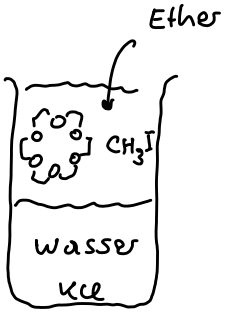
Lösl. in org. Lsgm.



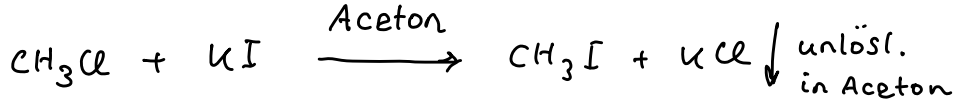
Tetrabutyl-ammonium-chlorid

$\equiv Bu_4N^{\oplus} Cl^{\ominus}$

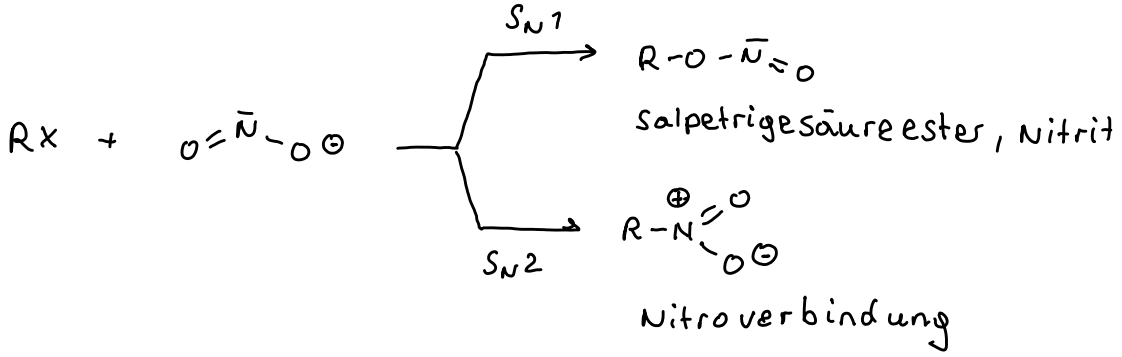
Lösl. in org. Lsgm.

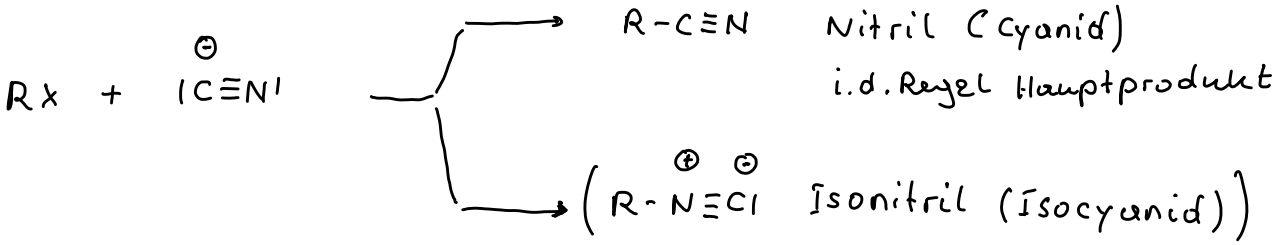


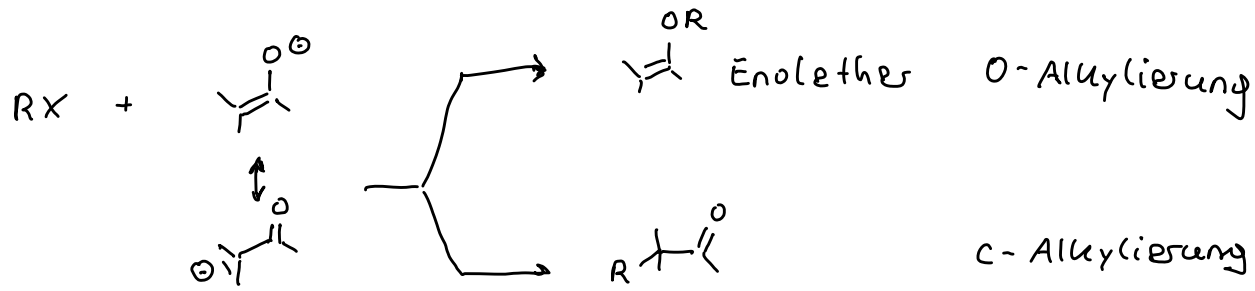
aber:



Ambidente Nucleophile







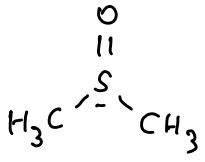
- prot. Lsgm. bremsen Reaktivität der Nucleophile

$$Nu^{\ominus} + H\text{-}Y \rightarrow Nu\cdots H\text{-}Y$$

- polare (dipolar aprot.) Lsgm. erhöhen Reaktivität mit steigender Polarität

Lsgm.	CH_3OH	DMSO	DMF	CH_3CN	HMPT
k_{rel}	1	1300	2800	5000	200 000

wichtige dipolar aprot. Lsgm.:

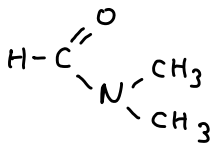


$\mu = 4.0$ D

Sdp. 189 °C

DMSO

Dimethylsulfoxid

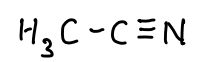


$\mu = 3.2$ D

Sdp. 153 °C

DMF

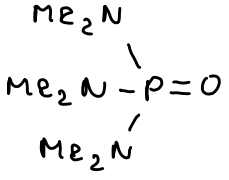
Dimethylformamid



$\mu = 3.5$ D

Sdp. 82 °C

Acetonitril



$\mu = 5.5$ D

HMPT

Hexamethylphosphorsäure triamid.

carcinogen

Zum Vgl. H_2O : $\mu = 1{,}72\ D$, CH_3OH : $\mu = 1{,}70\ D$

Synthetisch wichtige Beispiele:

1. $ROH \longrightarrow RX$

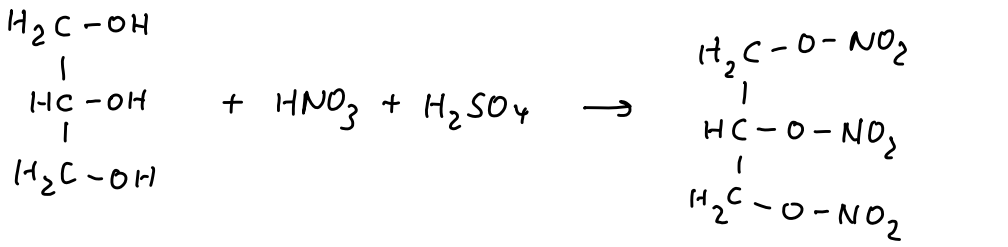
a) $ROH + HBr \rightleftharpoons RBr + H_2O$

b) $ROH + SOCl_2 \rightarrow R\text{-}Cl + SO_2 + HCl$

c) $ROH + PX_3 \rightarrow R\text{-}X + H_3PO_4 \qquad X = Cl, Br, I$

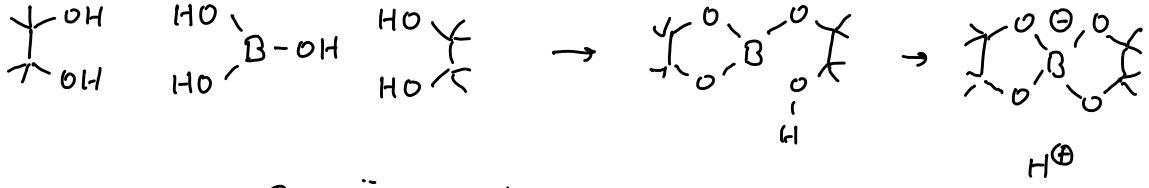
d) $ROH + PCl_5 \rightarrow R\text{-}Cl + HCl + POCl_3$

ad a)



Glycerintrinitrat
Nitroglycerin

andese: Nitrocellulose,
Pentaerythroltetranitrat (Nitropenta)

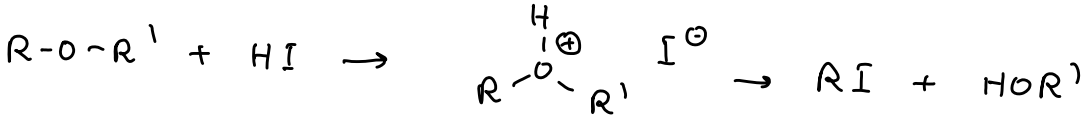


Borsäureester

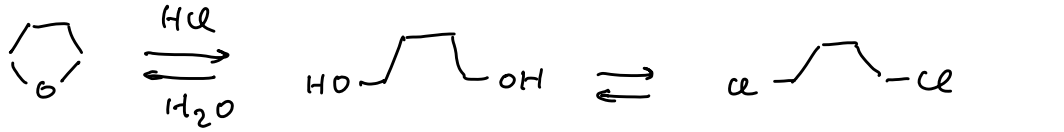
~~Mitsunobu~~

~~Mukayama~~

2. saure Veretherung - Etherspaltung

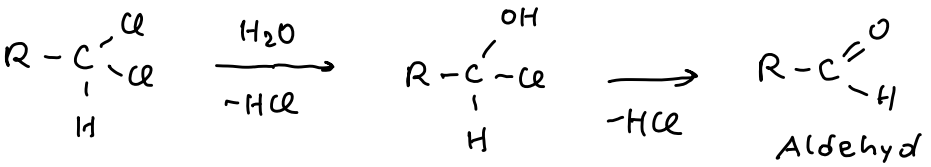


z.B.

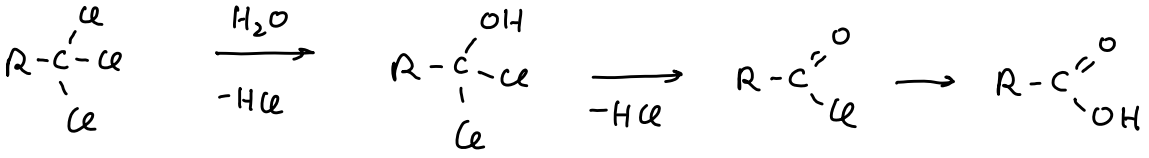


1,4-Dichlorbuten

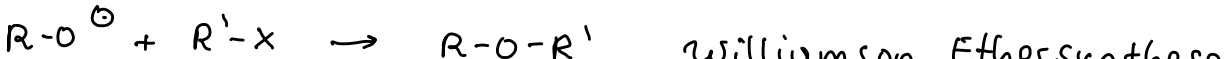
3. Hydrolyse



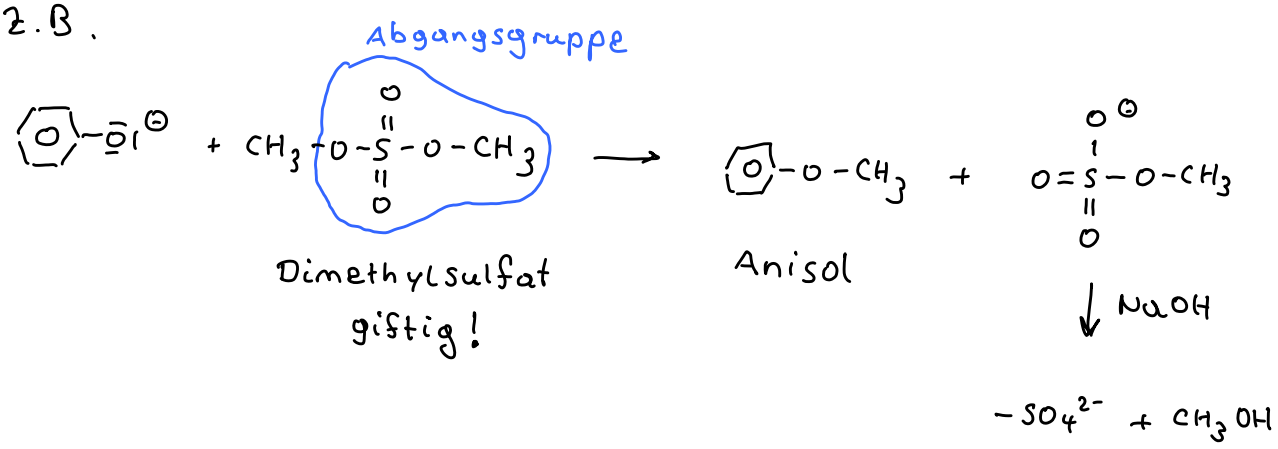
Aldehyd



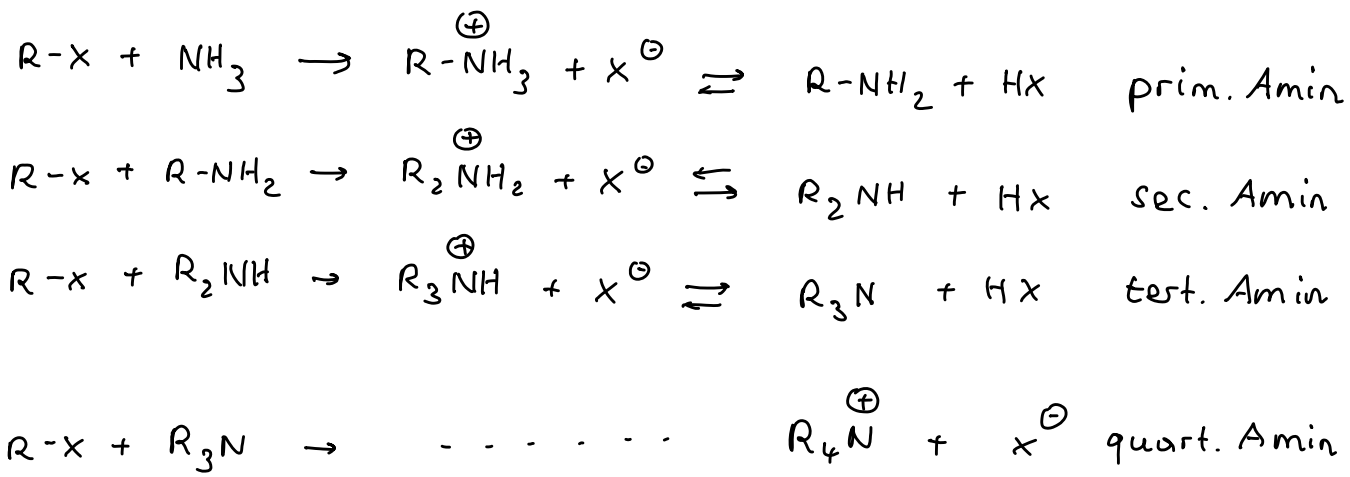
4. Alkylierung von Alkoholen und Phenolen



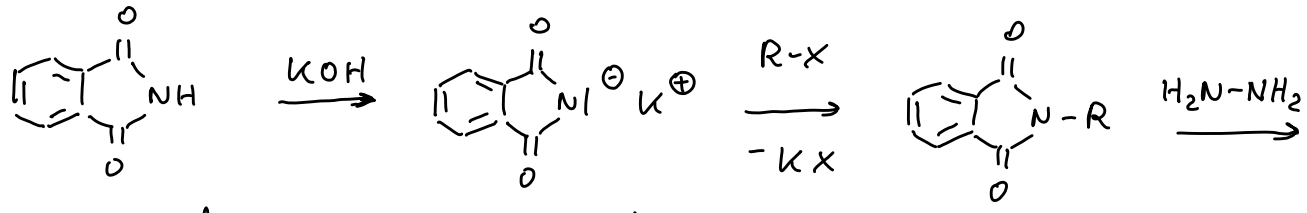
z.B.



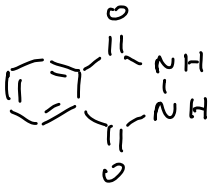
5. Alkylierung von Ammoniak und Aminen



Gabriel Synthese (für prim. Amine)



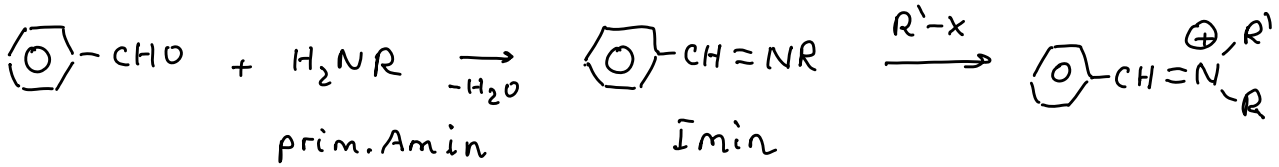
Phthalimid — resonz stab. Imid



+ H_2NR

prim. Amin

für sek. Amine:

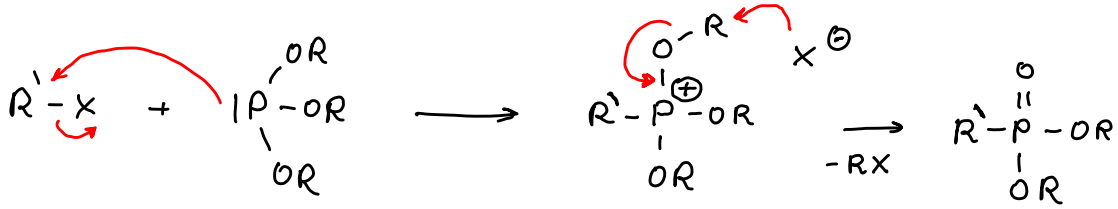


prim. Amin — Imin

$\xrightarrow{H_2O}$ $H-N(R')(R)$ sek. Amin

6. Alkyliesung von Phosphorverbindungen

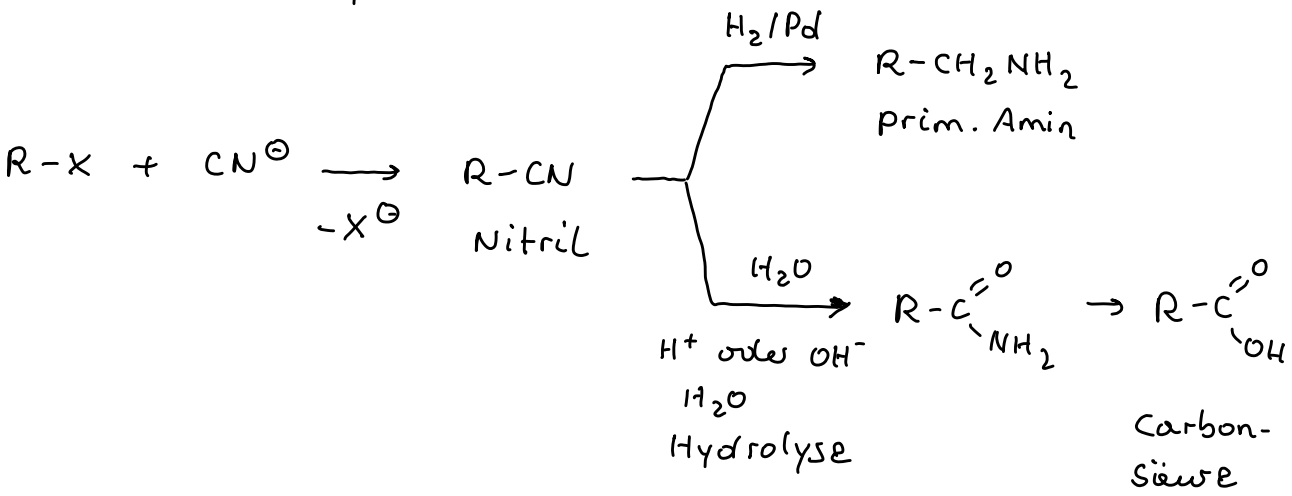
Michaelis - Arbuzov

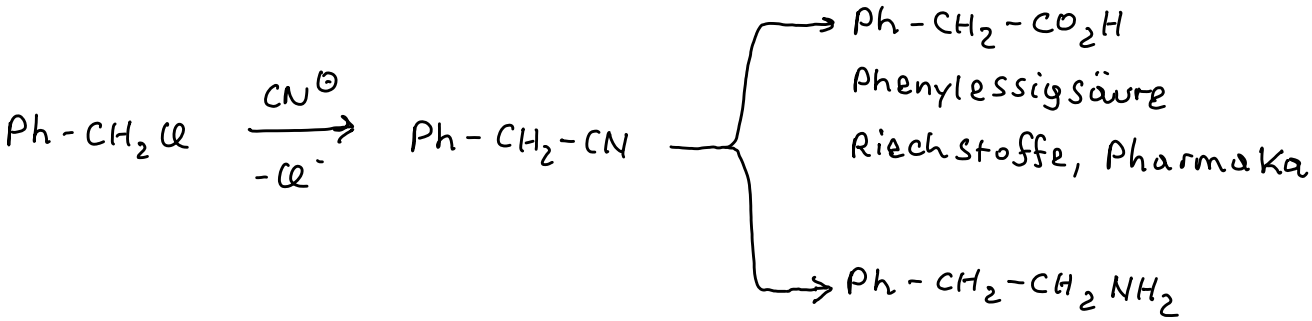


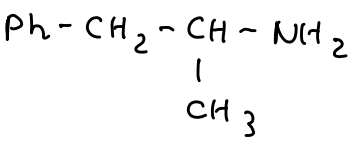
Trialkylphosphit

Phosphonat

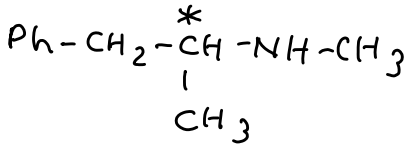
7. Kolbe Nitrilsynthese





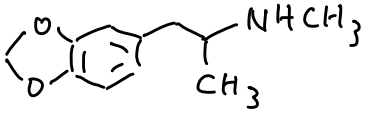


Amphetamin



Methamphetamin

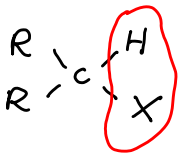
Crystal Meth

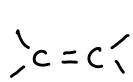


Ecstacy

Eliminierungen D3

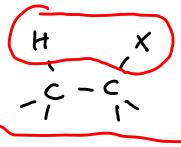
11.11.2013





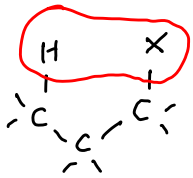
α - Eliminierung

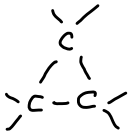
1,1 - Eliminierung



β - Eliminierung

1,2 - Eliminierung



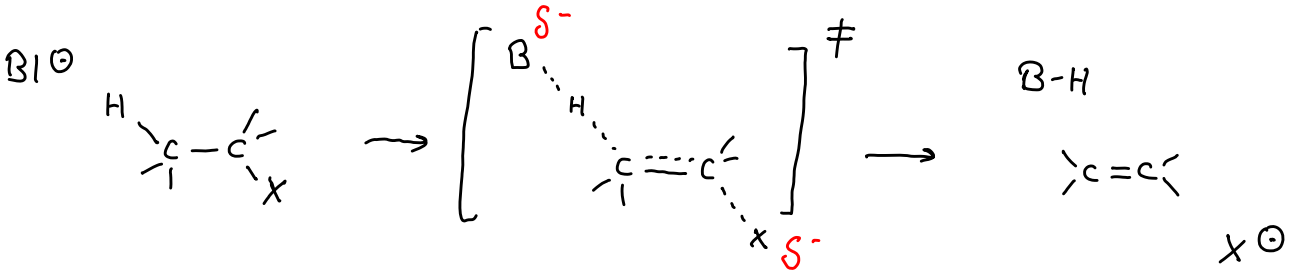


γ - Eliminierung

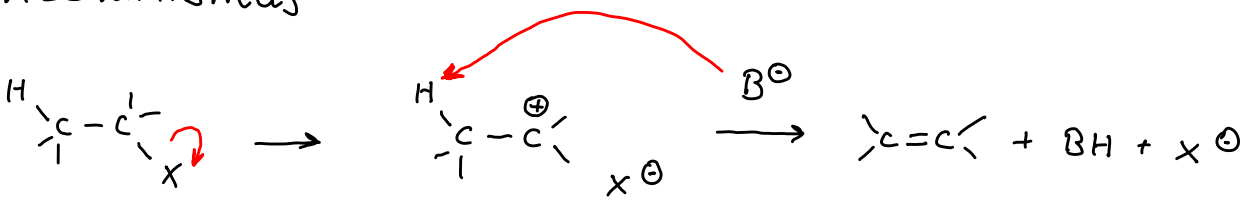
1,3 - Eliminierung

Mechanismen β-Eliminierung

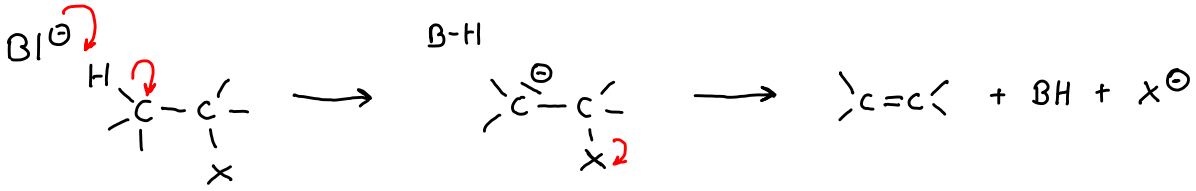
- E2 Mechanismus



- E1 Mechanismus

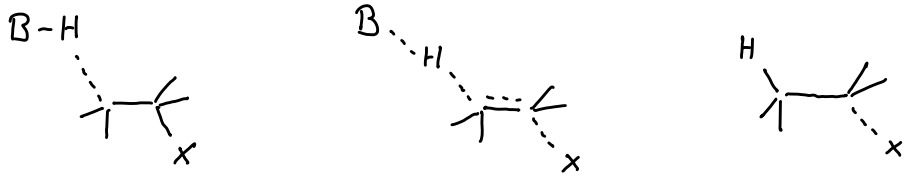


- $E1_{cb}$ Mechanismus



zunehmender C-H - Bindungsbruch ←

Übergangs zustände



Mechanismen $E1_{cb}$ E2 E1

→ zunehmender C-X Bindungsbruch

Reaktivität

1. Abgangsgruppe X
2. Base $B|^{\ominus}$
3. elektron. u. sterische Effekte (Subst. im Substrat)
4. Lösungsmittel-Effekte

E1 mechanismus wird begünstigt durch:

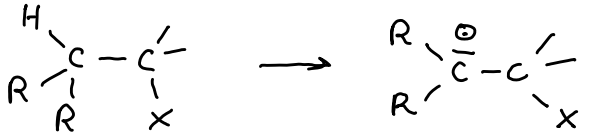
gute Abgangsgr. X

kationen-stab. subst. z.B. R = Ph

polare Lsgm. (DMSO, DMF, TFA, ... CF_3CH_2OH)

$E1_{cb}$ wird begünstigt durch

$B|^{\ominus}$



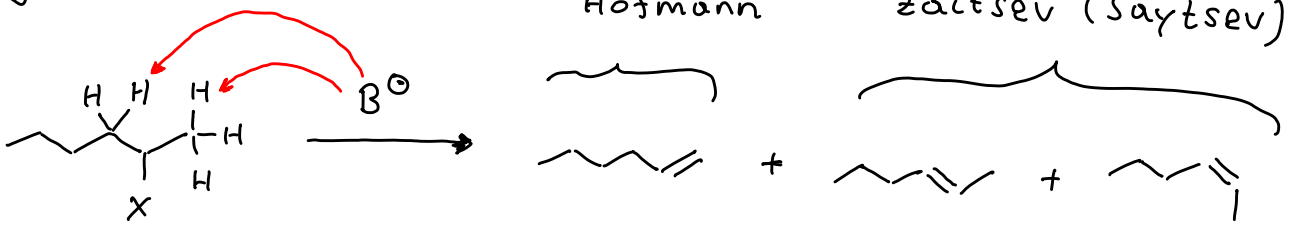
sehr starke (oder gehinderte) Basen (NaH, t-BuO$^{\ominus}$)

Anionenstab. Subst. R =  , $-NO_2$, $-SO_3R$, $-CN$

Stark elektronen ziehende Abgangsgr. $-\overset{\oplus}{N}R_3$

Schlechte Abgangsgr. X

Regiochemie



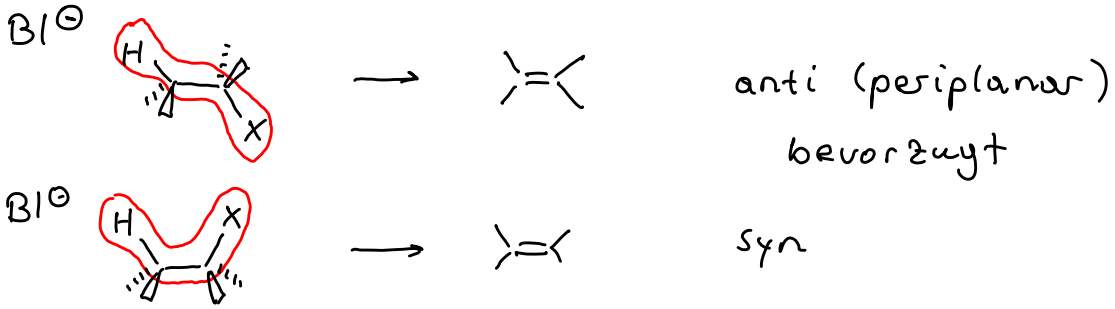
2-subst. Hexan

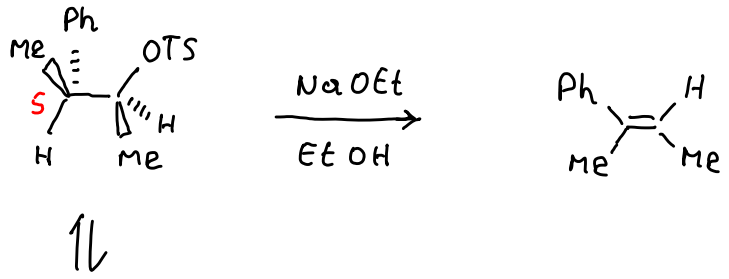
X	B⊖				Mech.
I	$MeO^\ominus/MeOH$	19%	63%	18%	E2
Cl	"	33%	50%	17%	E2/$E1_{cb}$
F	"	69%	21%	9%	$E1_{cb}$
I	$t\text{-}BuO^\ominus/t\text{-}BuOH$	78%	15%	7%	$E1_{cb}$

gute Abgangsgr. => E1 oder E2 → höher subst. Olefin
Saytsev stabiler

schlechte Abg.gr => $E1_{cb}$ → weniger subst. Olefin
gehinderte Base Hofmann

Stereochemie

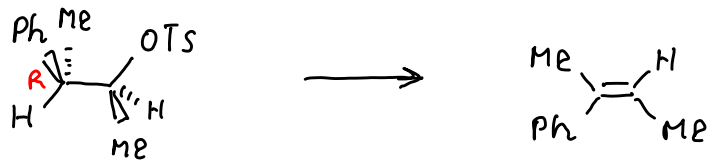




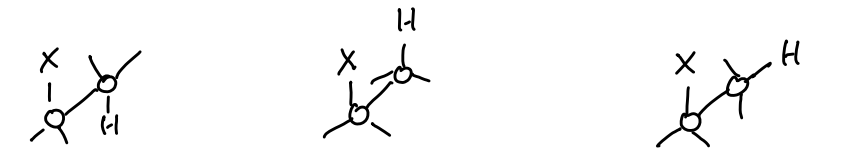
Ts : $-SO_2-C_6H_4-CH_3$

Et : CH_2CH_3

Me : CH_3



anderes Enantiomer



anti-periplanar

günstig

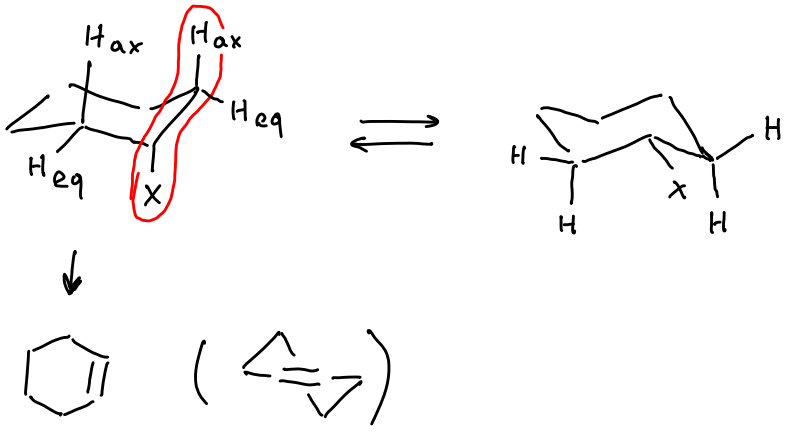
syn periplanar

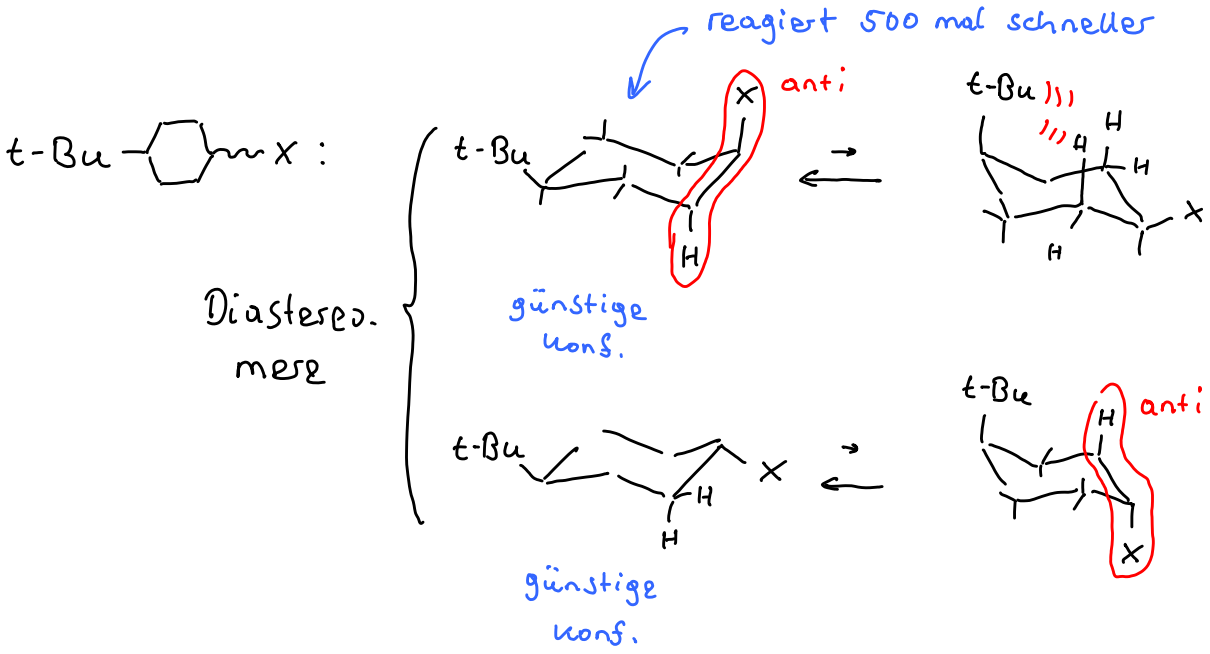
weniger günstig

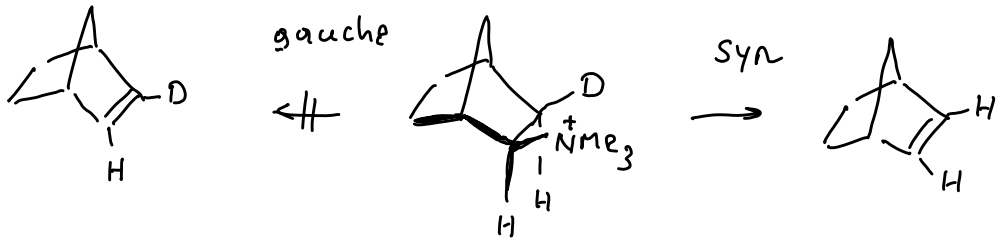
gauche

ungünstig

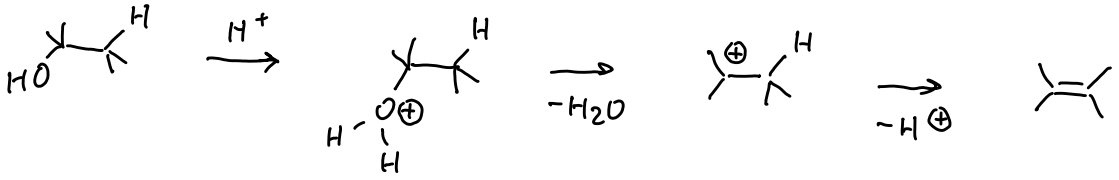
in cyclischen Systemen

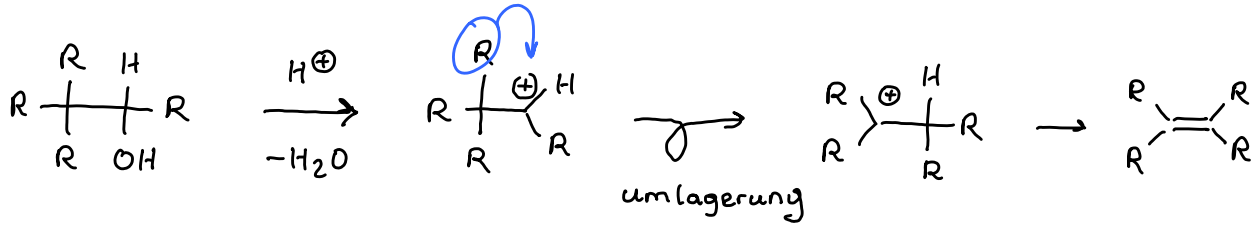






Dehydratisierung von Alkoholen



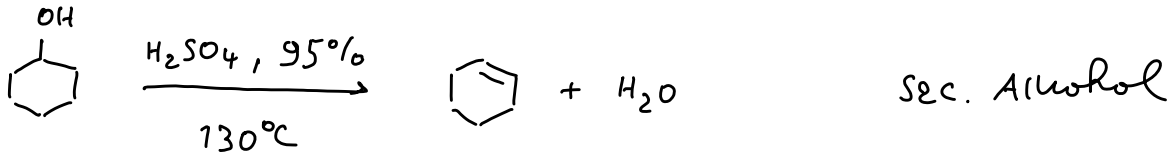


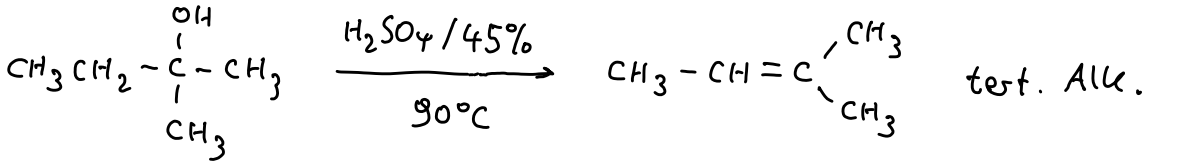
konkrete Beispiele

nucl. Subst. $CH_3CH_2OH \xrightarrow[140°C,\ -H_2O]{H_2SO_4} CH_3CH_2\text{-}OSO_2OH \xrightarrow{CH_3CH_2OH}$

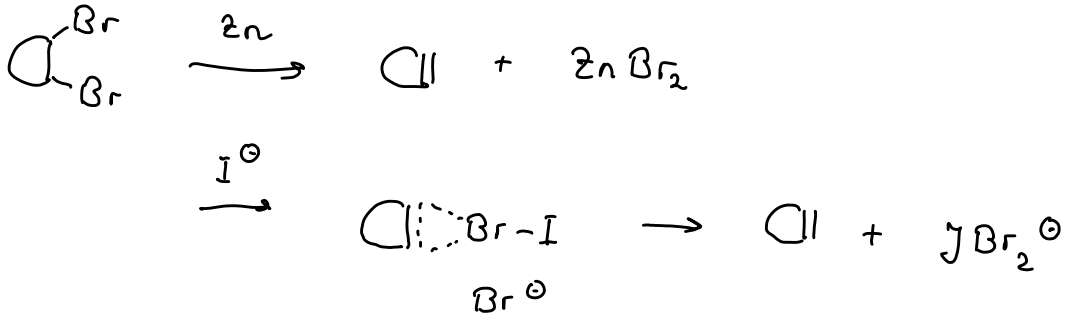
$$CH_3CH_2OCH_2CH_3 + H_2O + H_2SO_4$$

Eliminierung: $CH_3CH_2OH \xrightarrow[170°C]{H_2SO_4} CH_2=CH_2 + H_2O$ prim. Alkohol

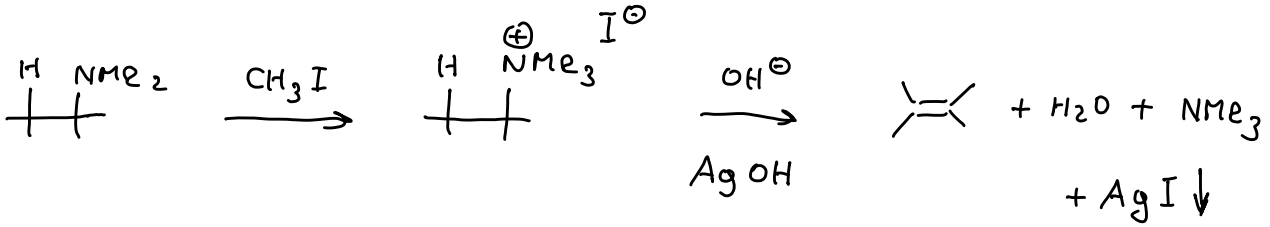




andere β-Eliminierungen

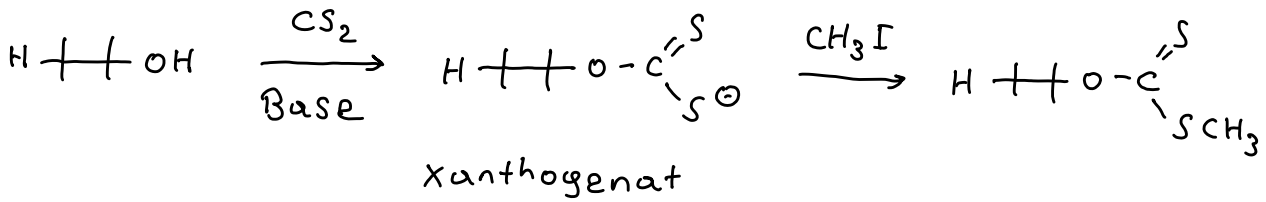


Hofmann Eliminierung (Abbau)

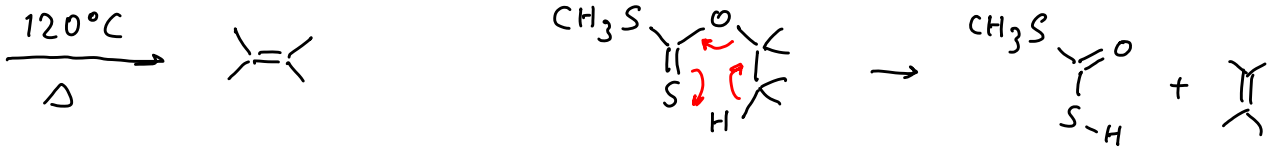


Regiochemie: Hofmann-Produkt

Thermische cis-Eliminierung



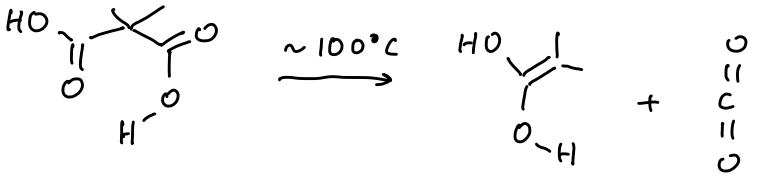
Xanthogenat

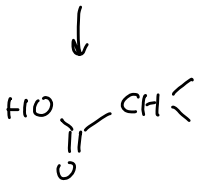


Mechanismus

Acetat Pyrolyse

Keton - Spaltung (Decarboxylierung von 1,3-Ketocarbonsäuren)





subst. Essigsäure

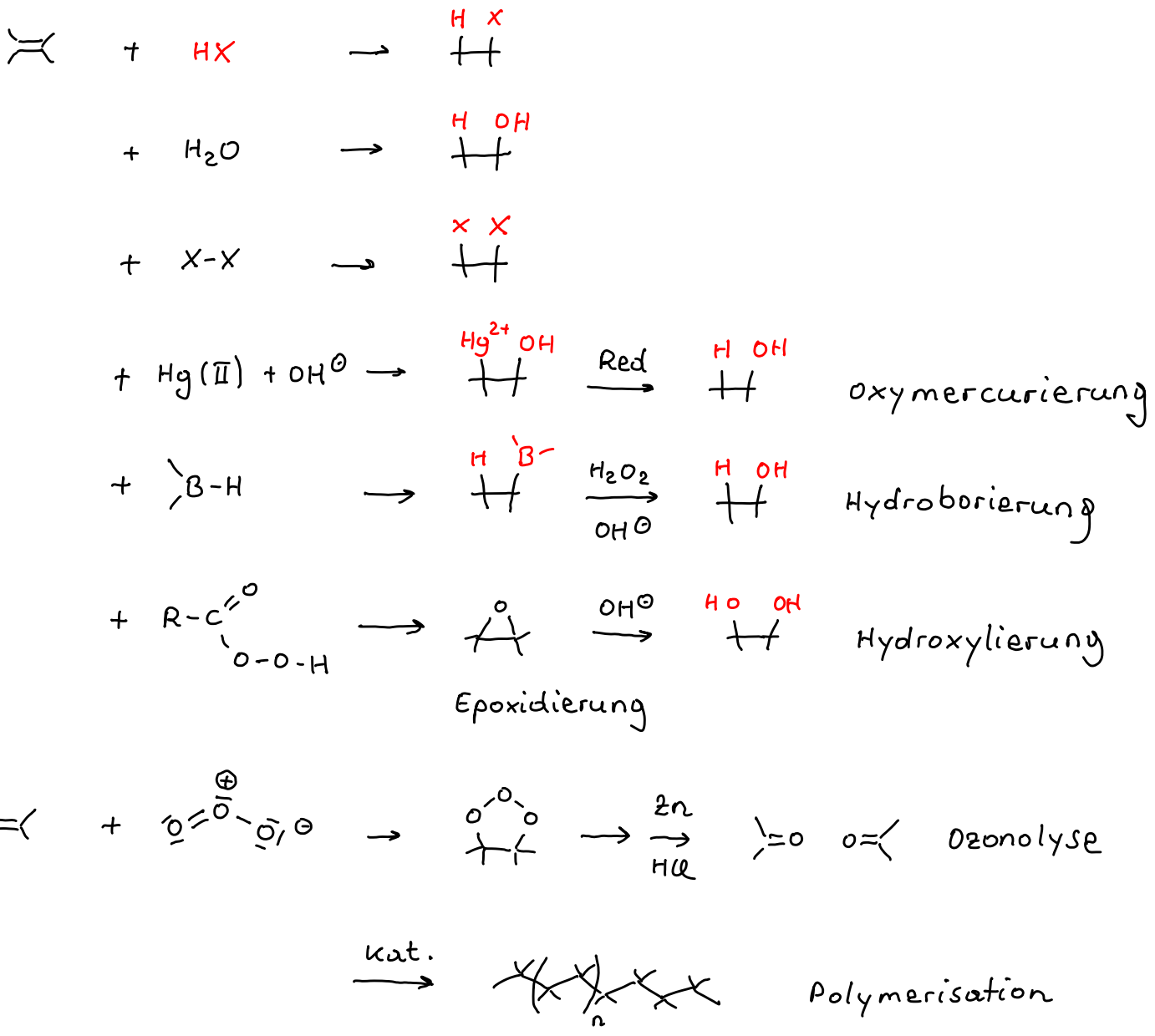
13.11.2013

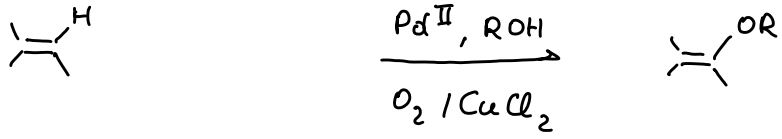
Additionen an C=C - Bindungen D.4.

