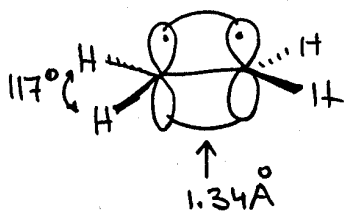


4. Gruppe : Alkene und Alkine

①

1. Alkene

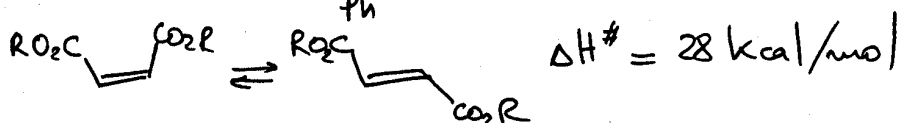
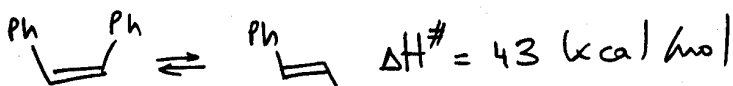
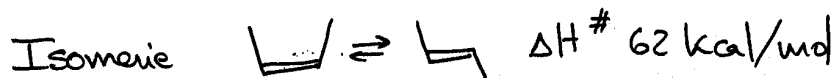
1.1. Struktur und Isomerie der Alkene



$$C-C : 83 \text{ kcal/mol}$$

$$C=C : 83 + 63 = 146 \text{ kcal/mol}$$

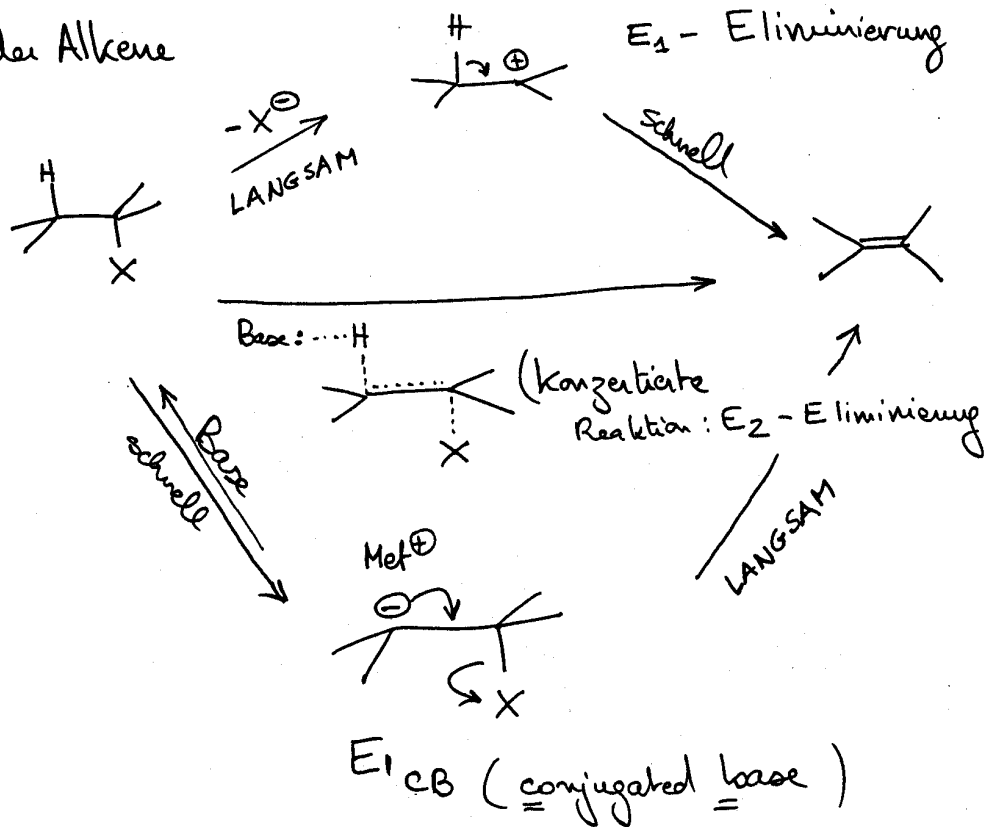
Doppelbindungs Anteil



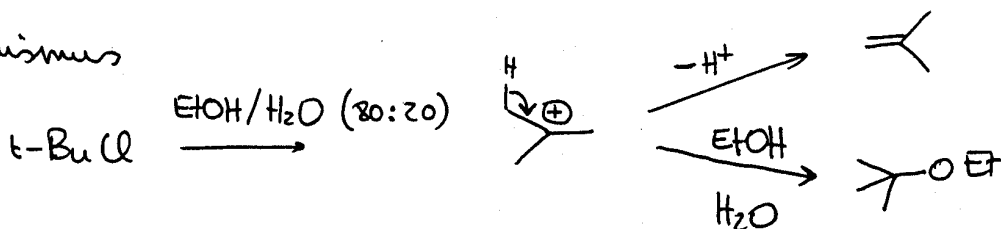
Saytzeff-Regel: Substituierte C=C Bindungen sind stabiler als Endständige (Hyperkonjugation)

1.2. Darstellung der Alkene

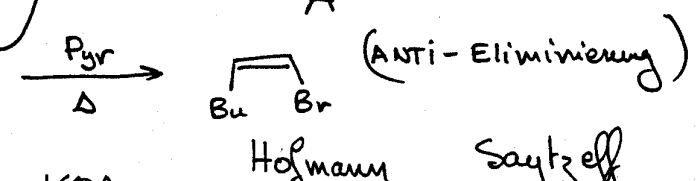
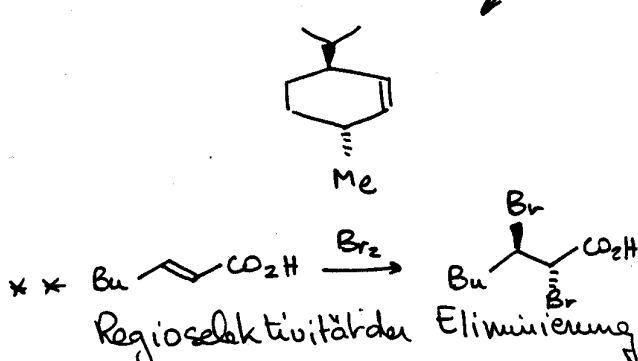
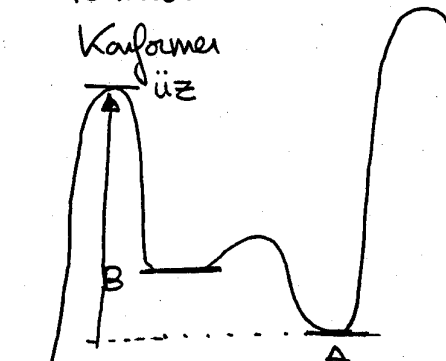
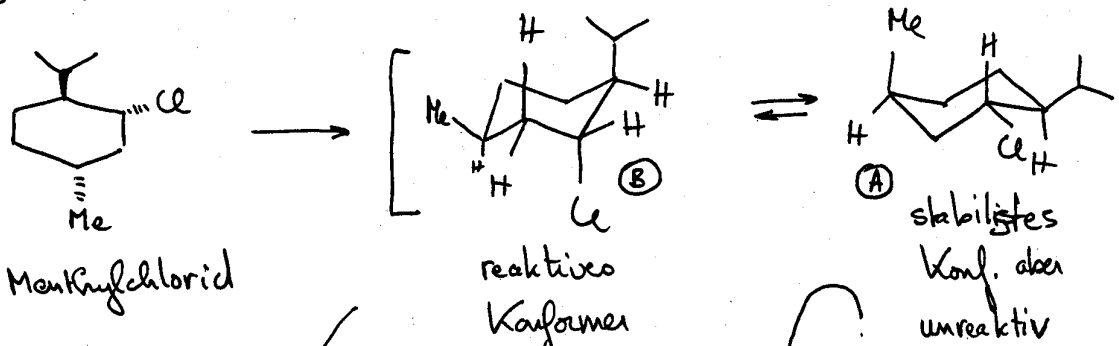
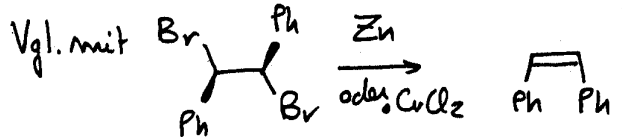
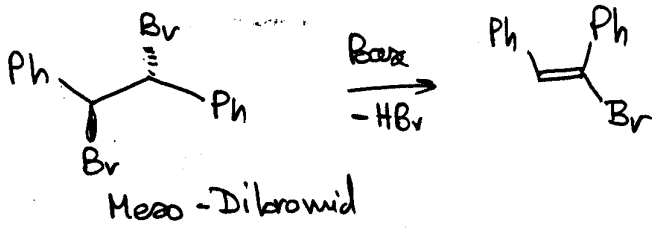
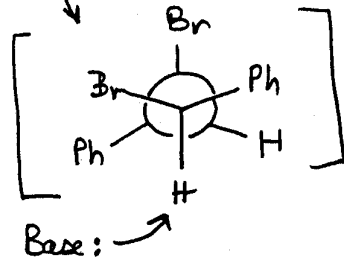
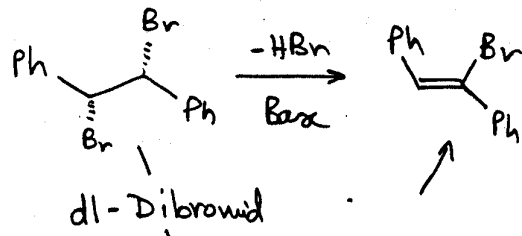
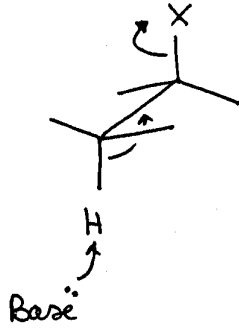
1.2.1. Mechanismen der Eliminierung von H-X