- electrophile Additionen
- nucleophile Additionen
- radikalische Additionen
- metallvermittelte Additionen

---

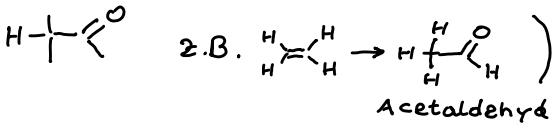
synthetisch wichtige Reaktionen

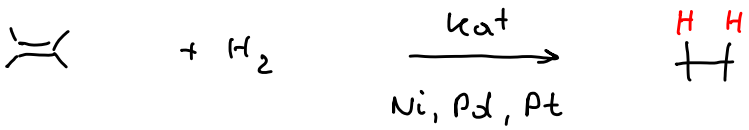




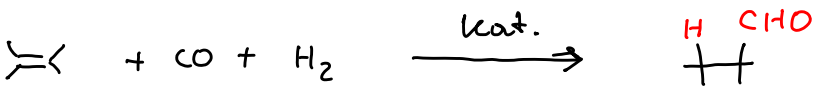
Oxypalladierung

(Wacker-Prozess für R=H

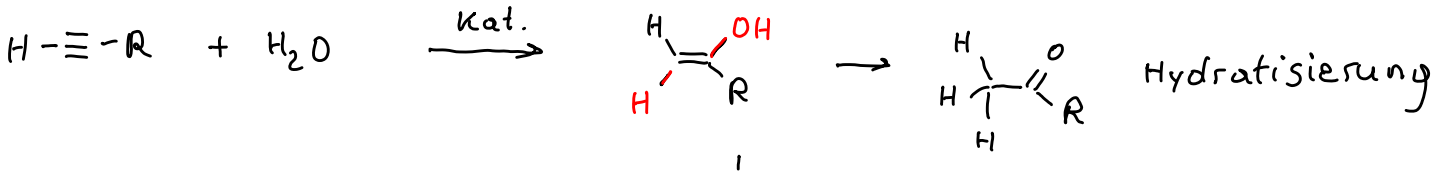




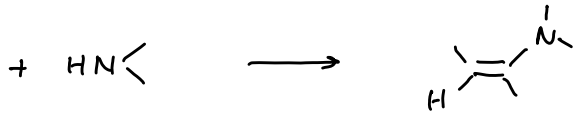
kat. Hydrierung



Hydroformylierung

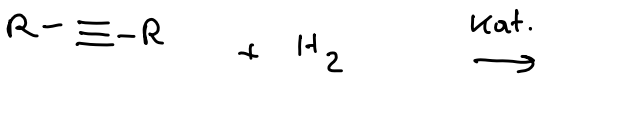


Hydratisierung



Aminierung

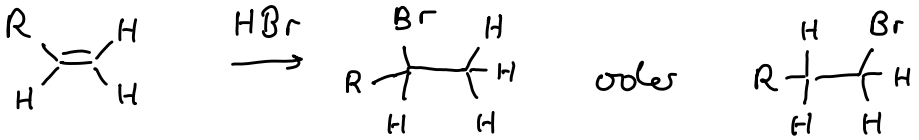
Halogenierung



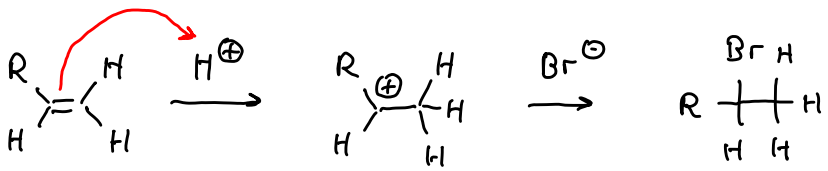
cis-Hydrierung

(Lindlar)

- electrophile / radikal. Addition



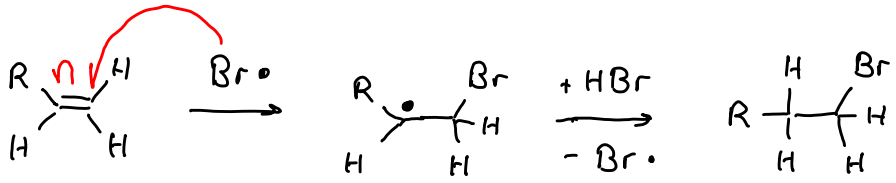
Mechanismus:



stab. kation

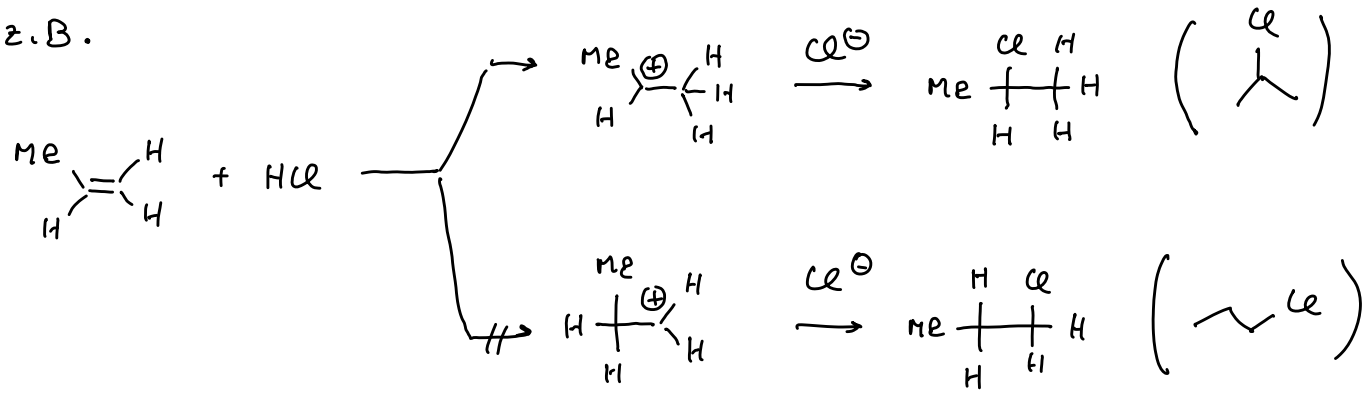
Markownikoff

radikalisch: H-Br + R· → R-H + Br· Radikalstart

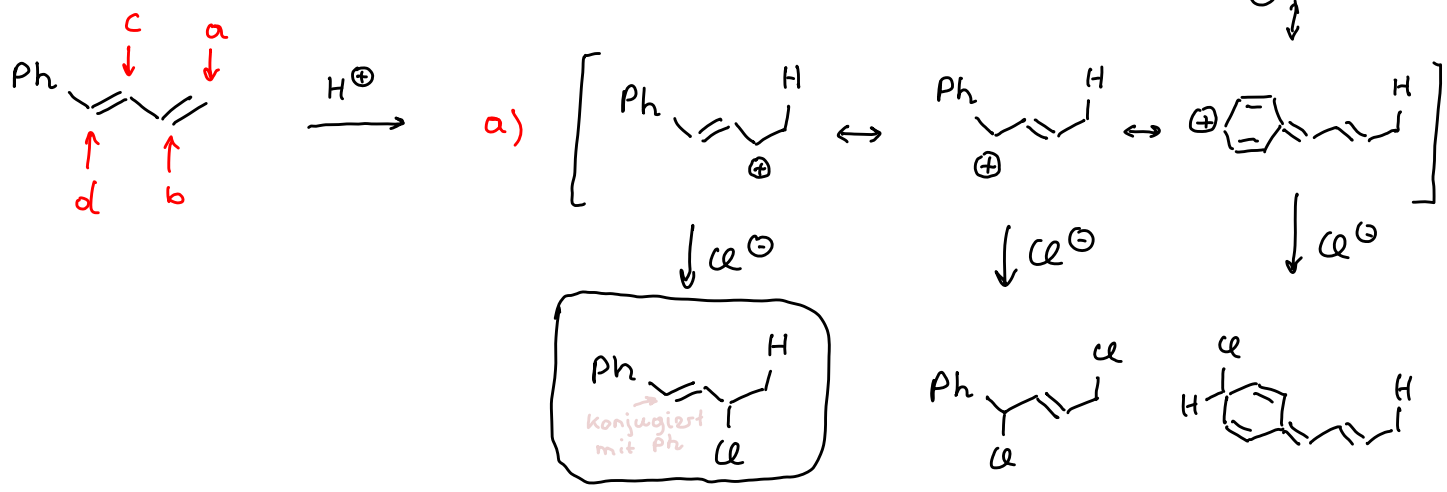


stab. Radikal anti-Markownikoff

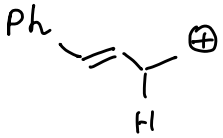
z.B.

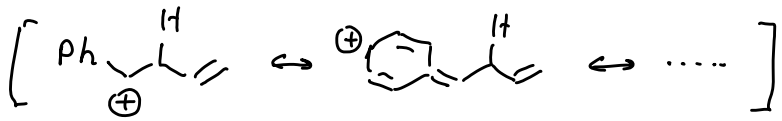


Beispiel Regioselektivität

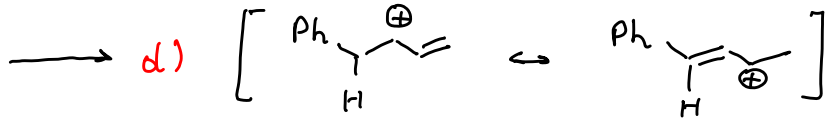


98% Ausbeute

→ b)  primkat. ungünstig

→ c) 

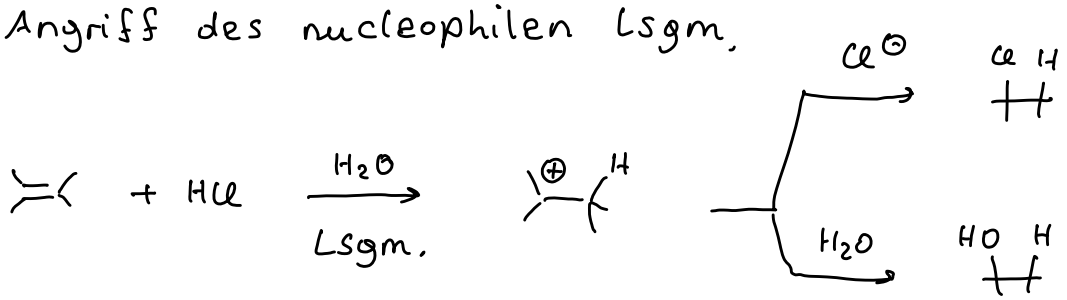
Benzyl- u. sek.



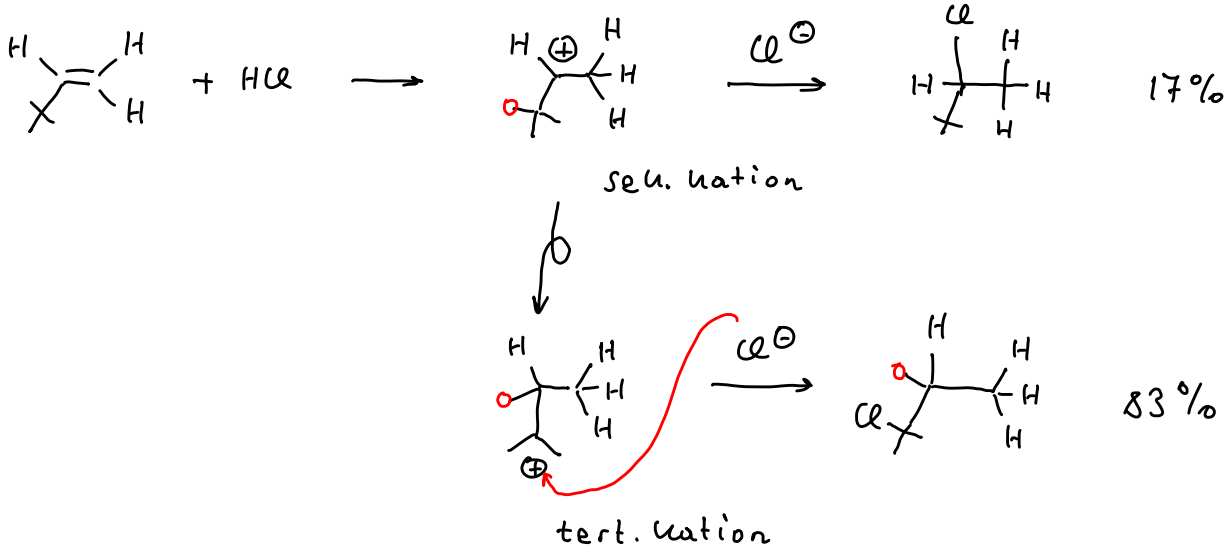
Allyl-kat.

Nebenreaktionen:

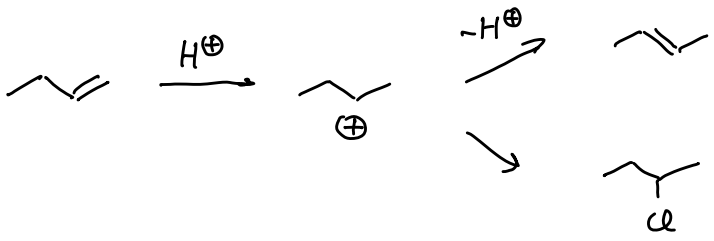
- Angriff des nucleophilen Lsgm.



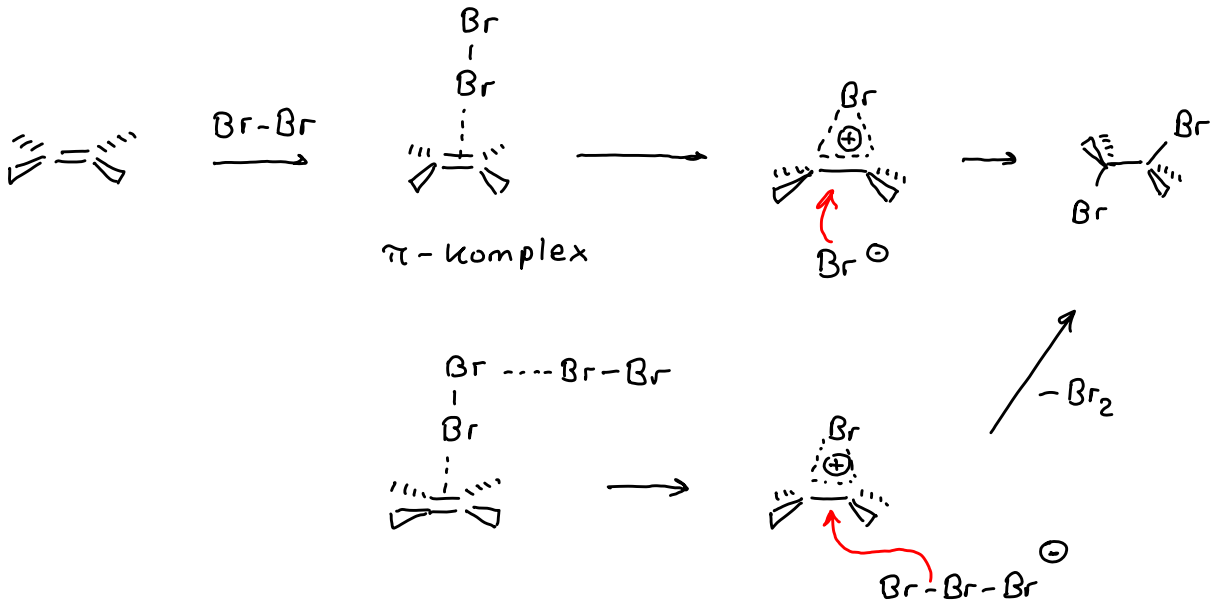
- Umlagerungen



- Eliminierungen / Subst.



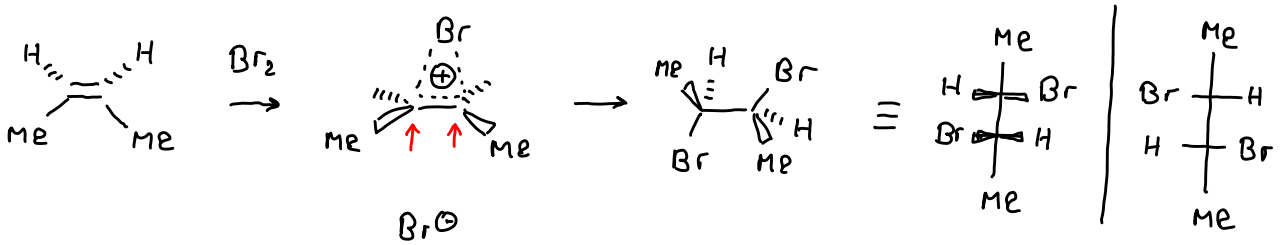
Addition von X_2



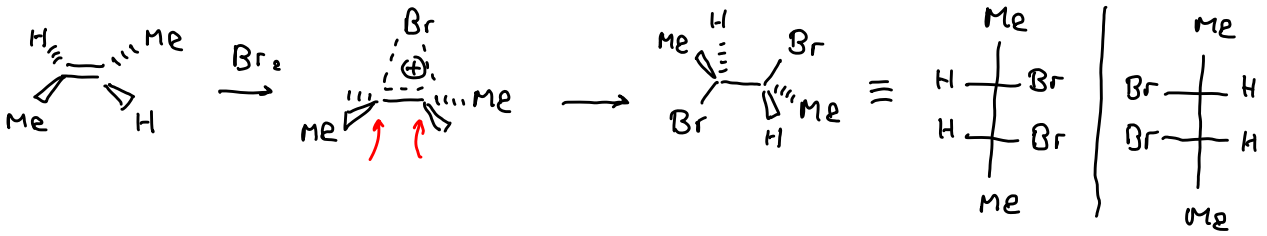
Beispiele für anti-Addition

1. 

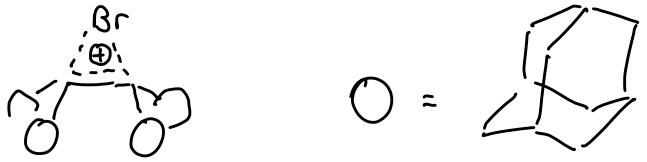
trans-Addukt

2. 

d,l-Dibromid
Racemat

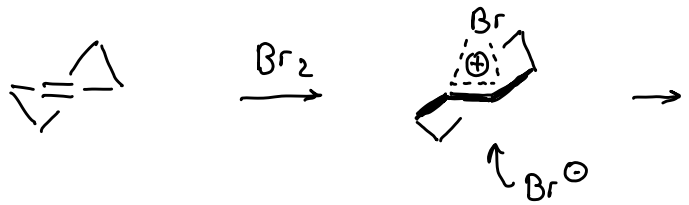


meso-Dibromid

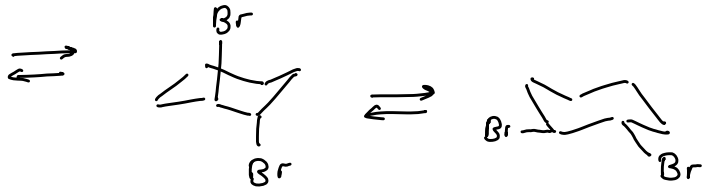
3. 

(Adamantyl)

Addition an Cyclohexene



Cyclohexan
Twist-konform.



Sessel-konformation

bis-axial

bis-equatorial
günstiges

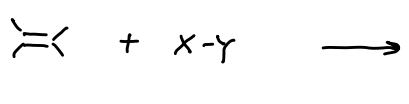
Wiederholung

20.11.2013

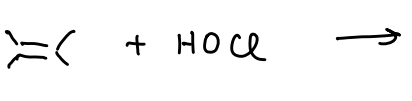
- Addition von HX
  - Markownikoff — elektrophil
  - anti " — radikalisch
  - benzyl > allyl > tert. alkyl — Regioselektivität
  - Wolfenreaktionen, umlag., nucl. Add., Eliminierung
- Addition von X_2
  - Mechanismus
  - Stereochemie

---

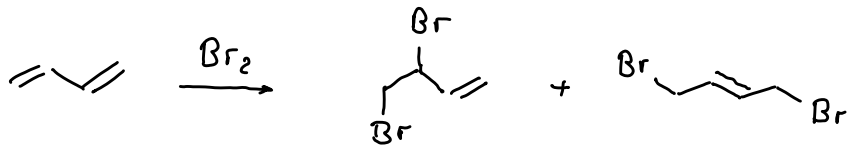
gemischte Halogene, Hypohalogenide



Cl-Br
I-Cl

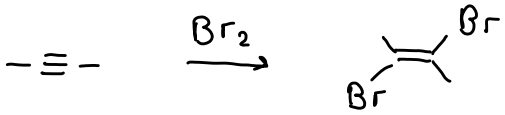


Diene



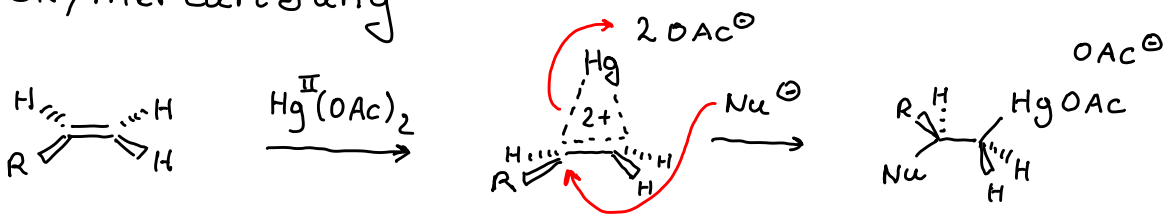
1,2-Addition 1,4-Addition

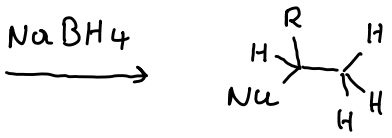
Alkine



trans (meistens)

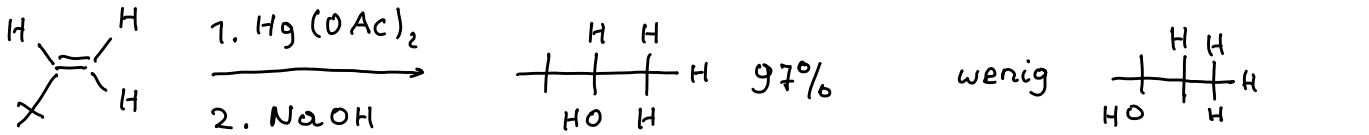
Oxymercurierung

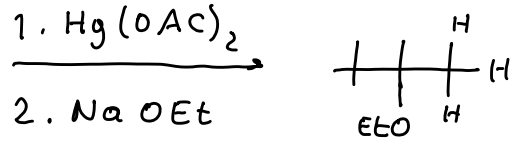




Ac = $-\overset{\overset{O}{\|}}{C}-CH_3$ $Nu^{\ominus} = OH^{\ominus}, RO^{\ominus}, RCO_2^{\ominus}$

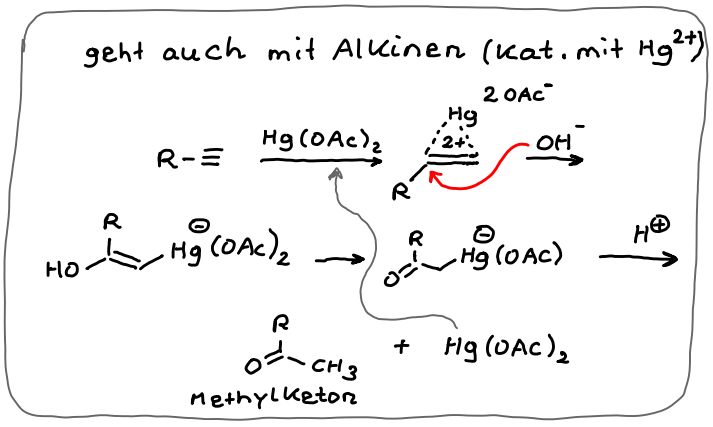
z.B.



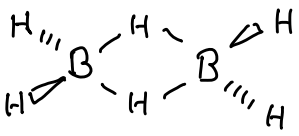


Vorteile gegen Säure kat. Anlagerung

- mildere Bedingungen
- keine umlag. oder Elimin.
- höhere Stereoselektivität



Hydroborierung



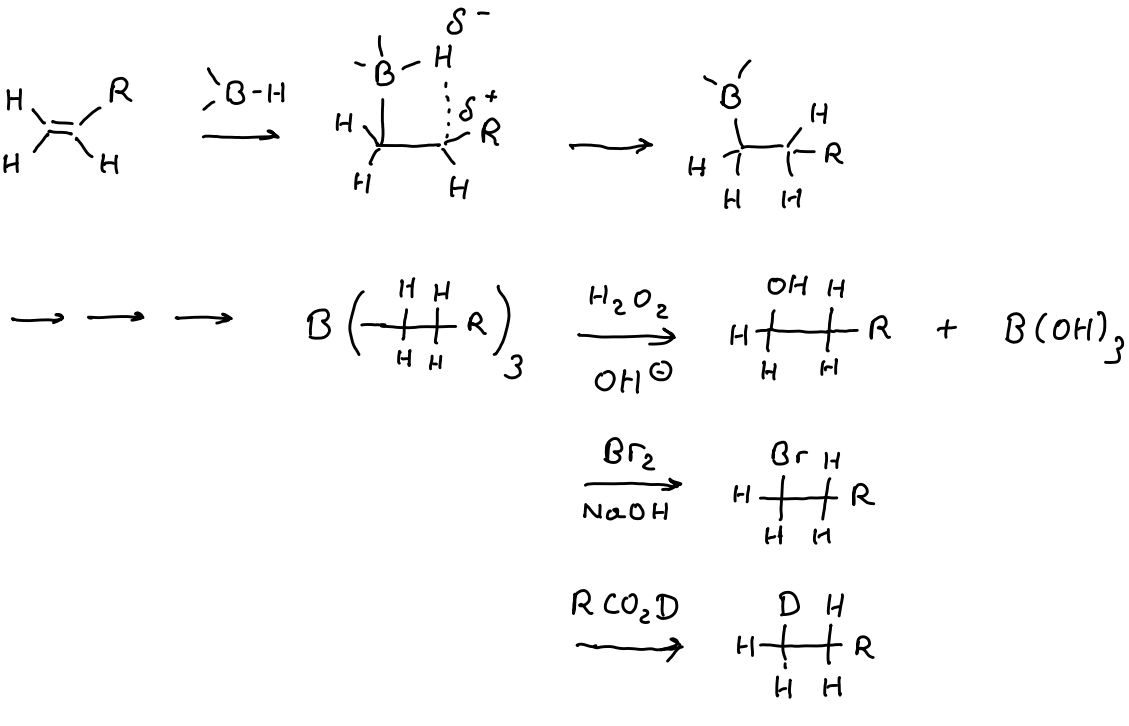
Diboran

Herstellung in situ:

$$3\ NaBH_4 + BF_3 \longrightarrow 3\ NaF + 2\ B_2H_6$$

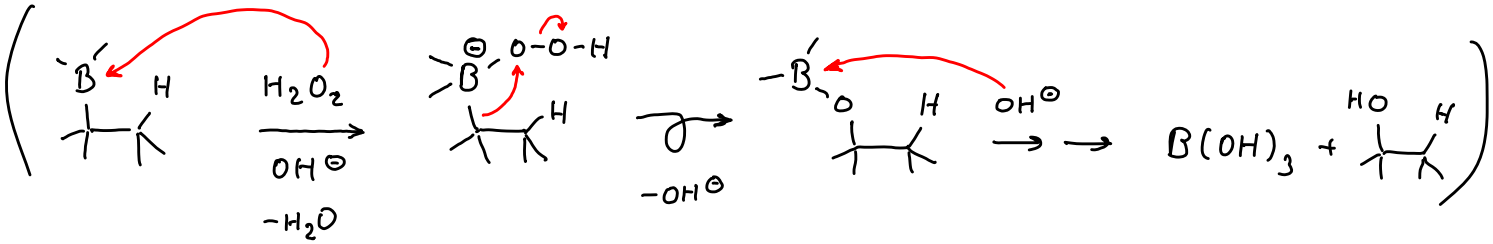
$$B_2H_6 + Et_2O \longrightarrow H_3B \cdots OEt_2 \quad \text{(Ether Komplex)}$$

vereinfachte Schreibweise

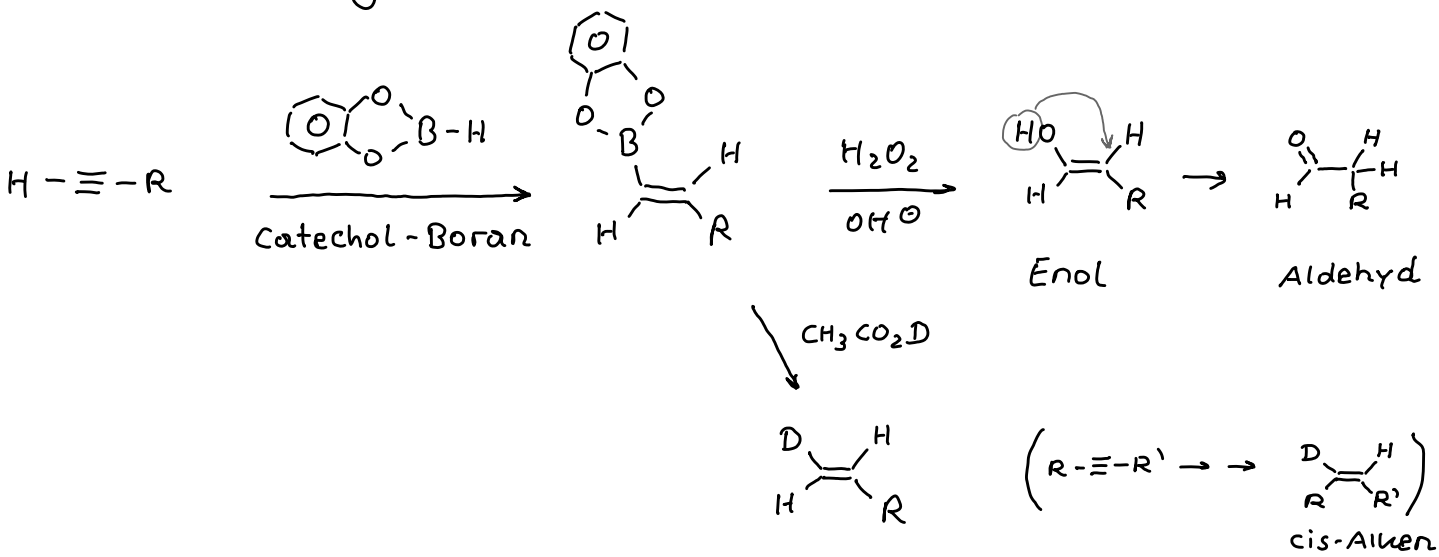


Regiochemie: anti-Markoffnikoff

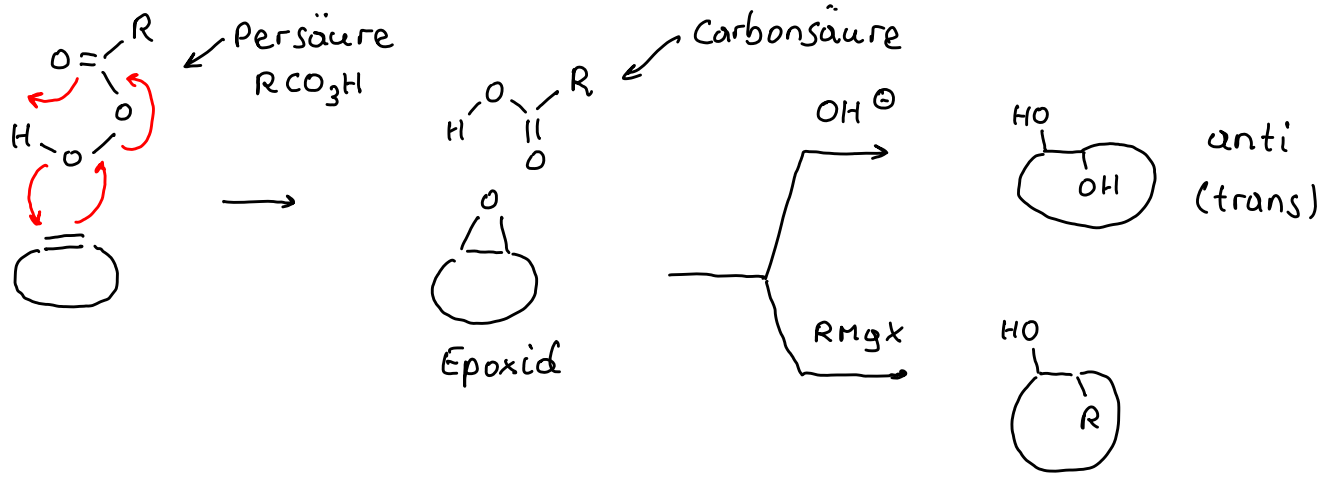
Stereochemie: cis-selektiv



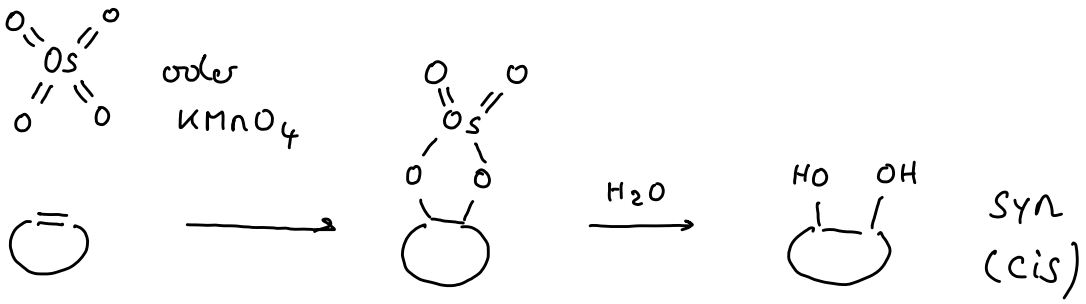
Hydroborierung von Alkinen



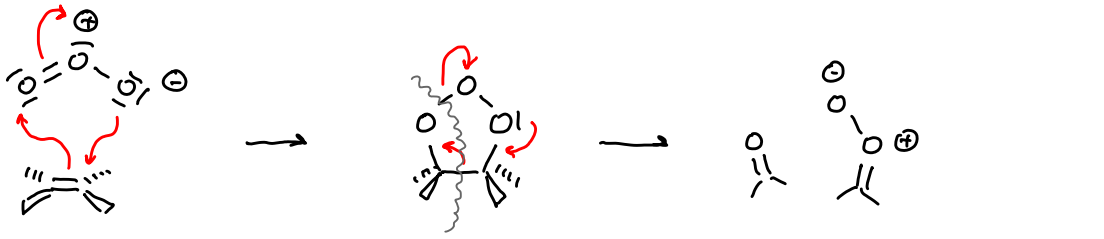
Epoxidierung / Hydroxylierung (Prilezhaev-Reaktion)



Hydroxylierung

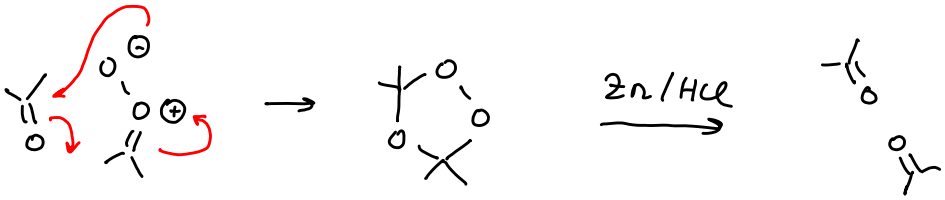


Ozonolyse (Carl Harries, Kiel 1904-1916)



Primärozonid

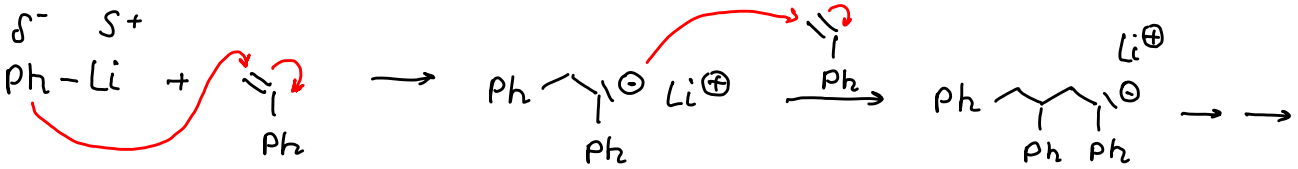
Carbonyl-Ylid



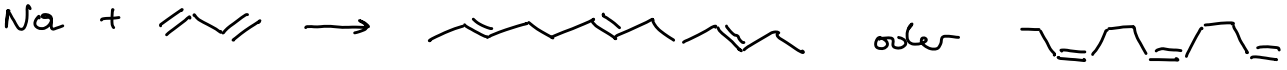
Sekundärozonid

Nucleophile Additionen

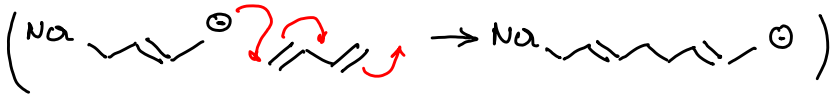
- anionische Polymerisation von Olefinen



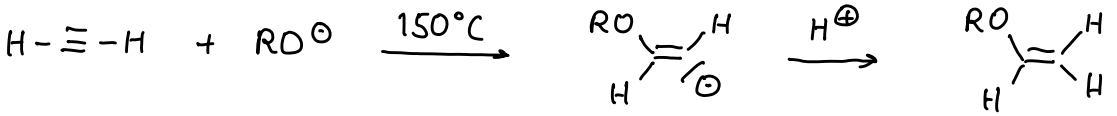
Lebende Polymerisation



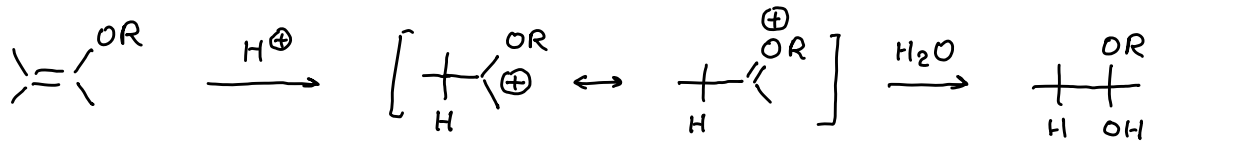
BUNA (Butadien-Natrium)



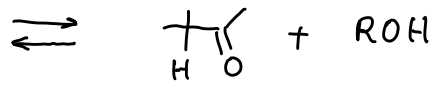
nucleophile Add. an $-C\equiv C-$



Vinylether

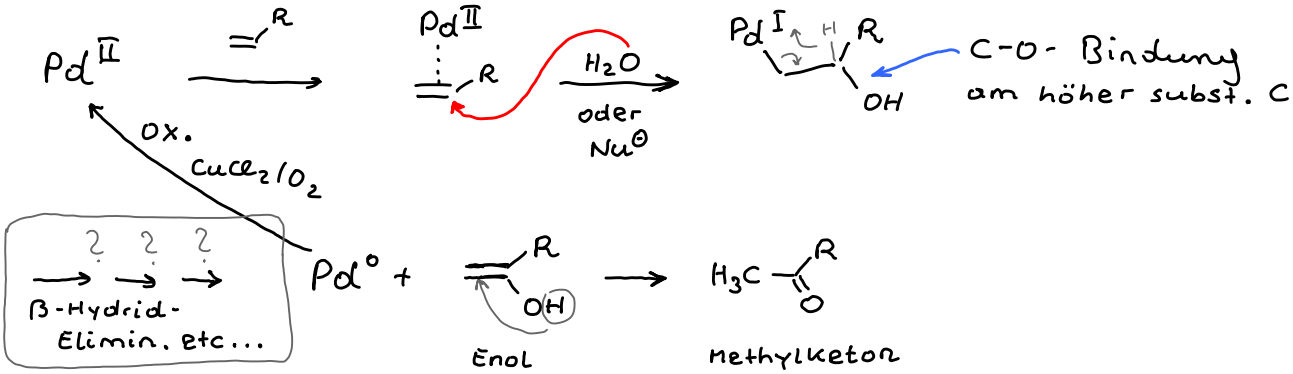


Halbacetal



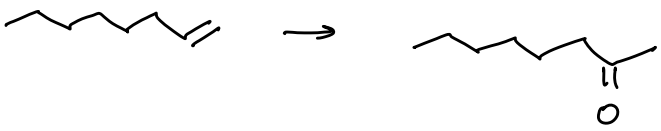
Metallkatalysierte Umsetzungen mit Olefinen

- Oxypalladierung (meistens mit 1-fach subst. Alkenen)

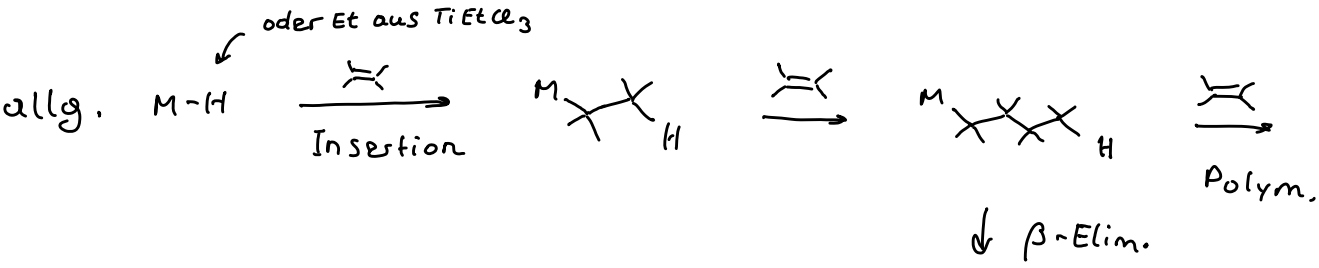


großtechn. (Wacker) $CH_2=CH_2$ (Ethylen) $\xrightarrow[H_2O,\ O_2]{Pd^{II}}$ $CH_3-C(=O)-H$ (Acetaldehyd)

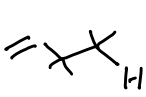
Labor:

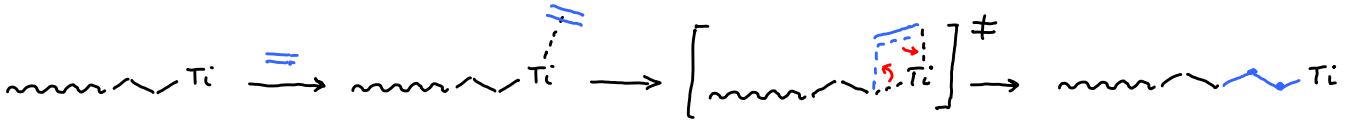


- Metall-kat. Polym. (Ziegler/Natta, Metallocen)



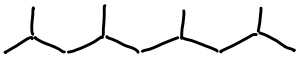
$M = TiCl_4 / AlEt_3 \rightarrow TiEtCl_3$



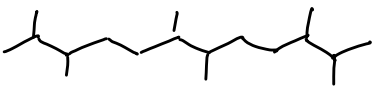


25.11.2013

Regioselektivität Bsp. $=$



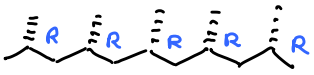
Kopf - Schwanz



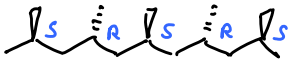
Kopf-Kopf + Schwanz-Schwanz

selten

Stereoselektivität

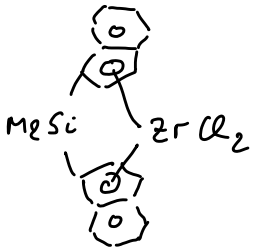


isotaktisch



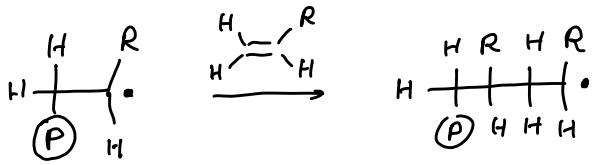
syndiotaktisch

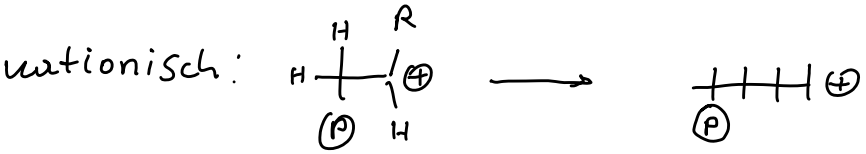
ataktisch

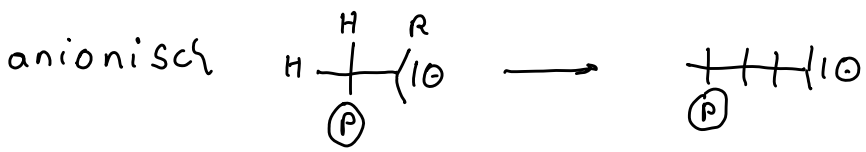


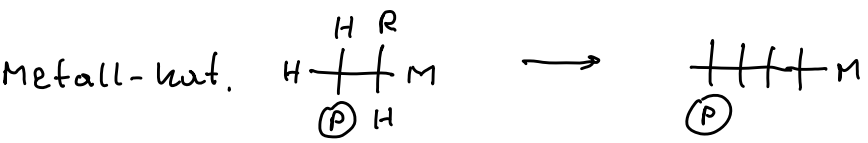
C_2-Symm. chiraler kat.

Übersicht: Polym. von Olefinen

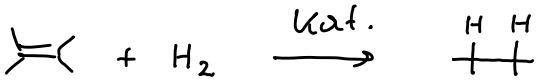
radikal.: 





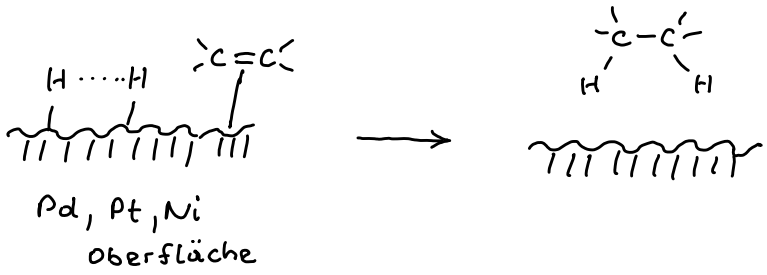


Hydrierung von Alkenen



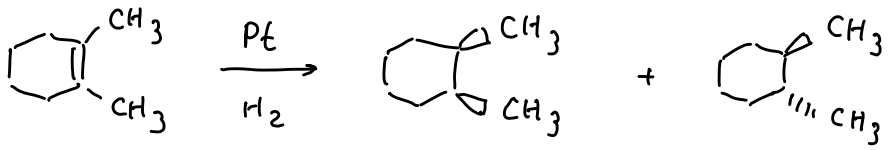
Kat. Raney-Ni, Pd/C, PtO
Pt/C ....

Mechanismus



Syn.-Add.

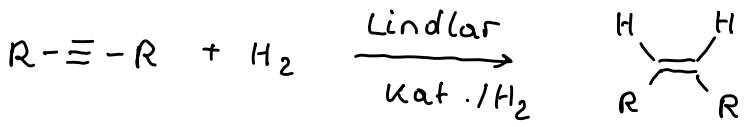
z.B.



70-85 % syn

30-15 % anti

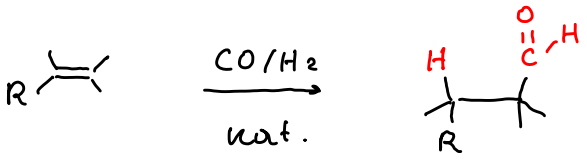
Hydrierung von Alkinen



Lindlar:
$Pd/BaSO_4$
"vergiftet" durch
PbO oder Chinolin

(enantioselektive Hydrierung
Wilkinson-Kat.)

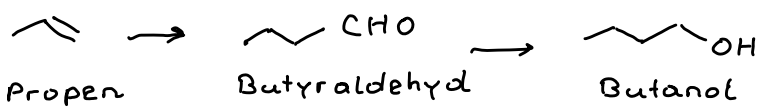
Hydroformylierung von Olefinen (Oxosynthese)



Kat. z.B.
$Co_2(CO)_8$, $RhH(CO)(PPh_3)_3$

Mechanismus: kompliziert

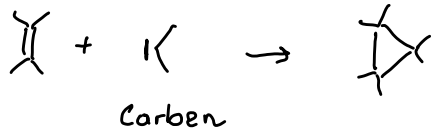
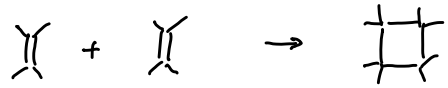
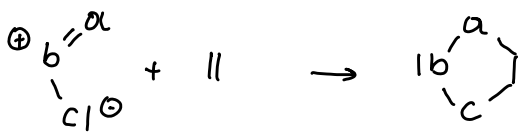
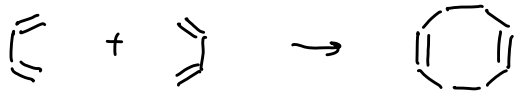
z.B.