E_1 - Mechanismus

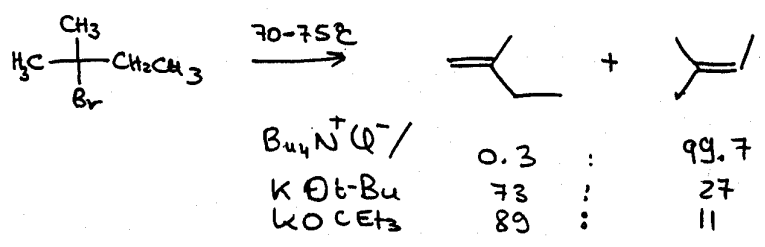


E₂ : Anti-Eliminierung (2)



$\text{CH}_3\text{CH}_2-\text{CH}(\text{X})-\text{CH}_3$	$\xrightarrow[\text{EtOH}]{\text{KOAc}}$	$\text{CH}_3\text{CH}_2-\text{CH}=\text{CH}_2$	Saytzeff	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$
X = I		30		70
X = N ⁺ Me ₃		98		2
X = S ⁺ Me ₂		87		13

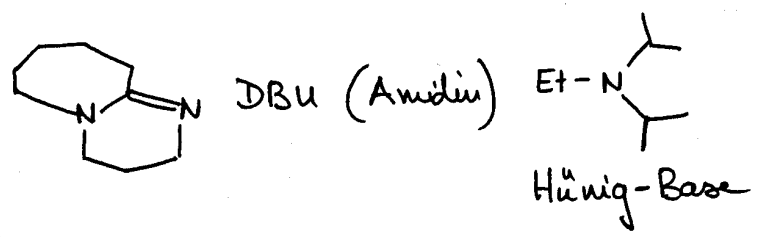
Basenstärke / Abhängigkeit



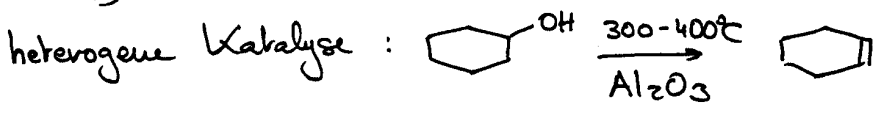
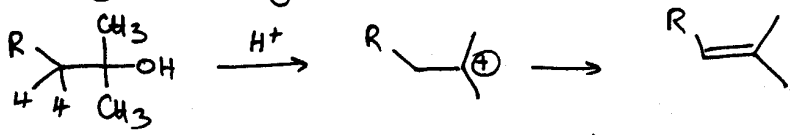
Elimin./Subst.

<chem>CC(Br)C</chem>	$\text{NBu}_4^+ \text{Cl}^-$	96%
	EtONa/EtOH	100%
<chem>CC(C)C(Br)C</chem>	$\text{NBu}_4^+ \text{Cl}^-$	0%
	NaOEt	75%
<chem>CCCC(Br)C</chem>	$\text{NBu}_4^+ \text{Cl}^-$	0%
	NaOEt	10%

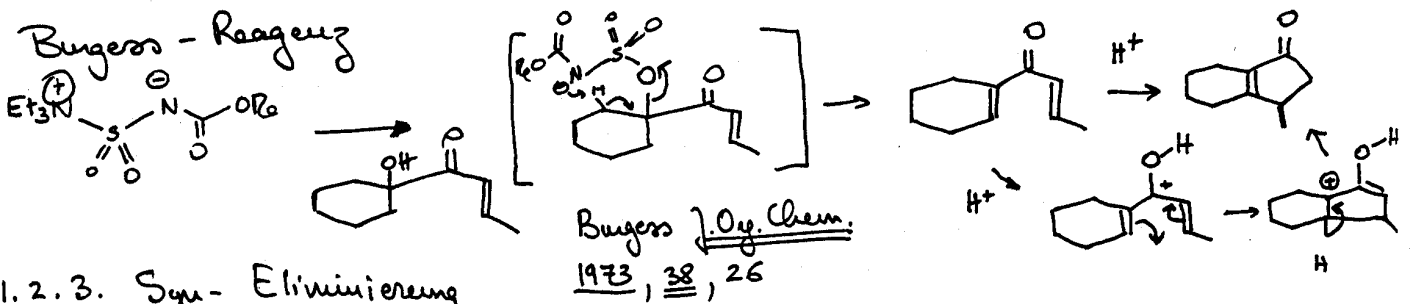
Base für Eliminierungen:



1.2.2. Dehydatisierung von Alkoholen

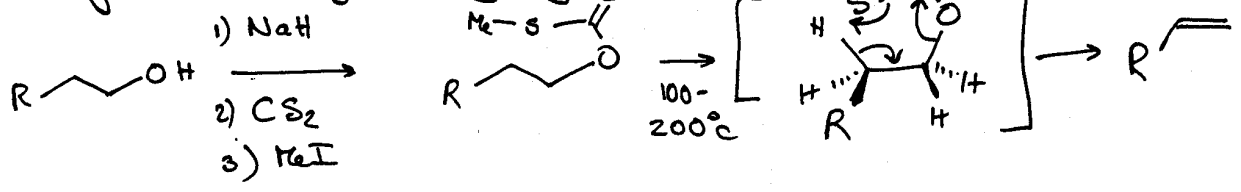


Burgess-Reagenz

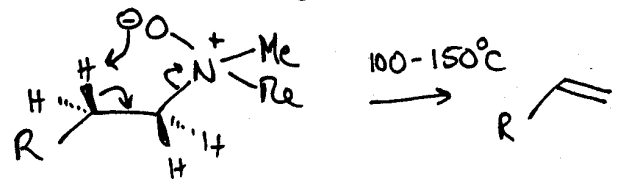


1.2.3. Syn-Eliminierung

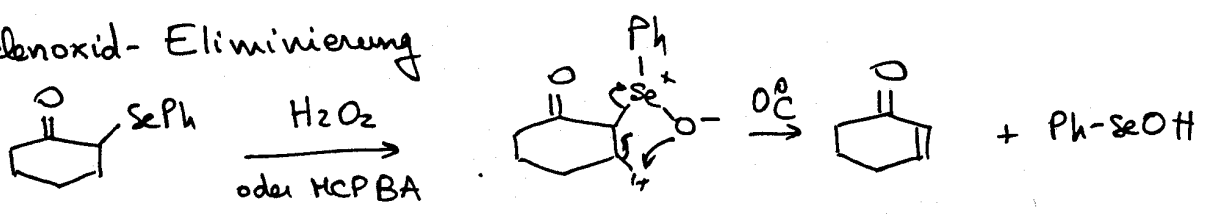
Chugaev-Xanthogenat-Pyrolyse



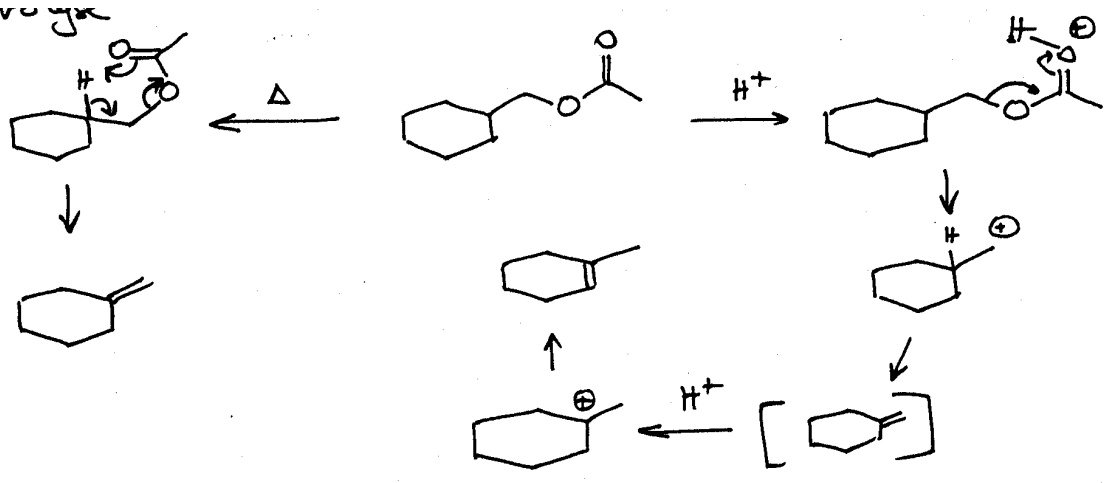
Cope-Eliminierung (Aminoxid-Pyrolyse)