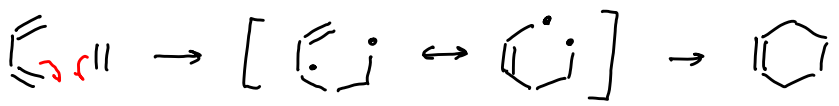
wichtigste industrielle Anwendung

Cycloadditionen D.4.4

- Einteilung, Nomenklatur

		Zahl der El.	Zahl Atome	
[2+2]			2+1	
			2+2	
[4+2]			2+3	1,3-dipolare Cycloadd.
			4+2	Diels-Alder
[4+4]			4+4	

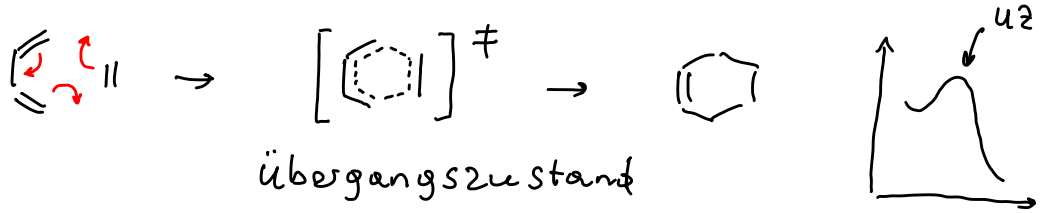
- Mechanismen Bsp. Diels-Alder

a) radikalisch 

diradikal. Zwischenstufe

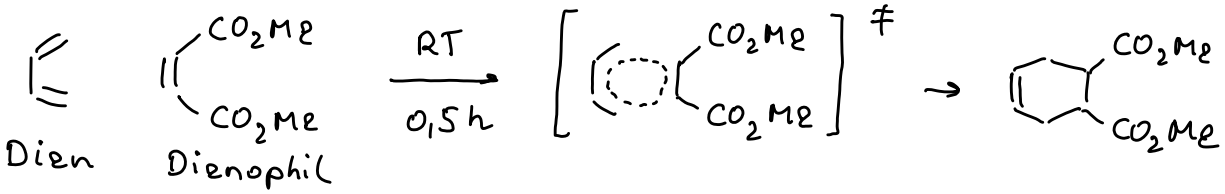
b) dipolar: 

dipolare Zwischenstufe

c) konzertiert 

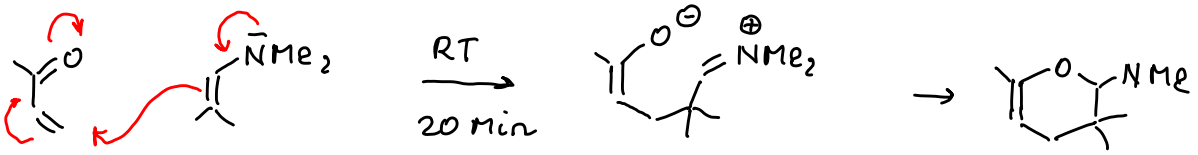
Beispiele:

- konzertiert:



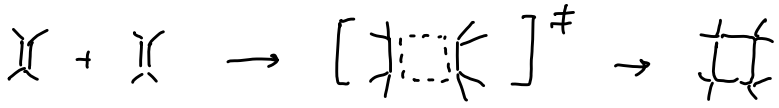
Dien Dienophil

- stufenweise:



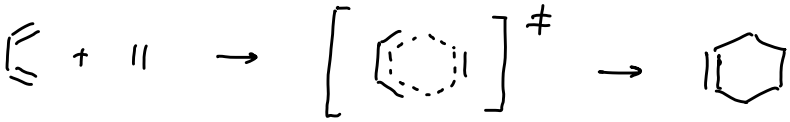
Stereochem. Regeln (Woodward-Hoffmann)
gelten nur für konzertierte (pericyclische) Reaktionen

1. Orbitalsymmetrie (Woodward-Hoffmann)
2. Grenzorbitale (Fukui)
3. Aromatizität von üz (Dewar, Zimmerman)

[2+2] 

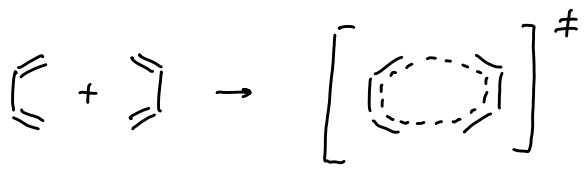
4 El. delok. im üz
antiarom., destab.

thermisch verboten
photochem. erlaubt

[4+2] 

6 El. delok. im üz
aromatisch, stabilisiert

thermisch erlaubt
photochem. verboten

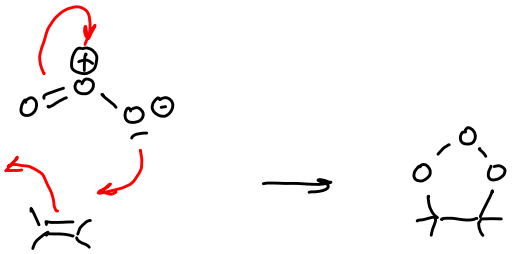
[4+4] 

photochem. erlaubt

therm. verboten

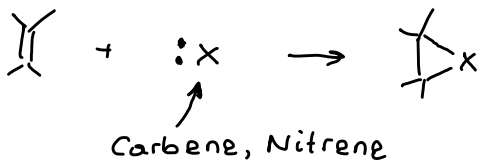
8 El. antiarom. üZ

Zahl der beteiligten El. = Zahl der Verschiebungspfeile ×2

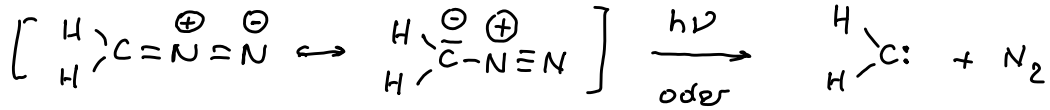


3 Verschiebungspf.
6 El.
arom. üZ
thermisch erlaubt

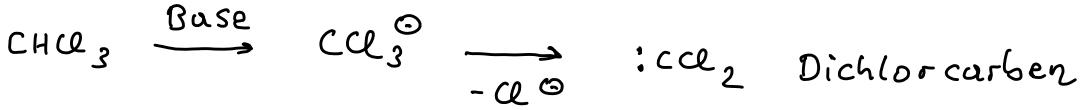
1+2 Cycloadditionen



- Herstellung von Carbenen

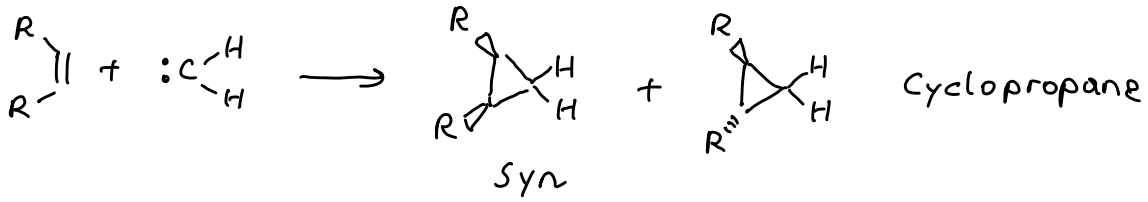


Methylen



Dichlorcarben

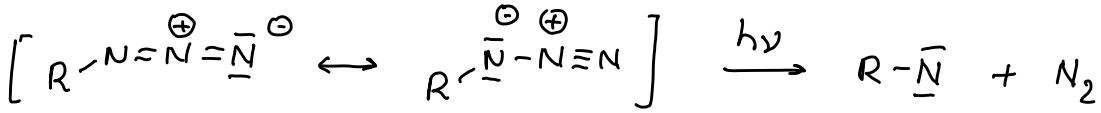
- Cycloadditionen von Carbenen



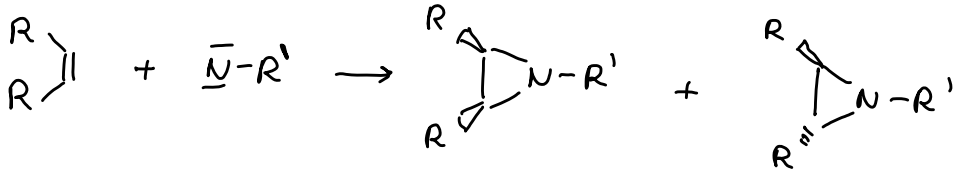
Cyclopropane

Syn

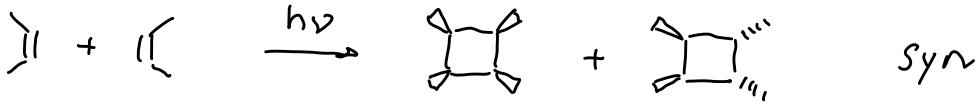
Nitrene $\underline{N}$-R



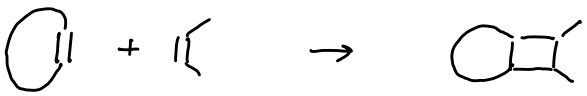
Nitren

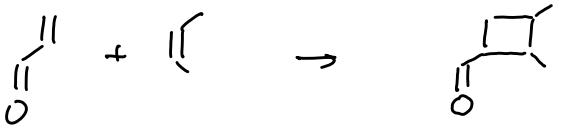


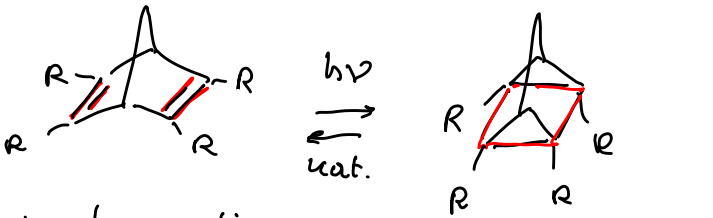
2+2 Cycloadditionen



Syn

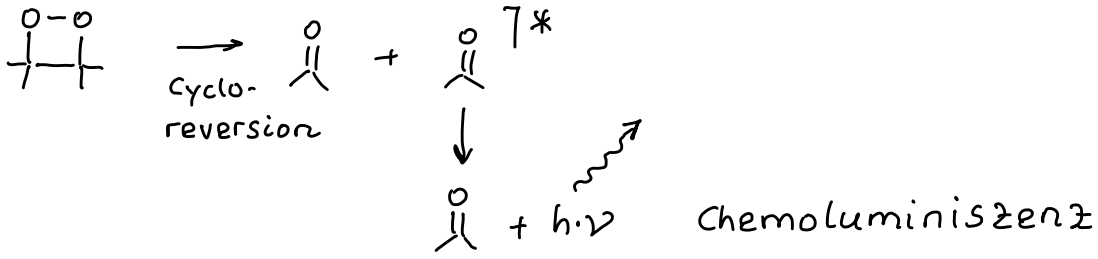






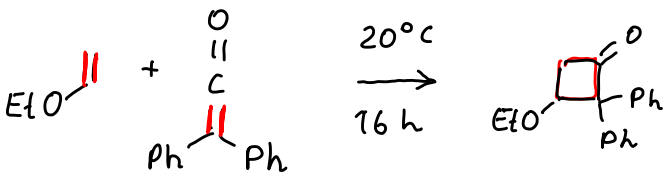
Norbornadien

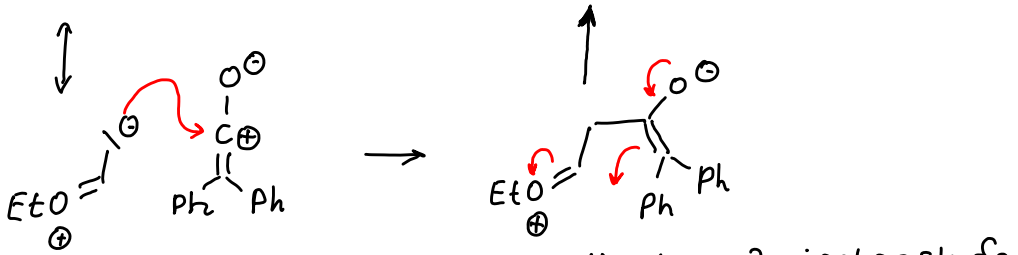
Quadricyclan



Chemoluminiszenz

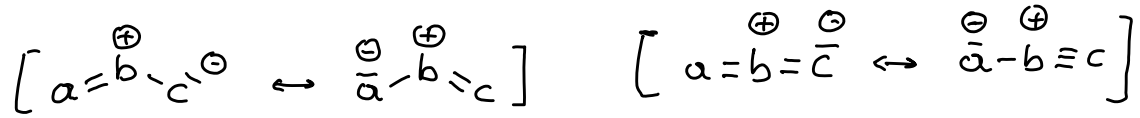
stufenweise, thermische Reaktion:





dipolare Zwischenstufe

1,3-dipolare Cycloadditionen



Allyl-Typ | Propargyl-Typ

27.11.2013

Wiederholung Cycloadditionen

- Einteilung, Nomenklatur
- Mechanismen (pericyclisch (konzertiert), stufenweise)
- Aromatizität von üZ (thermisch, photochemisch)
- Beispiele:

1+2, 2+2 } [2+2]

3+2, 4+2 } [4+2] 1,3-dipolare Cycloadd. / Diels-Alder

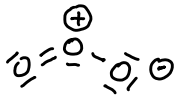
1,3-dipolare Cycloadd.

Allyl-Typ

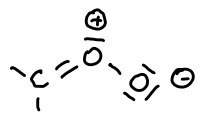
12 Spezies für a,b,c = C,N,O

Propargyl-Typ

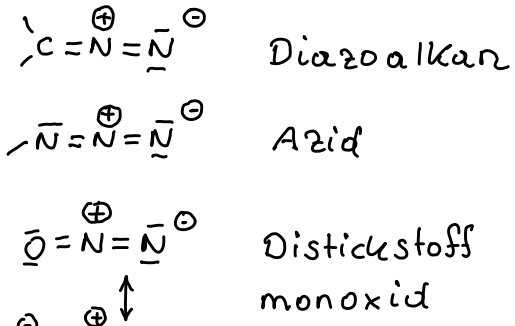
6 Spezies



Ozon



Carbonyl-ylid



Diazoalkan

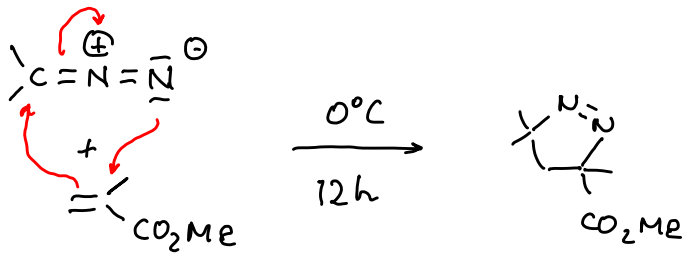
Azid

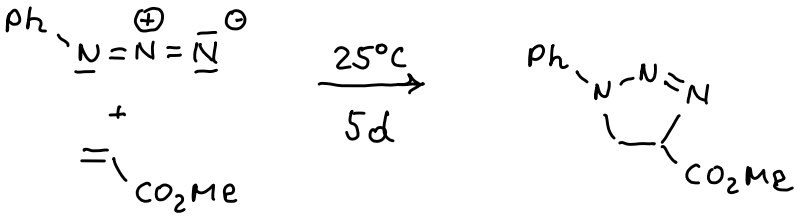
Distickstoffmonoxid Lachgas

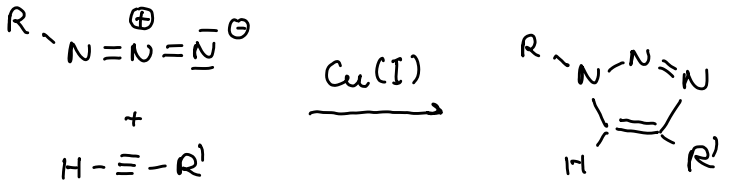
reaktionsträge

Anwendung: Herstellung von 5-Ring-Heterocyclen

z.B.







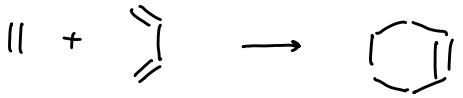
regioselektiv

"Click-Reaktion"

nicht pericyclisch (stufenweise)

Diels-Alder 1928 in Kiel entdeckt

1950 Nobelpreis



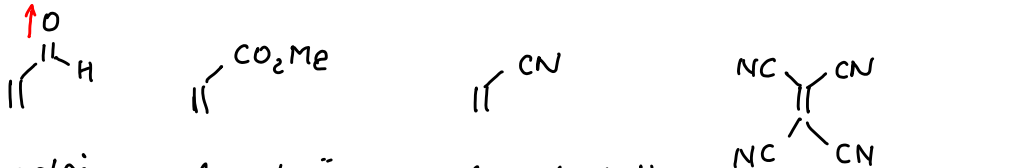
Dienophil Dien

Reaktivität: normaler Elektronenbedarf

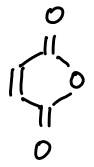
(inverser El. " " , selten)

Dienophil: elektronenarm (elektronenziehende Subst.)

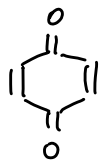
z.B.



Acrolein Acrylsäure-methylester Acrylnitril TCNE

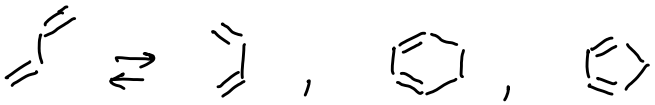


Maleinsäure-anhydrid

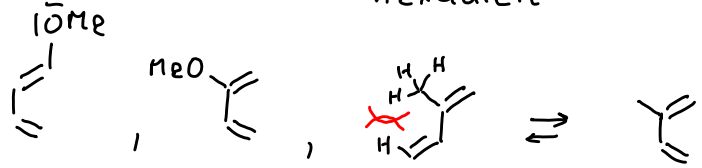


p-Chinon

Dien: elektronenreich, cis-fixiert

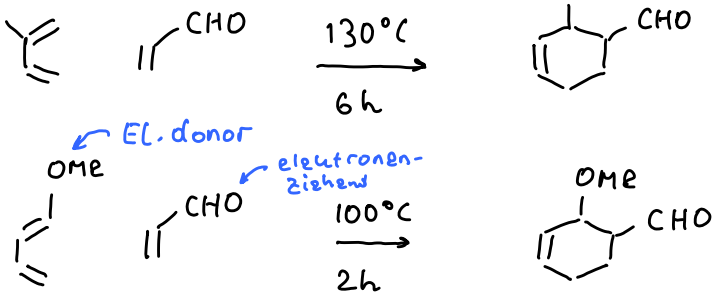
z.B. 

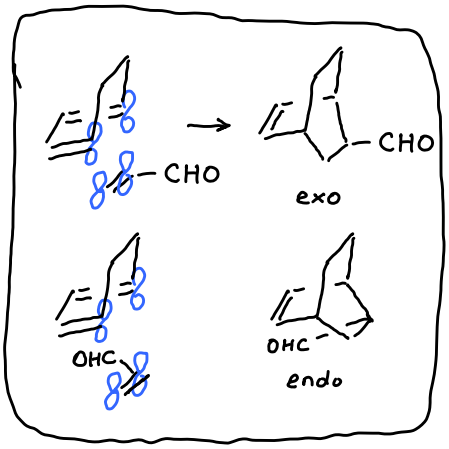
1,3-Cyclohexadien, Cyclopentadien

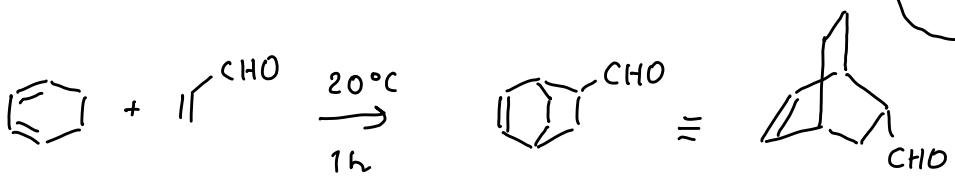


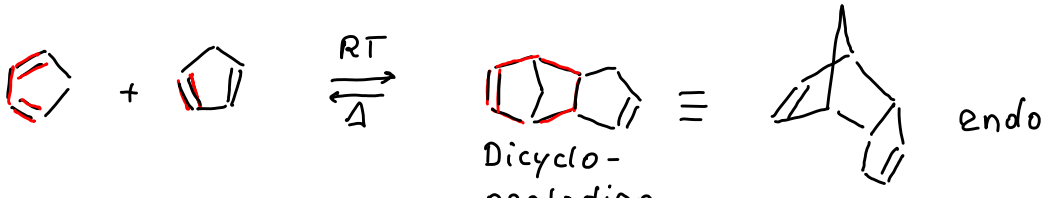
Isopren

Beispiele:

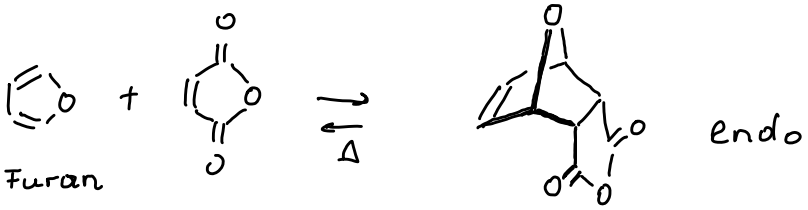


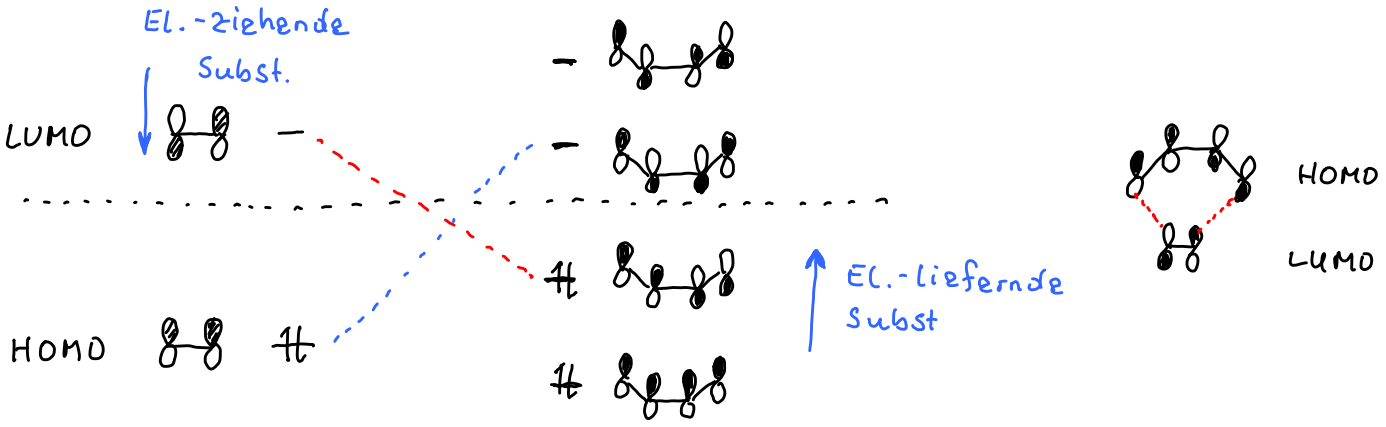






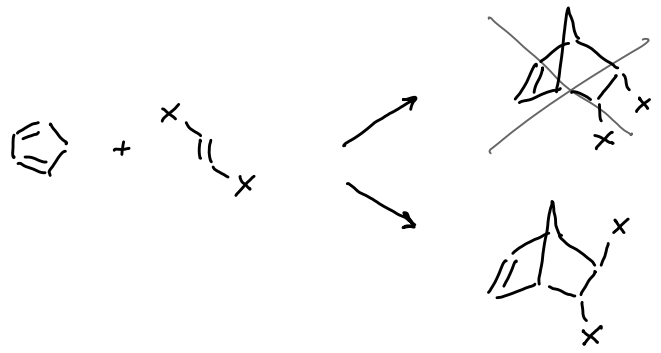
Dicyclopentadien





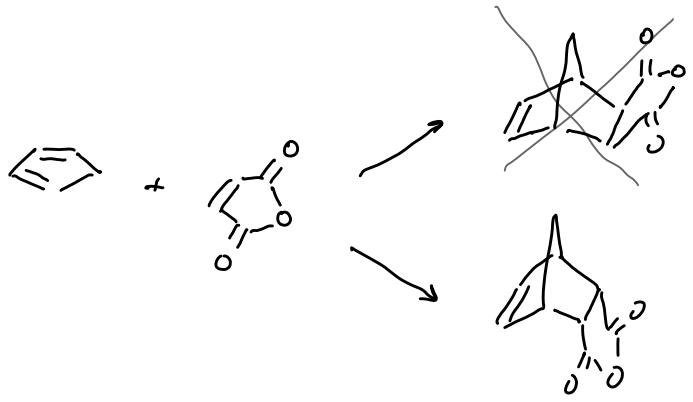
Wechselwirkung stärker je geringer $\Delta E_{HOMO-LUMO}$

Stereochemie Regeln:

1. 

Stereochemie der Edukte bleibt erhalten

Syn-Addition

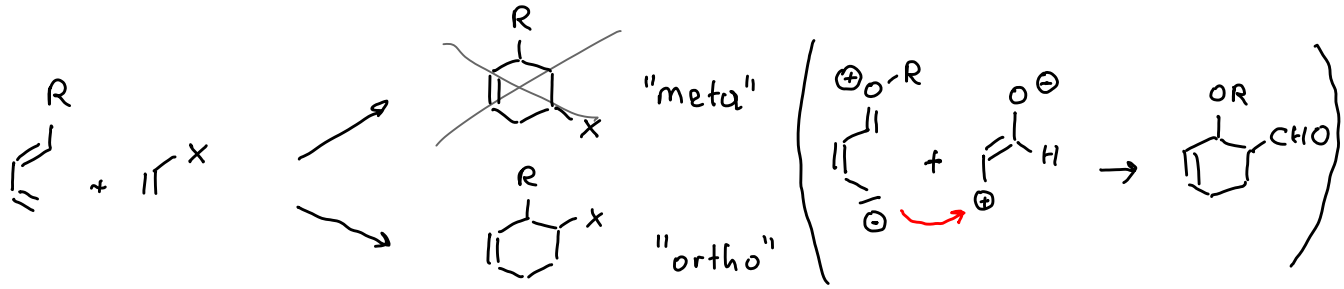
2. 

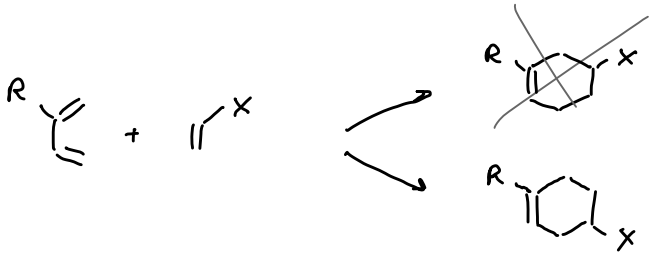
meist endo

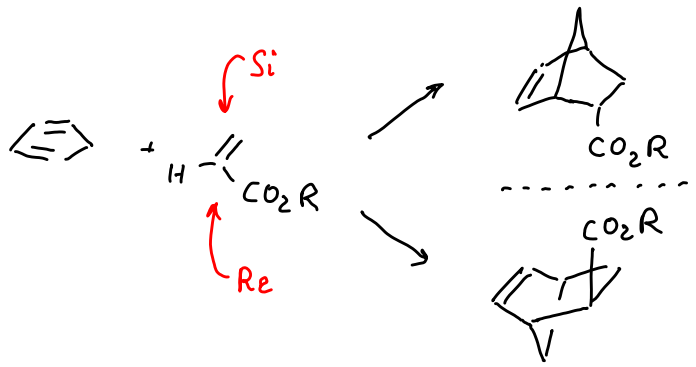
kinetisch kontrolliert

exo ist thermodyn. stabiler

thermodyn. Kontrolle

3. 



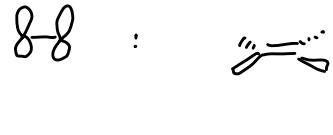
4. 

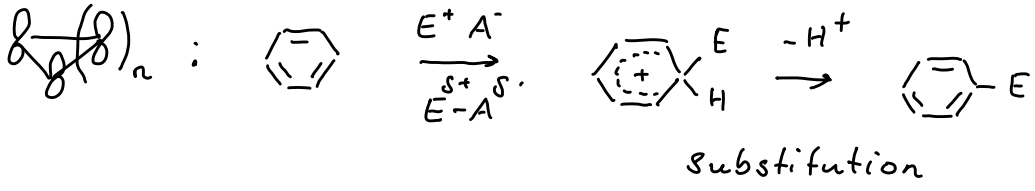
Enantiomere werden im gleichen Verhältnis gebildet (Racemat)

2. Dez. 2013

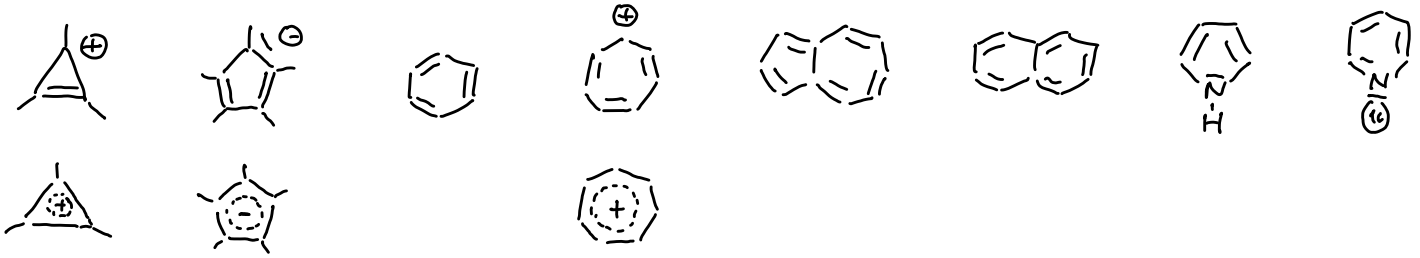
Electrophile Aromatensubst. D.5.1

elektronische Struktur u. Reaktivität ungesättigter Verb.

Olefine 

Aromaten 

Beispiele für Aromaten:



Cyclopentadienyl Anion

Tropylium-kation

Azulen

Pyrrol

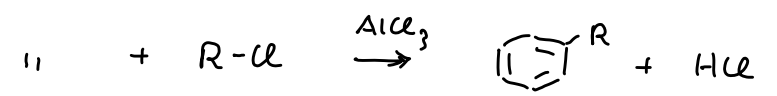
Pyridin

electrophile Subst.

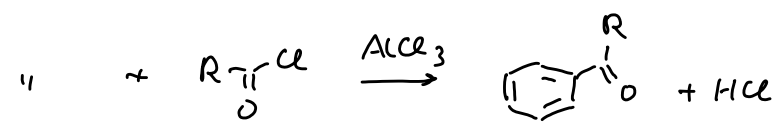
Nitrierung

Sulfonierung

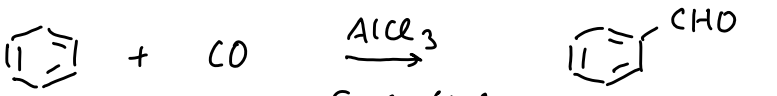
Chlorierung



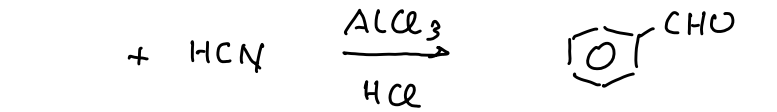
Friedel-Crafts-Alk.



" " Acylierung

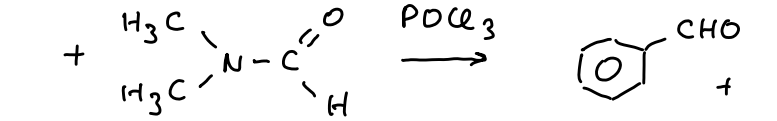


Gattermann-Koch



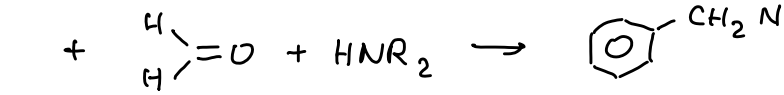
Gattermann

~~Houben-Hoesch~~

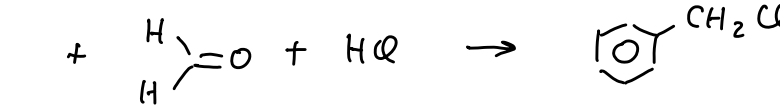


Vilsmeyer

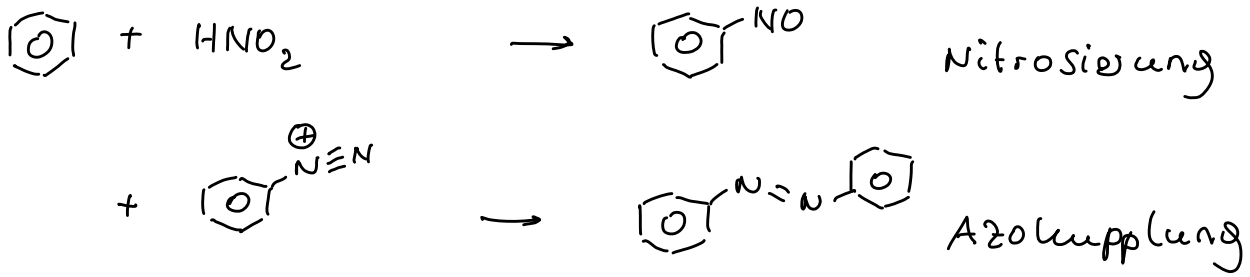
Hydroxymethylierung



Aminomethylierung



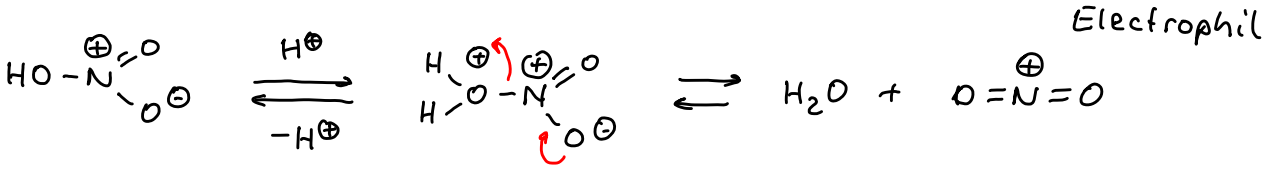
Chlormethylierung



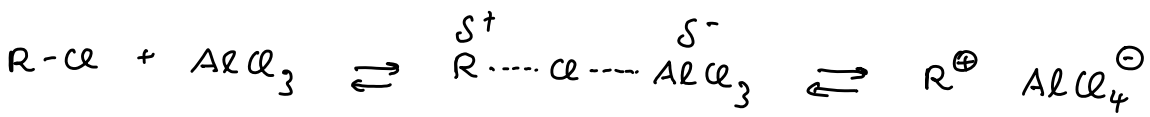
Mechanismus (3 Schritte)

a) Erzeugen des Electrophils E^+ bzw. $E^{\delta+}$

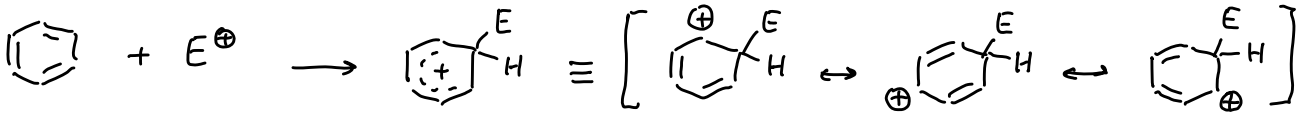
z.B. Protonierung



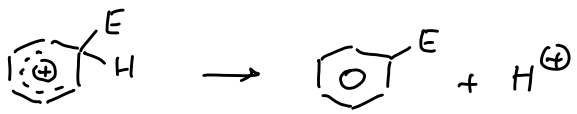
z.B. Ionisierung mit Lewis-Säure



b) electrophile Addition



c) Proton-Abspaltung



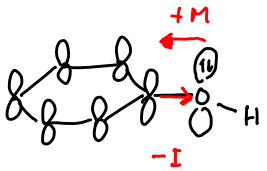
Einfluss von Subst. auf Reaktivität u. Regioselekt.

- Subst. die Reaktivität erhöhen

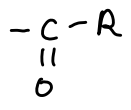
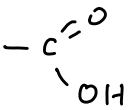
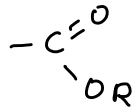
Alkyl: $-CH_3$, $-C_2H_5$ .... $+I$

$-OH < -NH_2 < -NHR < -NR_2$ $+M, -I$

$-\ddot{O}|^{\ominus}$ $+M, +I$



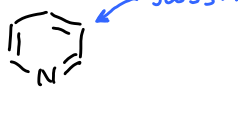
- deaktivierende Subst.

 ,  ,  , $-C\equiv N$, $-NO_2$ $-M, -I$

$-F$, $-Cl$, $-Br$ $+M, -I$

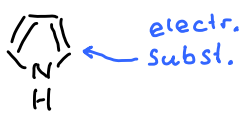
$-\overset{\oplus}{N}R_3$, $-\overset{\oplus}{N}HR_2$ $-I$

- Heteroatome im Ring



Pyridin

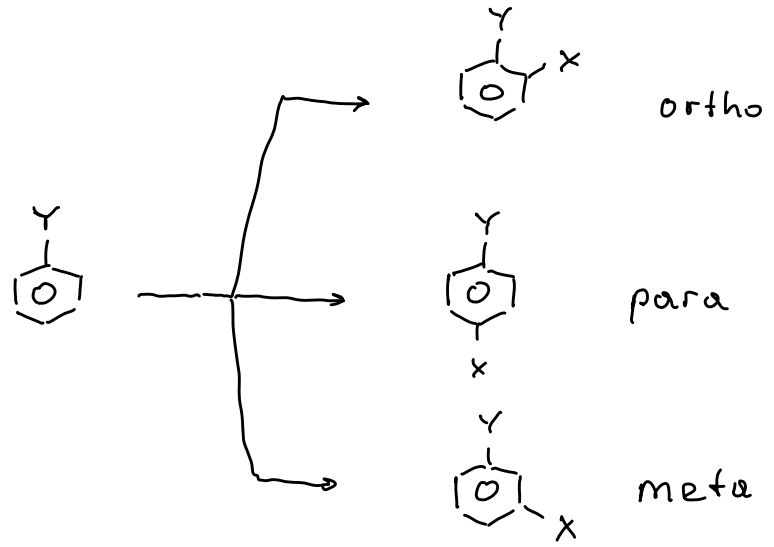
desaktiviert



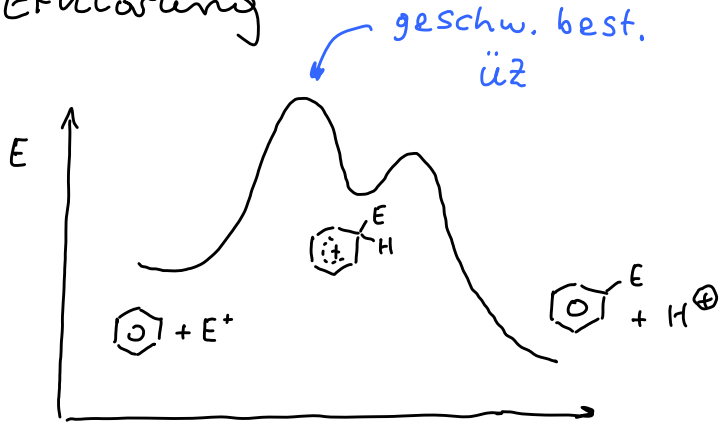
Pyrrol

aktiviert

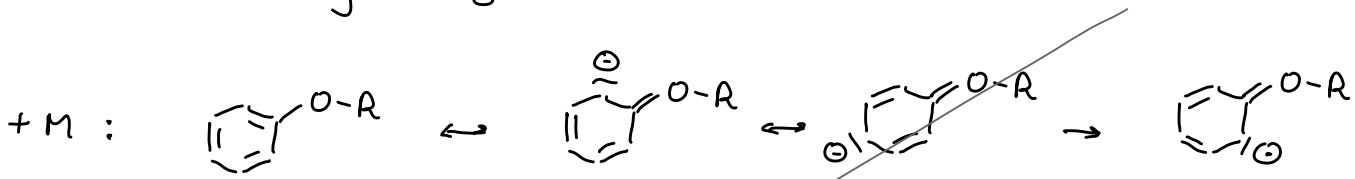
Regioselektivität (Zweitsubstitution)



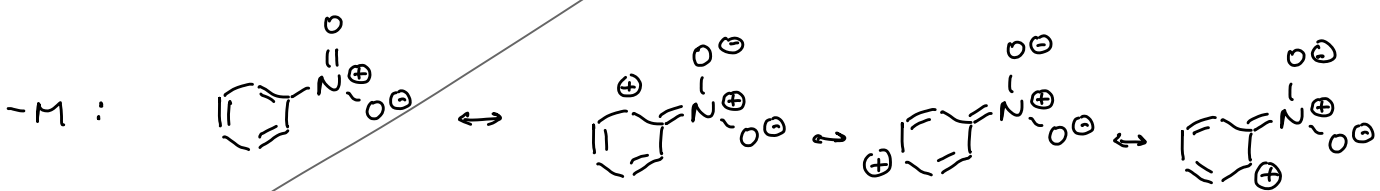
Erklärung



Betrachtung ausgehend vom Edukt



⇒ akt. in o,p-Position

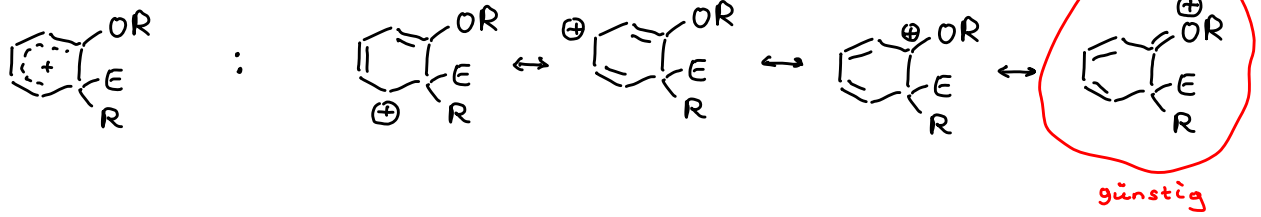


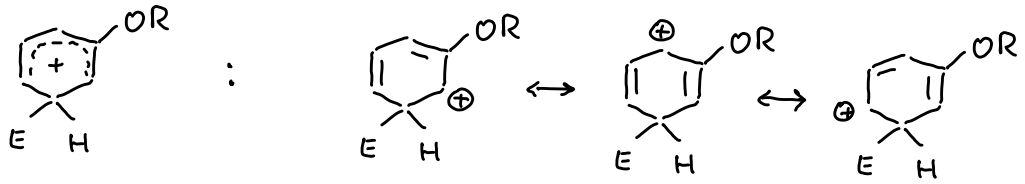
⇒ desakt. in o,p-Pos.

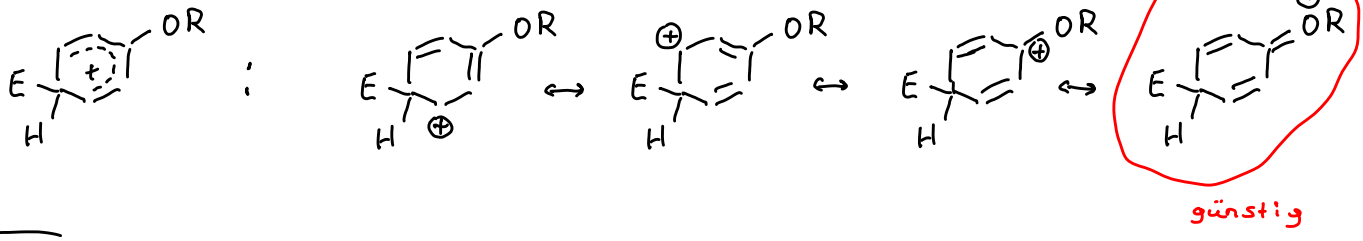
Betrachtung ausgehend vom σ-Komplex

Hammond Prinzip 1. Schritt endotherm => üz Produkt-ähnlich

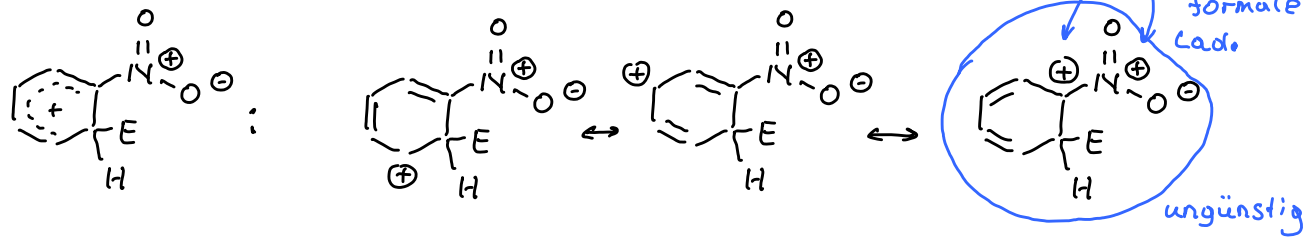
+M

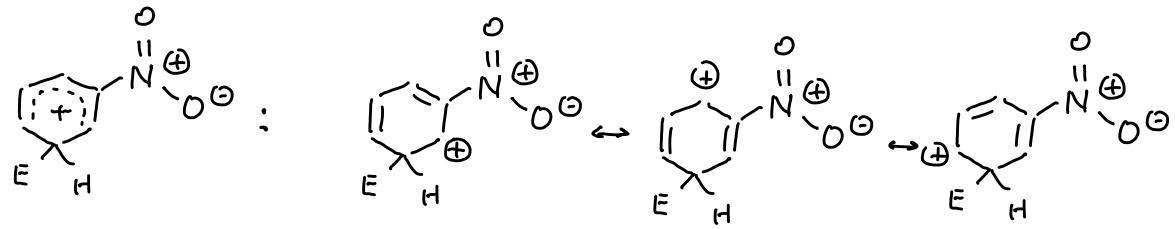
o: 

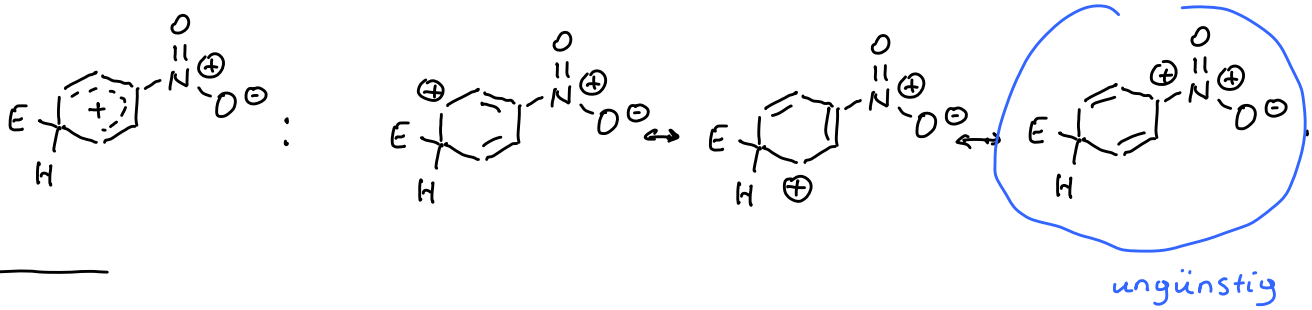
m: 

p: 

-M

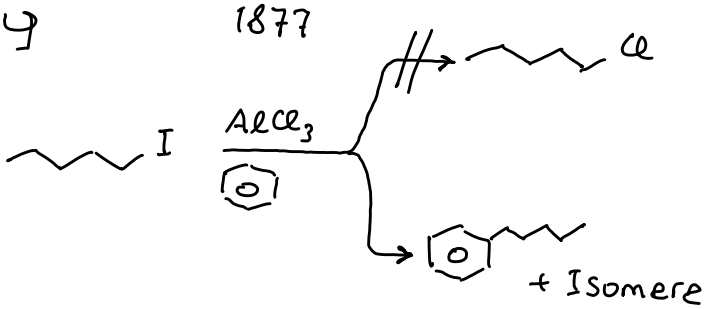
o: 

m: 

p: 

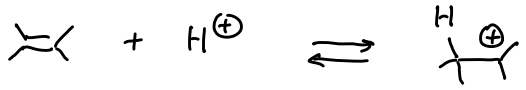
Friedel-Crafts-Alkylierung

1877



a) $R\text{-}Cl + AlCl_3 \rightarrow \overset{\delta+}{R} \cdots Cl \cdots \overset{\delta-}{AlCl_3}$ Kat. Mengen $AlCl_3$

$R\text{-}OH + H^{\oplus} \rightleftharpoons R^{\oplus} + H_2O$

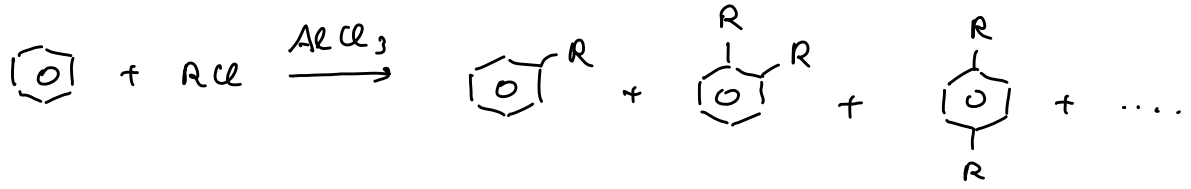


Lewis-Säuren

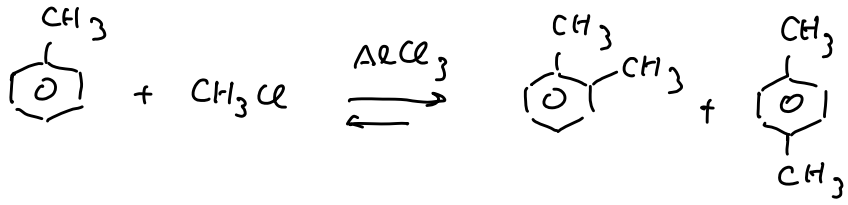
$SbF_5 > AlCl_3 > FeCl_3 > SnCl_4 > TiCl_4 > ZnCl_2$

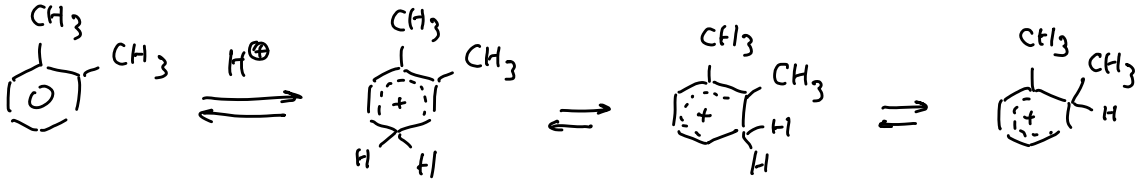
Probleme:

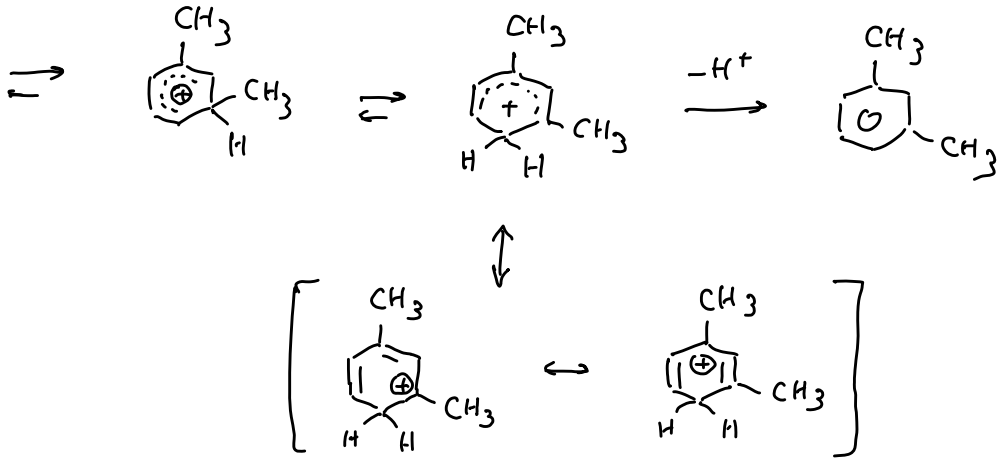
a) Mehrfachsubst.



b) Reversibilität

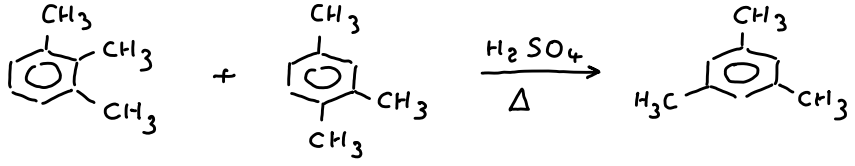






stabilstes Kation im Gleichgew.