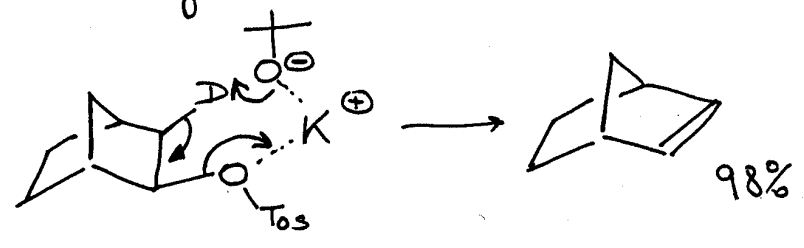
Selenoxid-Eliminierung



ESR-lysozym

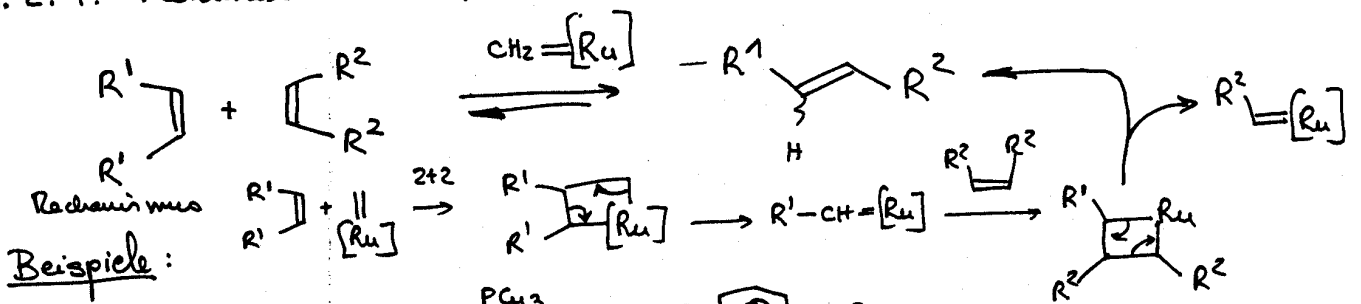


Sym-Eliminierung



1.2.4. Metathese von Olefinen

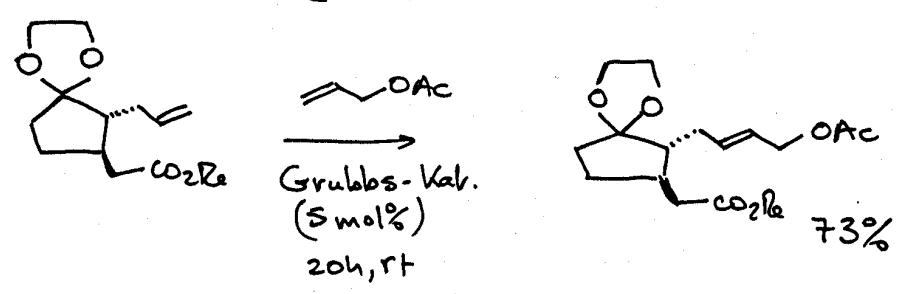
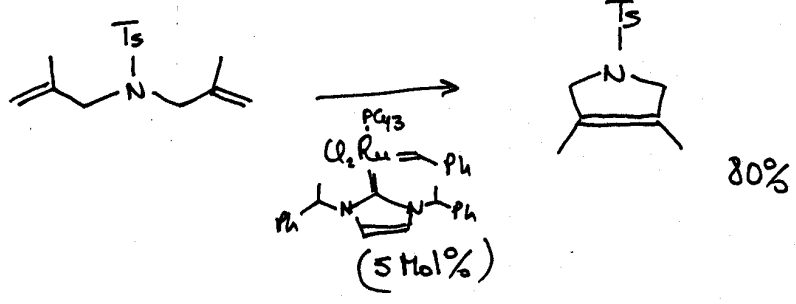
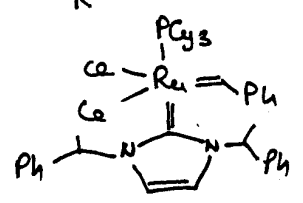
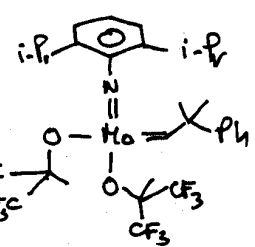
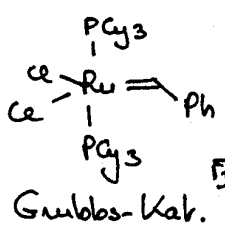
1990: Schrock, Grubbs



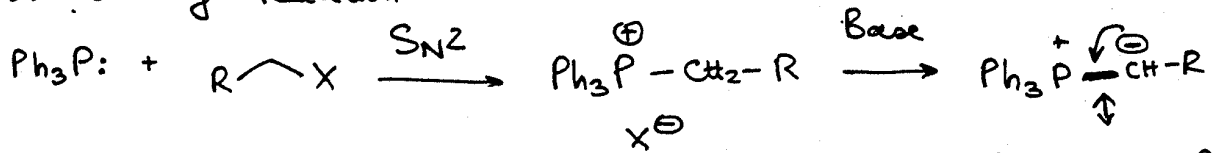
Beispiele:

Katalysatoren:

Maier *Angew. Chem.*
Int. Ed.
2000, 39, 2073

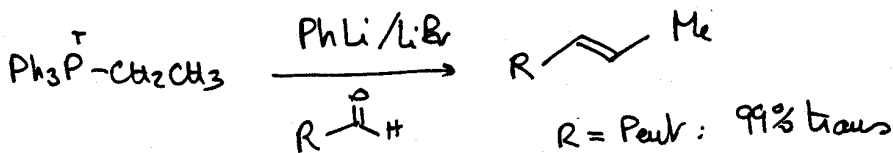
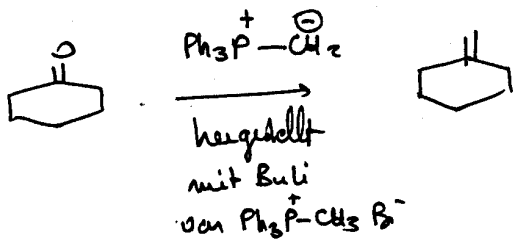
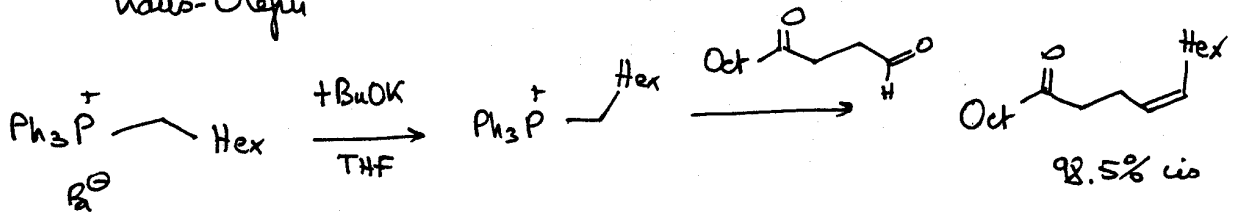
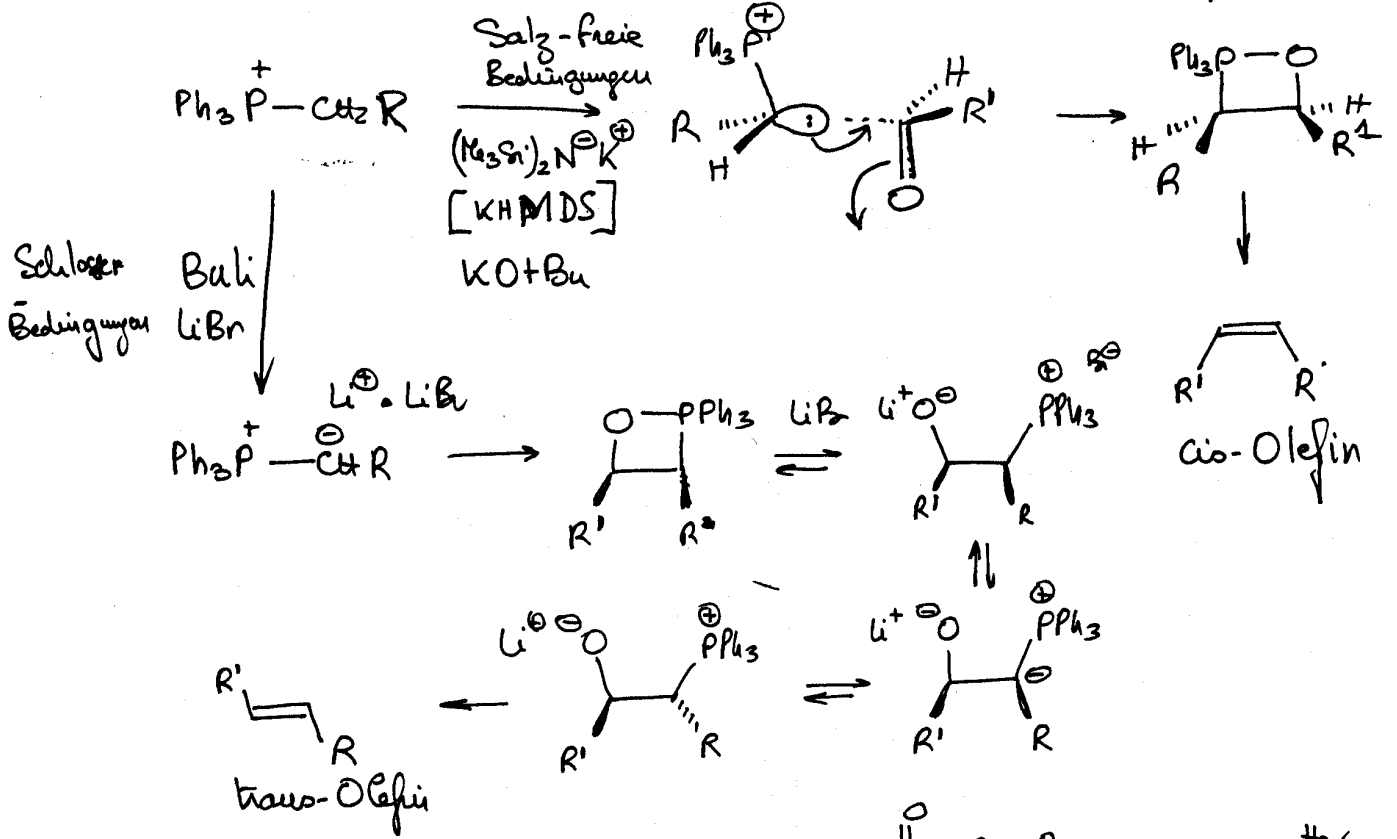


1.2.1. Wittig-Reaktion

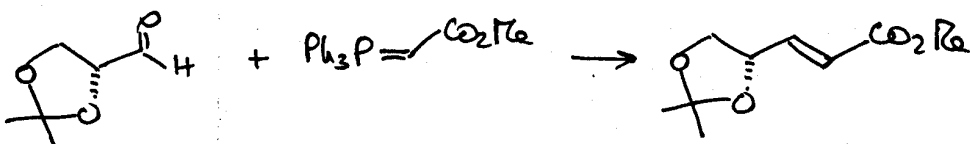


- Erzeugung des Ylids ist essentiell für die Stereoselektivität der Reaktion mit Carbonyl-Verbindungen

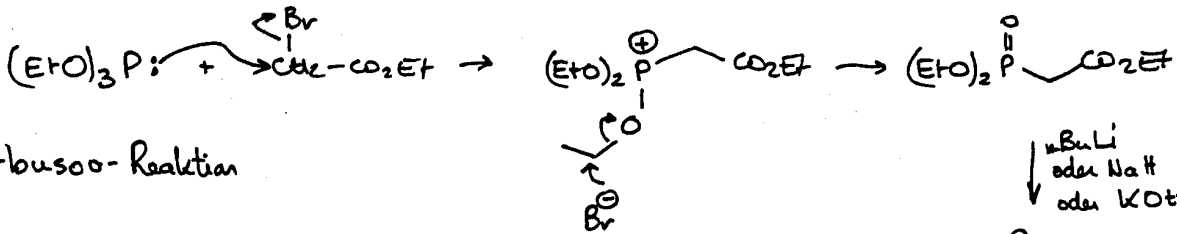
Phosphor-Ylid (Phosphoran)



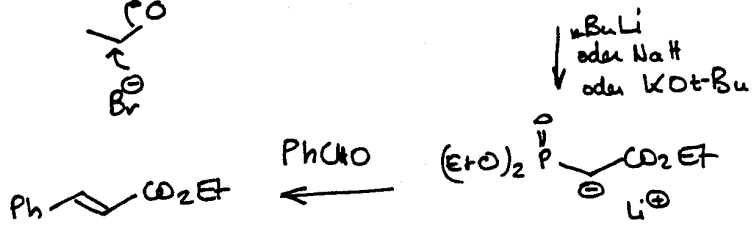
Stabilisierte Ylide geben die trans-Verbindung



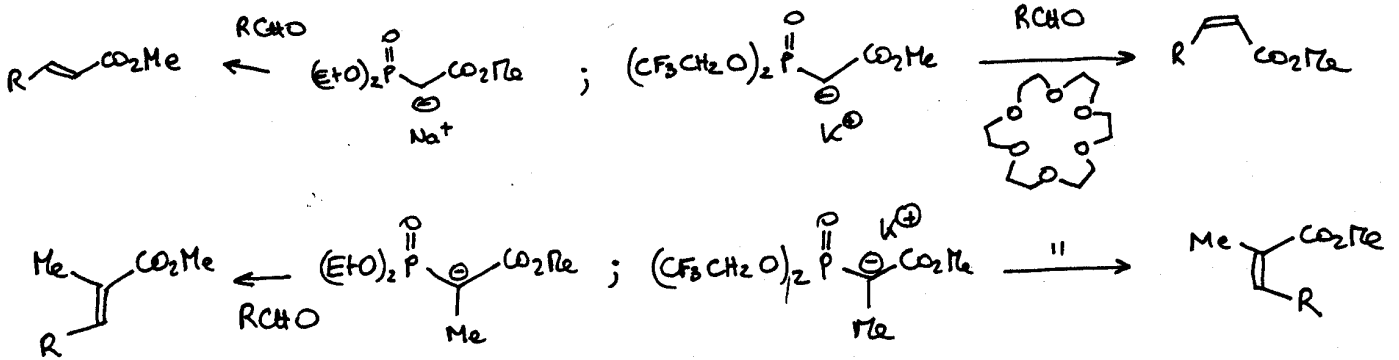
Horner-Wadsworth-Emmons-Reaktion



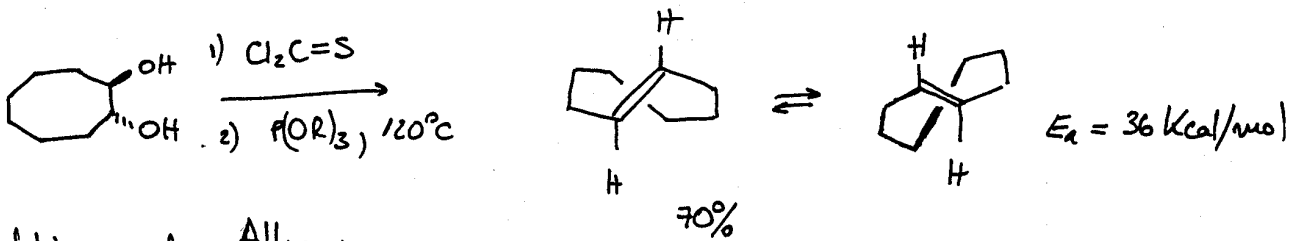
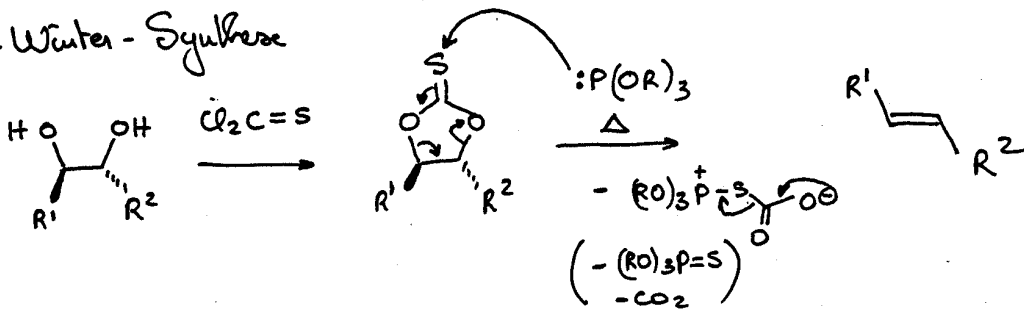
Arbusso-Reaktion