Anwendung



Mesitylen

Wiederholung 9.12.2013

elektron. Struktur

Reaktivität

wichtige (Namens-) Reaktionen

Mechanismus

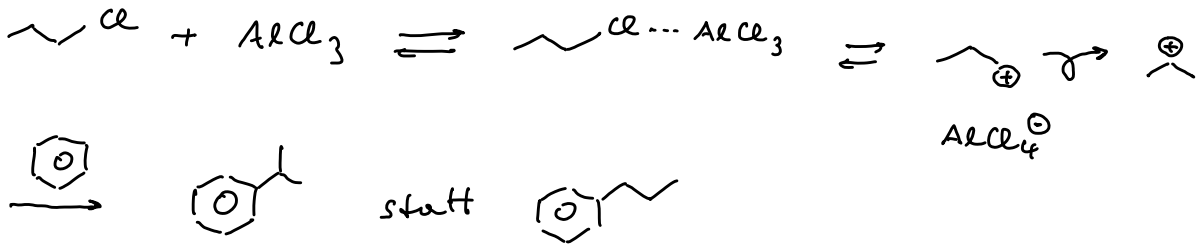
- Erzeugen des Electrophils
- electrophile Add.
- Proton-Abspaltung

Reaktivität u. Zweitsubst.

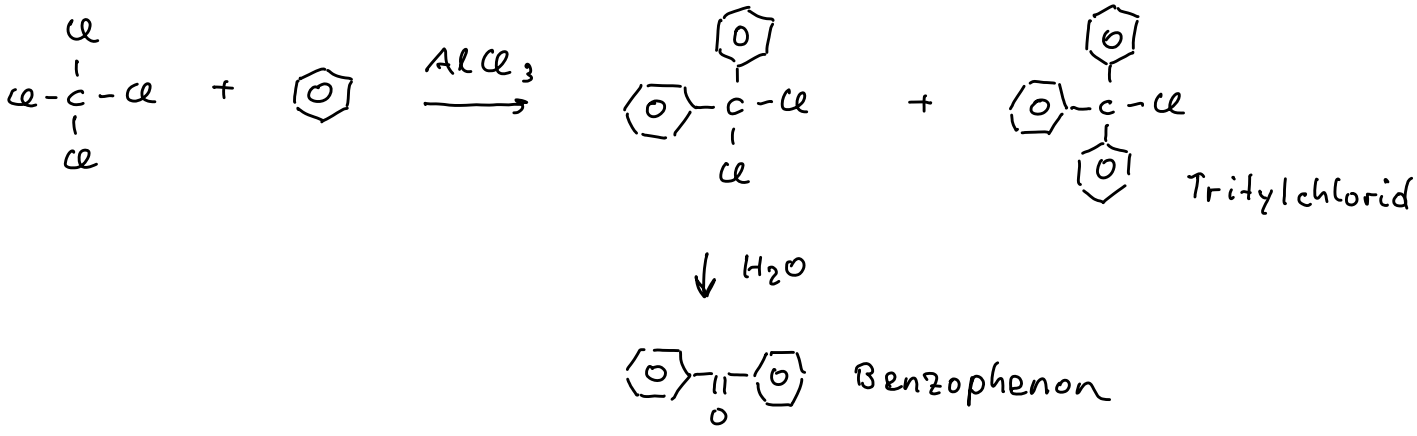
Reaktionen:

- Friedel-Crafts-Alkylierung
  - allg.
  - Nebenreaktionen

- umlagerungen

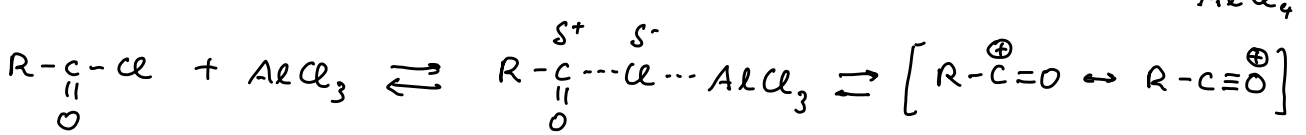


spez. Anwendungen

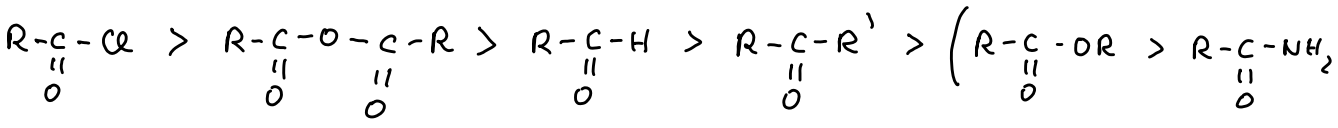


Friedel-Crafts-Acylierung

a) Erzeugung Electrophil:

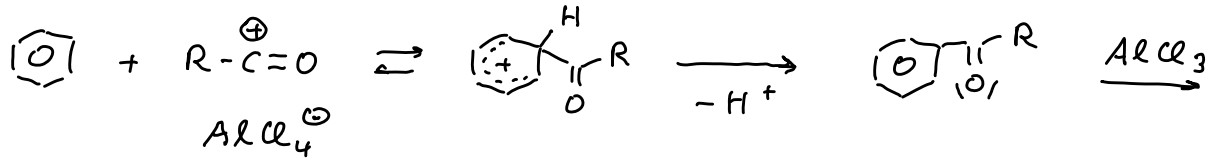


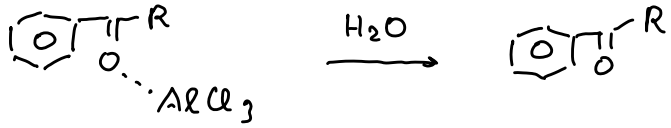
enolere Carbonylverb.



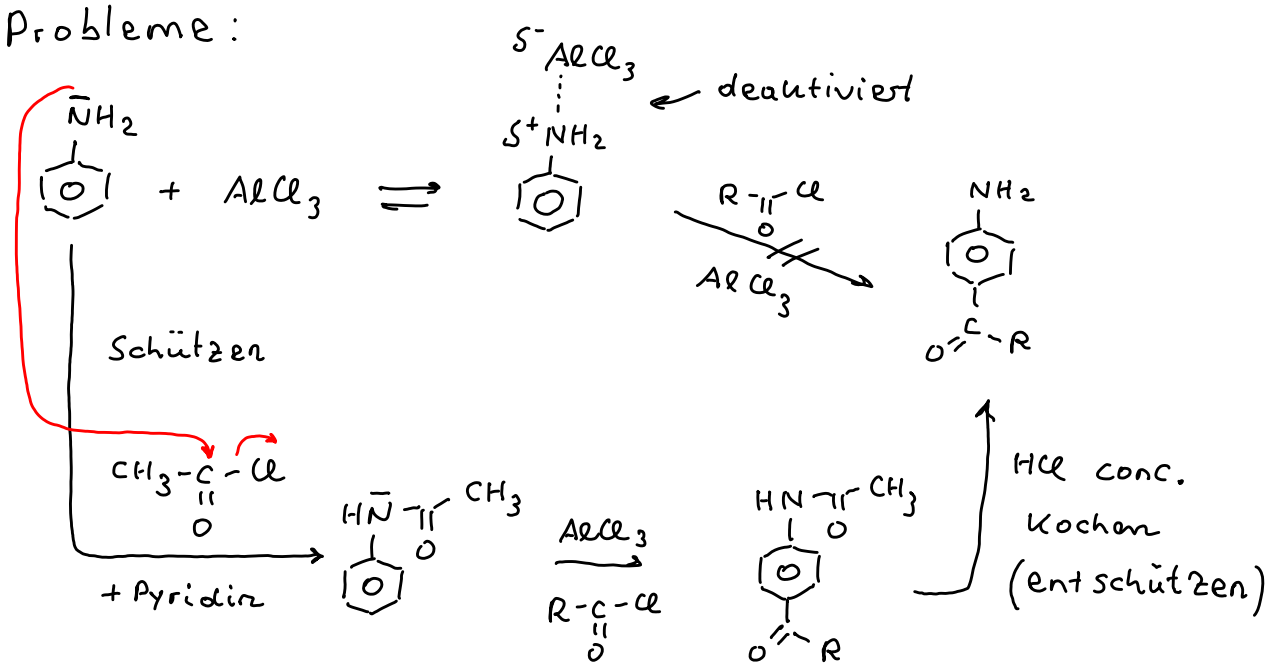
b) electrophile Add.

C) Absp. Proton

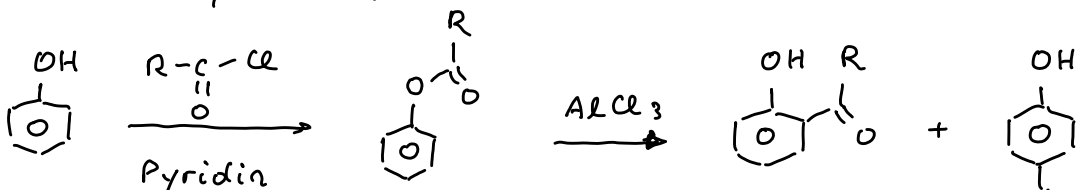


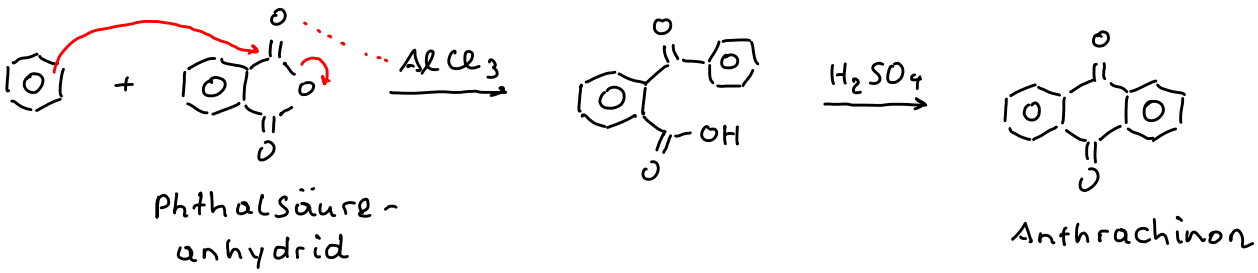


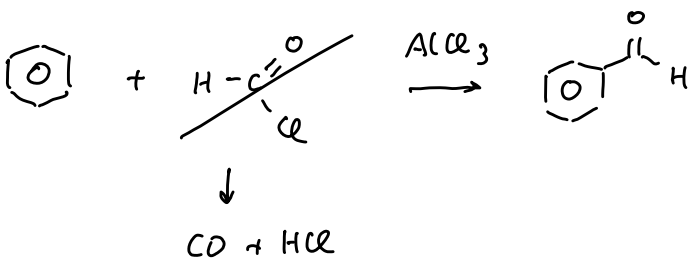
Probleme:



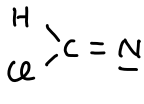
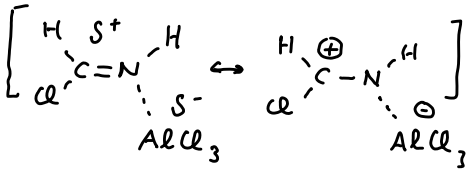
Spezielle Systeme:

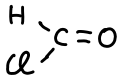




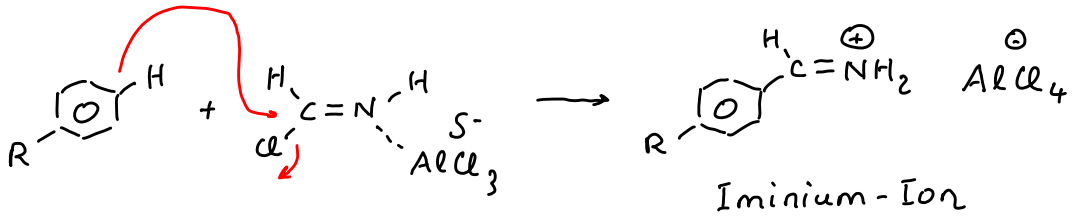


Gattermann

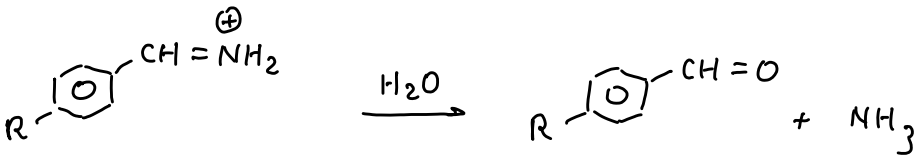
a) $H-C\equiv N| + HCl \rightleftharpoons$  $\xrightarrow[\text{Kat.}]{AlCl_3}$ 

isoelectron. zu  stabil

b), c)



d)

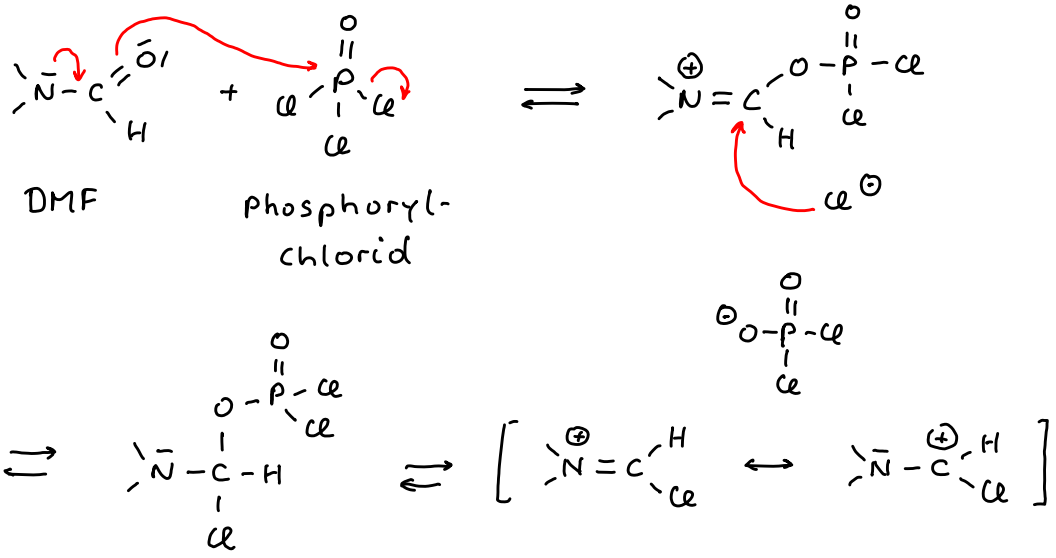


geht nur mit aktivierten Aromaten

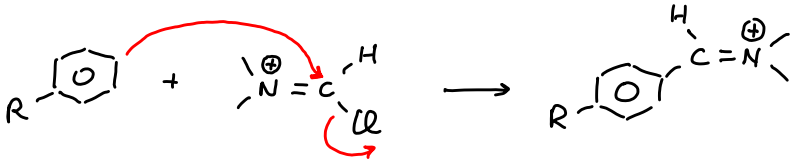
z.B. R = OCH_3, (-OH), nicht: $-NH_2$

Vilsmeier

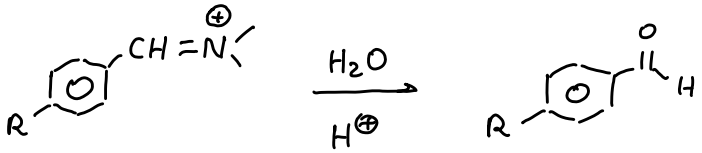
a)



b)
c)

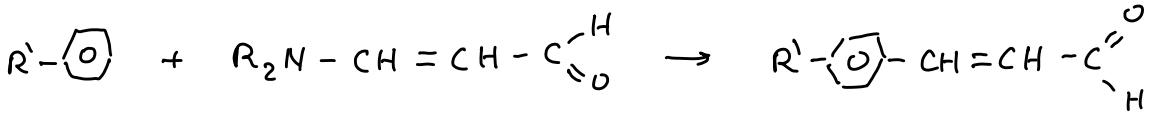


d)

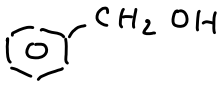


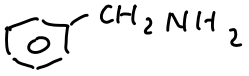
geht auch R = NH_2, NHR, NR_2

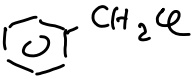
vinyloge Formamide

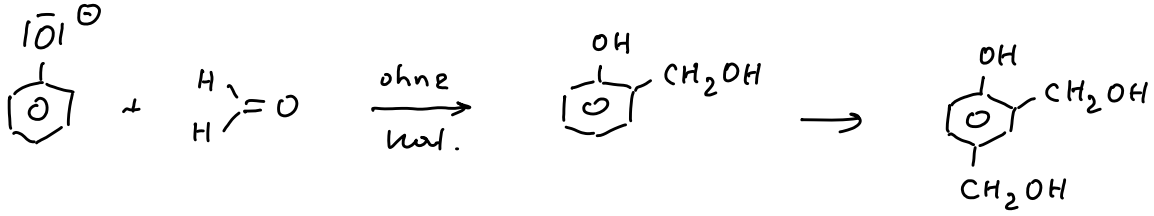


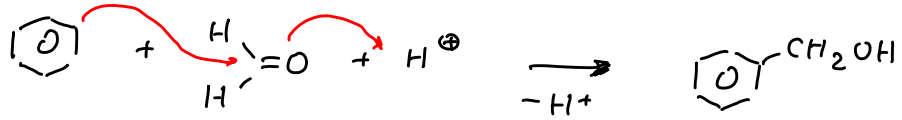
Reaktionen mit Formaldehyd

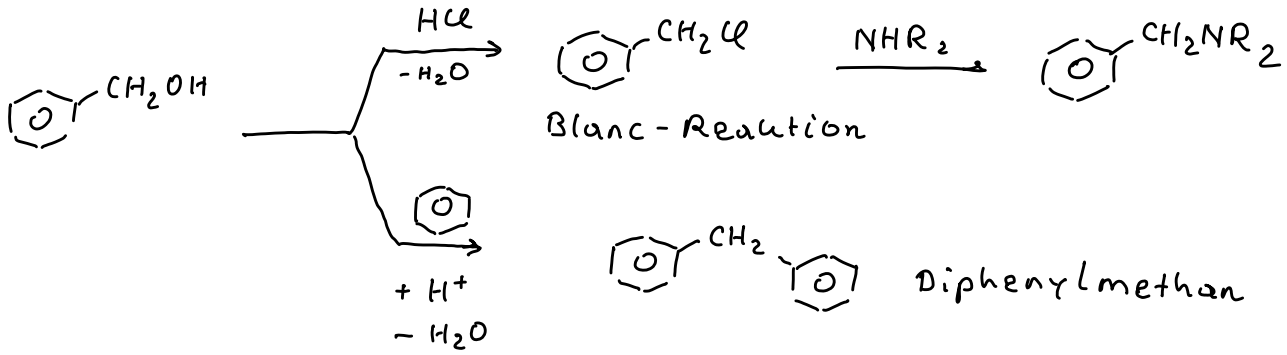
Hydroxymethylierung 

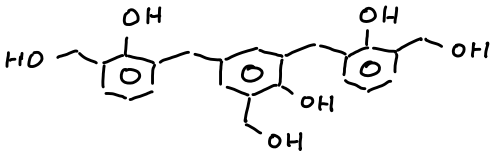
Aminomethylierung 

Chlormethylierung 





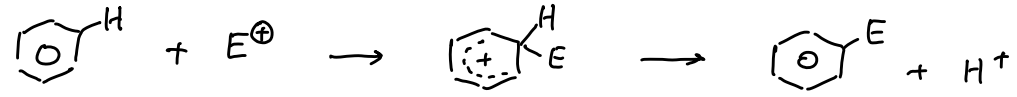


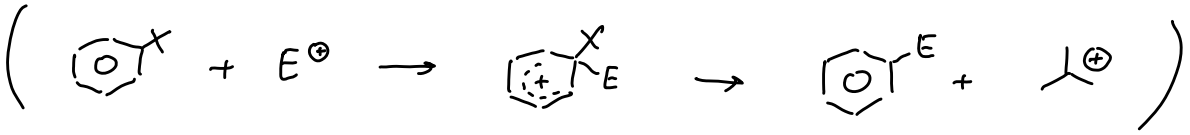


Phenol-Formaldehyd-Harze,
Phenoplaste, Resole, Resite, (OSB-Pl.)
Bakelit

Nucleophile Aromatensubst. D.5.2

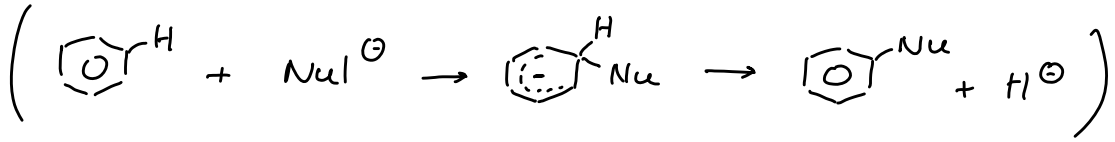
electrophile Aromatensubst

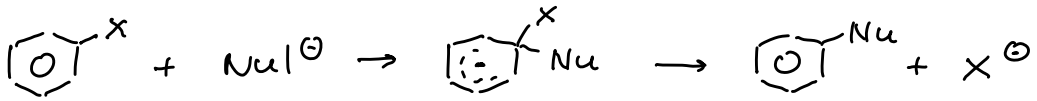


()

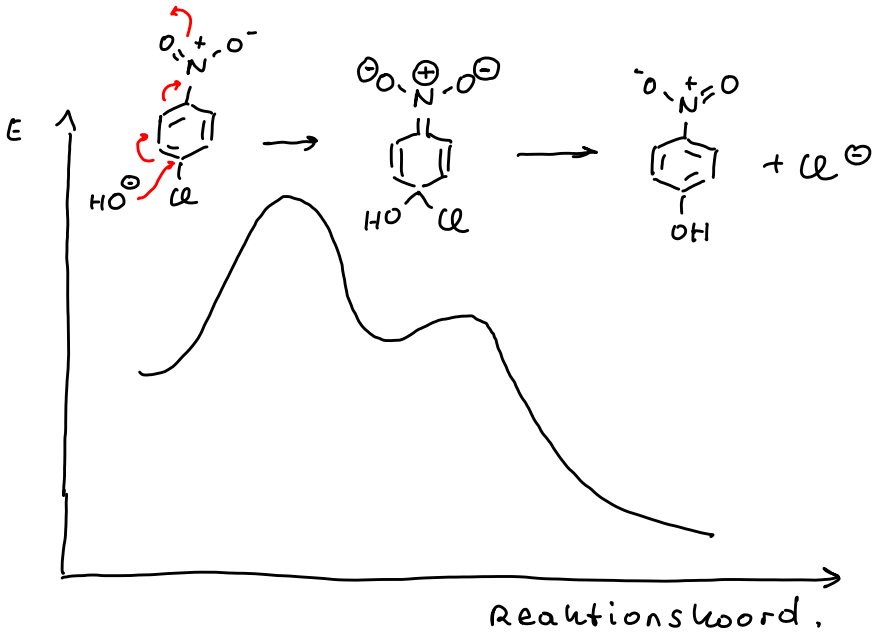
Aktivierung durch +I, +M subst. in o,p-Stellung

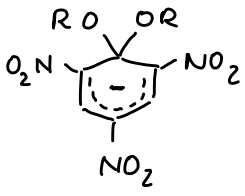
nucleophile Aromatensubst

()



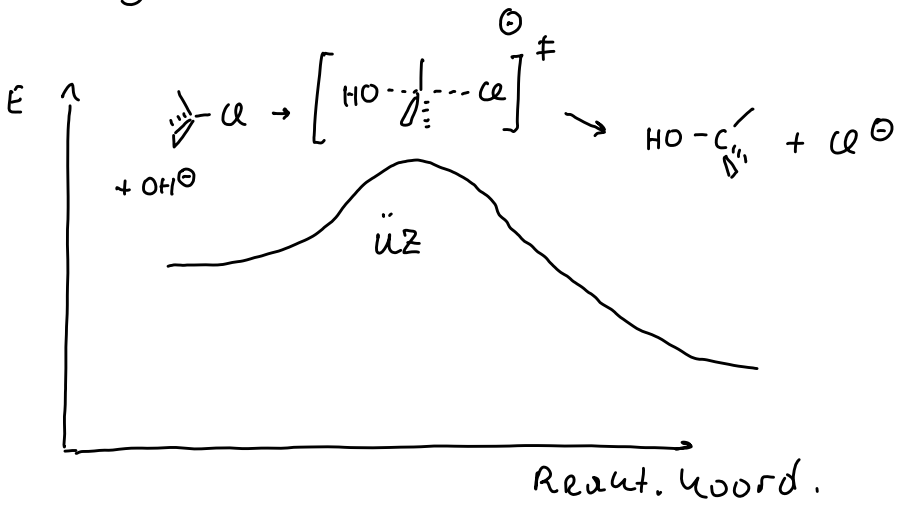
Aktivierung durch -I, -M subst. in o,p-Stellung





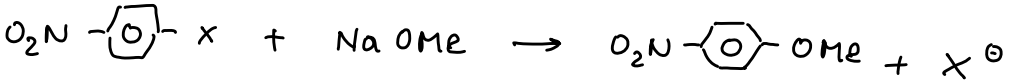
Meisenheimer Komplexe stabil

Vergleich S_N2:



aktivierende Subst.

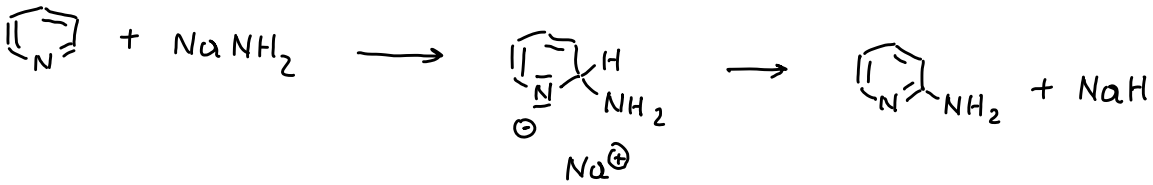
$-\overset{\oplus}{N}\equiv N$ > $-NO_2$ > $-C\equiv N$ > $-CHO$ > Cl

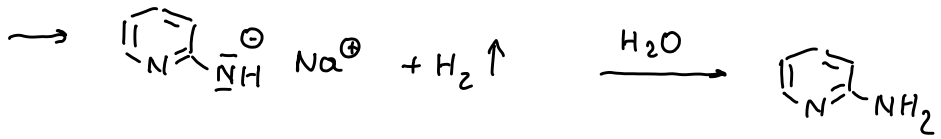


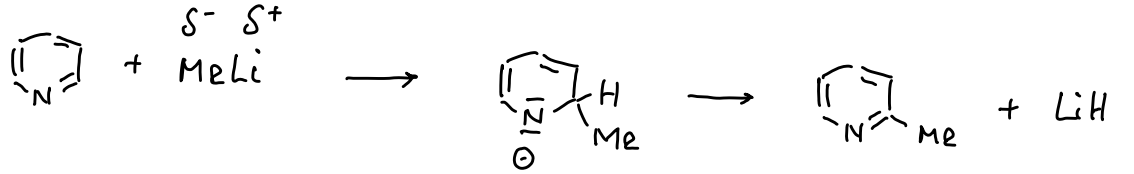
$F^\ominus$ >> $Cl^\ominus$ > $Br^\ominus$ > $I^\ominus$ (vgl S_N2: $I^\ominus > Br^\ominus > Cl^\ominus > F^\ominus$)

312 1.0 0,74 0,36

Chichibabin (Tschi....



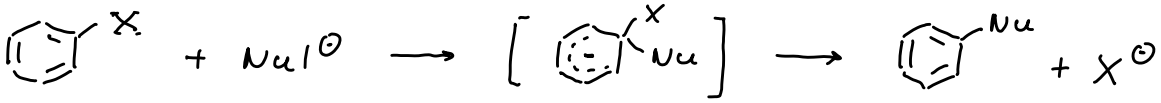




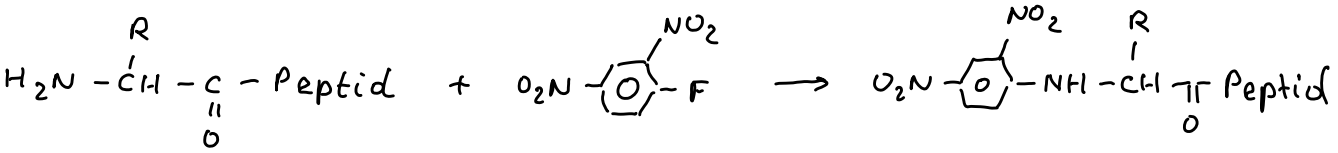
α-Picolin

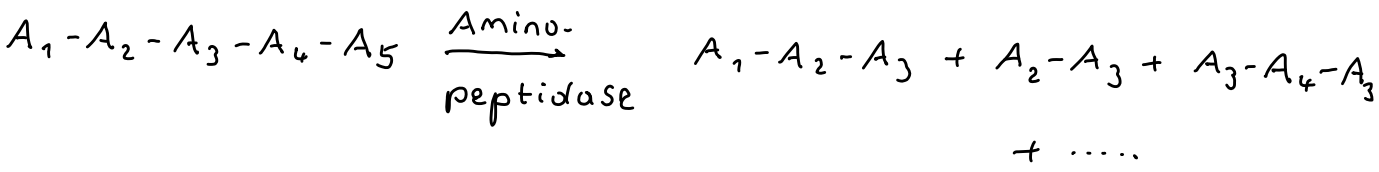
16.12.2013

Wiederholung

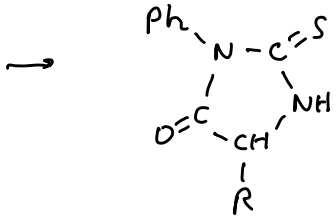


Protein-Sequenzanalyse nach Sanger

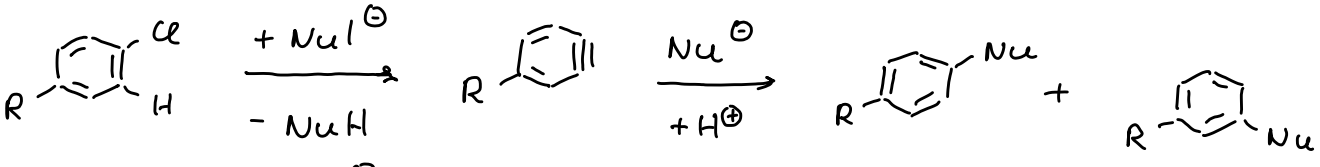




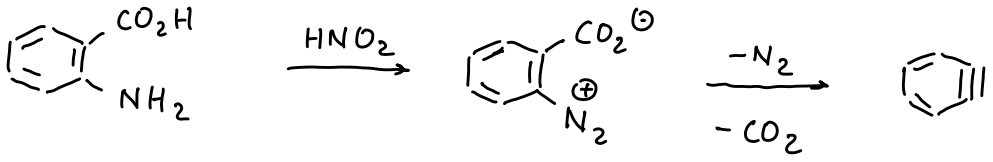
Edmann-Abbau

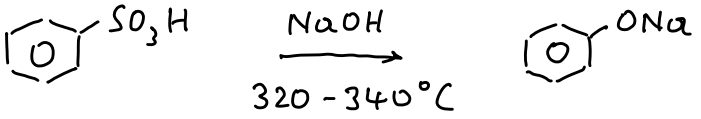


Eliminierung-Addition (Arin-Mechanismus)

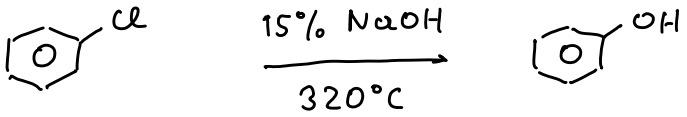


Arin
Dehydrobenzol
Benzyn

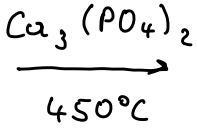




Kekule, Wurtz 1867

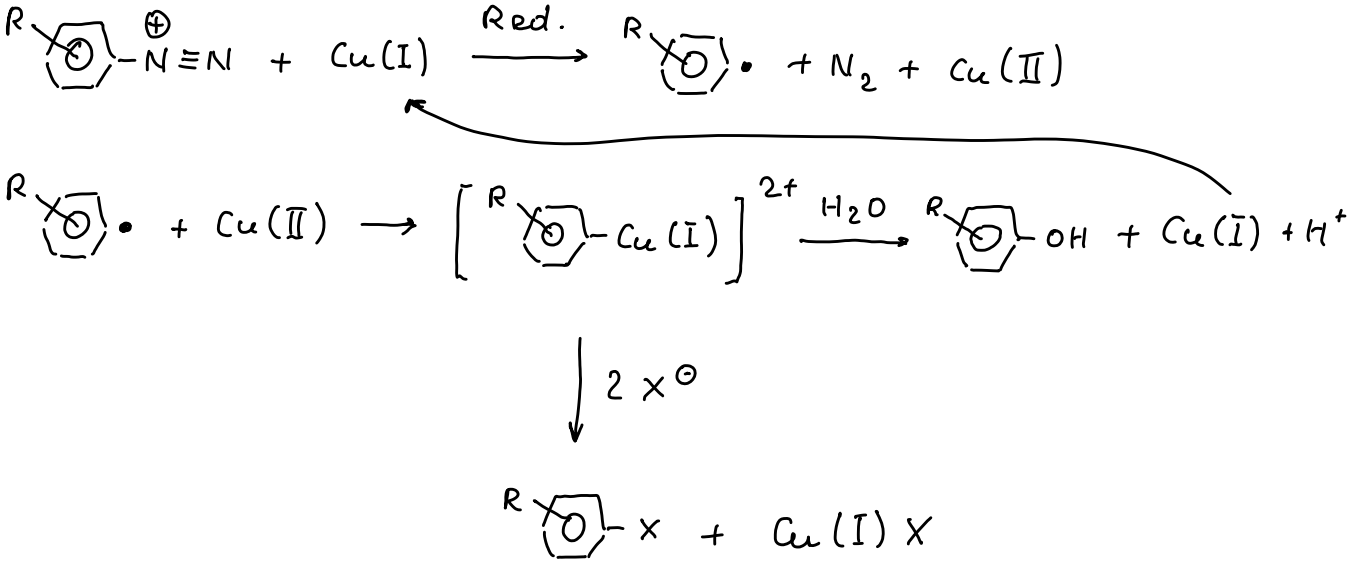


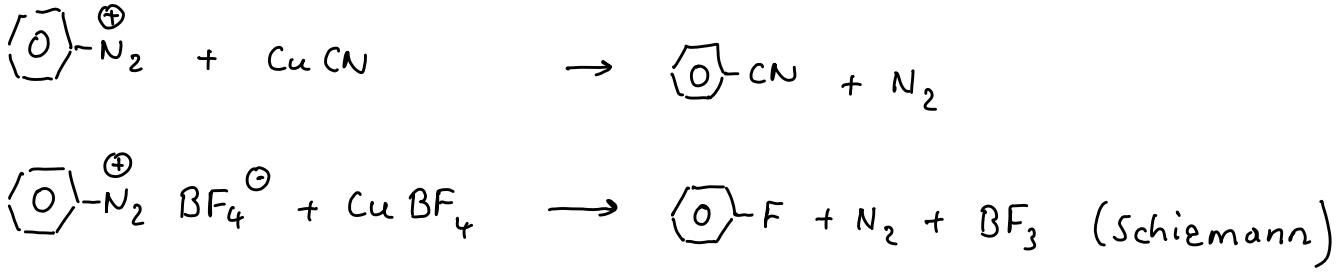
Raschig-Hoover 1915



~ Mio t/a

Kupfer-kat.: Sandmeyer





(Schiemann)

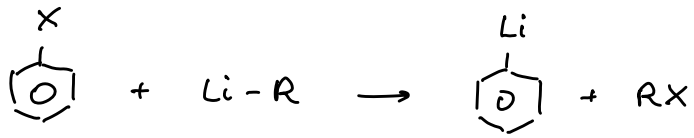
Metallvermittelte Subst. am Aromaten D.S.3

- Metallierung von Aromaten
  - Halogen-Metall-Austausch
  - direkte Metallierung
  - Transmetallierung

(- Kupplungsreaktionen (Kreuzkupplungen)
  - Heck
  - Stille
  - Suzuki
  - Sonogashira
  - Negishi)

Metallierung

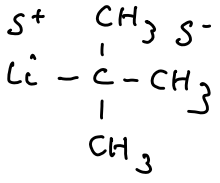
- Halogen-Metall-Austausch



Organolithium verb.

Grignard

organolithium-Basen (als Lsg. in Hexan)

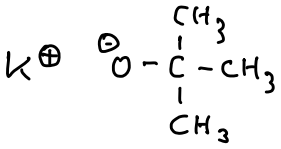
t-BuLi 

n-BuLi $Li-CH_2-CH_2-CH_2-CH_3$

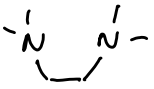
MeLi $Li-CH_3$

↑ Basen-Stärke

"beschleunigende Zusätze"



K-ot-Bu

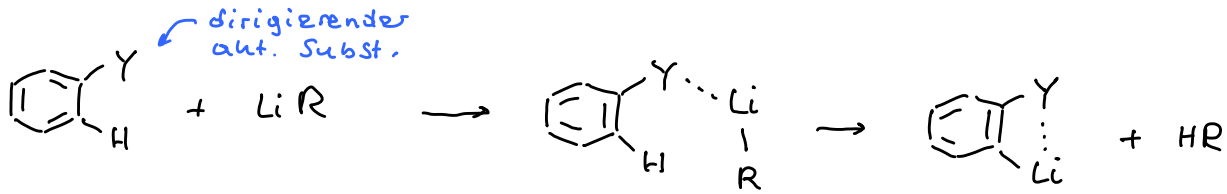


Tetramethyl-ethylendiamin

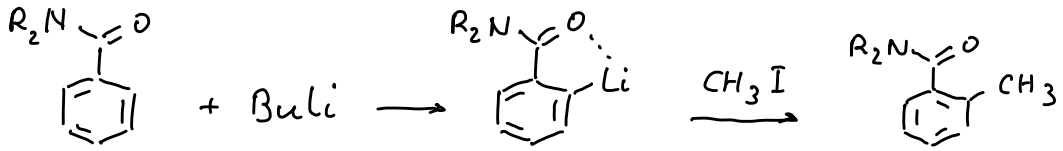
TMEDA

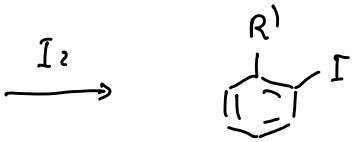
- direkte Metallierung arom. C-H Bind.

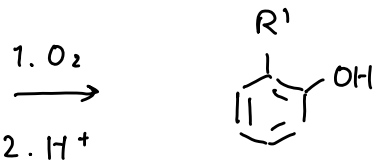
ortho-Metallierung

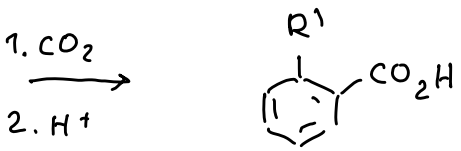


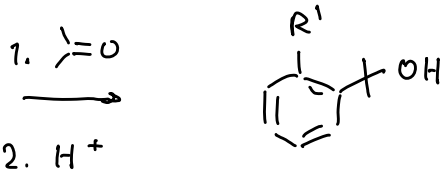
Y = OR, SR, NR_2, (CO_2R), 



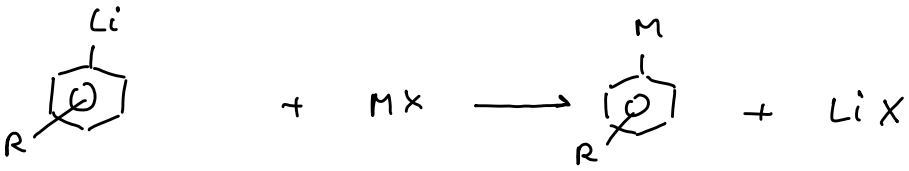


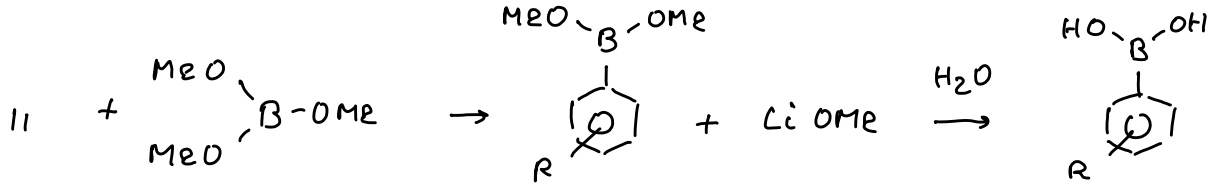


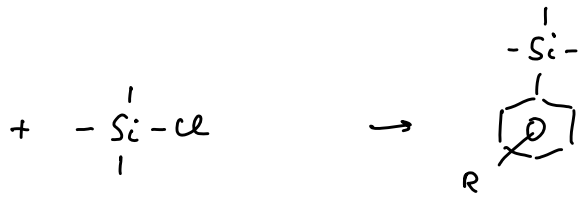


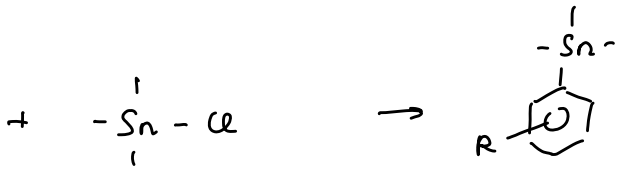


- Transmetallierung

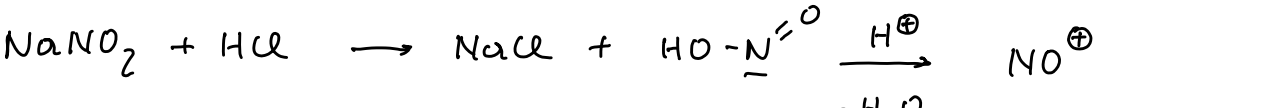


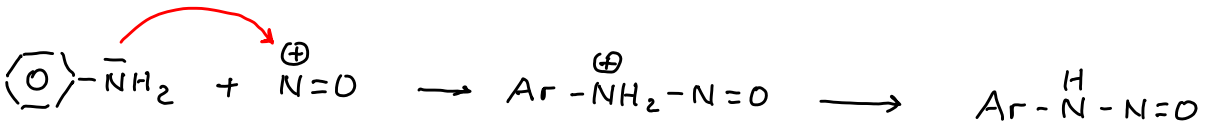


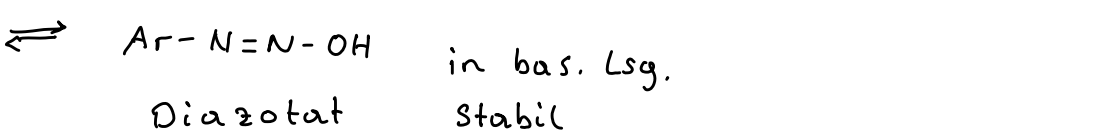




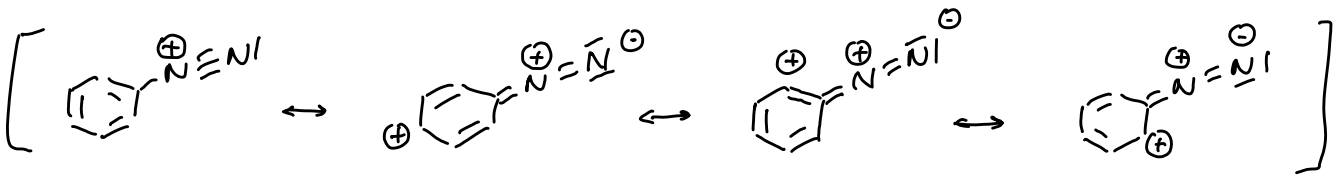
Aryldiazonium-Salze u. Diazokupplung D.8.3.3



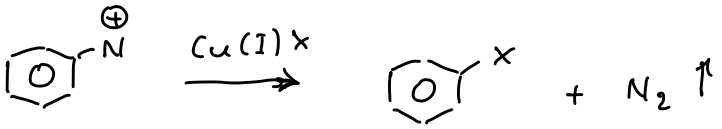




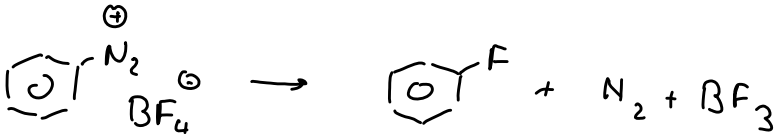
Mesomerie stabilisierung



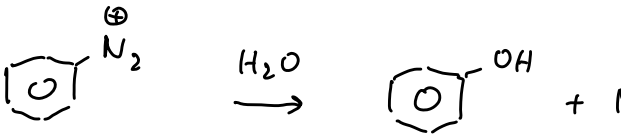
Reaktionen von Diazoniumsalzen



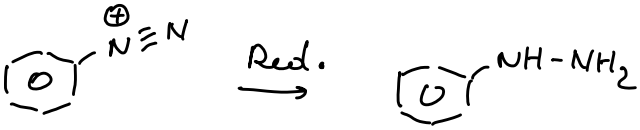
Sandmeyer



Schiemann



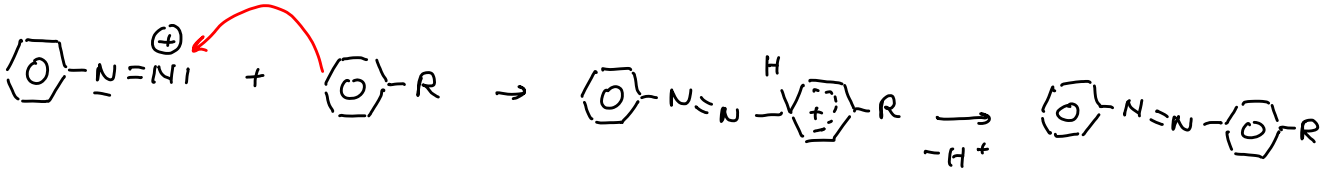
Verkochung



Red. zu Phenylhydrazin mit $SnCl_2$ oder Zn/HCl

Azokupplung (Azofarbstoffe)

relativ schwaches Electrophil

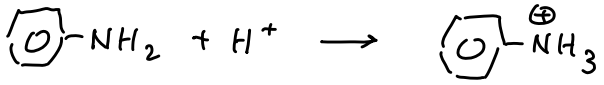


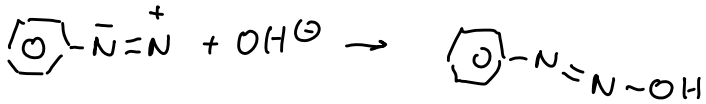
geht nur mit aut. Arom.