Still-Gennari-Variante

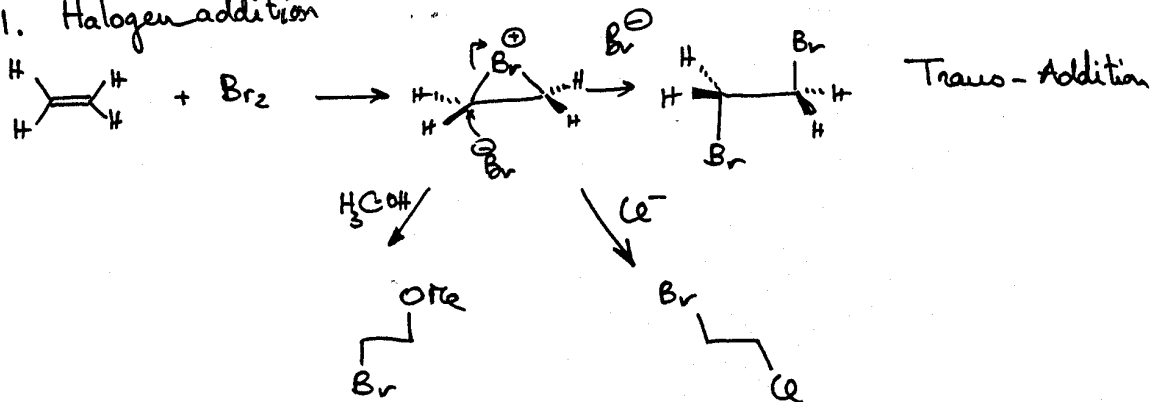


Corey-Winter-Synthese

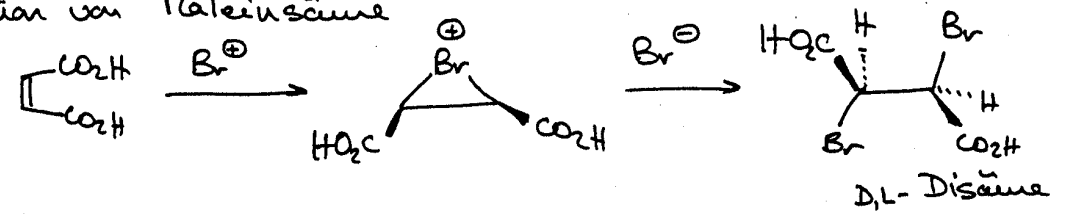


1.3. Reaktionen der Alkene

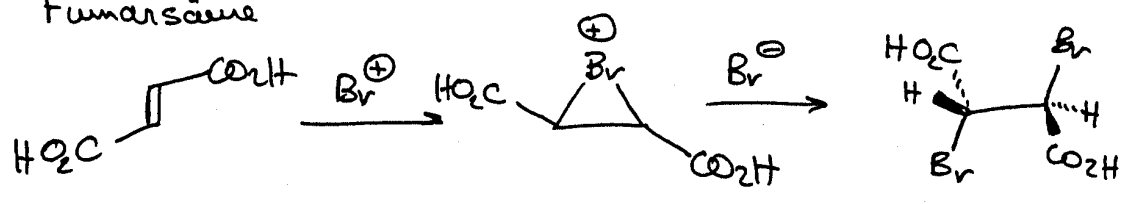
1.3.1. Halogenaddition



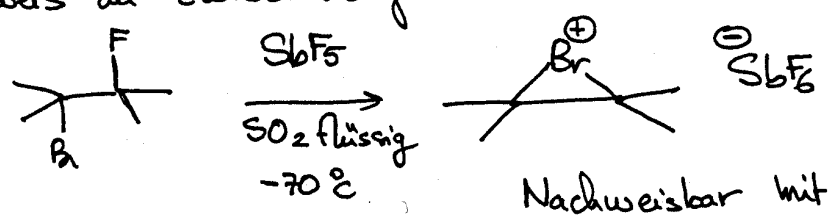
Reaktion von Maleinsäure



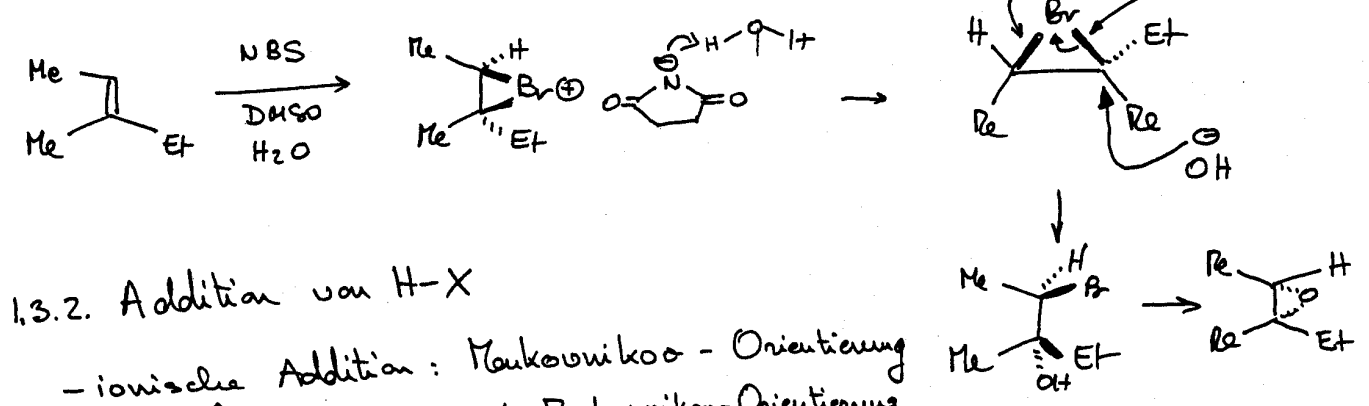
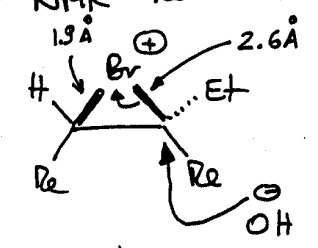
Fumarsäure



Nachweis der Zwischenstufe mit NMR

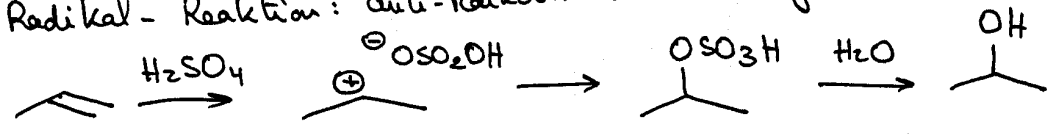


Nachweisbar mit NMR-Methoden



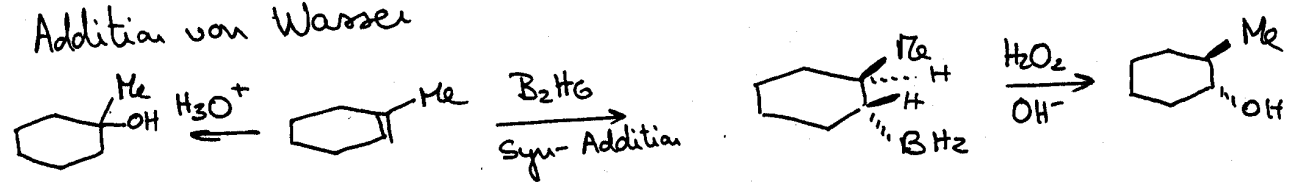
1.3.2. Addition von H-X

- ionische Addition: Markownikow-Orientierung
- Radikal-Reaktion: anti-Markownikow-Orientierung

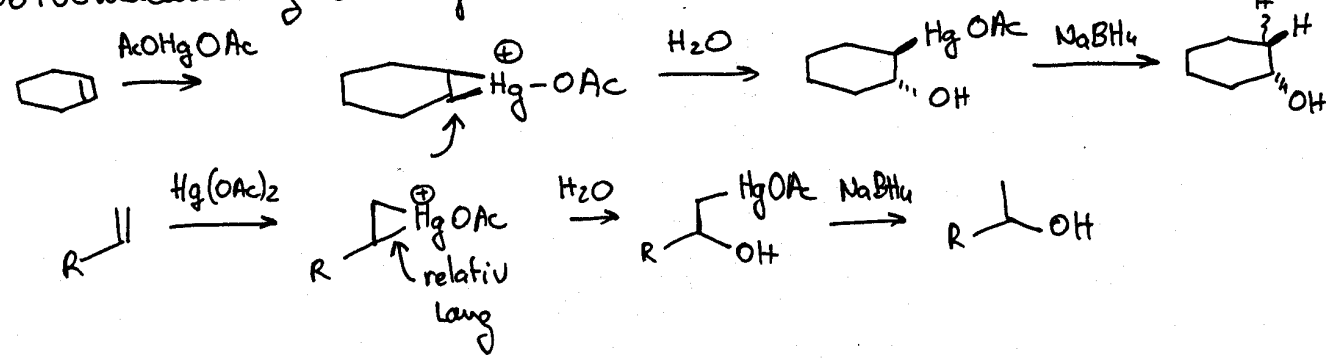


Reaktivität: HI > HBr > HCl

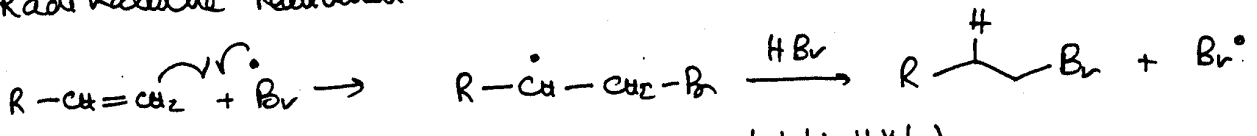
Addition von Wasser



Solvomercurierung von Olefinen

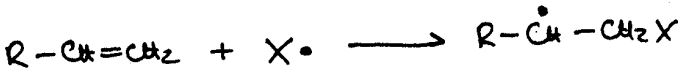


Radikalische Reaktionen

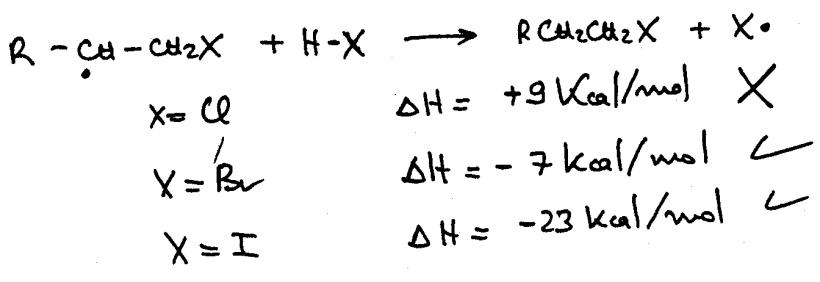


Kettenreaktion (Anti-Markownikoo Selektivität)