Azoverbindung

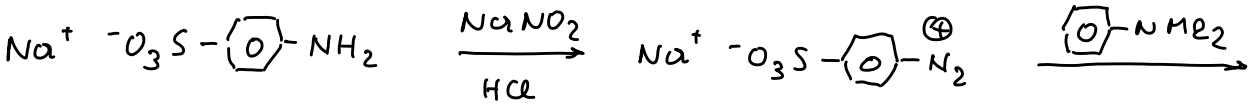
z.B. R = OH, OMe, NH_2, NR_2

pH-Wert:

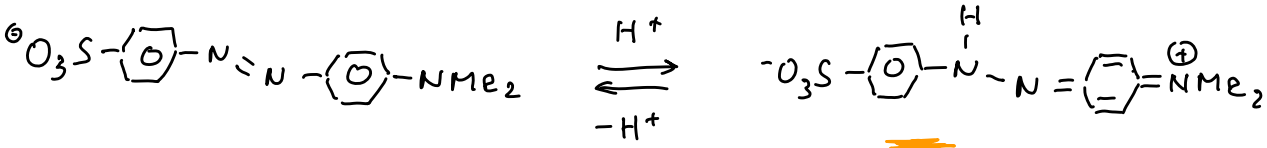
zu sauer: 

zu basisch: 

Beispiel: Azofarbstoff Methylorange



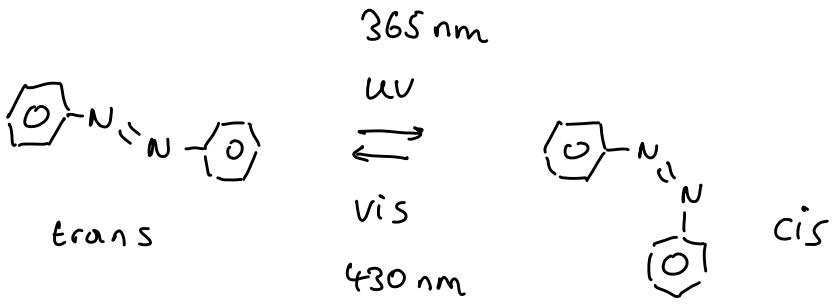
Sulfanilsäure



rot

gelb-orange

Photoschalter (molekulare Maschinen)



trans

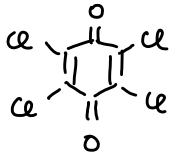
cis

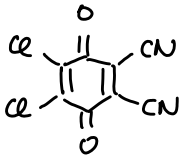
Oxidation, Dehydrierung D.6

Chemgapedia
organische Chemie
oxidationsreakt.

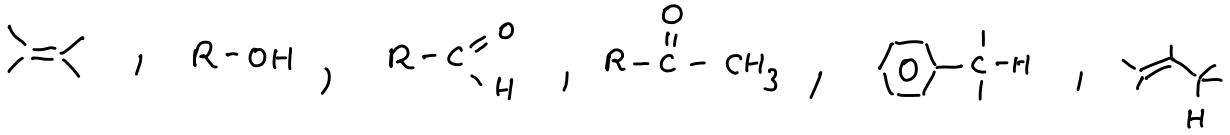
- gebräuchliche Ox.-Mittel

MnO_4^-	Permanganat	Cl_2 Chlor	
MnO_2	Mangandioxid	OCl^- Hypochlorid	
$Cr_2O_7^{2-}$	Dichromat	O_2 / kat.	Chloranil
CrO_3	Chromtrioxid	O_2 / hν	
OsO_4	Osmiumtetroxid	e^-	
H_2O_2	Wasserstoffperoxid		DDQ





- Substrate



- Einteilung

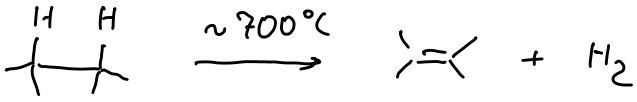
  - Entfernen von Elektronen ($R \xrightarrow{-e^-} R^{+\cdot} \xrightarrow{-e^-} R^{2+} \longrightarrow \longrightarrow R^{n+}$)
    Elektronentransfer

  - Entfernung von H_2 (Dehydrierung)

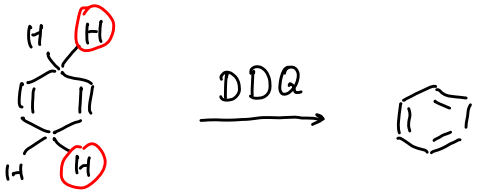
  - Ersatz von H durch O

  - Addition von O

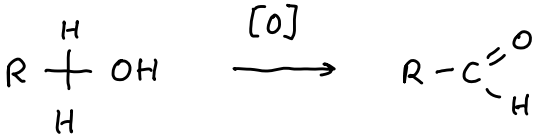
Entfernen von H_2 (Dehydrierung)



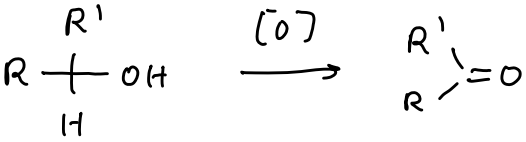
Cracken von Erdöl



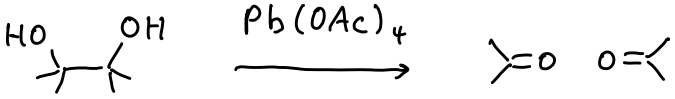
Aromatisierung



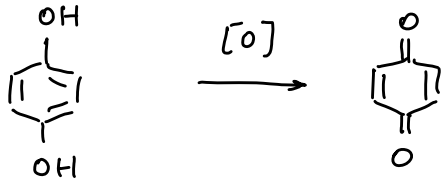
prim. Alkohol zu Aldehyd



sec. Alk. zu Keton

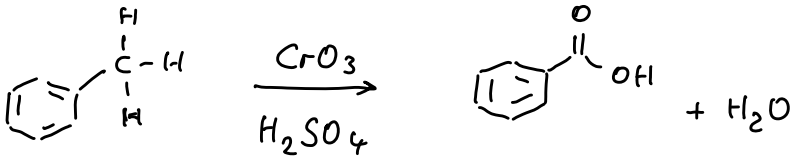


Glykol-Spaltung

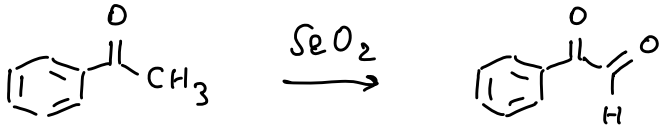


Phenole zu Chinonen

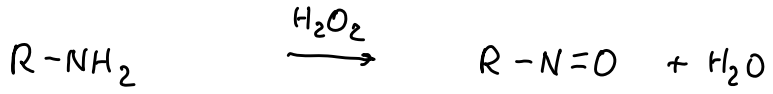
Ersatz H durch O



ox. benzylischer H's

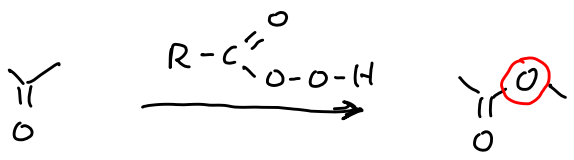


Methylketon zu Glyoxal

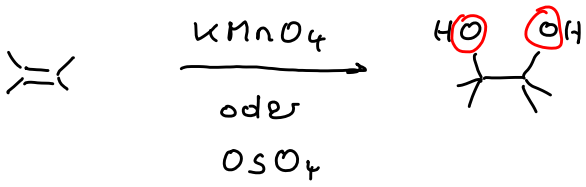


Amin zu Nitroso

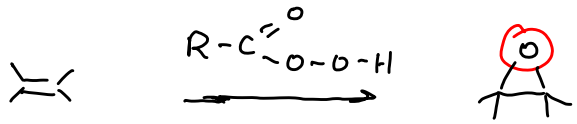
Addition von Sauerstoff



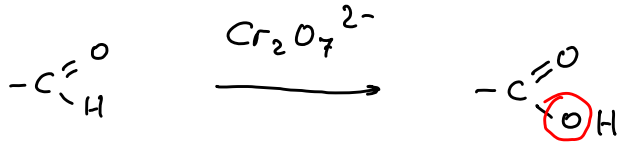
Keton zu Ester (Baeyer-Villiger)



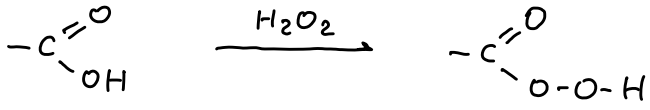
Alkene zu Diolen (Dihydroxylierung)



Alkene zu Oxiranen (Epoxidierung)



Aldehyde zu Carbonsäuren



Carbonsäuren zu Peroxycarbonsäuren

Sulfid → Sulfoxid → Sulfon

tert. Amin → Aminoxid

Oxidationszahlen

H (+1), O (-2), X (-1), C–C (0), C–C (0)

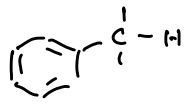
-4	CH_4
-3	H_3C-CH_3
-2	$H_2C=CH_2$, H_3C-OH
-1	$H-C\equiv C-H$, H_3C-CH_2-OH
0	$H_2C=O$
+1	CH_3-CHO
+2	HCO_2H
+3	H_3C-CO_2H
+4	CO_2, CCl_4

Oxidation von CH_2- u. CH_3-Gruppen

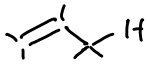
$-CH_3 \rightarrow -CH_2OH \rightarrow -CHO \rightarrow -CO_2H$

$-CH_2- \rightarrow -\underset{\displaystyle OH}{\underset{|}{C}}H- \rightarrow \overset{\displaystyle O}{\overset{\|}{C}}$

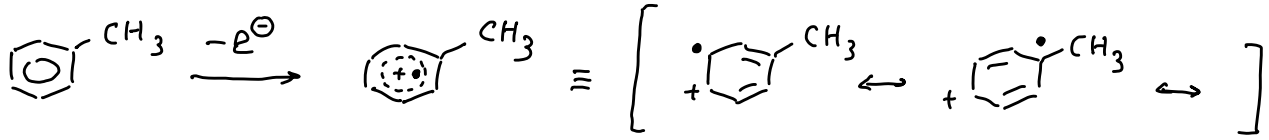
drastische Reaktionsbed. selektiv nur Benzyl- bzw Allyl-H

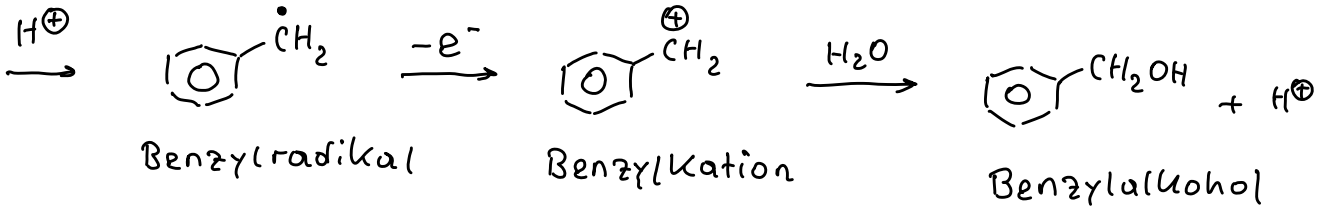


Benzyl-



Allyl-





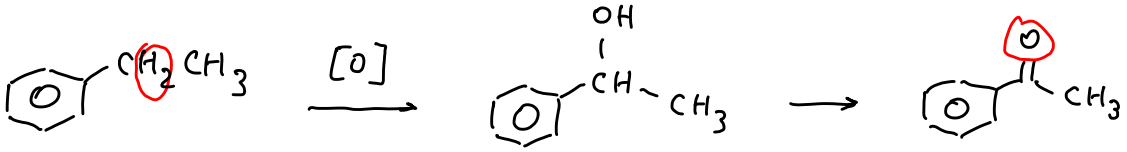
Benzylradikal

Benzylkation

Benzylalkohol

Benzaldehyd

Benzoesäure



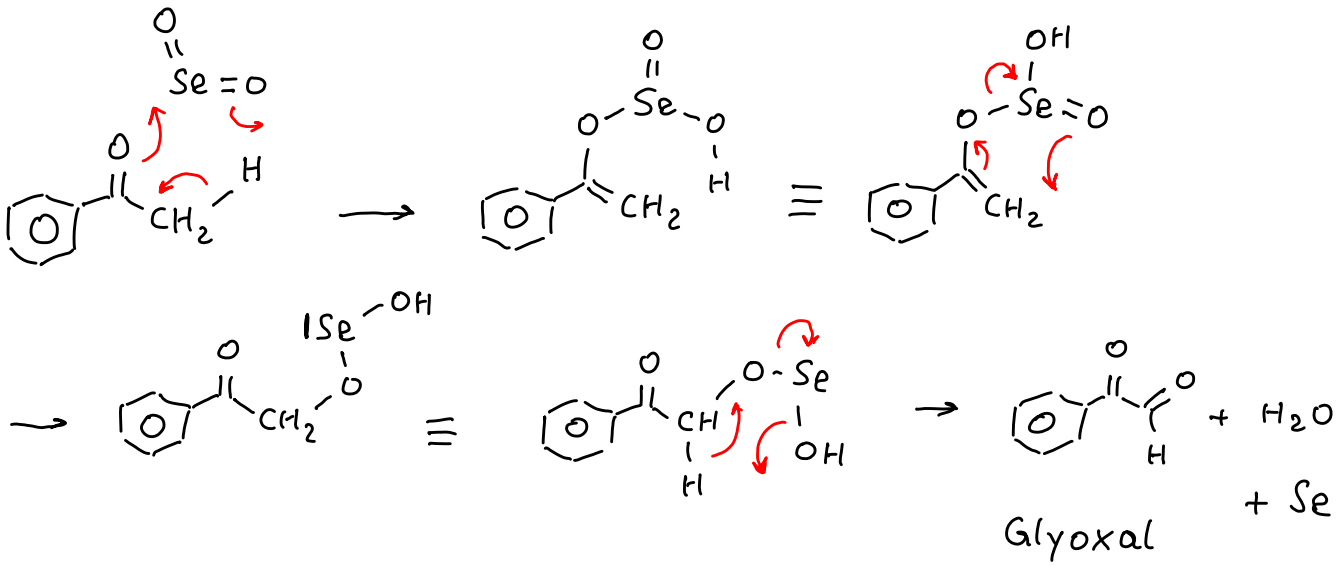
[O]: $KMnO_4$, $Cr_2O_7^{2-}$, Co^{2+}/O_2, Cu^{2+}/O_2

technisch

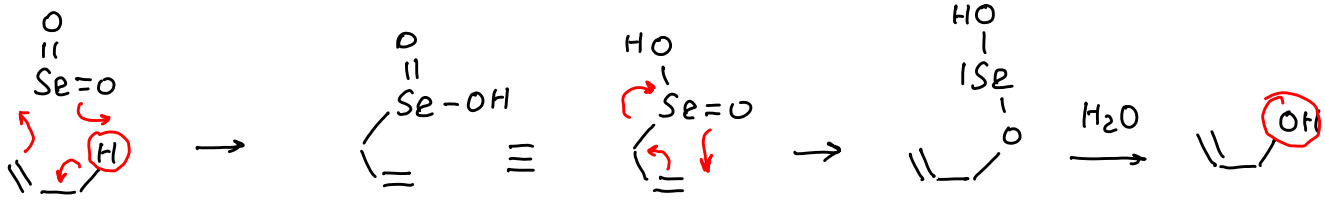
$H_2C=CH-CH_3$ (Propen) $\xrightarrow[350-400°C]{O_2/CuO}$ $H_2C=CH-CHO$ → D,L-Methionin (Tierernährung)

Acrylsäure (Polyacrylate)

Glyoxale aus Methylketon + Selendioxid

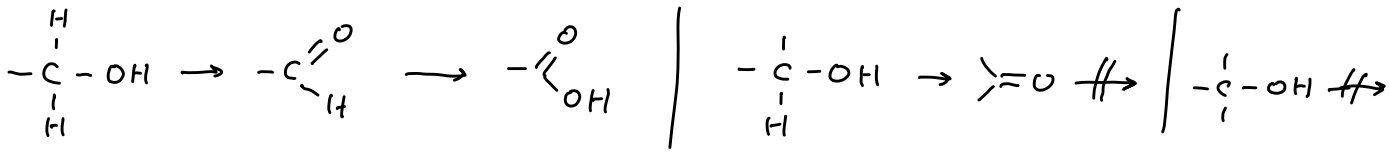


allylische Oxidation



Dehydrierung

Oxidation von Alkoholen

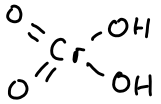


prim. Alk — Aldehyd — Carbon-säure | sek. Alk — Keton | tert. Alk.

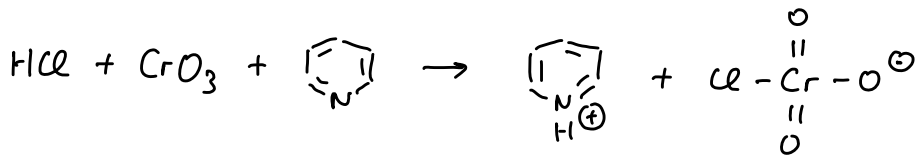
Oxidationsmittel

$Cr_2O_7^{2-} / H_2SO_4$ — Dichromat

CrO_3 / H_2SO_4 / Aceton — Chromsäure

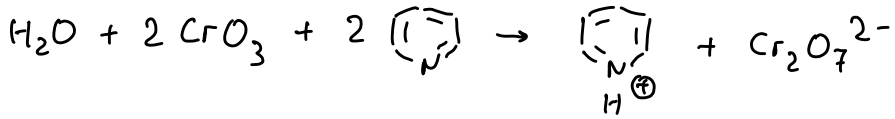


Jones Reagens



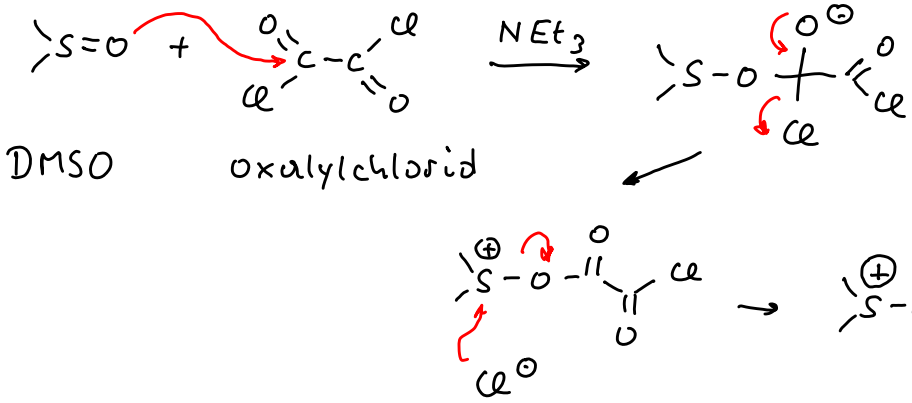
Pyridinium Chlorochromat

PCC



Pyridinium dichromat

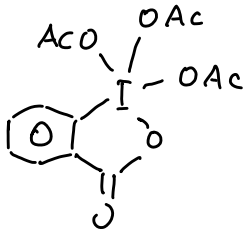
PDC



DMSO

Oxalylchlorid

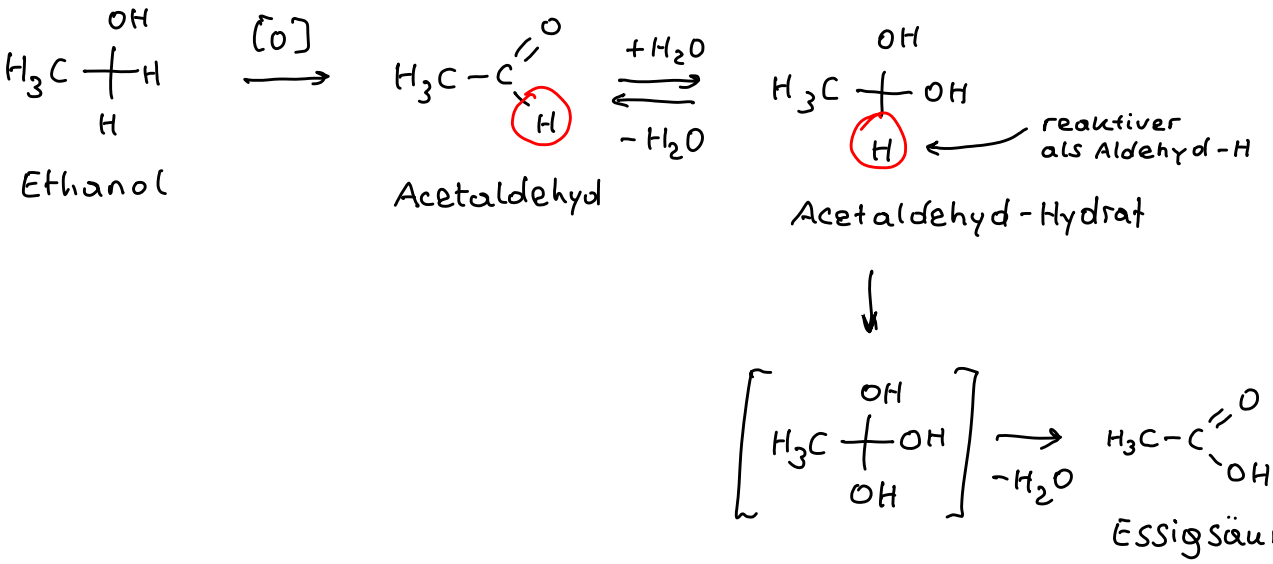
Dimethyl-chlor-sulfonium-Ion



ohne Mechanismus

Dess-Martin

Mechanismen



Ethanol

Acetaldehyd

Acetaldehyd-Hydrat

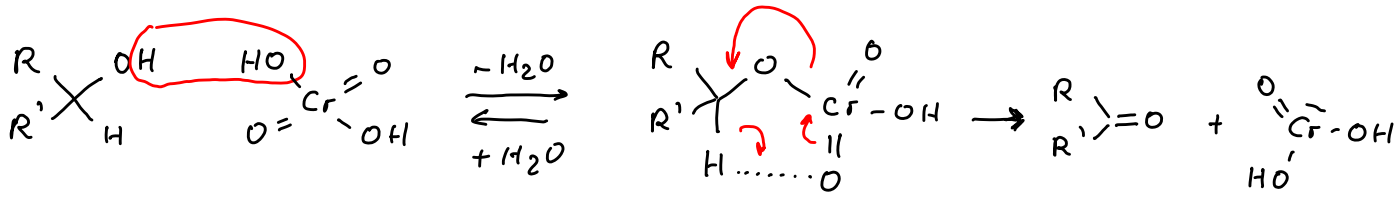
reaktiver als Aldehyd-H

Essigsäure

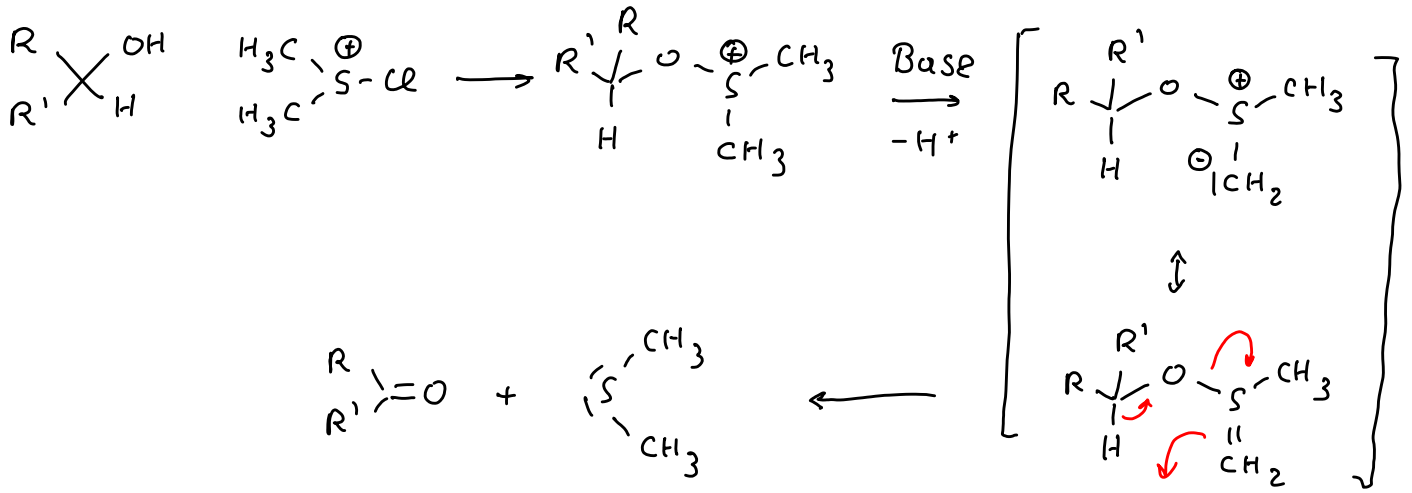
→ wasserfreie Bedingungen um Ox. auf Stufe des Aldehyds zu stoppen!

6.1.2014

Mechanismus Ox. von Alkoholen mit Chromsäure

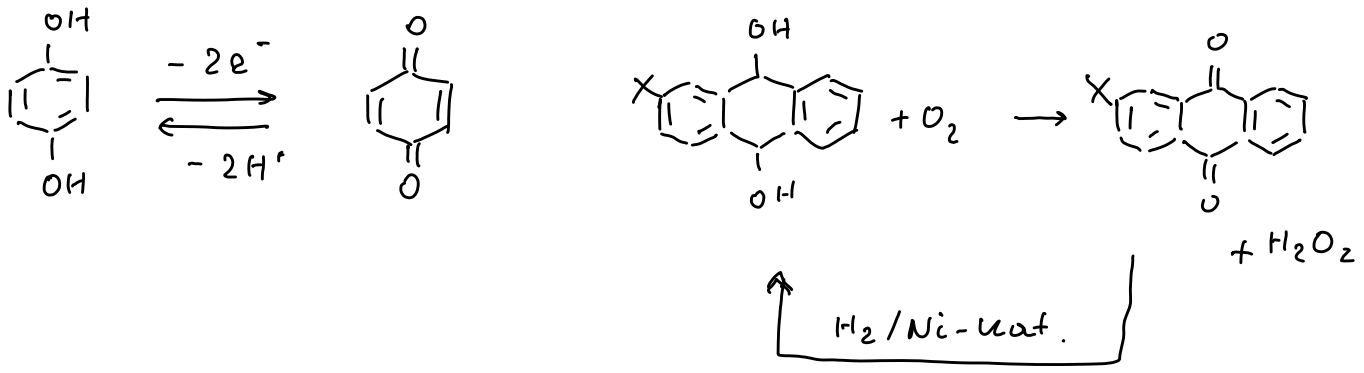


Mechanismus mit Dimethylchlorsulfonium (Swern-Oxidation)

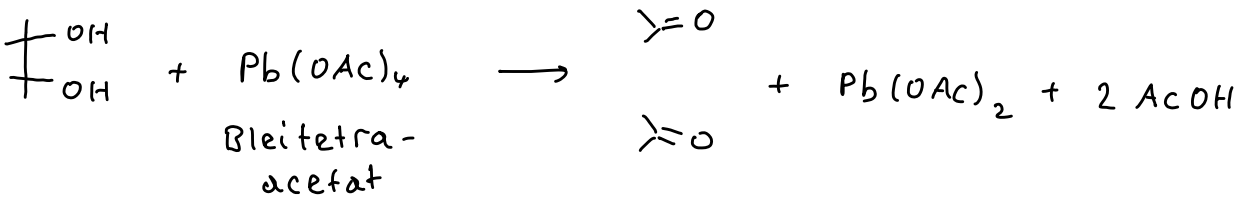


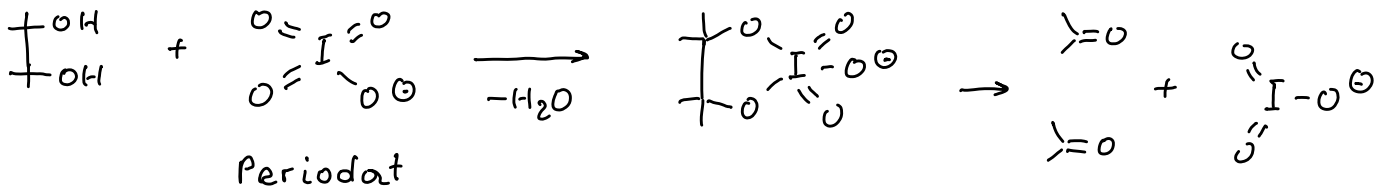
Dess-Martin (ohne Mechanismus)

Chinone aus -OH oder $-NH_2$ subst. Aromaten



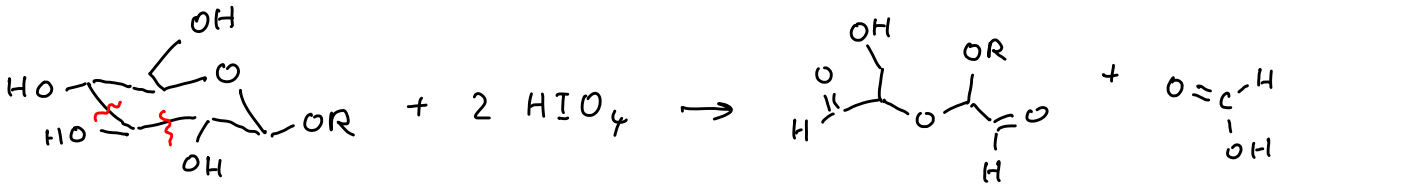
Glykolspaltung



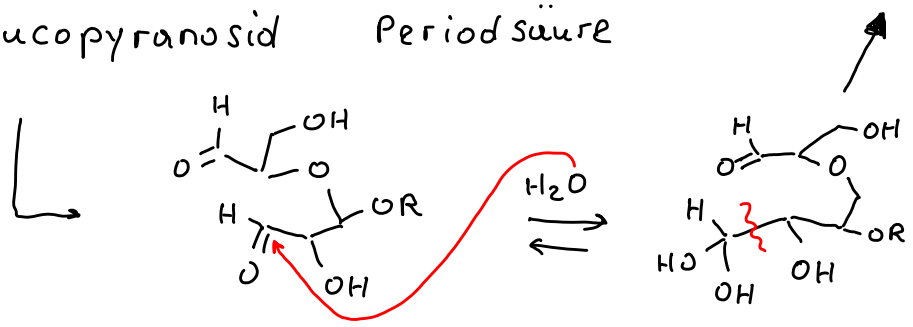


Periodat

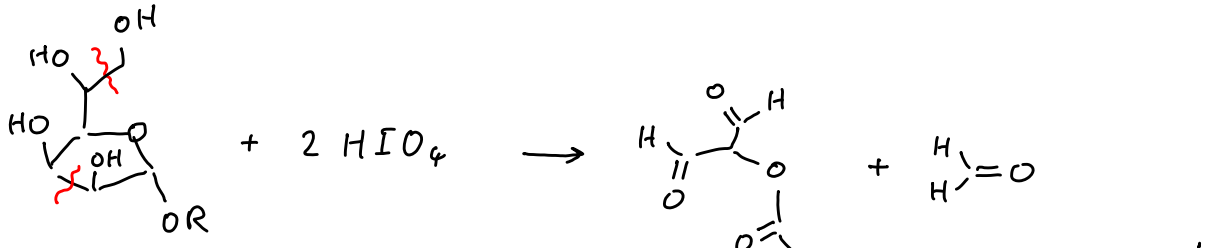
Glykolspaltung von Zuckern



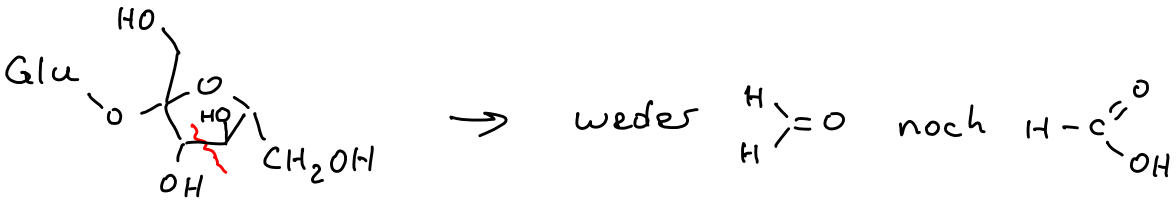
Glucopyranosid Periodsäure Ameisensäure



Hydrat



Furanosid Formaldehyd

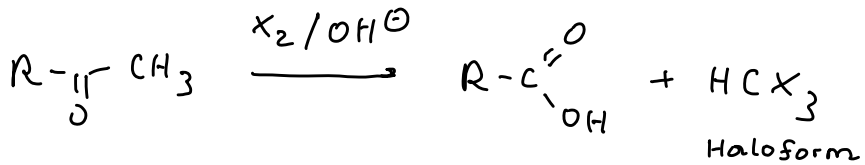


Saccharose

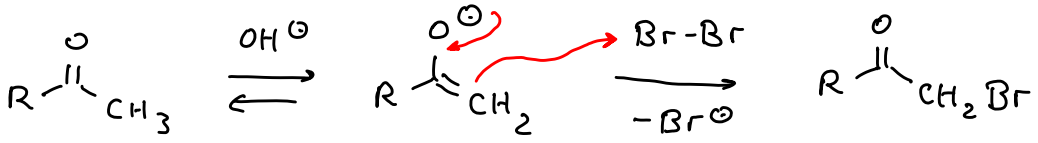
- Spaltung von Alkoholen und Ketonen

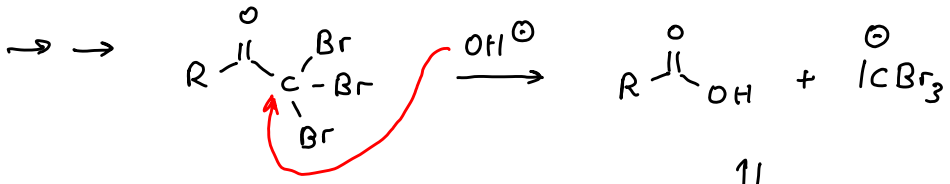
Haloform - Reaktion

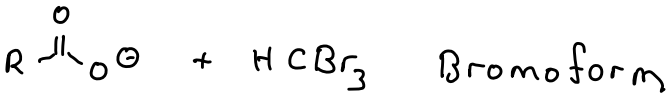
formal:



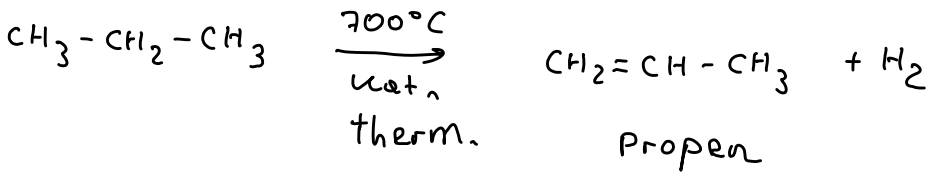
Mechanismus

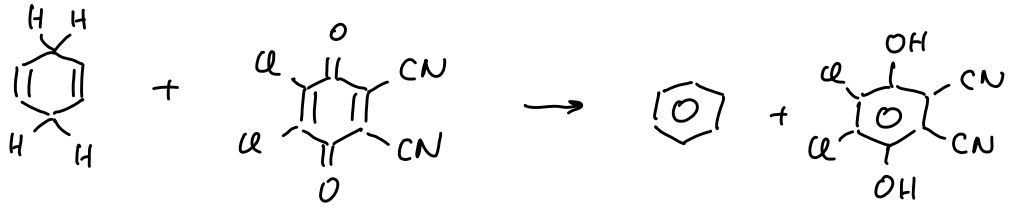






- Dehydrierung (Aromatisierung)

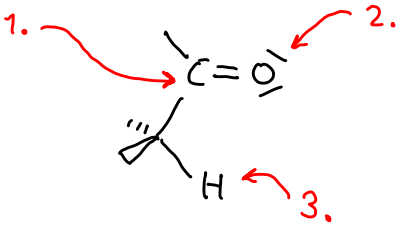


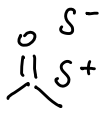
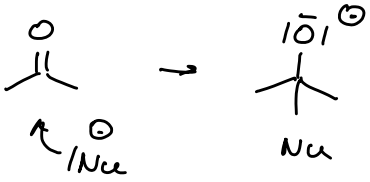


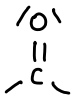
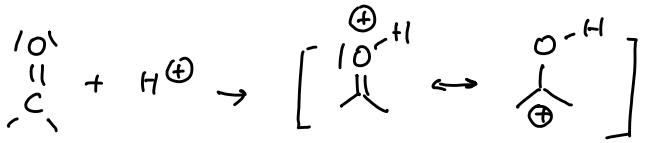
Reaktionen von Carbonylverb. I

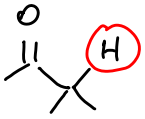
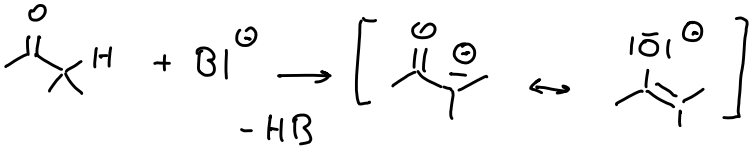
D.7.1

Reaktivität



1.  polarisierte Doppelbind.  nucleophile Addition

2.  freie El. paare am O 

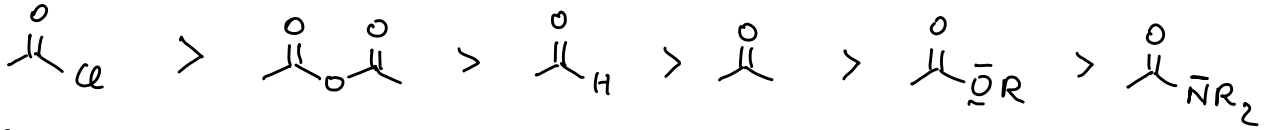
3.  acides H-Atom α-H Atom 

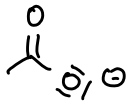
Enolat

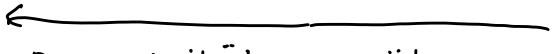
---

1. Nucleophile Addition

- Reaktivität von Carbonylverbindungen

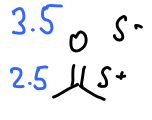


Säure-chlorid > Anhydrid > Aldehyd > Keton > Ester > Amid > Säure > 

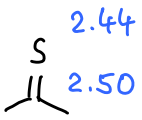


Reaktivität gegenüber Nucl.

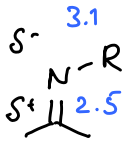
— heteroanaloge Carbonylverb.



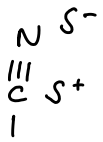
Carbonyl



Thiocarbonyl

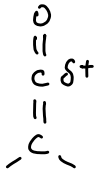


Azomethin
Imin
Schiffsche Base

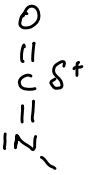


Nitrile

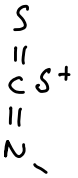
— Kumulene



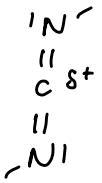
Keten



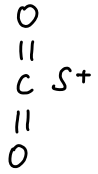
Isocyanat



Thioisocyanat



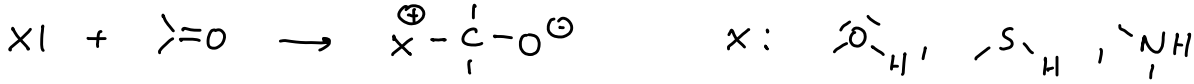
Carbodiimid



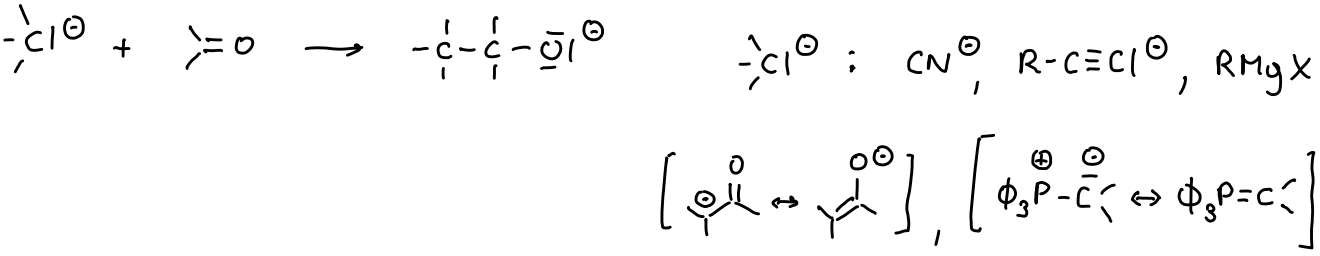
CO_2

Kapitelübersicht:

1. Heteroatom-Nucleophile



2. Kohlenstoff-Nucleophile

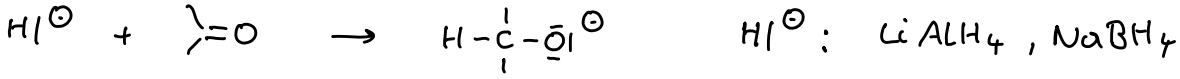


Enolat

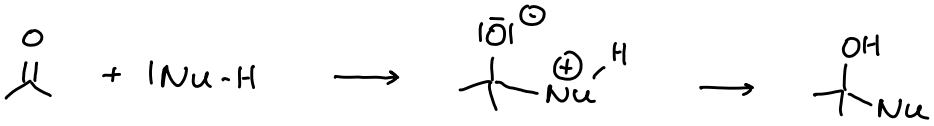
Phosphor-Ylid

Φ = Ph

3. Hydrid (Reduktion)



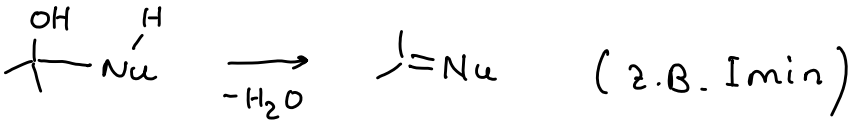
Nucleophile Addition von Heteroatom-Nucleophilen



Folgereaktionen:

a) am Nucleophil ist ein weiteres H : Eliminierung

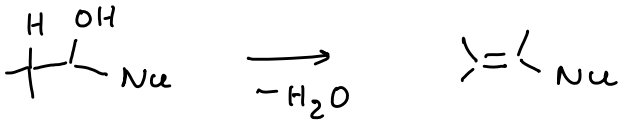
Nucleophil: $\bar{N}uH_2$



(z.B. Imin)

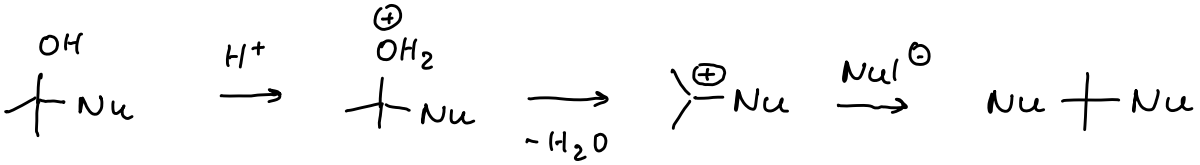
b) am Nucl. ist kein weiteres H

aber es gibt ein acides α-H : Eliminierung



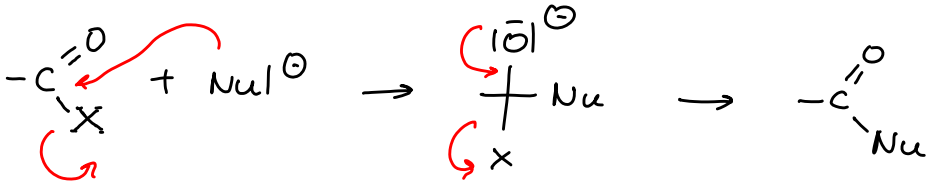
(z.B. Enamin)

c) kein weiteres H am Nu, kein α-H



(z.B. Acetal, Aminal)