Nur HBr - Anlagerung ist radikalisch möglich

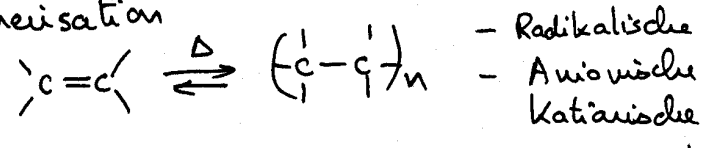


- X = Cl ΔH = -30 kcal/mol ✓
- X = Br ΔH = -9 kcal/mol ✓
- X = I ΔH = +3 kcal/mol ✗



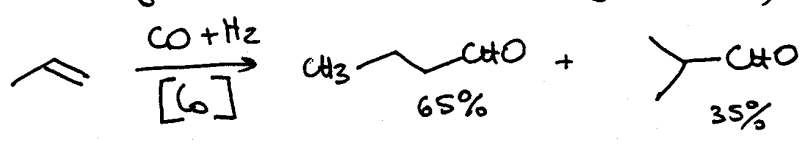
Beide Schlussschritte der Kettenreaktion sind exotherm.

1.3.3. Polymerisation

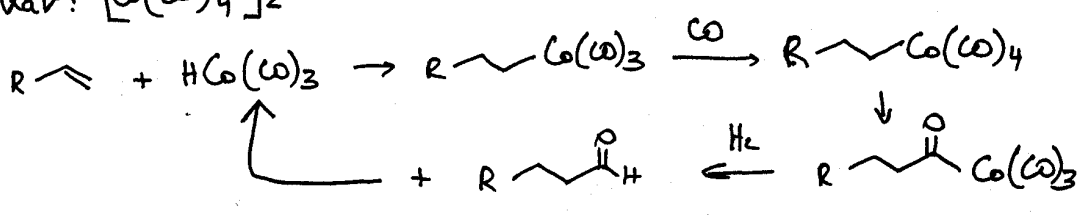


Polymerisationen sind möglich

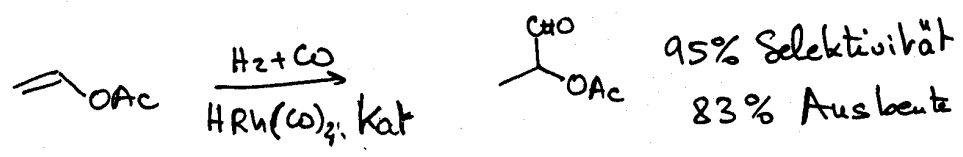
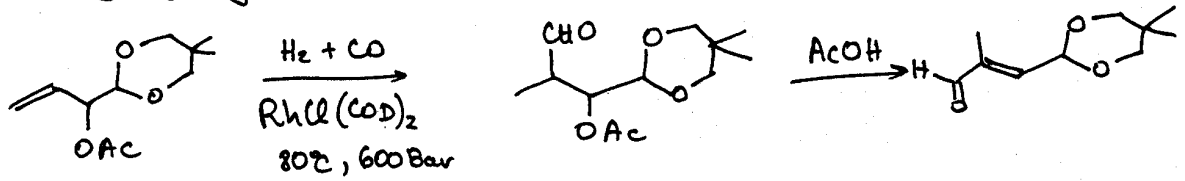
1.3.4. Oxo-Synthese (Hydroformylierungsreaktion)



Kat: $[Co(CO)_4]_2$

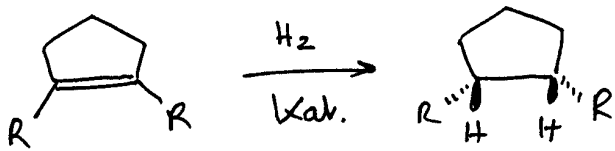


Moderne Hydroformylierung:



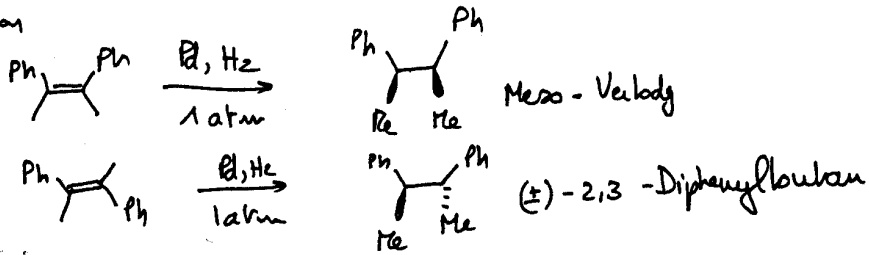
200 Bar, 60°C, NMP

1.3.5. Katalytische Hydrierung

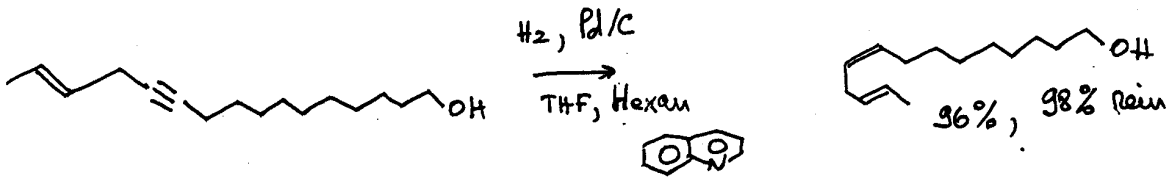


Heterogene Reduktion

Syn Addition

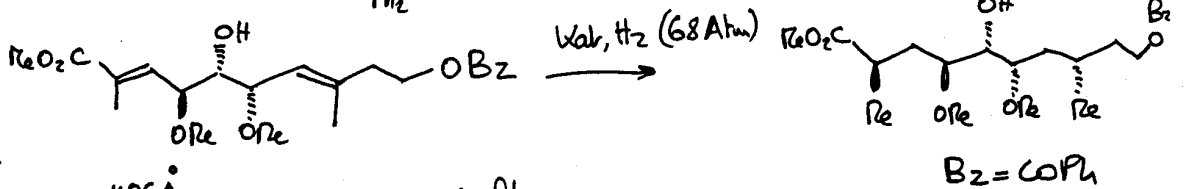
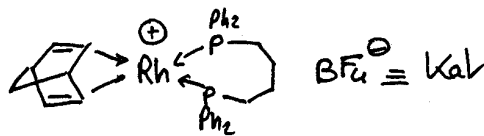
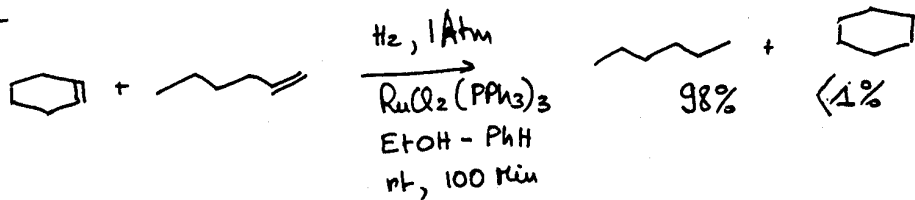


Lindlar - Reduktion

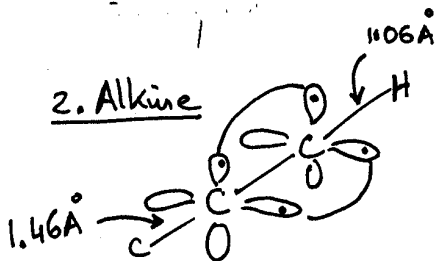


Homogene Katalyse

Selektivität



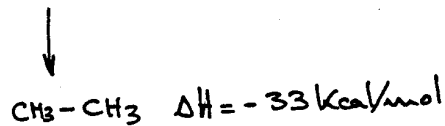
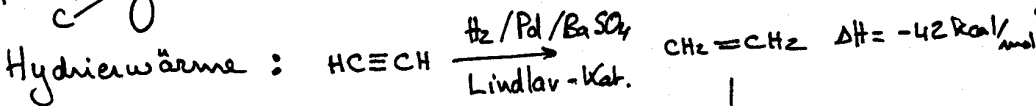
2. Alkine



z.B. Eigenschaften

Bindungsenergie:

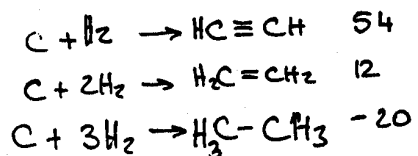
C-C	C=C	C≡C	
83	146	200	kcal/mol
		83	
		63	
		54	



$\equiv\text{C-H}$ ← acide C-H Bindung

<chem>CH_3-C#C-H</chem>	60
<chem>CH_2=C#C-H</chem>	>46
<chem>H-C#C-H</chem>	25

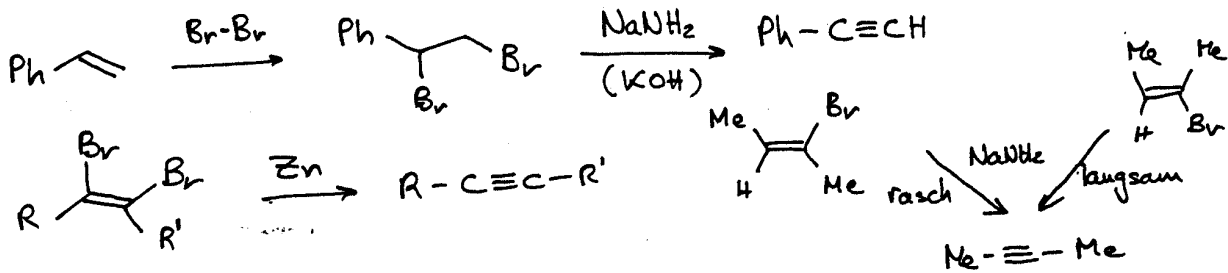
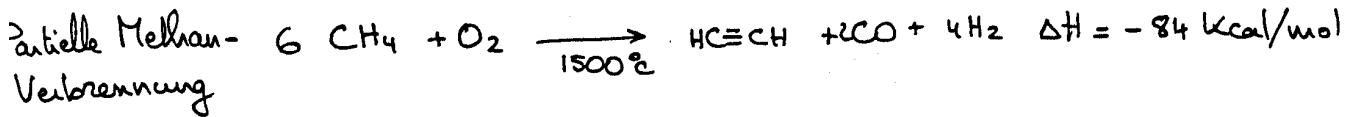
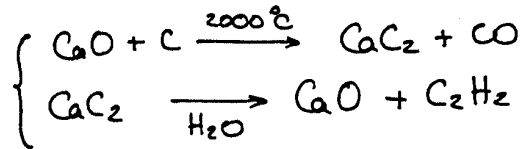
Acetylen ist eine endotherme Verbindung:



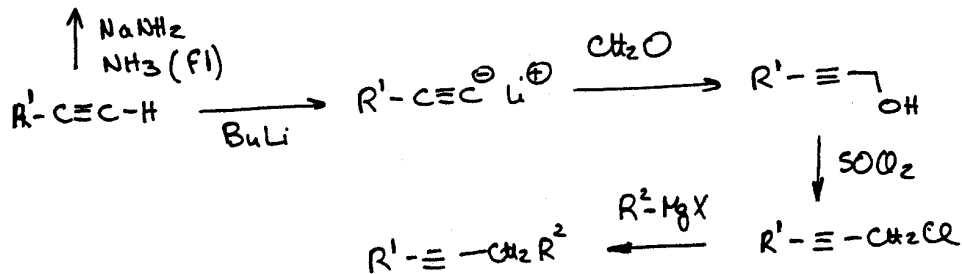
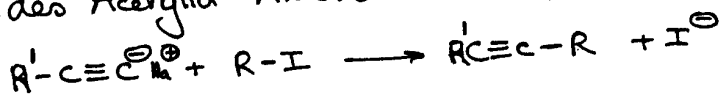
ΔH_f (kcal/mol)

2.2. Darstellung

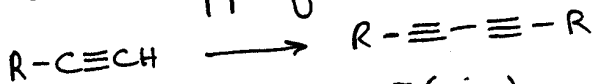
Technische Synthese



Alkylierung des Acetylid-Anions

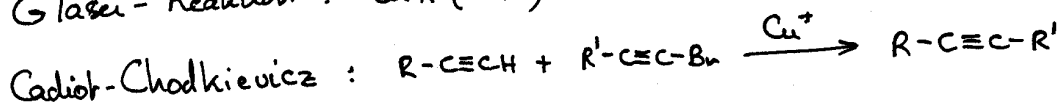


Oxidative Kupplung

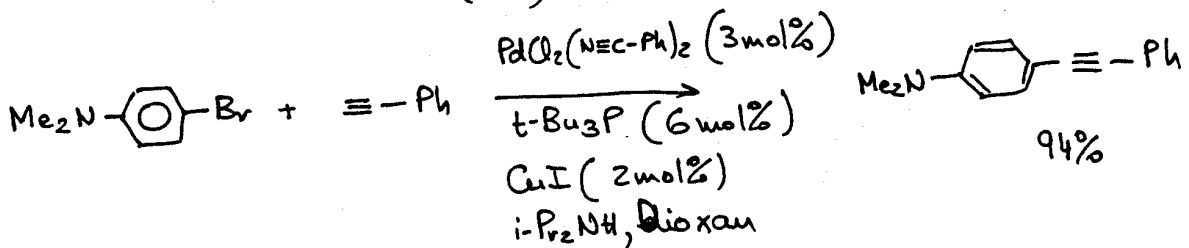
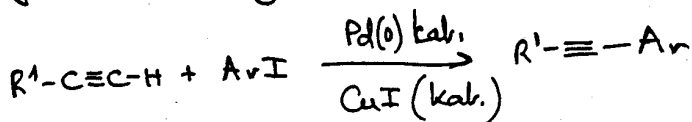


Eglinton-Reaktion: $\text{Cu}^{\text{II}}(\text{OAc})_2$ in Pyridin

Glaser-Reaktion: $\text{CuX}(\text{kat.}) \text{NH}_4\text{Cl} / \text{NH}_3 / \text{O}_2$



Sonogashira-Kreuzkupplung

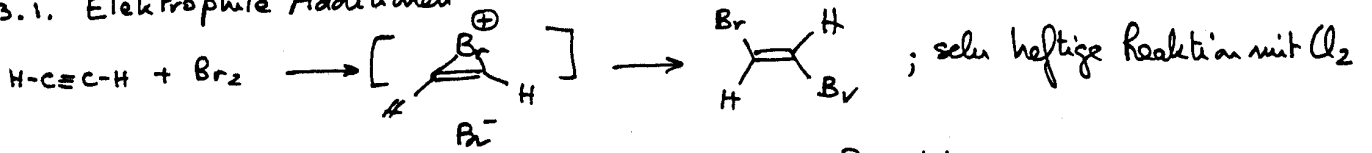


G.C. Fu Org. Lett. 2000, 2, 1729 rt, 1-15 h

2.3. Reaktionen

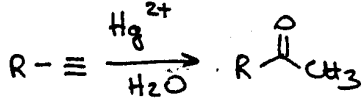
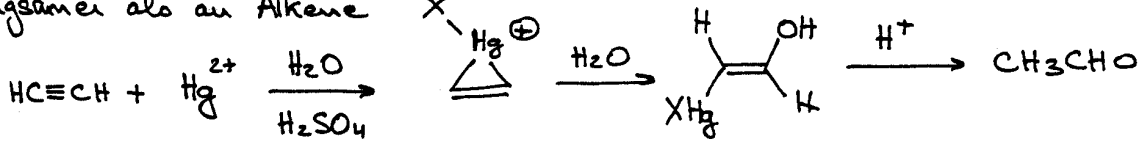
(11)

2.3.1. Elektrophile Additionen

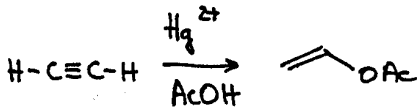
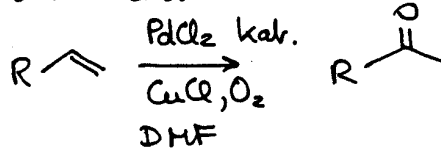