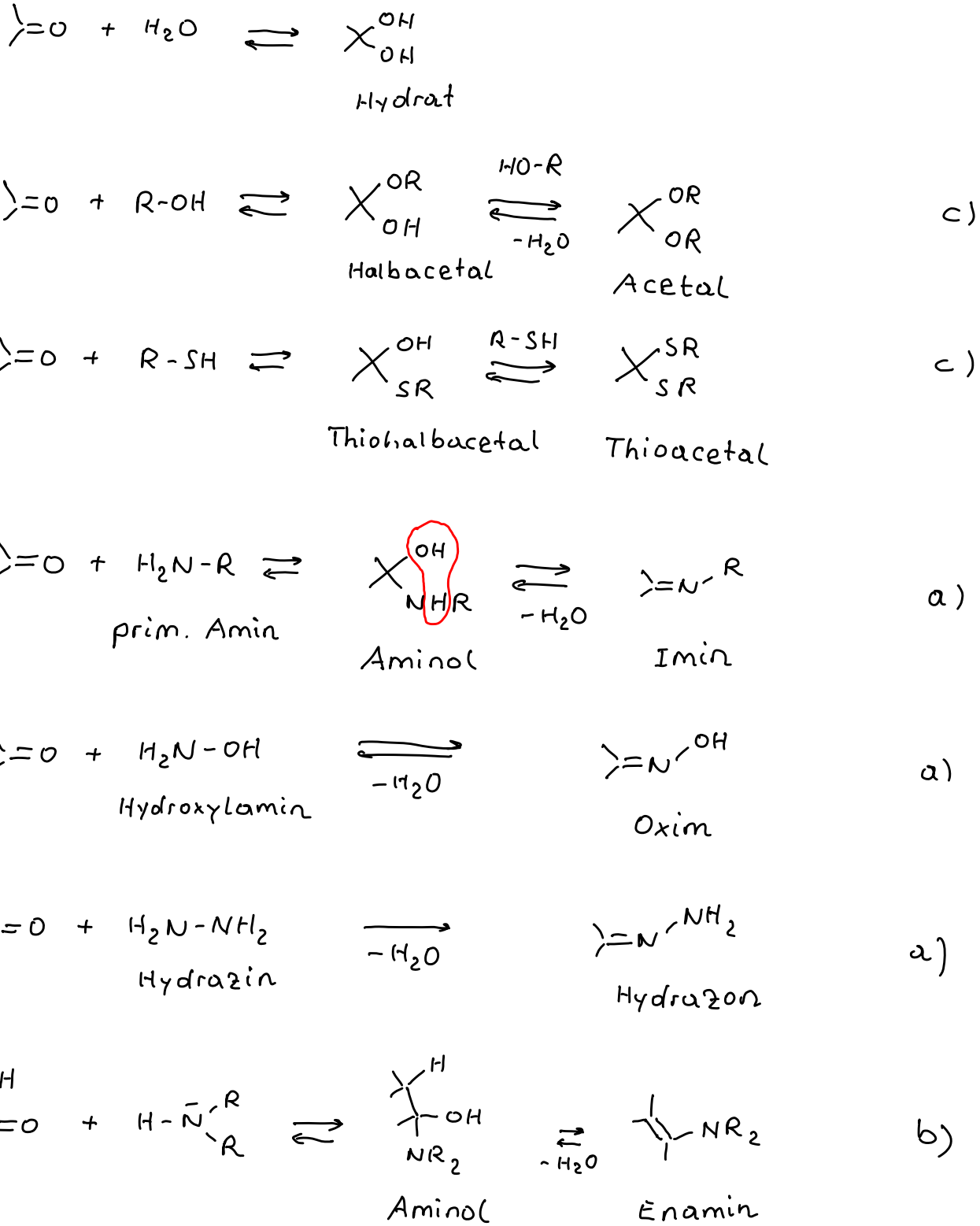
d) Gute Abgangsgruppe am Carbonyl-C



z.B. Esterverseifung

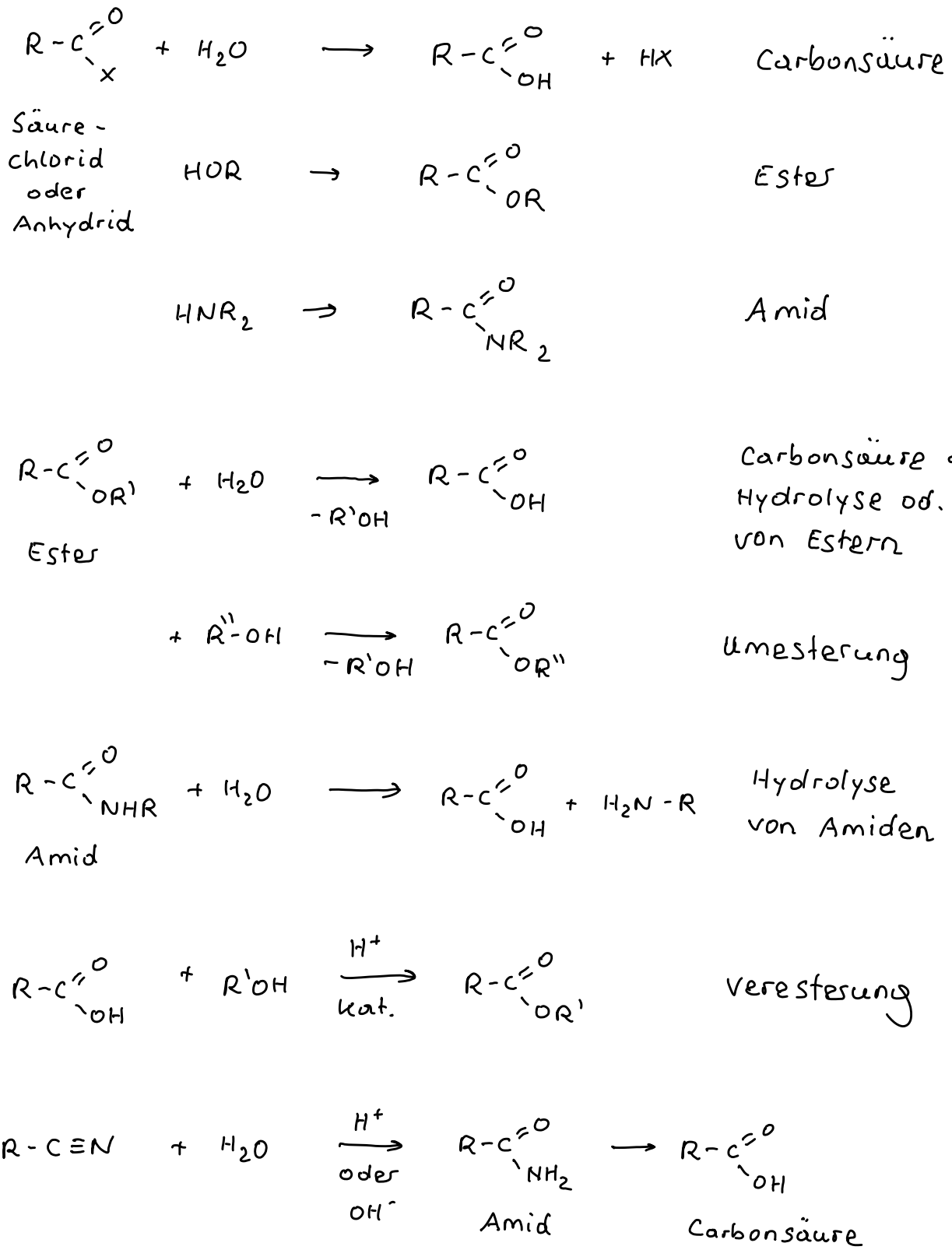
1. Heteroatom Nucleophile (Addition, Eliminierung)

Folgereakt. a), b), c)



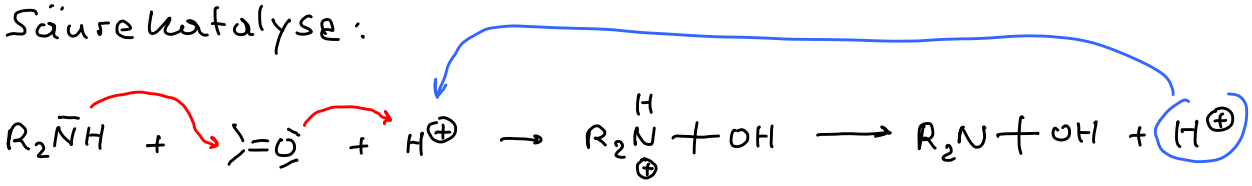
2. Heteroatom Nucleophile : Substitution

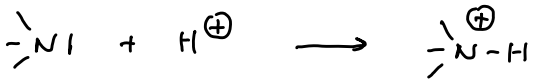
Folgereaktion d)



Mechanismus: Bsp. R_2NH + 

Säurekatalyse:

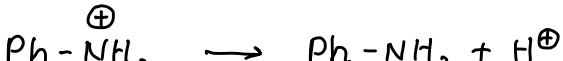




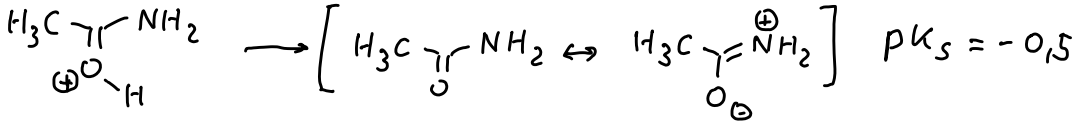
nucleophil — nicht nucleophil

optimales pH-wert: pK_S des protonierten Nucleophils

z.B. $CH_3NH_3^{\oplus} \longrightarrow CH_3NH_2 + H^{\oplus}$ $\quad pK_S = 10{,}6$

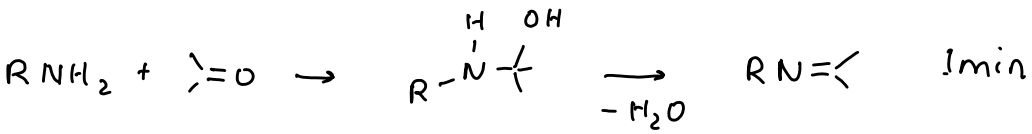


$pK_S = 3$

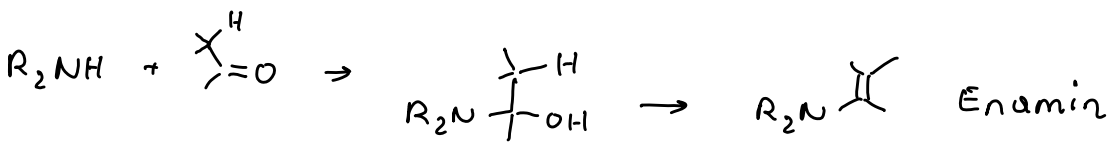


$pK_S = -0{,}5$

Beispiele:

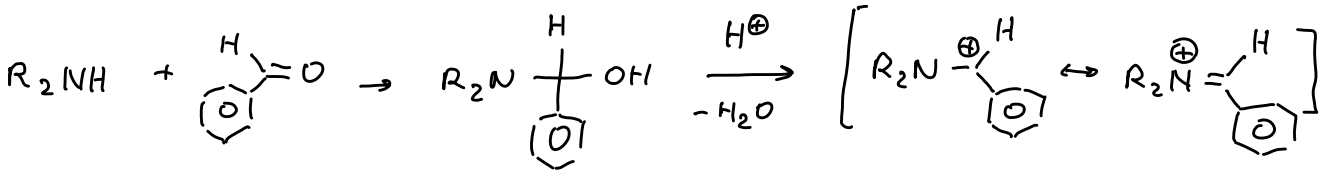


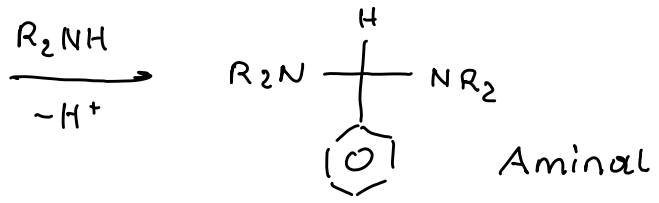
Imin



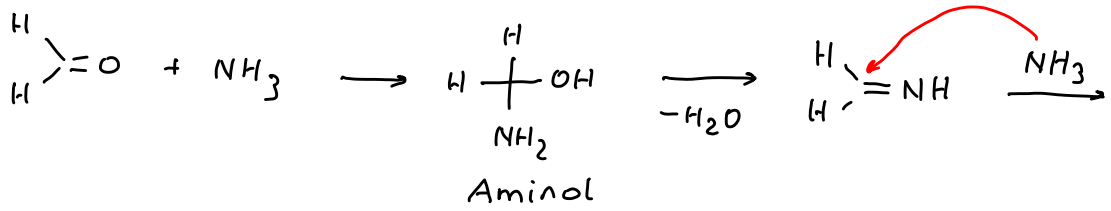
Enamin

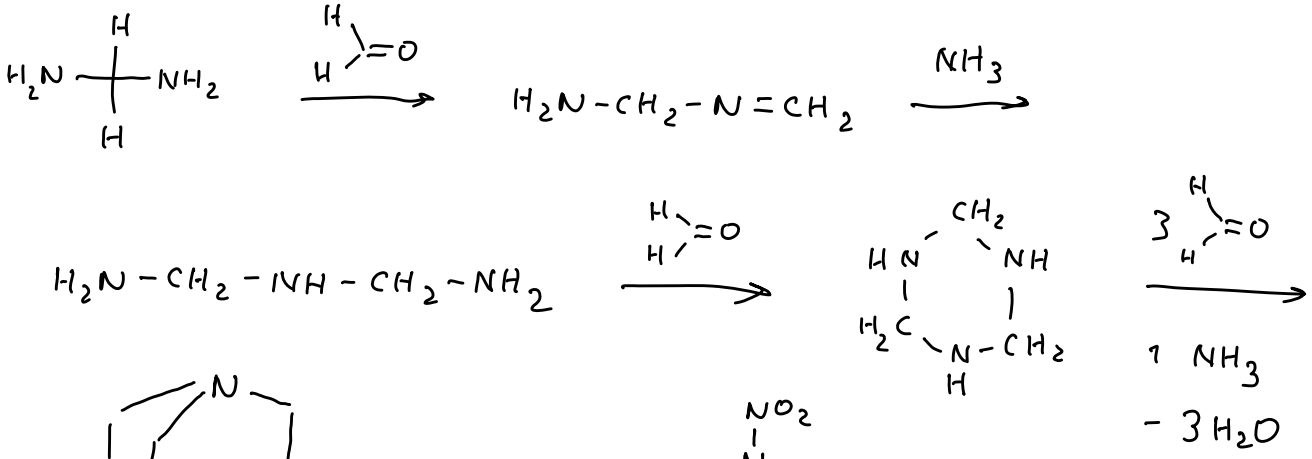
Sec. Amin + Carbonyl ohne α-H



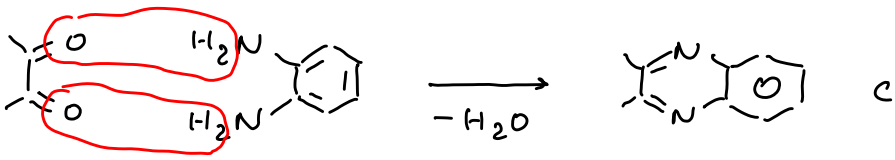


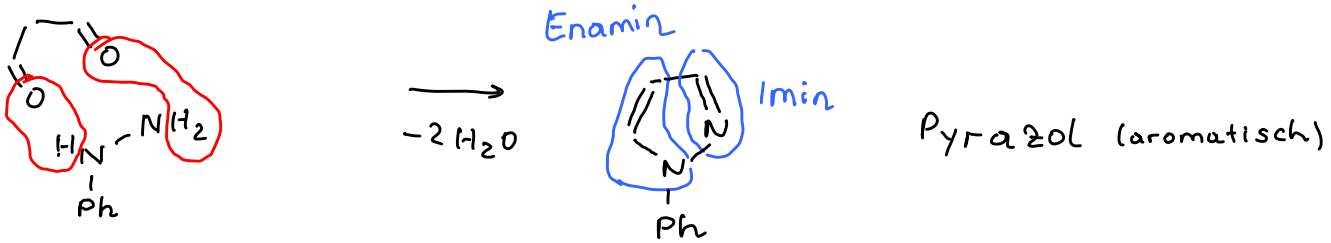
Bsp. Formaldehyd + Ammoniak

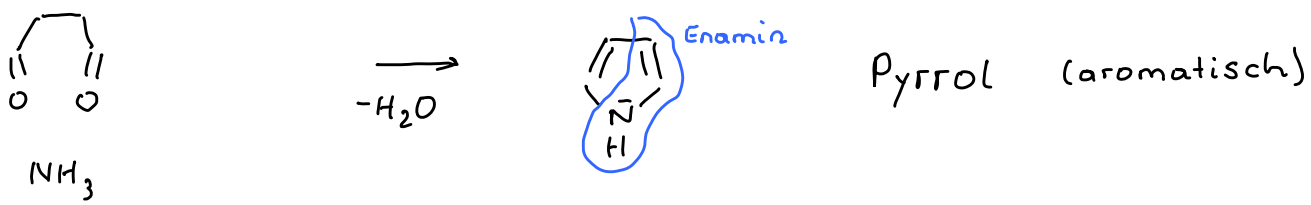




Bsp.: andere Heterocyclen

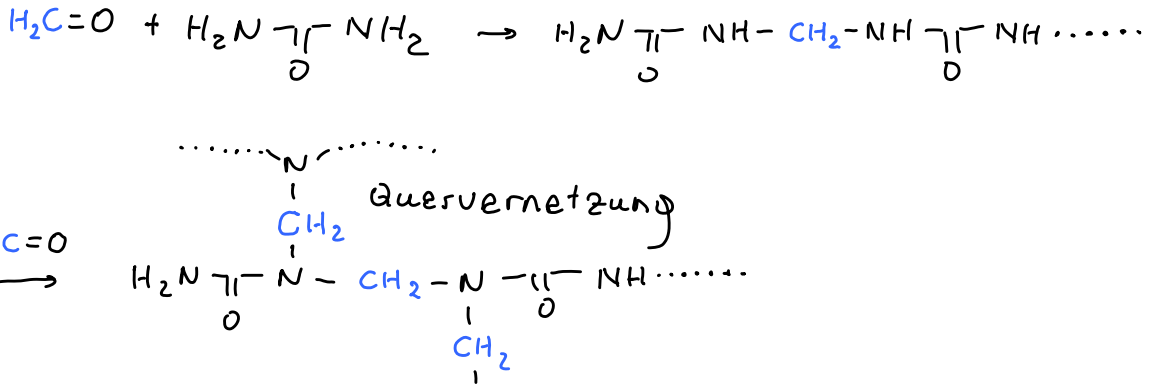




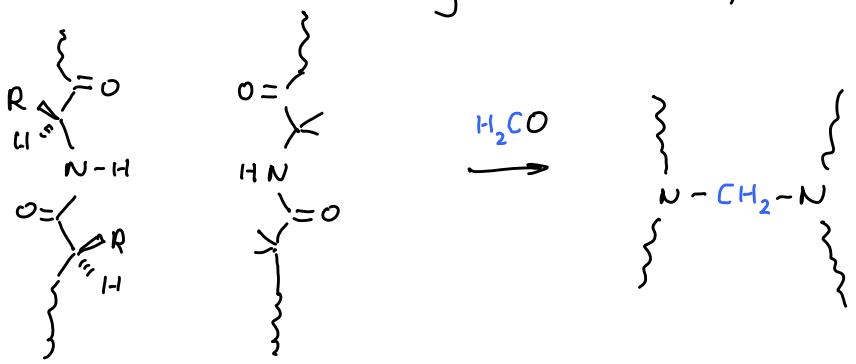


15.01.2014

Bsp. Aminoplaste



Bsp. Peptidvernetzung (Galalith)

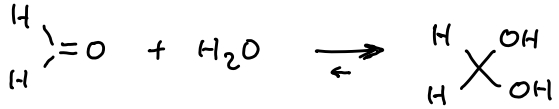


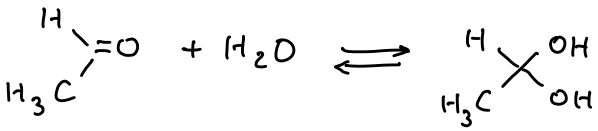
~~Osazone~~

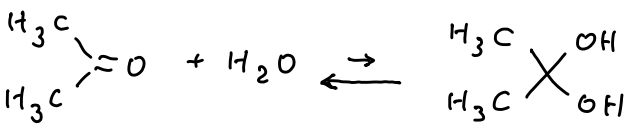
Ketone / Aldehyde + Wasser / Alkohole

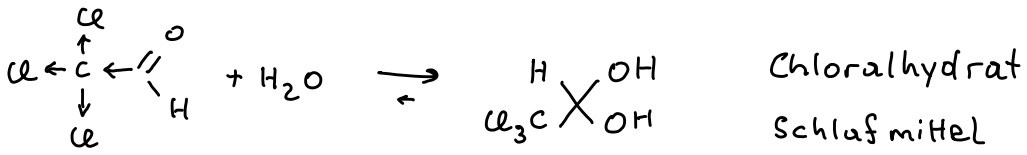
$$K = \frac{[\text{Hydrat}]}{[\text{Carbonylverb.}]}$$

Hydrate:

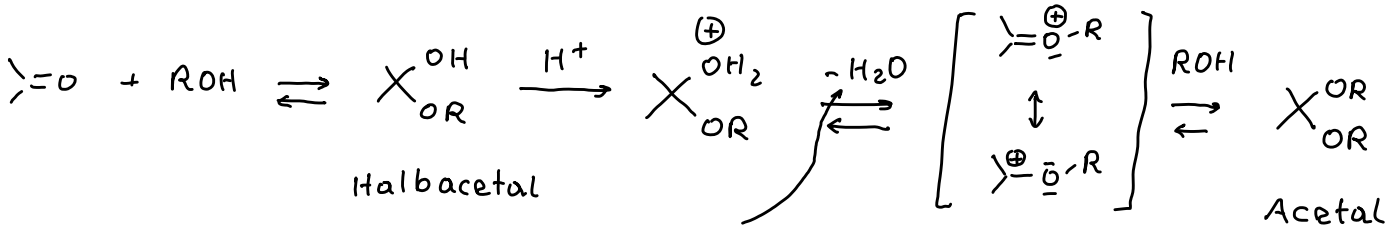




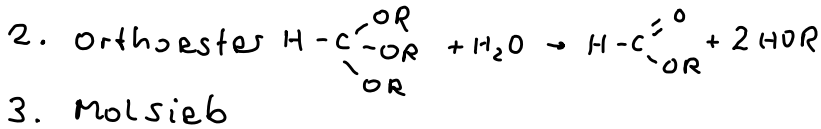




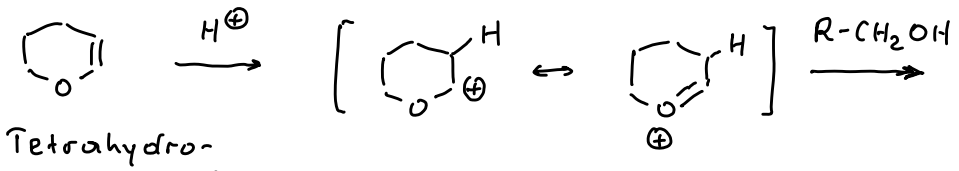
Acetale:



Wasser entziehen

1. "Schlepper" (Benzol)
2. Orthoester 
3. Molsieb

Bsp. Acetale als Schutzgruppen

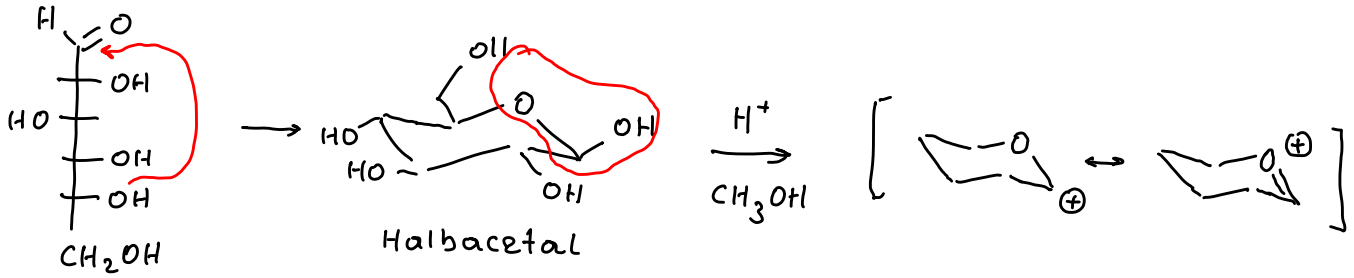


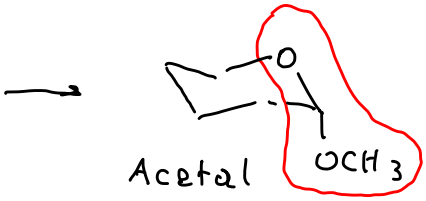
Tetrahydropyran THP

Schutzgruppe für Alk. z.B. gegen Ox.

Schutzgruppe
Aldehyde, Ketone
gegen Ox. oder nucl. Angriff
basenstabil, säurelabil

Bsp. Zuckerchemie

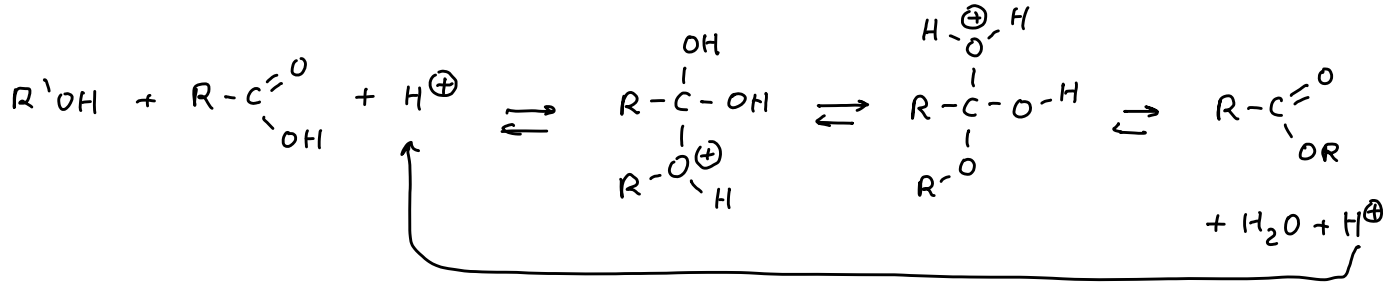




α-D-Methylglykosid

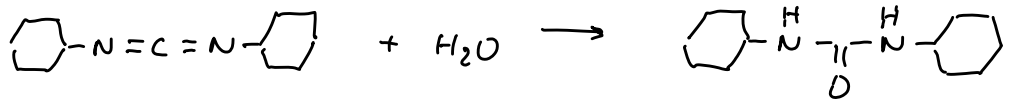
Substitution (Carbonsäurederivate + Heteroatom-Nucl.)

- veresterung



Gleichgew. Reakt. Überschuss ROH, wasser entziehen

z.B.

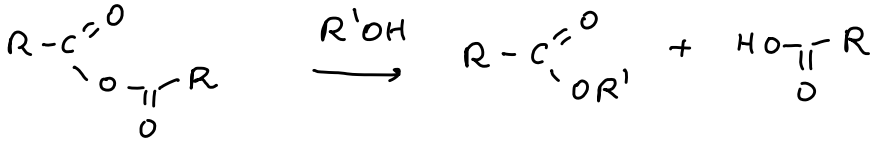


Dicyclohexyl-carbodiimid DCC

Harnstoff

- Umesterung (analog zu Veresterung)

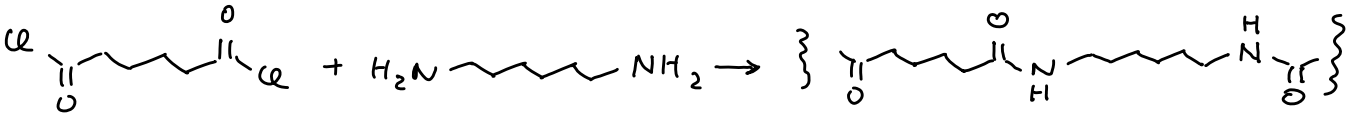
- Ester aus reaktiven Carbonsäurederivaten



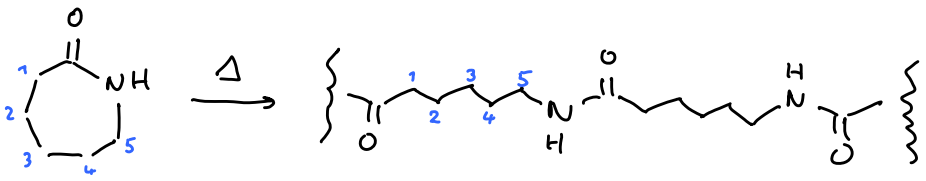
- Amide aus Carbonsäurederivaten

Anwendungen,

Beispiel Polyamide:

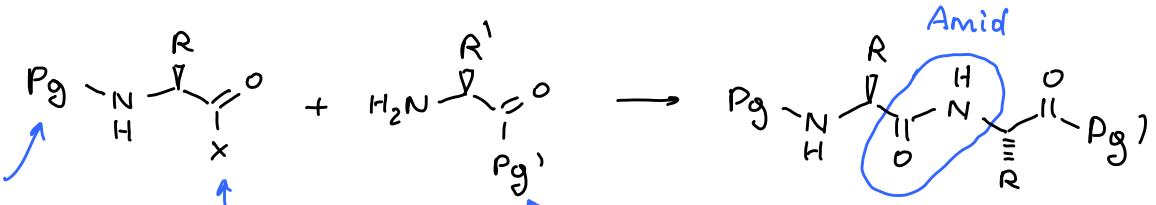


Adipinsaurechlorid Hexamethylendiamin Nylon 6,6



Perlon-G

Beispiel: Peptidsynthesen

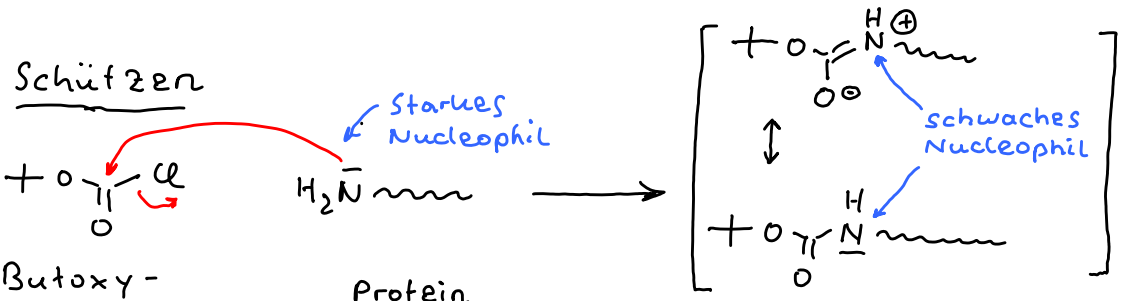


protecting group für Amin

aktivierte Carbonsäure z.B. Säurechlorid

protecting group für Carboxyl

Schützen

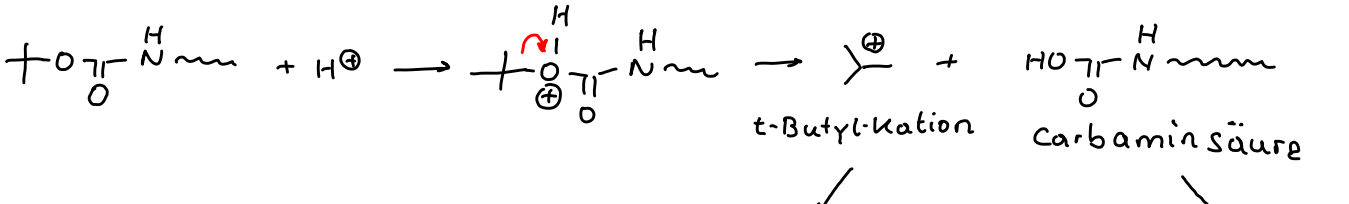


Butoxy-carbonylchlorid
boc-chlorid

Protein (N-Terminus)

geschütztes Protein
boc-Schutzgruppe
(Urethan)

Entschützen

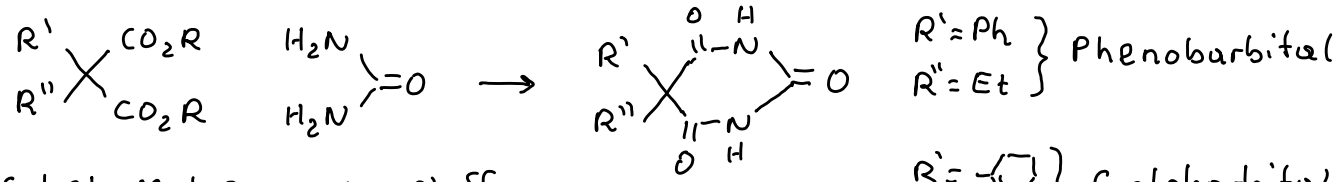


t-Butyl-Kation

Carbaminsäure

Protein

weitere Beispiele Reakt. von Amin mit Ester



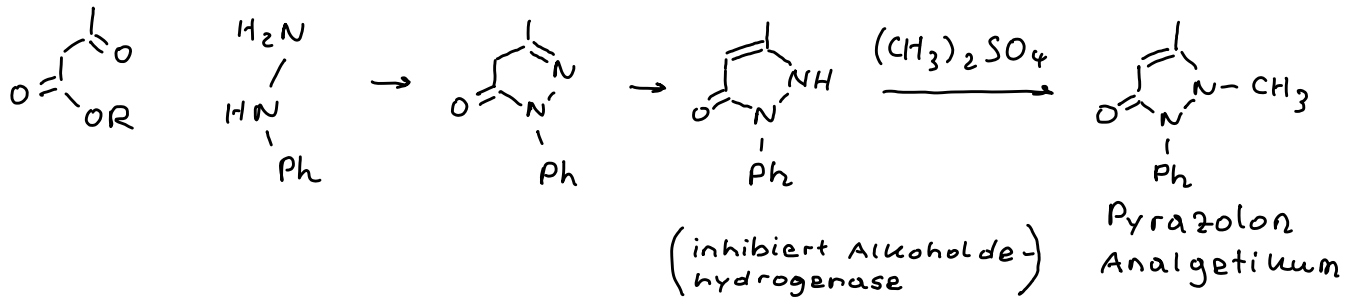
Subst. Malonsäure ester

Harnstoff

Barbiturate

R' = Ph, R'' = Et } Phenobarbital

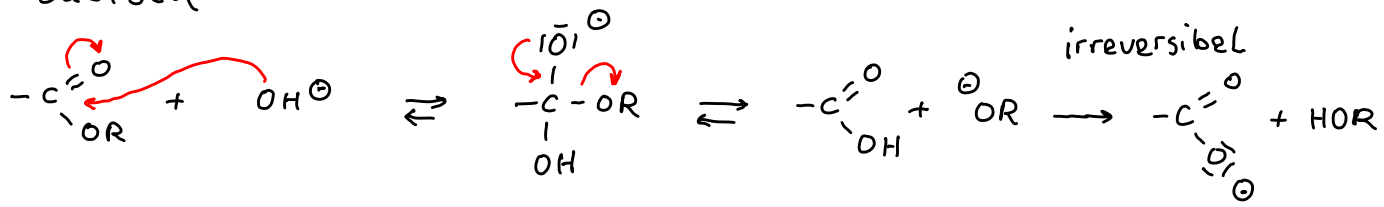
R' = , R'' = Et } Cyclobarbital (Barschel)



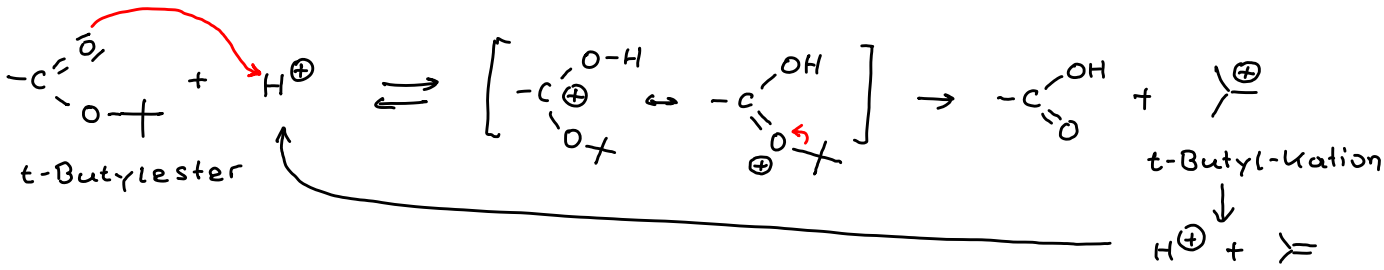
– Hydrolyse von Carbonsäurederivaten

Esterhydrolyse

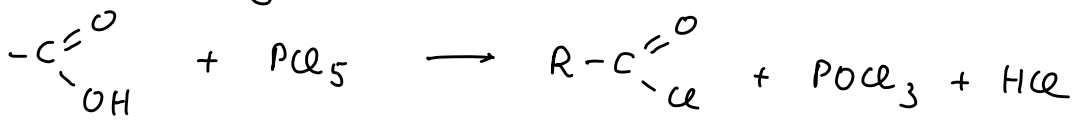
– basisch



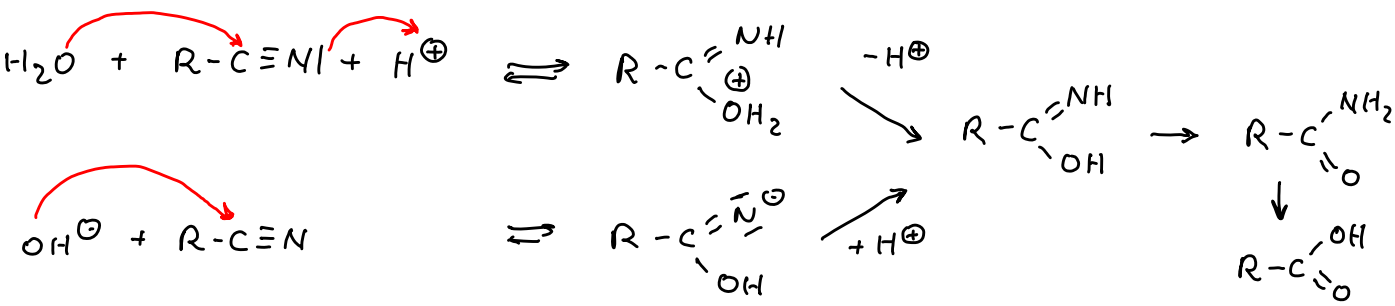
– sauer



– Darstellung von Säurechloriden

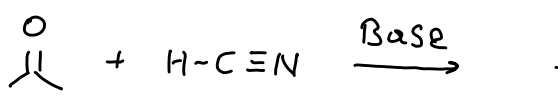


– Hydrolyse von Nitrilen

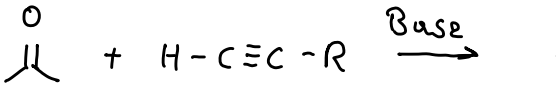


Reaktionen von Carbonylverb. mit Kohlenstoffnucleophilen

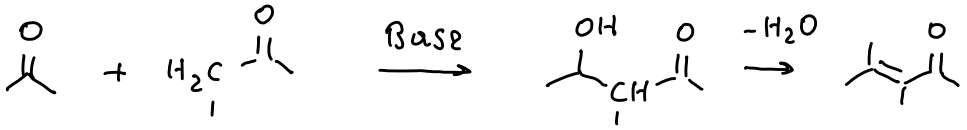
D.7.2



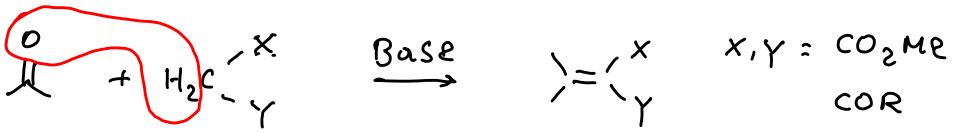
Cyanhydrin



Ethinylierung

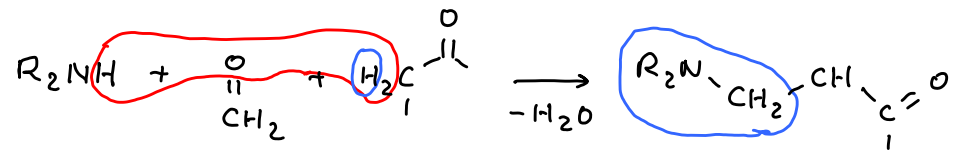


Aldol-Add. (kond.)

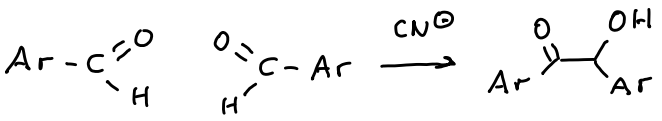


Knoevenagel

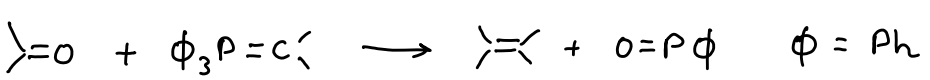
~~Erlenmeyer~~
~~Darzens~~ - Glycidester



Mannich-Reaktion
Aminomethylierung
C-H acider Verb.

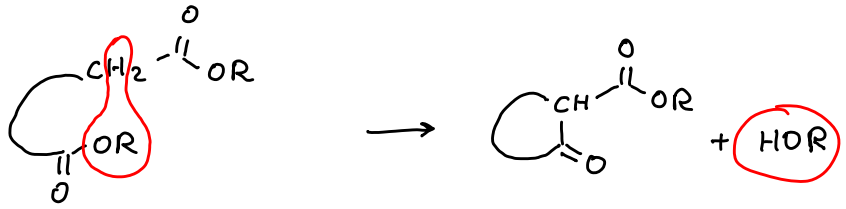


Benzoin-Kondensation

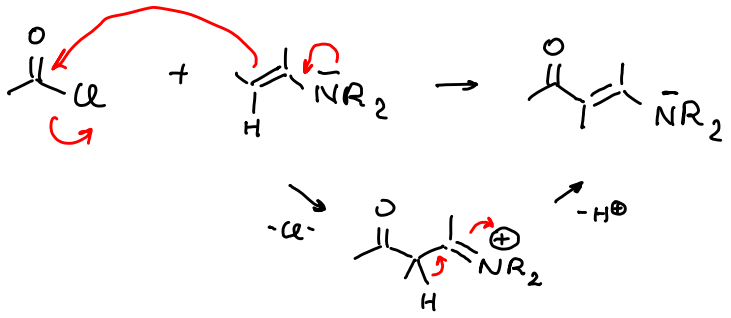


Wittig-Reaktion

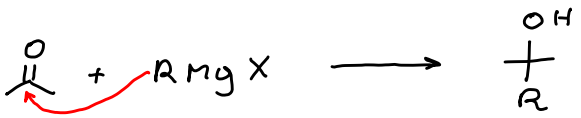
Claisen-Ester-Kond.



Dieckmann
(intramol. Claisen)



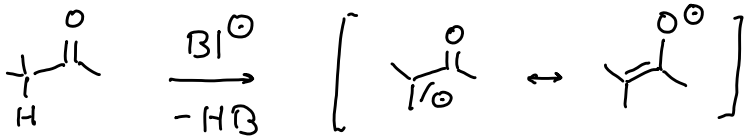
Acylierung von Enaminen



Addition von Grignard verbindungen (oder Li-org. verb.) an Carbonyle

---

Deprotonierung von Carbonyl mit α-H zu Enolat-Ion:



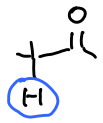
Enolat mesomerie-stab. Anion

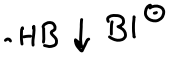
C-H acide verb.	pKs	Base
CH_4	~ 48	
H-C≡C-R	~ 26	BuLi, MeLi, LDA
$H_3C-C(=O)-OEt$	~ 24	K-O-t-Bu
$H_2C(CO_2Et)_2$	~ 13	NaOH, NEt_3

C-H acide Verb	pKs
$H_3C-C\equiv N$	~ 25
$H_2C(C\equiv N)_2$	~ 11
H_3C-NO_2	~ 10.2
(H_3C-CO_2H	4,7)

Enolat + Aldehyd / Keton

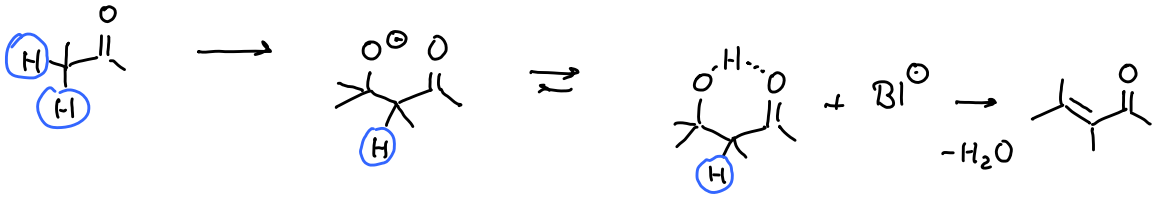
– ein α-H





Aldol-Add.

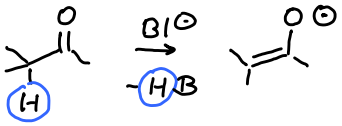
– zwei α-H

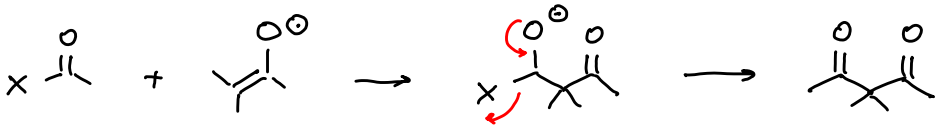


Aldol-Kond.

Enolat + Ester (od. Säurechlorid)

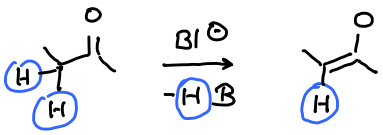
ein α-H in C-H acider komp.:

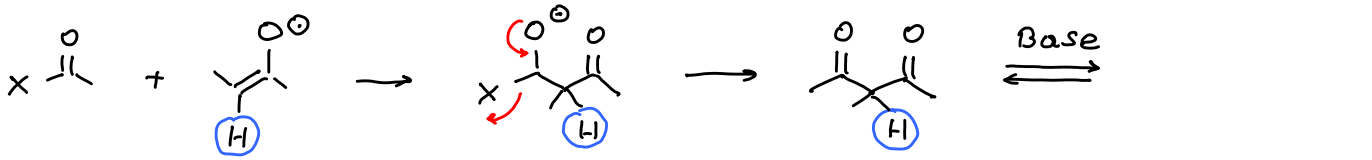


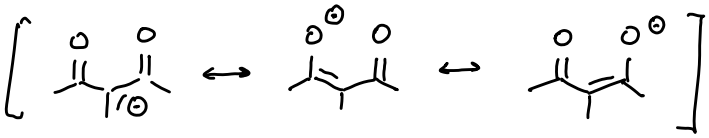


β-Dicarbonylverb.
(Claisen, Dieckmann)

zwei α-H's:

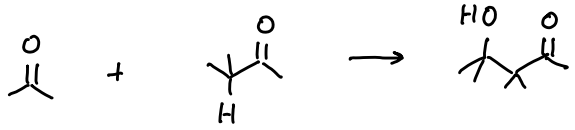




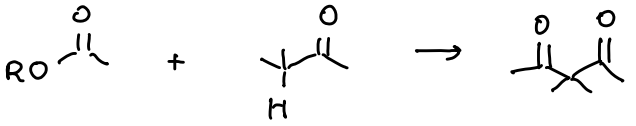


molare Mengen Hilfsbase notwendig

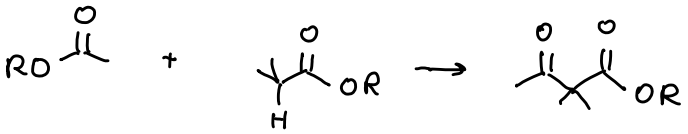
übersicht:



Keton/Aldehyd + Keton/Aldehyd ⇒ Aldol

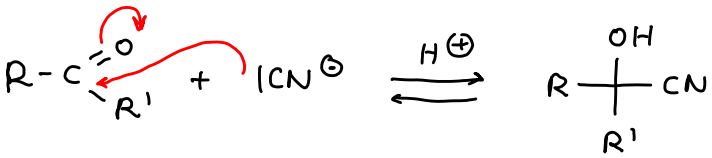


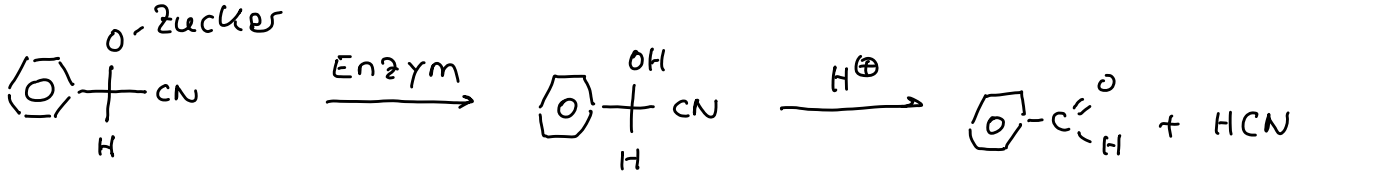
Ester + Keton/Aldehyd ⇒ Claisen



Ester + Ester ⇒ Claisen

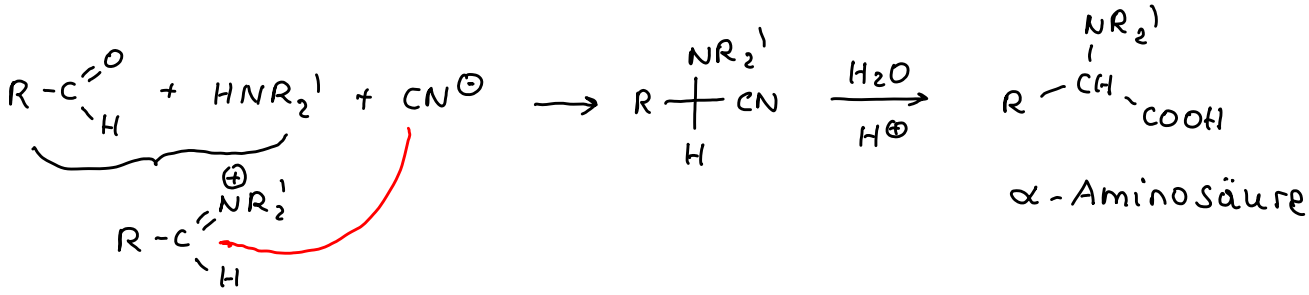
Cyanhydrine





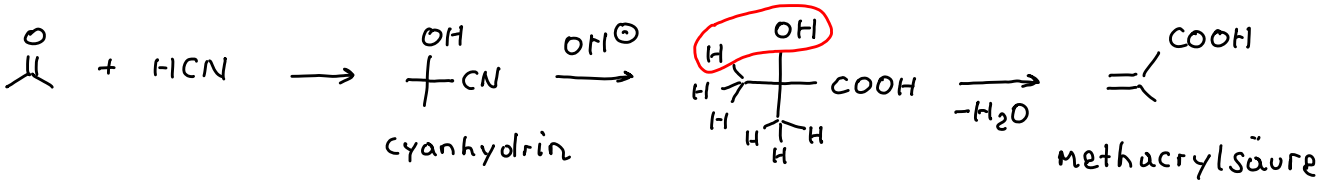
Amygdalin — Cyanhydrin — Benzaldehyd Blausäure

Strecker - Synthese

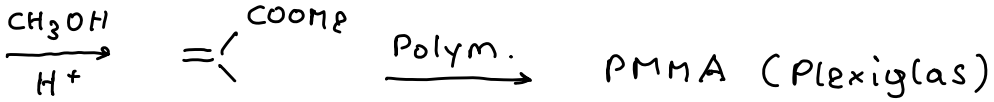


α-Aminosäure

Methacrylsäuremethylester

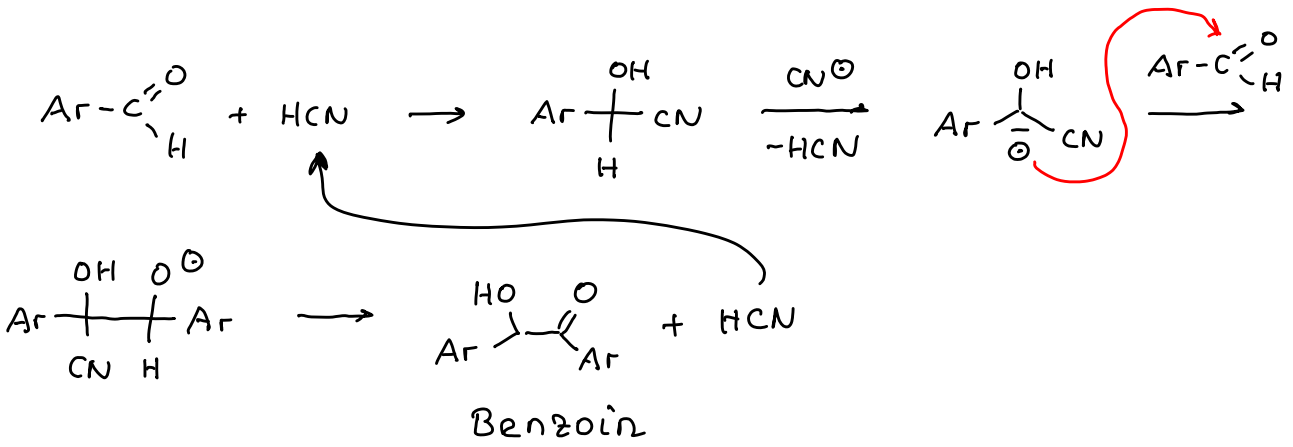


Cyanhydrin — Methacrylsäure



PMMA (Plexiglas)

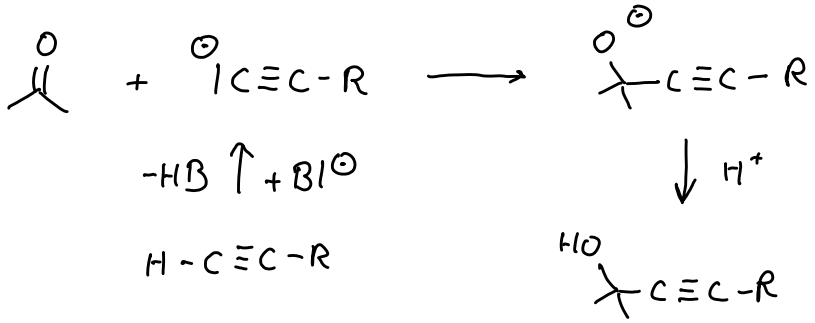
Benzoin-Reaktion



Benzoin

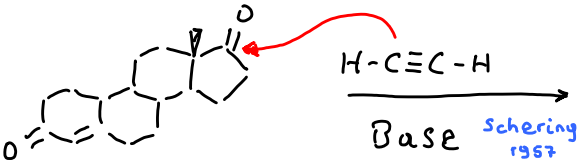
22.01.2014

Ethinylierung



Propargyl-Alkohol

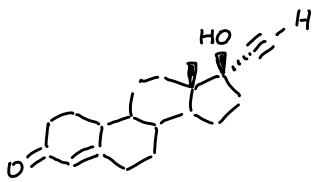
Beispiele:



östra-4-en-3,17-dion

Gestagen

wird im Verdauungsapparat abgebaut



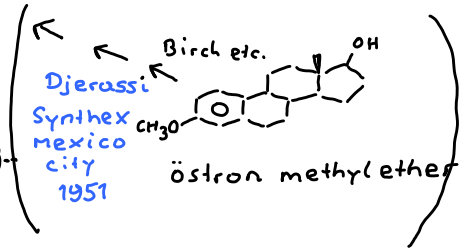
Norethindron

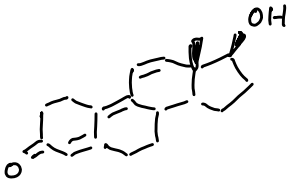
17-α-Ethinyl-19-nor-testosteron

Greory Pincus

Carl Djerassi

"Pille"

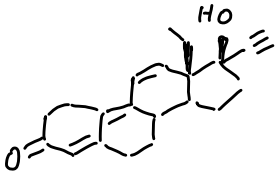




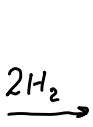
Trenbolon

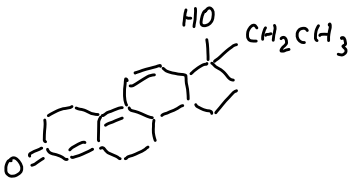
Anabolid

Verboten



Gestrionon



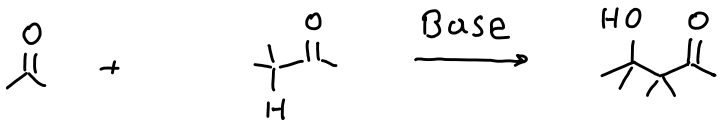


Tetrahydrogestrinon

(Designer-Anabolikum)

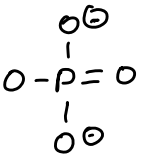
BALCO-Skandal

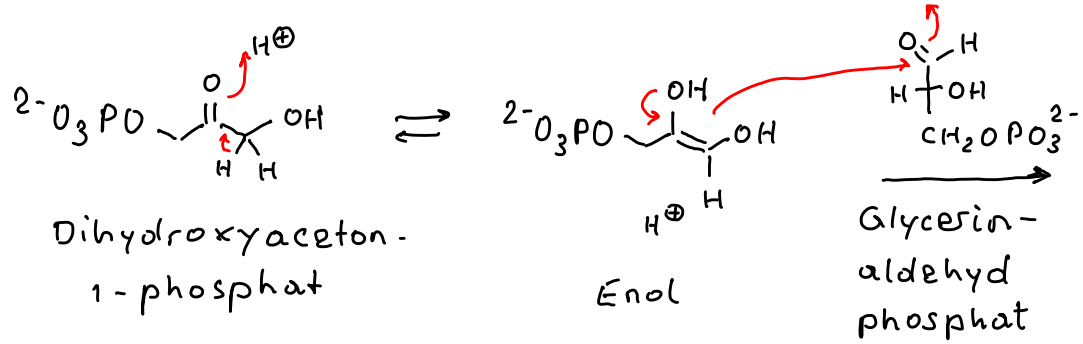
Aldol - Reaktion



Carbonyl-komponente | C-H-acide komp. | 3-Hydroxy-carbonyl (Aldol)

Bsp. Biosynth. der Fructose $^{2-}O_3PO$:



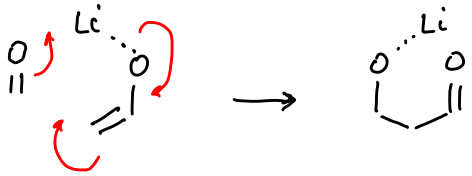


Dihydroxyaceton-1-phosphat | Enol | Glycerin-aldehyd phosphat

Aldolase Kat.

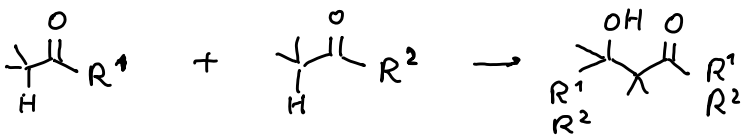
Fructose-1,6-diphosphat

Cyclischer Mechanismus der Aldol-Add.



Chemo- u. Regioselektivität

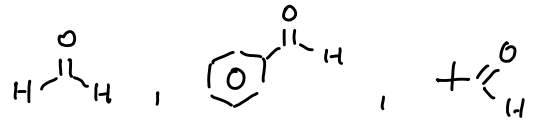
Problem:



4 Produkte möglich

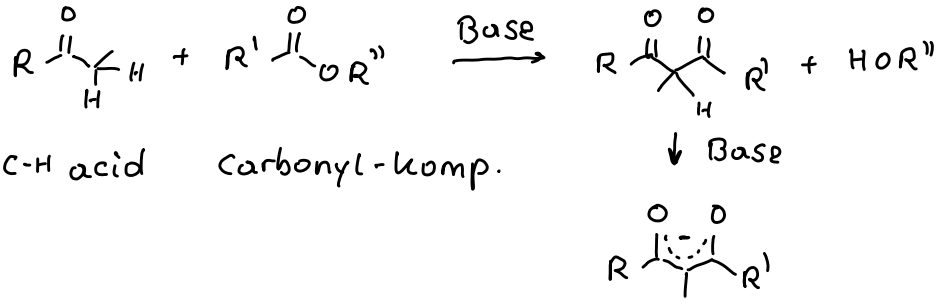
Lösung (Regeln):

- nicht enolisierbare Aldehyde (Ketone) (kein α-H)

z.B. 

- bei Reaktionen von Aldehyd mit Keton ist der carbonyl-aktivere Aldehyd meistens die Carbonylkomponente

- bei Reaktionen von enolisierbaren Aldehyden/Ketonen mit Estern, ist immer der Ester die Carbonylkomponente

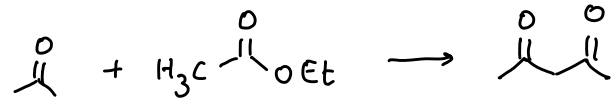


C-H acid Carbonyl-komp.

- doppelt aktivierte verb. sind immer C-H aktiv (Knoevenagel)

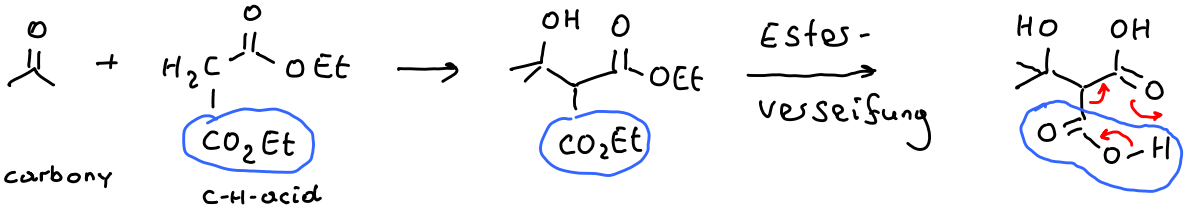
z.B. $H_2C(CO_2Et)_2$ Malonsäureester (C-H acid)

Bsp.

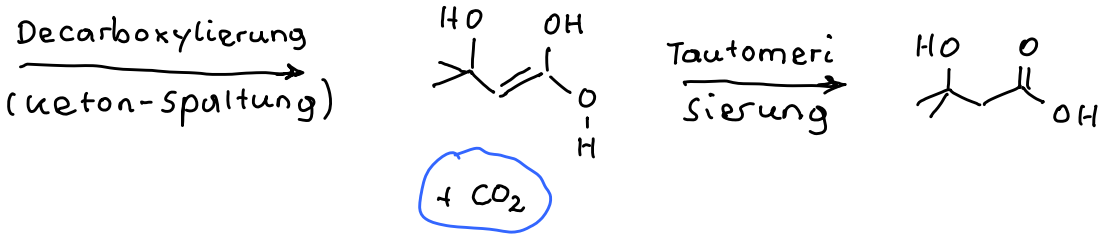


C-H-acid Carbonyl

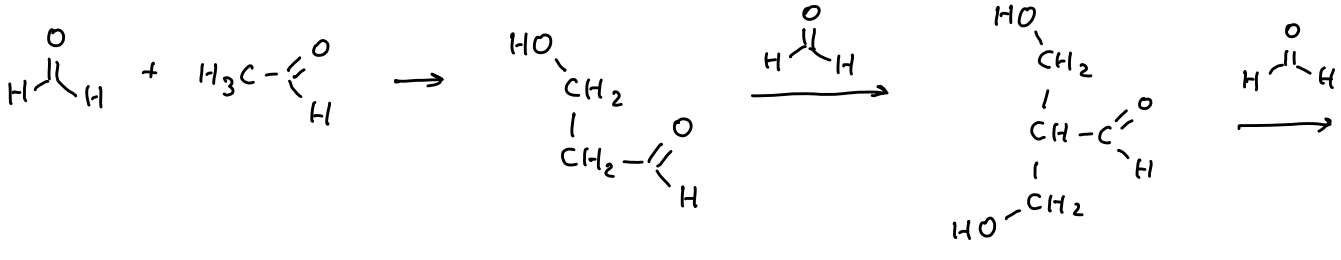
Umkehrung der Reaktivität mit doppelt akt. C-H acider komp.

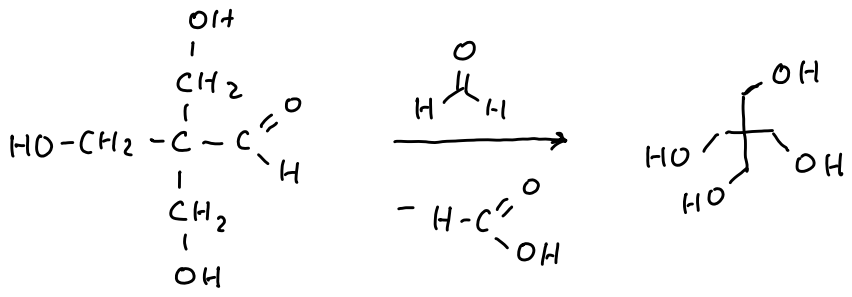


carbony C-H-acid



Beispiel (nicht enolisierbarer Aldehyd)



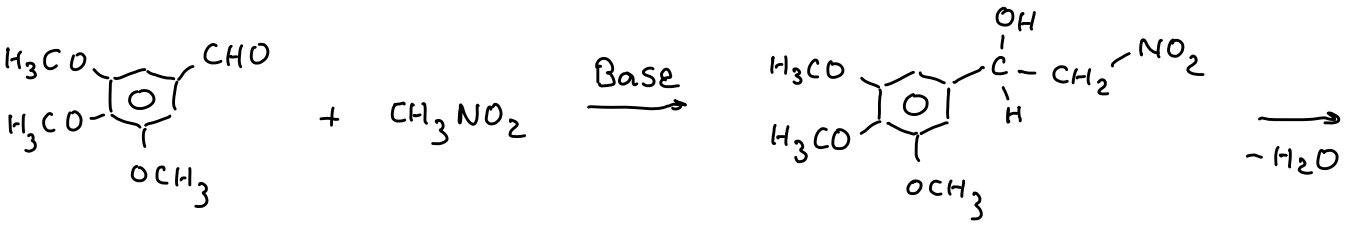


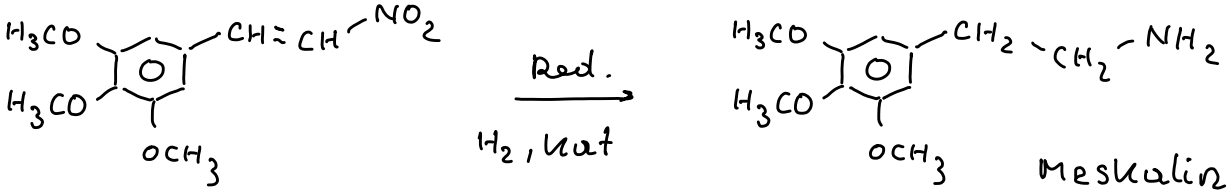
Pentaerythrit

300.000 t/a

Harze, Lacke, Weichmacher, Sprengstoff (Tetranitrat, Nitropenta)

Nitrile u. Nitroverbind. als C-H acide Komponenten

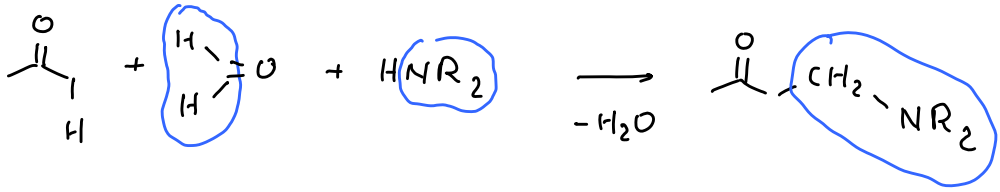




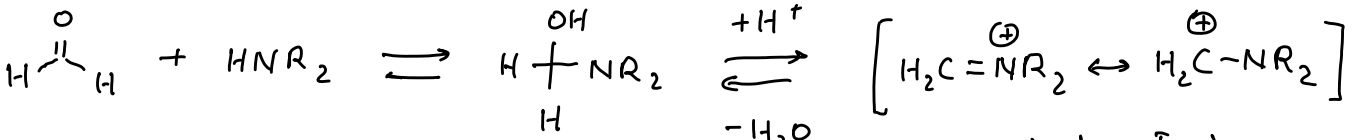
Meskalin

Knoevenagel (Mechanismus siehe Aldol)

Mannich-Reaktion (Aminomethylierung C-H-acider Verb.)

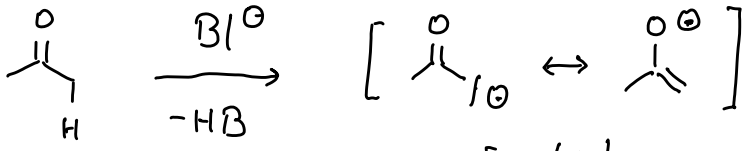


Mechanismus

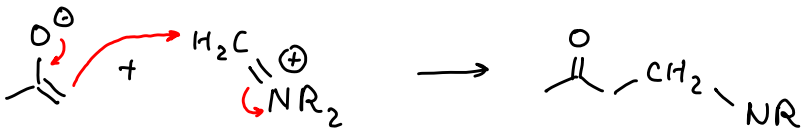


protoniertes Imin

Iminium-Ion

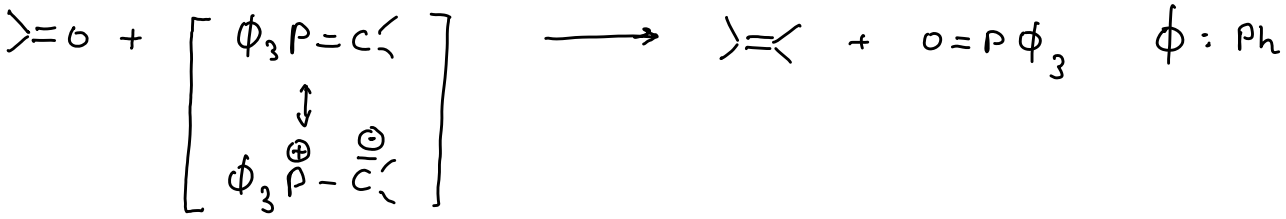


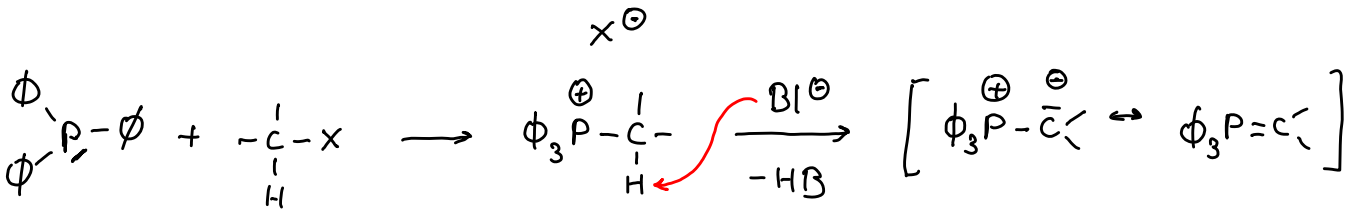
Enolat



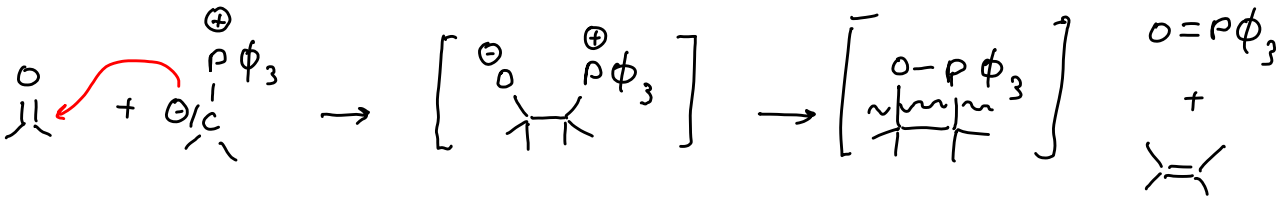
Enolat Iminium Ion

Wittig - Reaktion



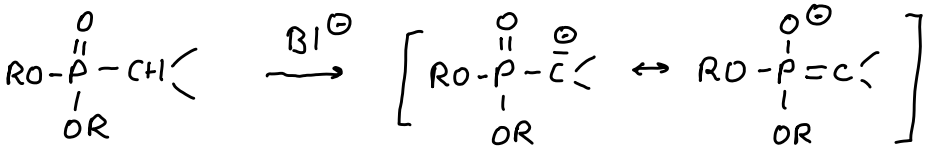


Triphenyl-phosphin Alkyl-halogenid Phosphonium-salz Phosphor Ylid

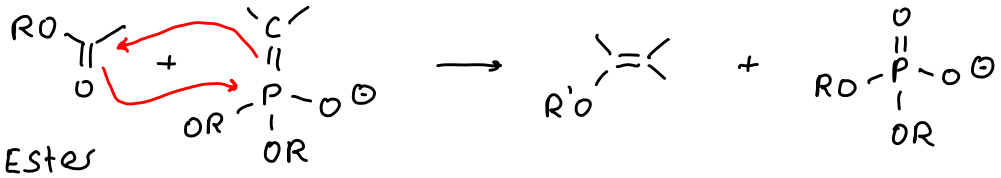


27.01.2014

Horner Variante (Horner-Wadsworth-Emmons)

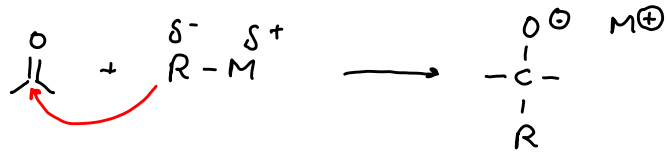


Alkylphosphon-Säureester Stärker nucleophil als Phosphorylid

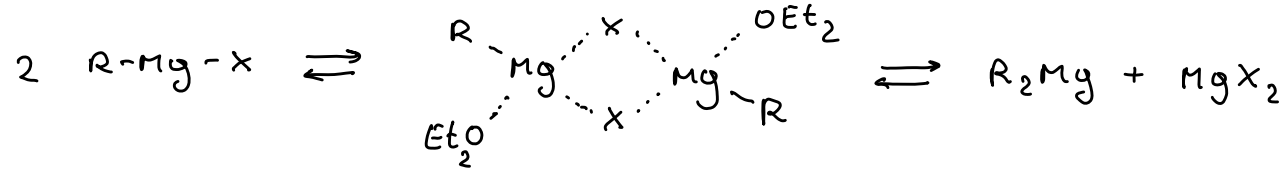


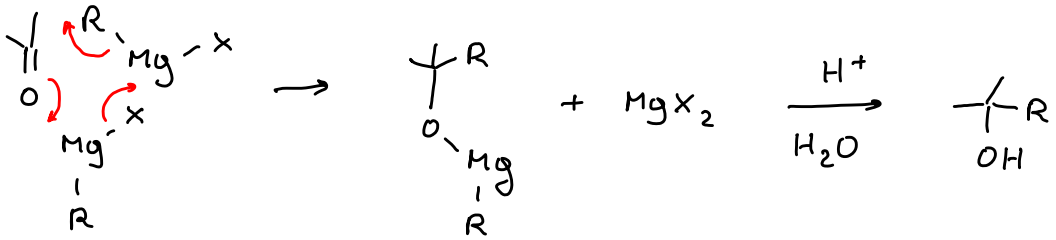
Ester

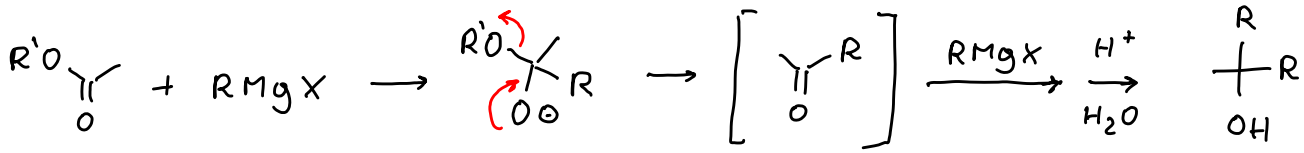
Reaktion von Carbonylverb. mit Organometallverb.



Grignard







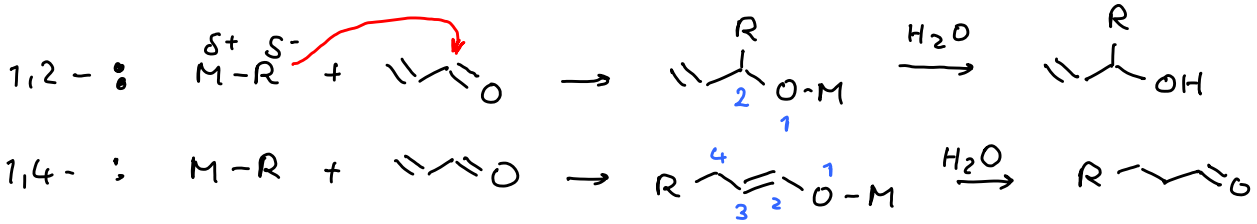
Ester

Keton
nicht isolierbar

Reaktionen vinyloger Carbonylverb D.7.4 und vinyloger Nucleophile

Add. von Nucl. an α,β-ungesättigte Carbonylverb.

1,2 - vs. 1,4 - Addition:

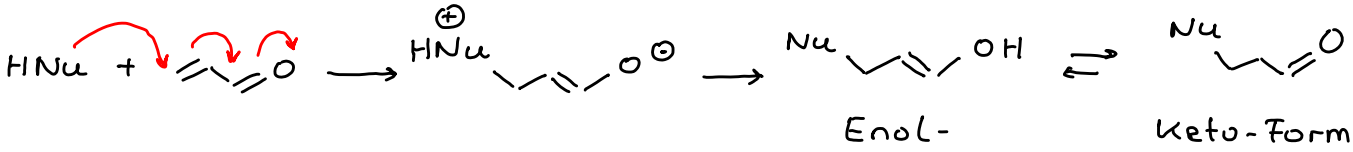


1,2 - Add. : harte Nucleophile z.B. BuLi, MeLi, RMgX

1,4 - " : weiche "  , R_2CuLi

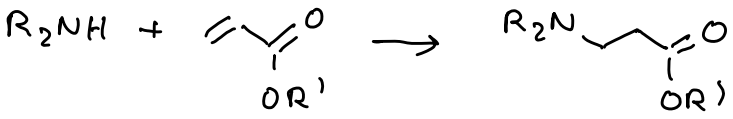
Enolat Cuprat

Mechanismus:

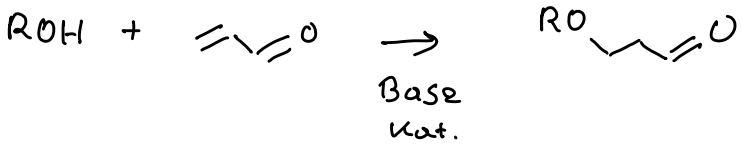


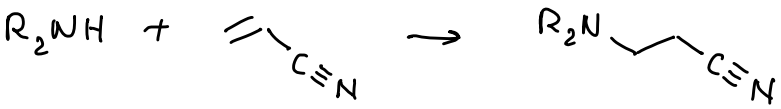
Enol- Keto-Form

z.B.:



Acrylsäureester

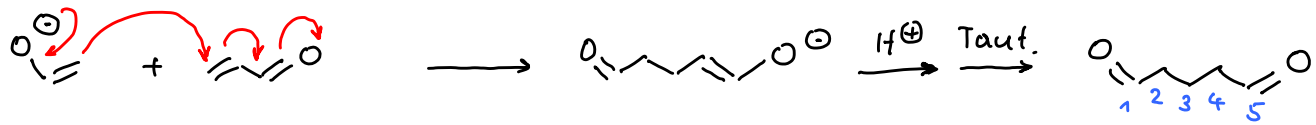




Acrylnitril

Addition v. C-H-aciden Verb. an α,β-ungesättigte Carbonylverb.

Michael - Addition



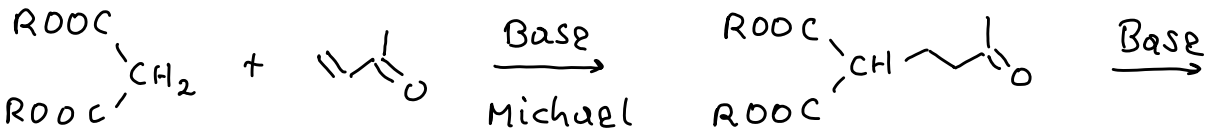
Enolat vinyloge Carbonylverb. Enolat 1,5-difunktionelle Verb.

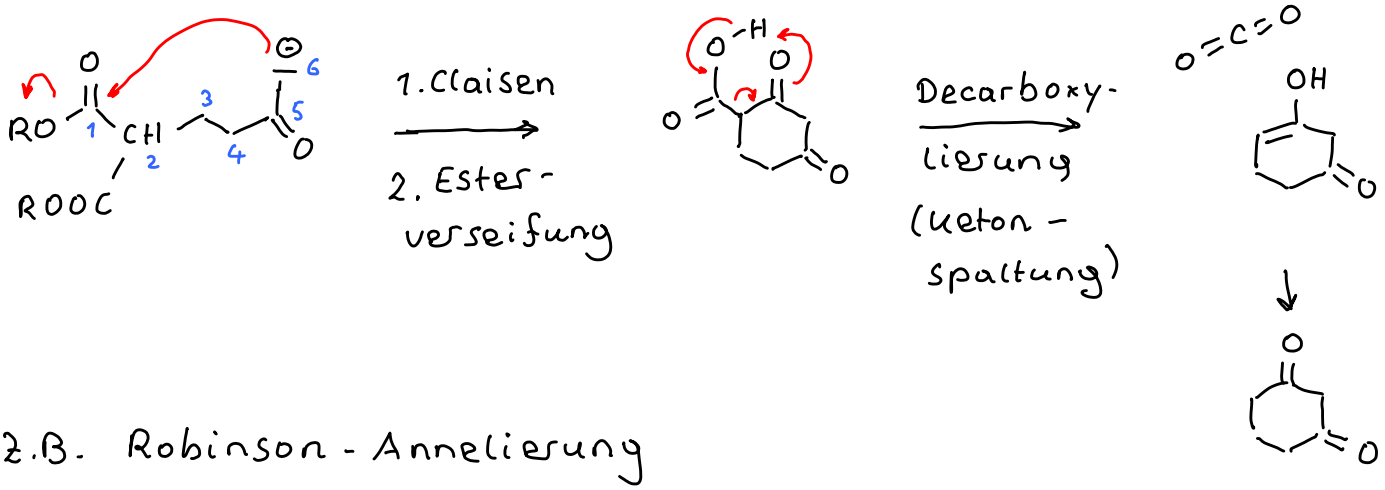
Michael-Akzeptor

Kombinierte Carbonylreaktionen

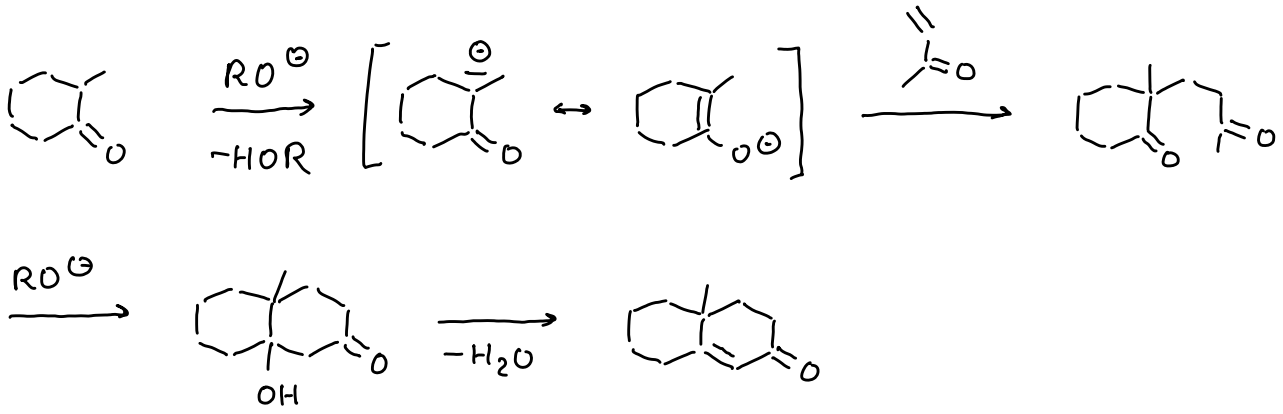
Michael/Aldol Michael/Claisen Michael/Dieckmann

z.B.

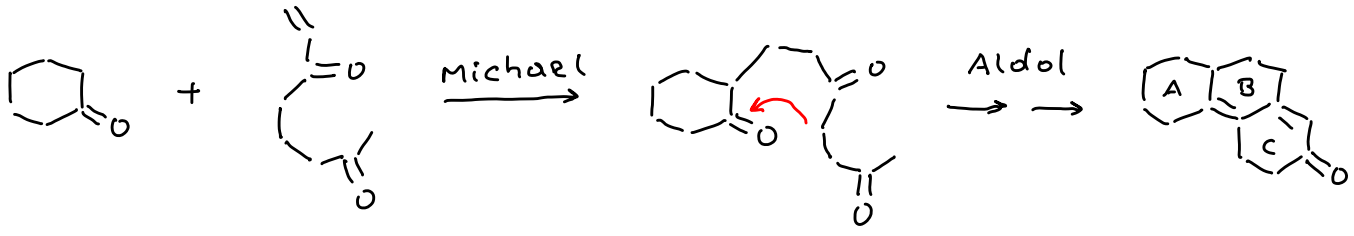




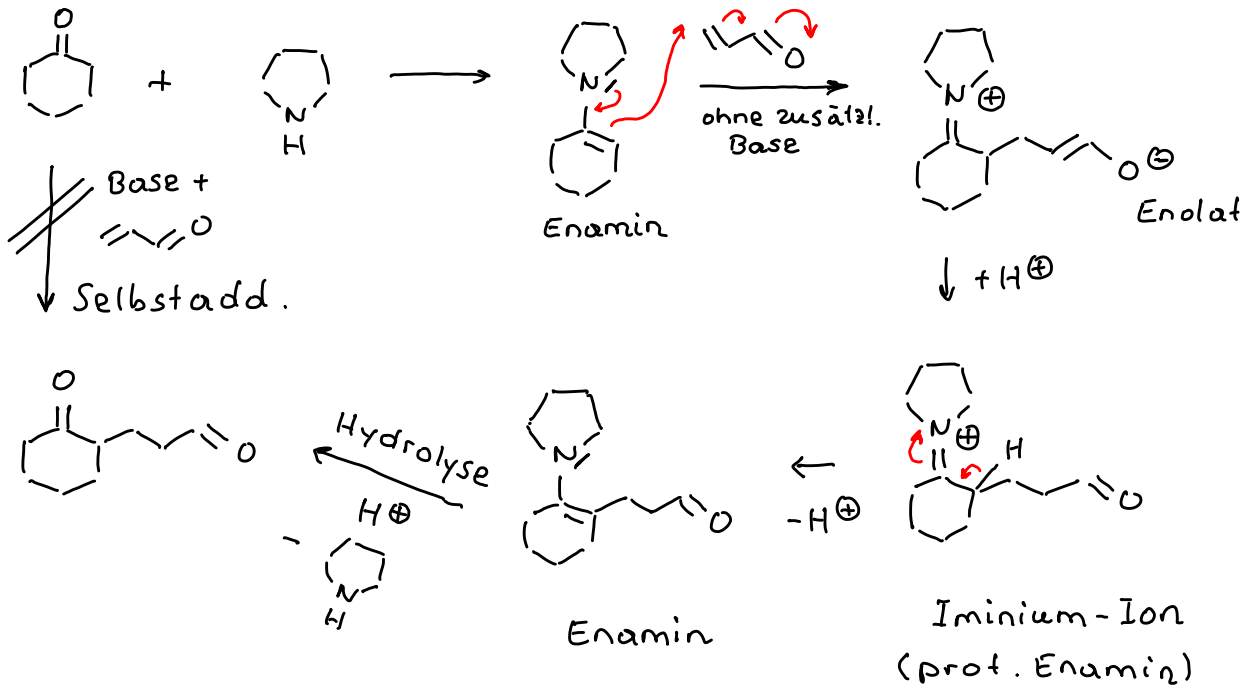
z.B. Robinson-Annelierung



z.B.



z.B. Stork-Enamin Trick



Reduktion von Carbonylverb. D.7.3

$\rangle C{=}O \rightarrow H{-}C{-}OH$ Keton zu sec. Alkohol

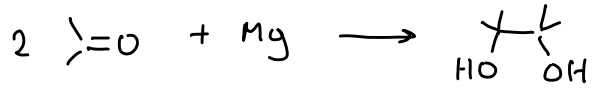
$H\rangle C{=}O \rightarrow H{-}\underset{H}{C}{-}OH$ Aldehyd " prim "

$-C(=O)Cl \rightarrow -C(=O)H$ Säurechlorid zu Aldehyd (Rosenmund)

$-C(=O)NR_2 \rightarrow -NR_2$ Amid zu Amin

$R\overset{I}{-}C(=O)H + \overset{I}{-}C(=O)H \xrightarrow{OH^-} \overset{III}{-}C(=O)OH + \overset{-I}{-}CH_2{-}OH$ Cannizarro (Disproportionierung)

~~Claisen-Tishenko~~
Leuckart-Wallach
Bouveault Blanc



Pinakol

Clemmensen (Zn/H^+)

Wolff-Kishner (H_2N-NH_2)

McMurry

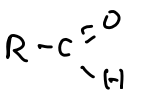
Reduktion (allgemein)

a) H_2 + Edelmetall Kat.
(Ni, Pd, Pt)

b) Komplexe Hydride
$LiAlH_4$, $NaBH_4$, DIBAH (DIBAL)

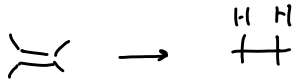
c) unedle Metalle
Li, Na, K, Mg, Zn
z.B. Birch

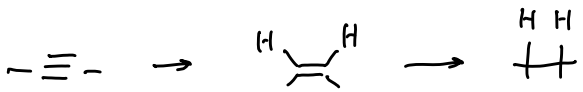
d) niedervalente C, N, S, P-verb.


, $HN=NH$, $Na_2S_2O_4$, $Na_2S_2O_3$, PR_3

---

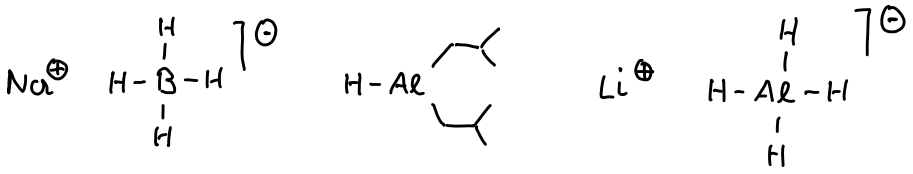
a) Kat. Hydrierung (H_2/Kat.)

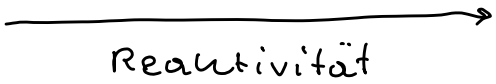




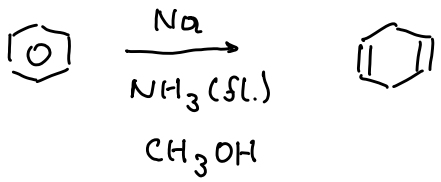
b) komplexe Hydride

$NaBH_4$, DIBAL , $LiAlH_4$

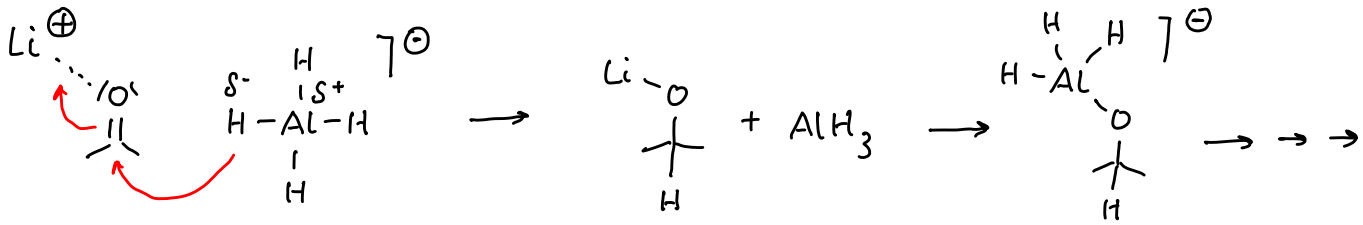


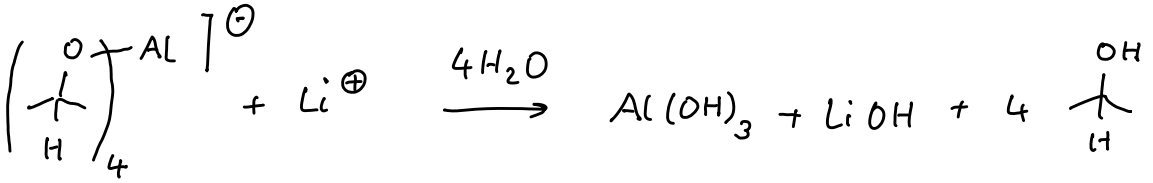


c) Birch - Reduktion

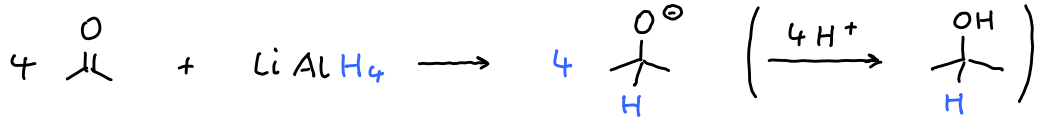


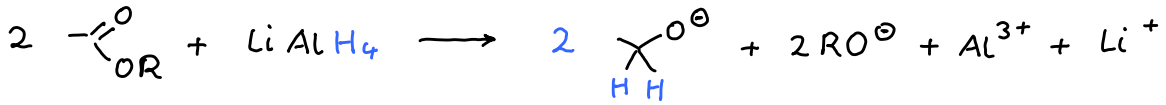
Mechanismus, komplexe Hydride





Stöchiometrie

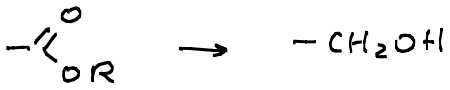




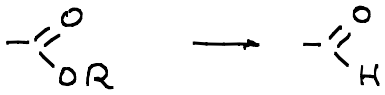
29.01.2014

Reaktivität

$LiAlH_4$, $NaBH_4$

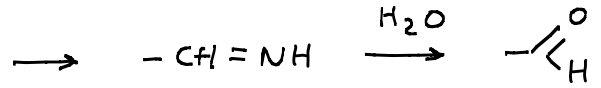


$LiAlH_4$

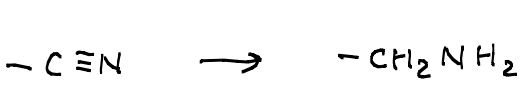


DIBAL

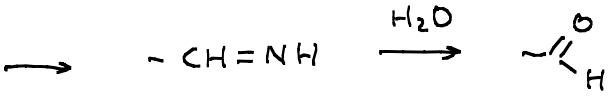
$LiAlH_4$



DIBAH

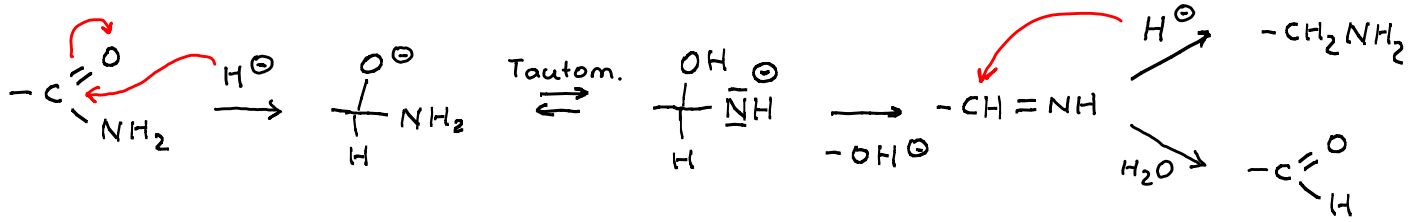


$LiAlH_4$

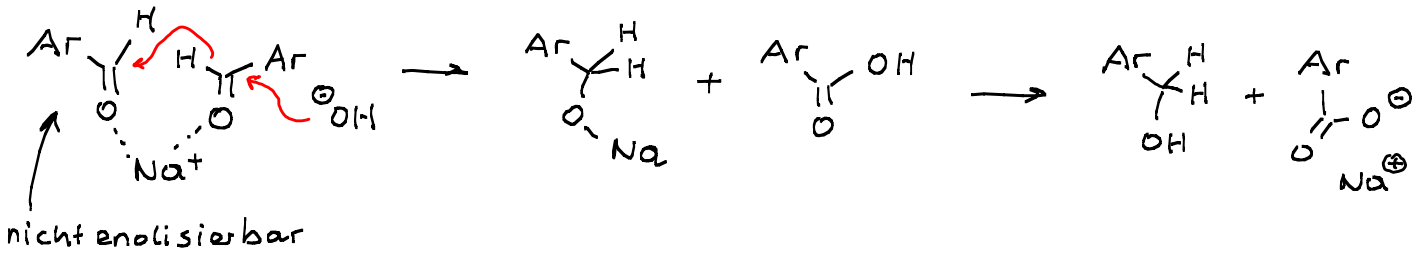


DIBAL

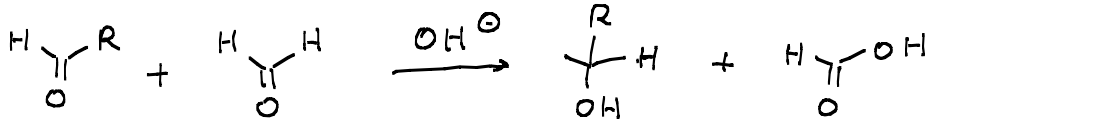
Mechanismus Reduktion Carbonsäureamid



- Cannizzaro



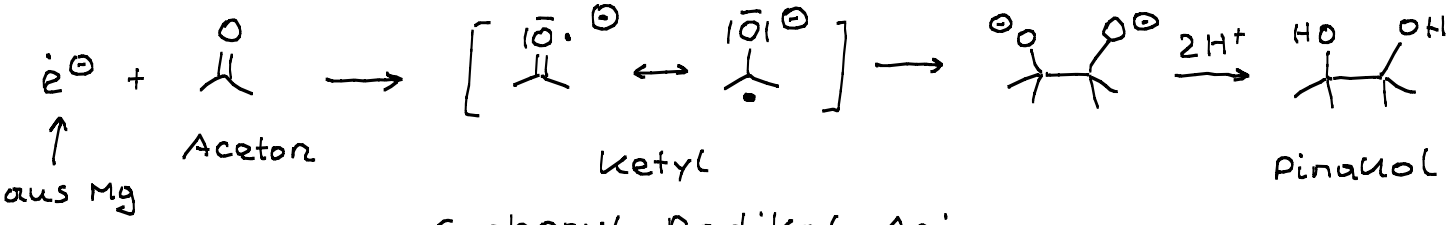
nicht enolisierbar



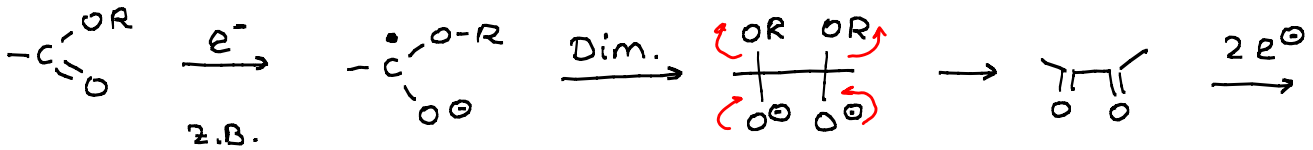
Formaldehyd
(Red-Mittel)