Elektrophile Additionen an Alkine sind langsamer als an Alkene

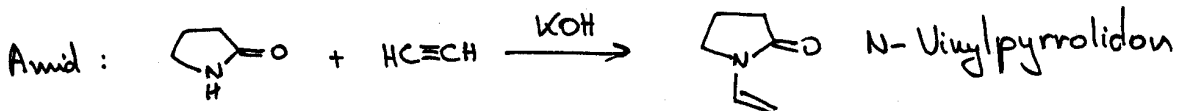
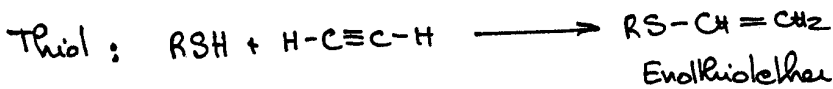
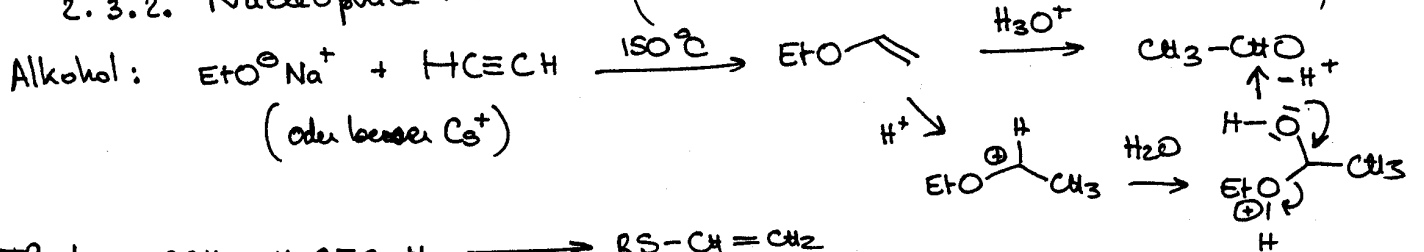
trans-Produkt



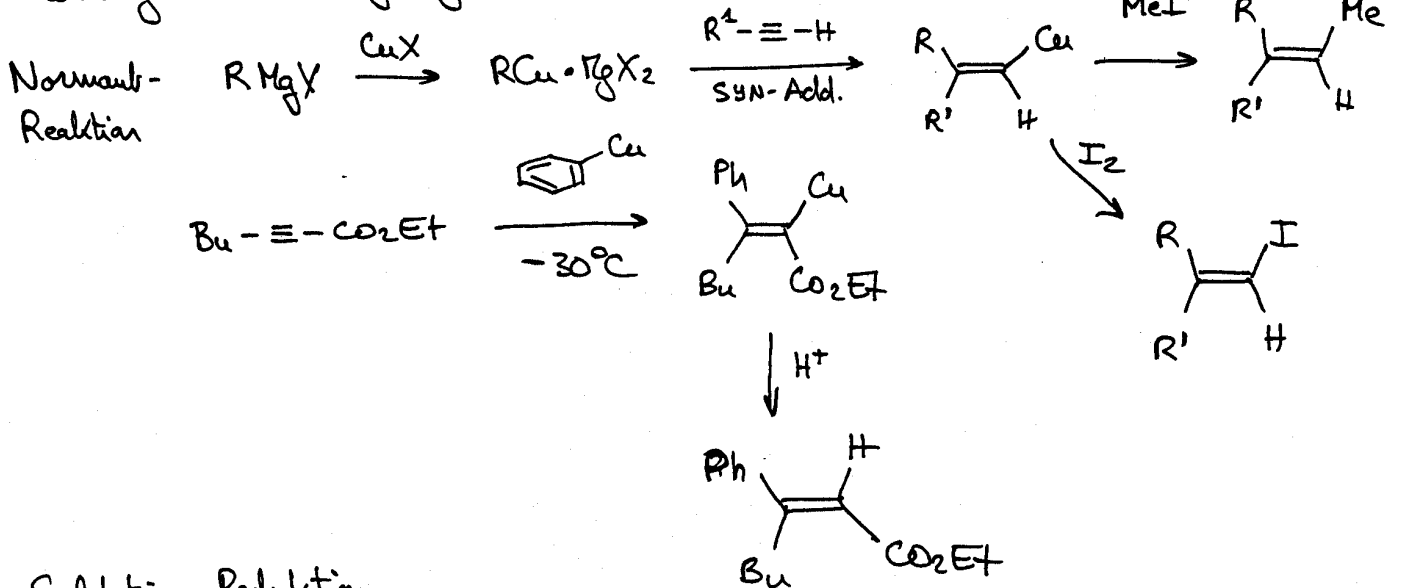
Vgl. mit der Wacker-Reaktion:



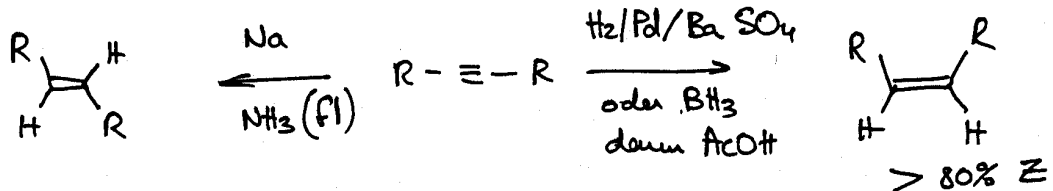
2.3.2. Nucleophile Additionen (an Alkine sind leichter als bei Olefinen)

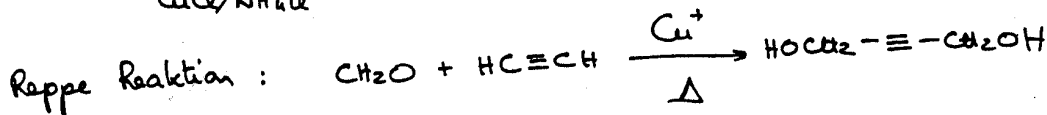
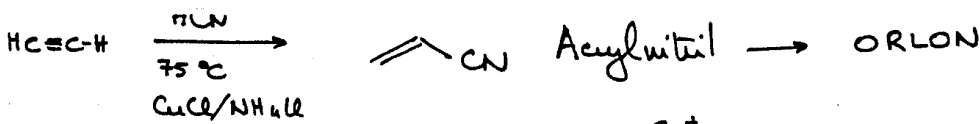


Rehaltorganische Reagenzien:

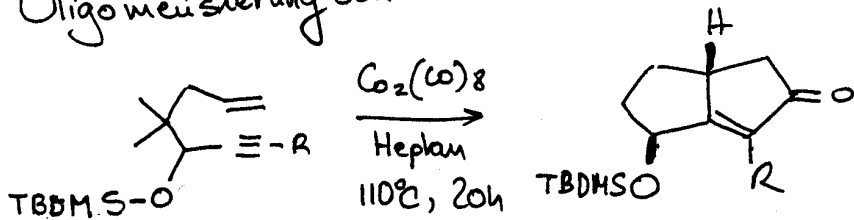


Selektive Reduktion

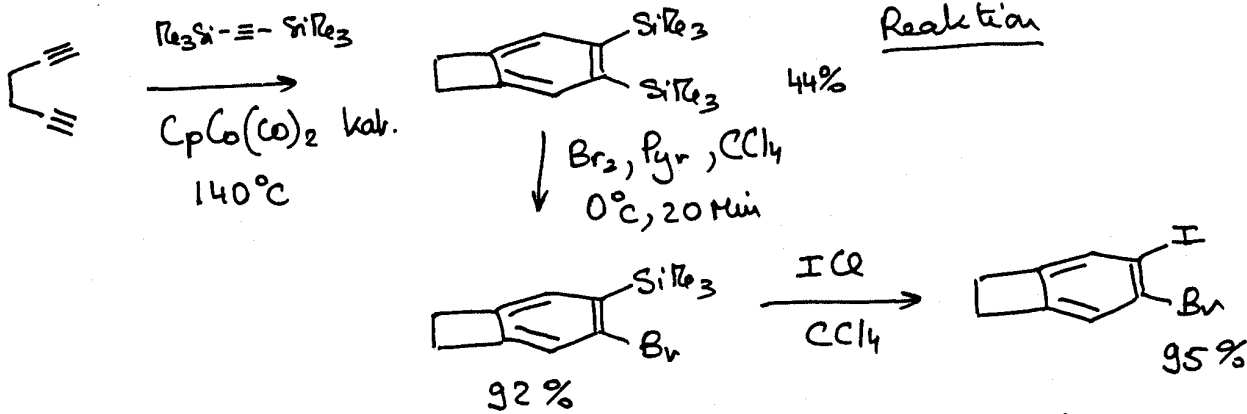




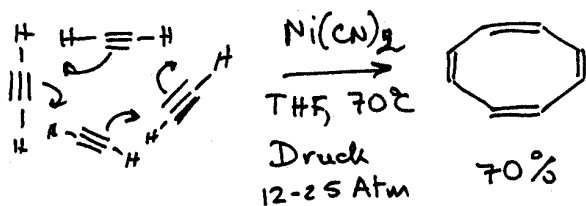
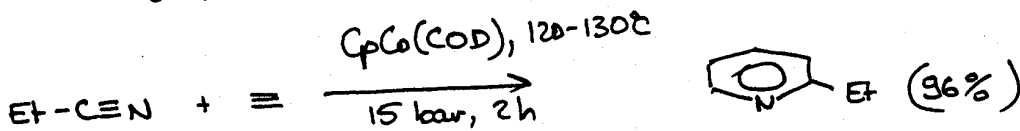