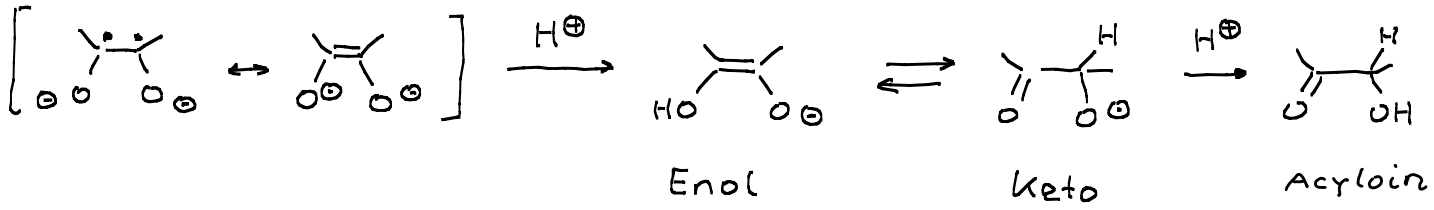
Ameisensäure

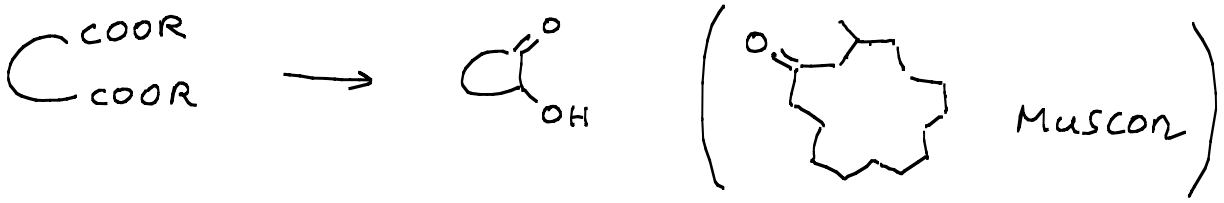
– Pinakol



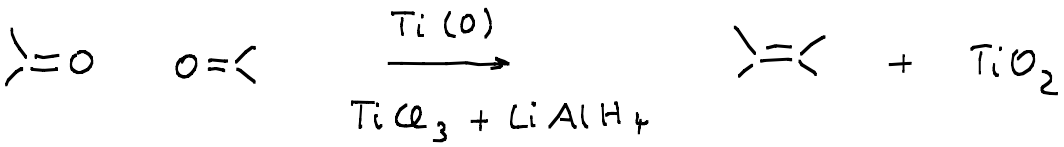
– Acyloin-Kondensation

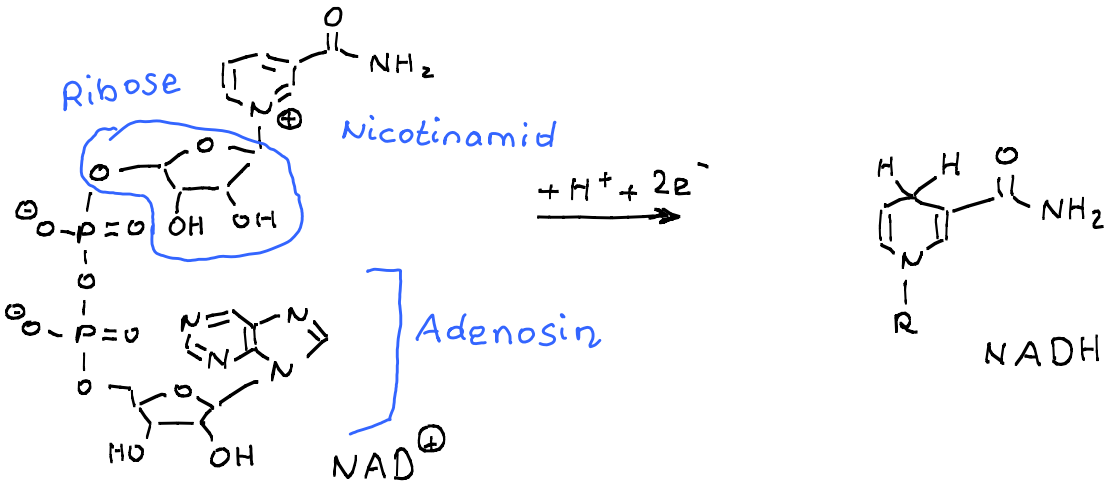


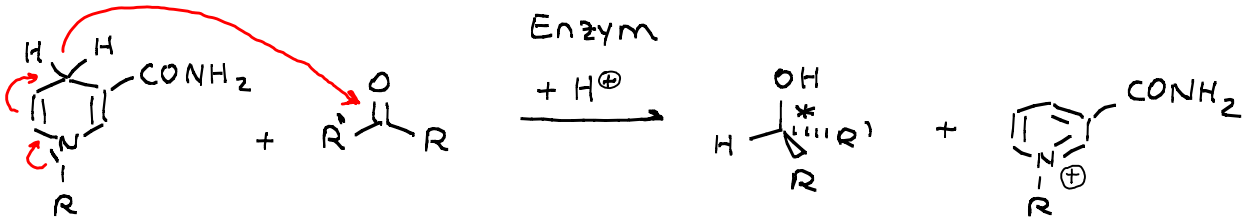




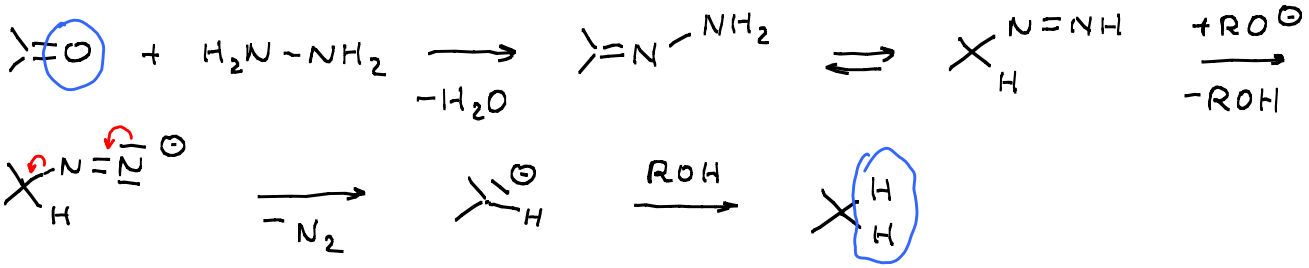
– McMurry



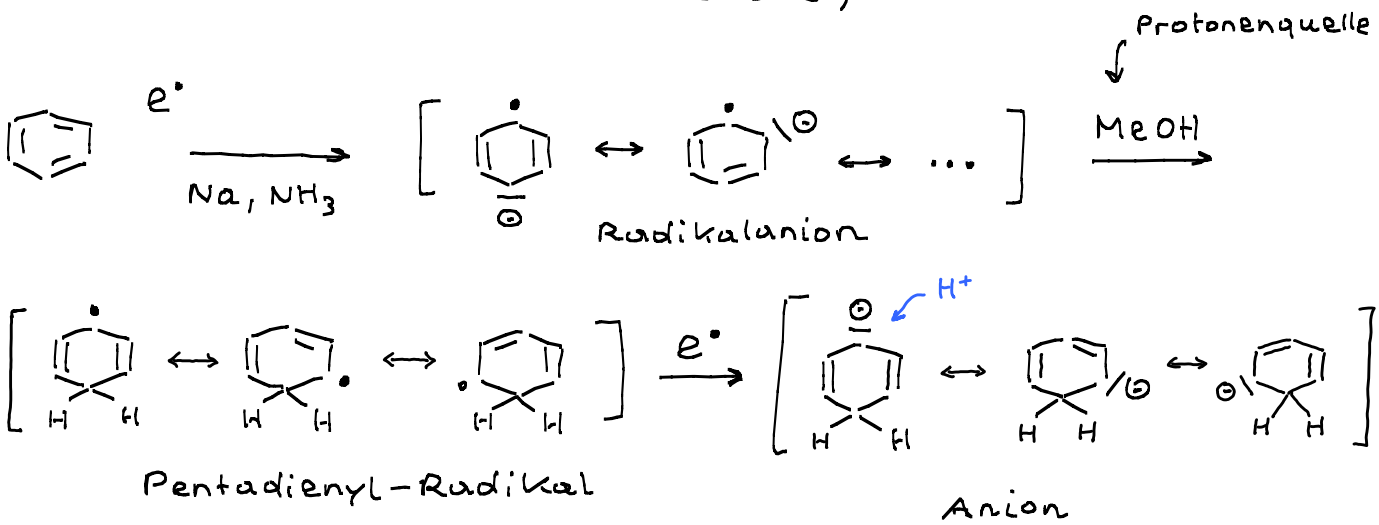




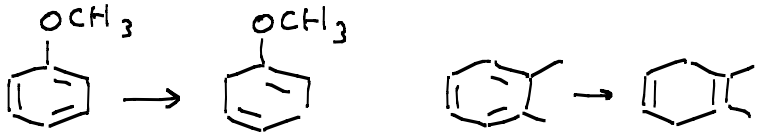
Wolff-Kishner



Birch-Reduktion (Mechanismus)

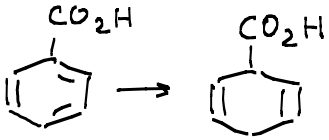


Beispiele:



+ M-Subst.

+ I-Subst.

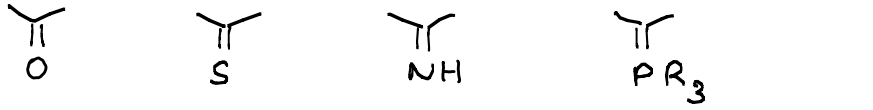


-I-Subst.

Reaktionen heteroanaloger Carbonylverb.

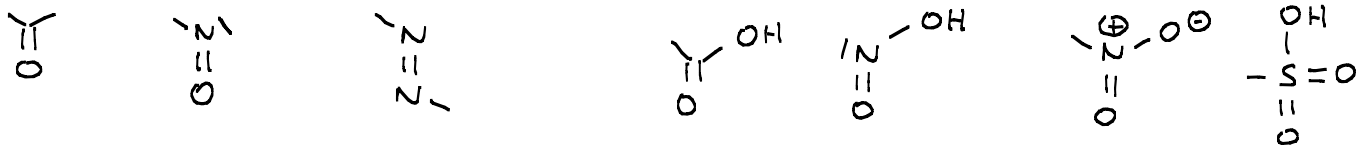
D 8.1-4

isoelektron. Austausch von O



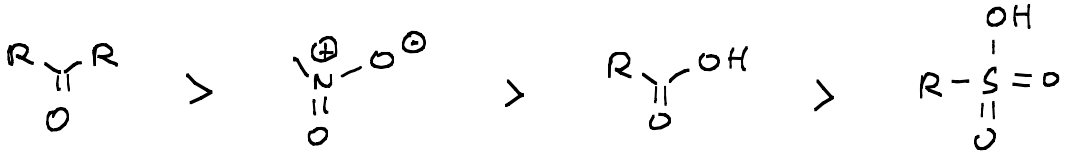
Thion Imin Phoshorylid

isoelektron. Austausch von C

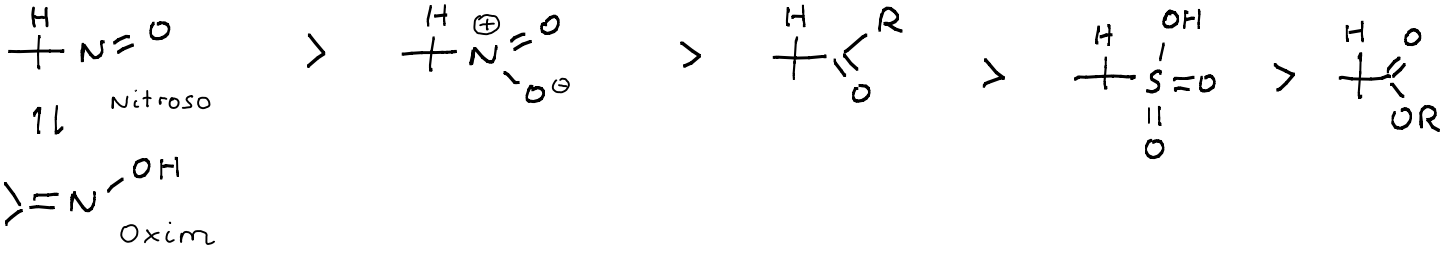


Nitroso Azo salpetrige Säure Nitroverb. Sulfonsäure

(Hetero) Carbonylreaktivität



C-H - Acidität



1l

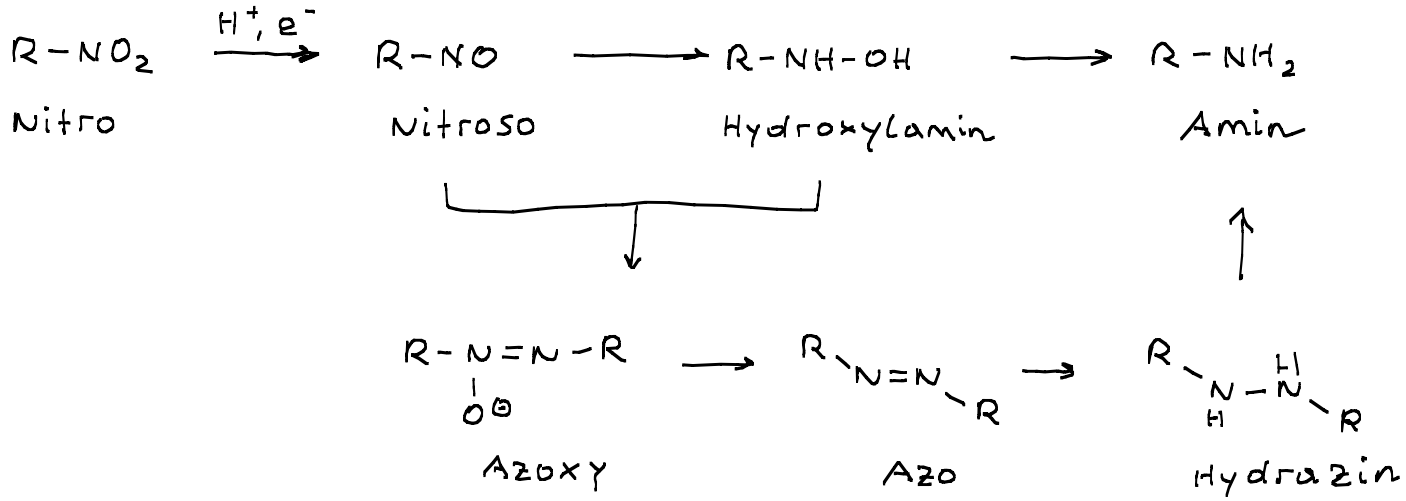
$\rangle = N - OH$

Oxim

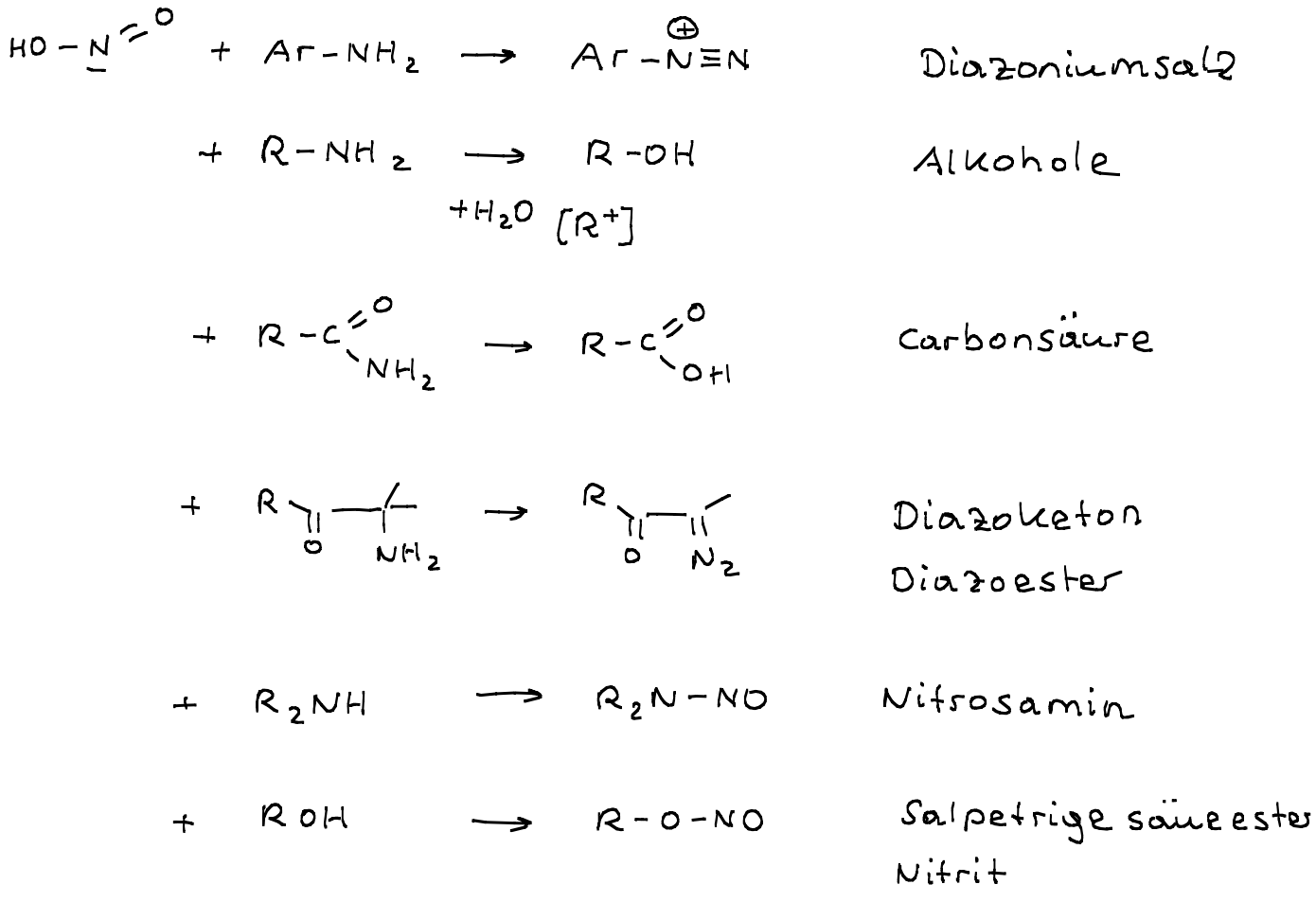
Reaktionen, Übersicht

1. Reduktion von Nitroverb.
2. Reaktionen von salpetriger Säure
(3. Reaktionen v. Diazoniumsalzen)
4. Reaktionen v. Diazomethan

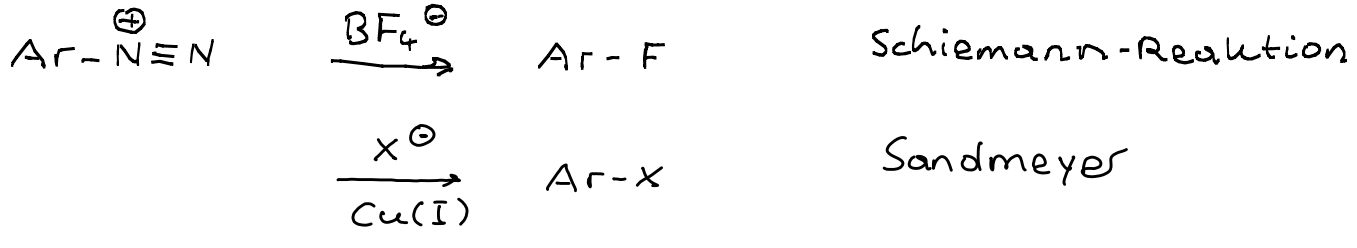
— Reduktion von Nitroverb.

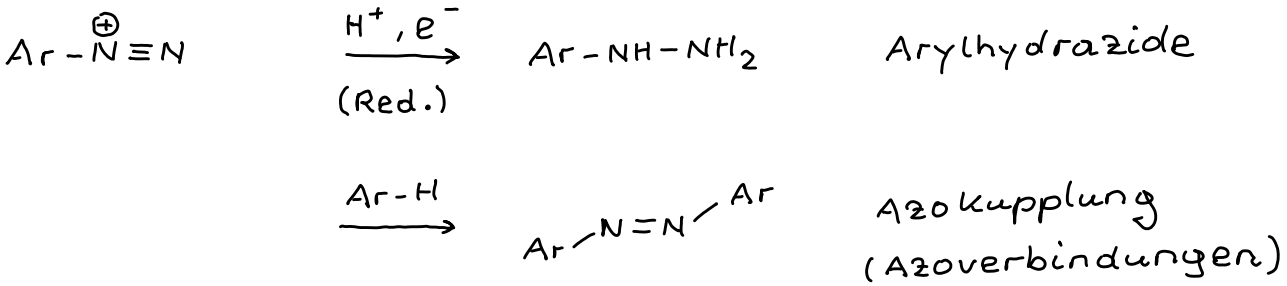


— Reakt. von Salpetriger Säure



— Reaktionen v. Diazoniumsalzen

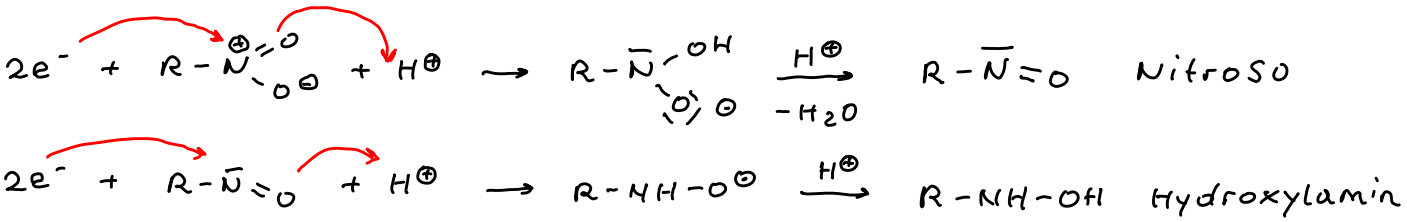




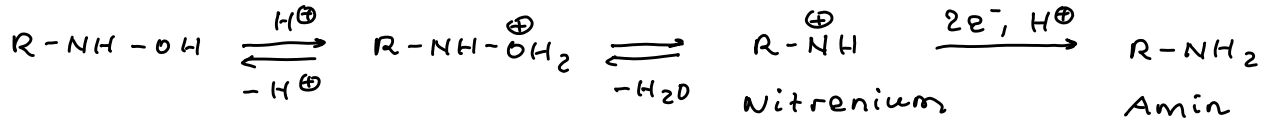
03. 02. 2014

Reduktion von Nitroverb.

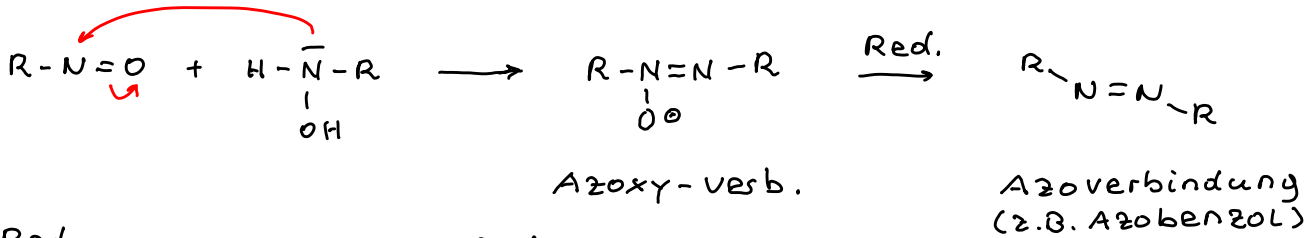
Red.-Mittel: Sn^{2+}, Zn, Fe (Ni, Pd, Pt/H_2)

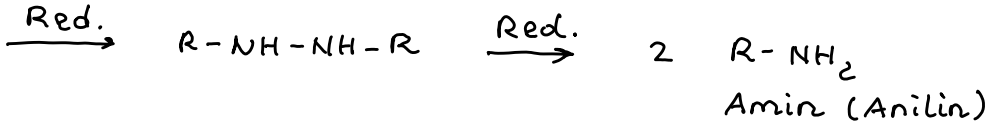


stark sauer:

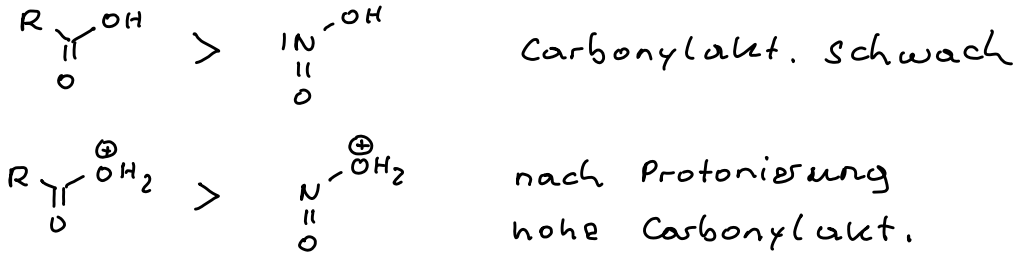


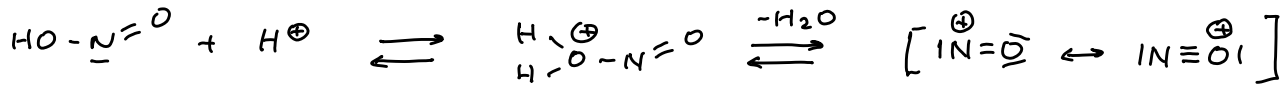
bas. Milieu





- Reaktionen der salpetrigen Säure HNO_2

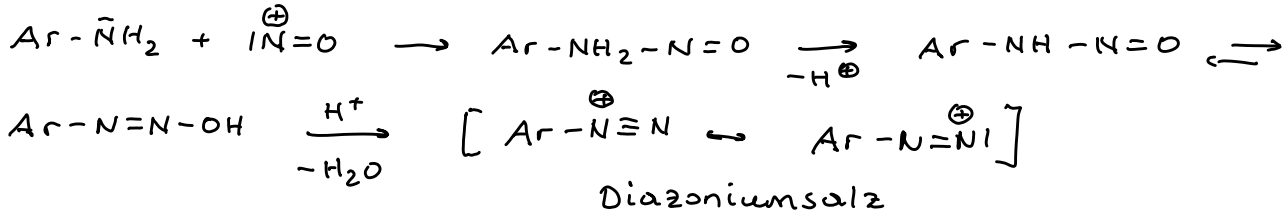




Nitrosylkation

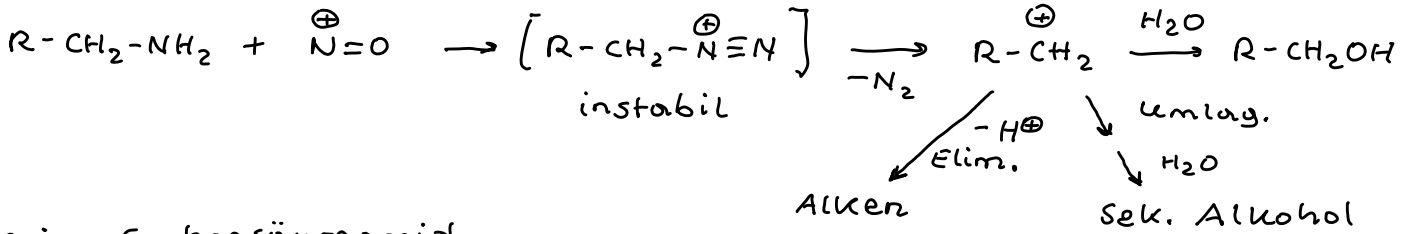
$NO^+ BF_4^-$ käufl.

Reaktionen mit arom. Aminen



Diazoniumsalz

- prim. Amine

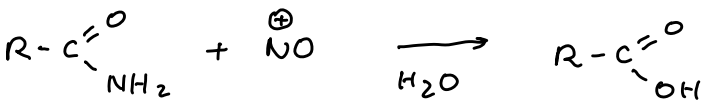


instabil

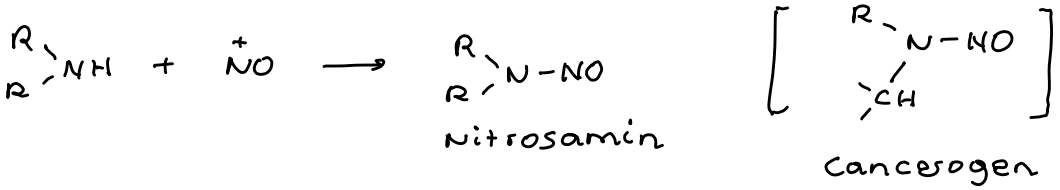
Alken

sek. Alkohol

- prim. Carbonsäureamid



- sek. Amine



Nitrosamin

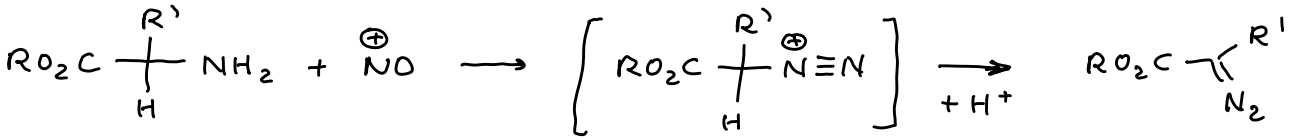
cancerogen

$R = CH_3$ Leber

C_2H_5 Lunge

C_3H_7 Blase, Magen

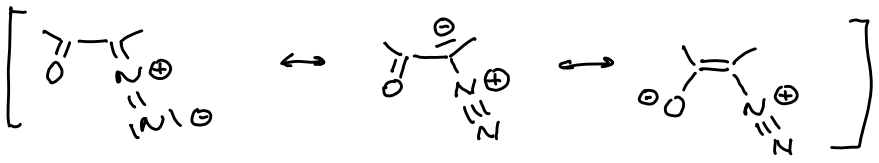
- α-Aminosäureester, α-Aminoketone



α-Aminosäureester

Diazoniumsalz

Diazoester



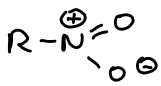
Diazocarbonylverb.

Mesomerie-stab.

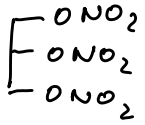
- mit Alkoholen

Nitrit, salpetrige Säure Ester

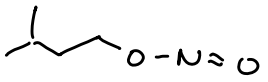
Nomenklatur



Nitroverb.



Glycerintrinitrat
Salpetersäureester

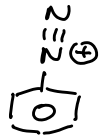


Amylnitrit
(salpetrige Säure Ester)

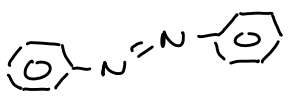
- Reaktionen mit Diazoniumsalzen

siehe elektrophile Arom. subst. (Sandmeyer, Schiemann verkochen...)

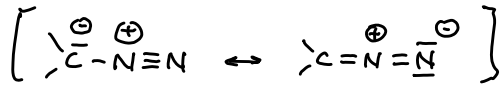
Nomenklatur



Diazonium-Salz

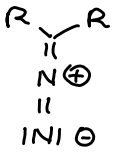


Azobenzol
(Azo-verb.)

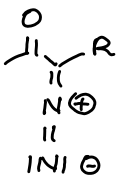


Diazoverbindung

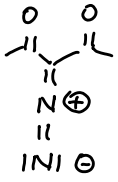
- Reaktionen von Diazoverb.



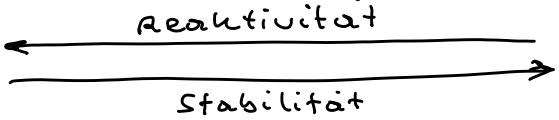
Dialkyl- od. diaryl-Diazo



α-Diazoketon
" ester

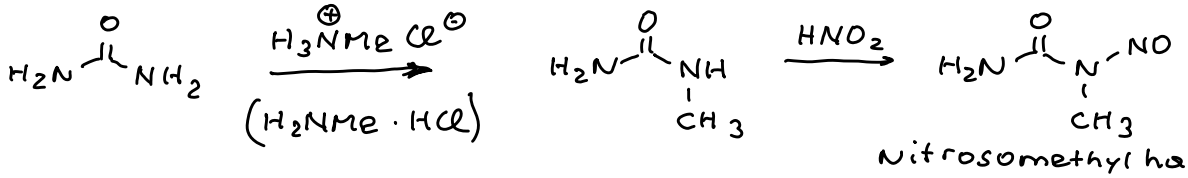


α-Diazodiketon

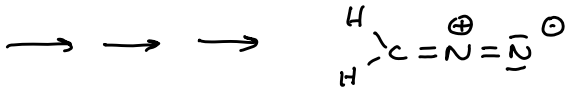


Herstellung

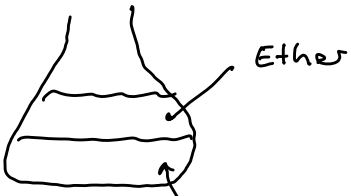
1. Diazoalkane aus Nitrosamiden



Nitrosomethylharnstoff



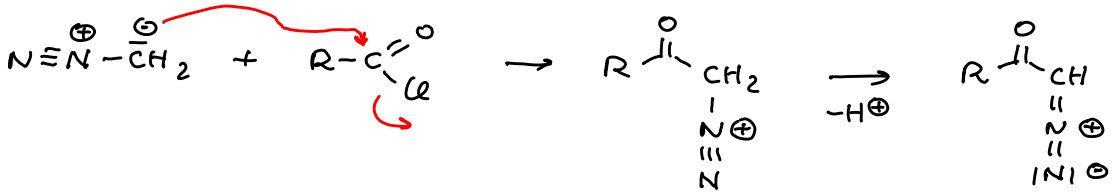
Diazomethan



2. α-Diazocarbonylverb. aus α-Aminosäureester oder α-Aminoketon

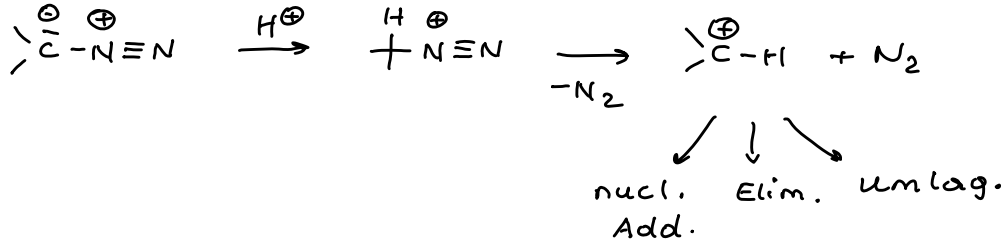
S. oben

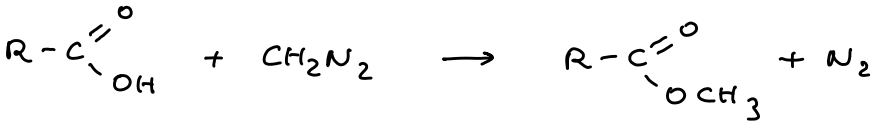
3. α-Diazoketone aus Diazoalkan + Säurechlorid



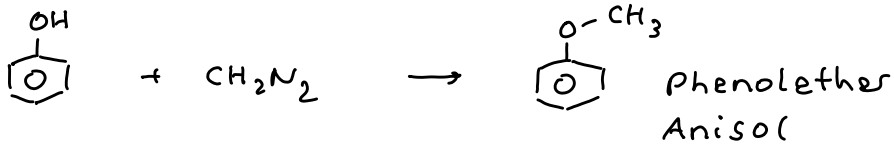
Reaktionen von Diazoverb.

1. mit $H^{\oplus}$

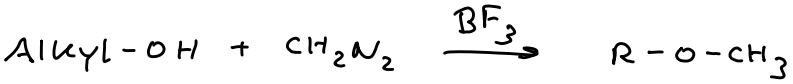




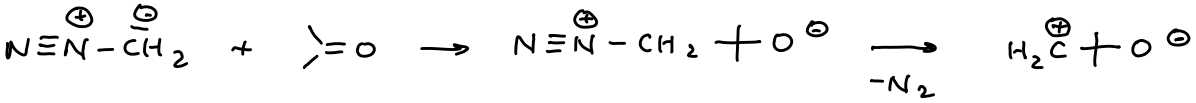
Methylester

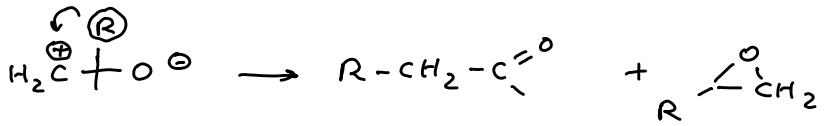


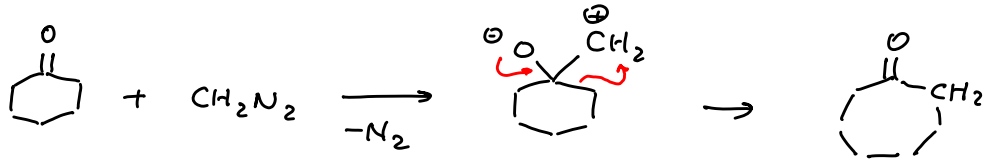
Phenolether
Anisol



2. Reakt. mit Carbonylverb.

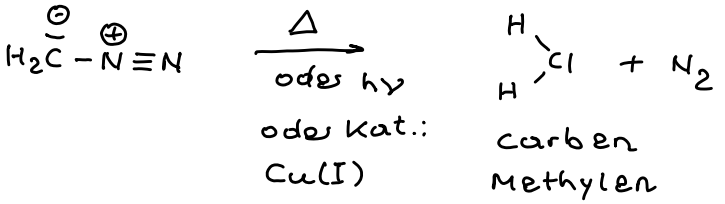


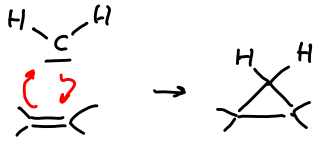




3. 1,3-diplolare Cycloadd.

Siehe Add. an C=C-Bind.

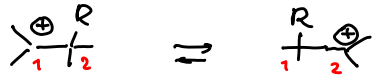
4. 

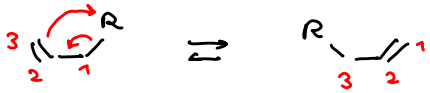


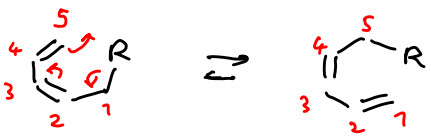
Umlagerungen D. 9.1 - 9.2

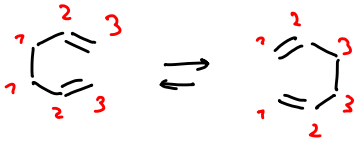
- Systematik nach Position

sigmatrope Umlagerungen


1,2- wagner meerwein


1,3- sigmatrop

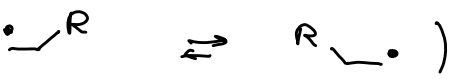

1,5- sigmatrop


3,3- Cope-Umlag.
Claisen-Umlag.

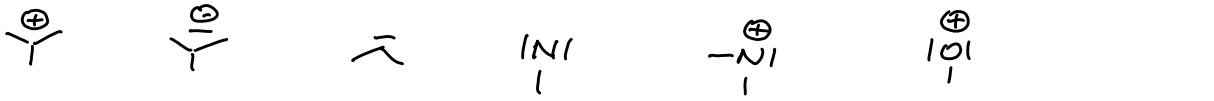
Klassifizierung nach Element

- am C-Atom
- am N- "
- am O- "

- Klassifizierung nach Art der Zwischenstufe

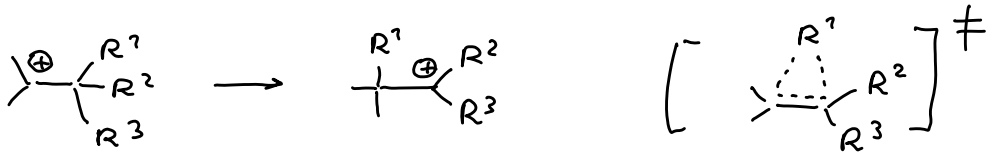
kationisch  (anionisch  radikal.  neutral )

1,2 - Umlagerungen am C, N, O



Carbeniumionen	Carbanion	Carben	Nitren	Nitrenium	Oxenium Ion
a)	b)	c)	d)	e)	f)
↑ Wagner-Meerwein	—	—	Hofmann ~~Lossen~~ Curtius	Beckmann	Hock'sche Phenolsynth. Baeyer-Villiger

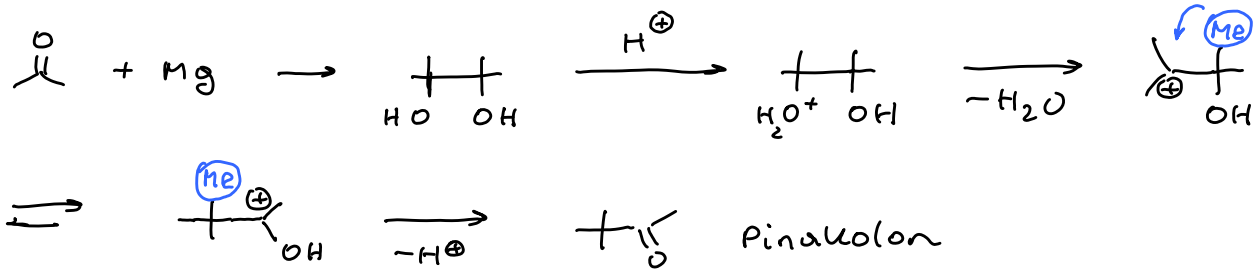
Wagner Meerwein

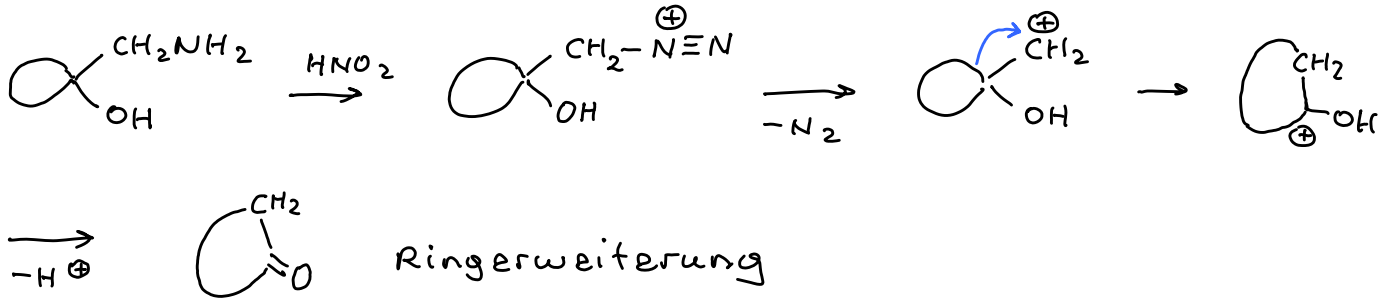


Wanderungstendenz

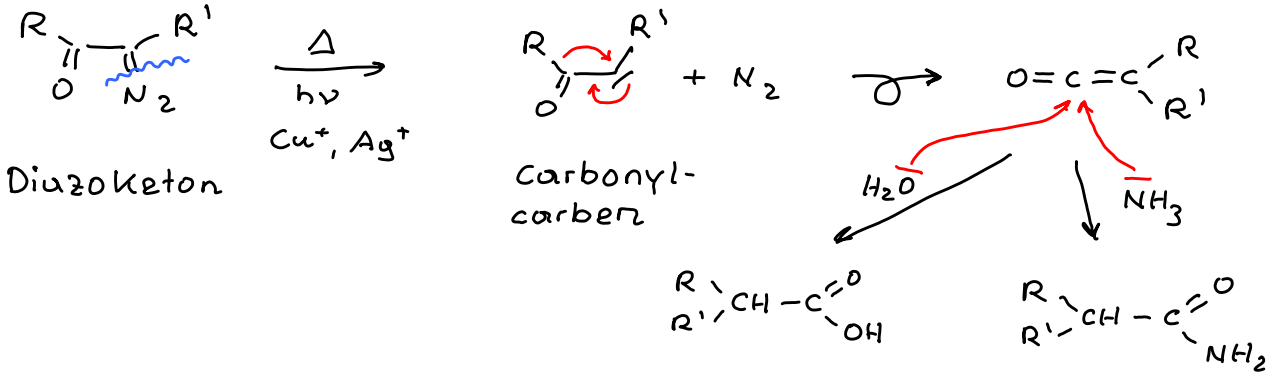
Ph > t-Bu > i-Pr > Et > Me > H

Pinakolon-Umlag.

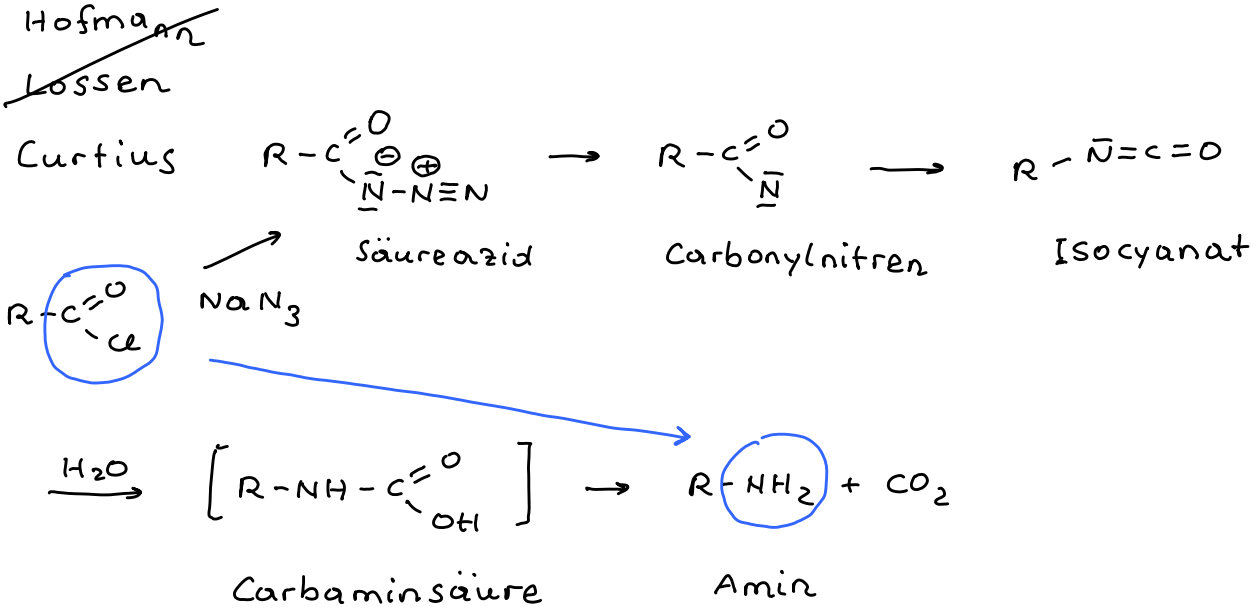




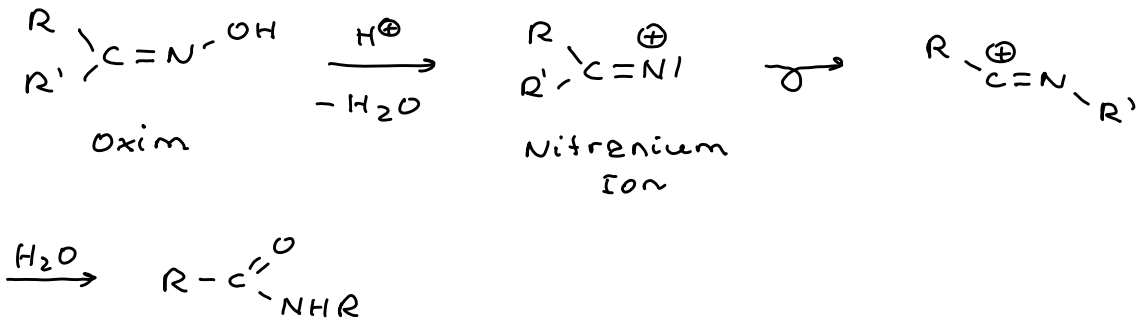
Wolff - Umlagerung



Hofmann Lossen / Curtius



Beckmann



industriell: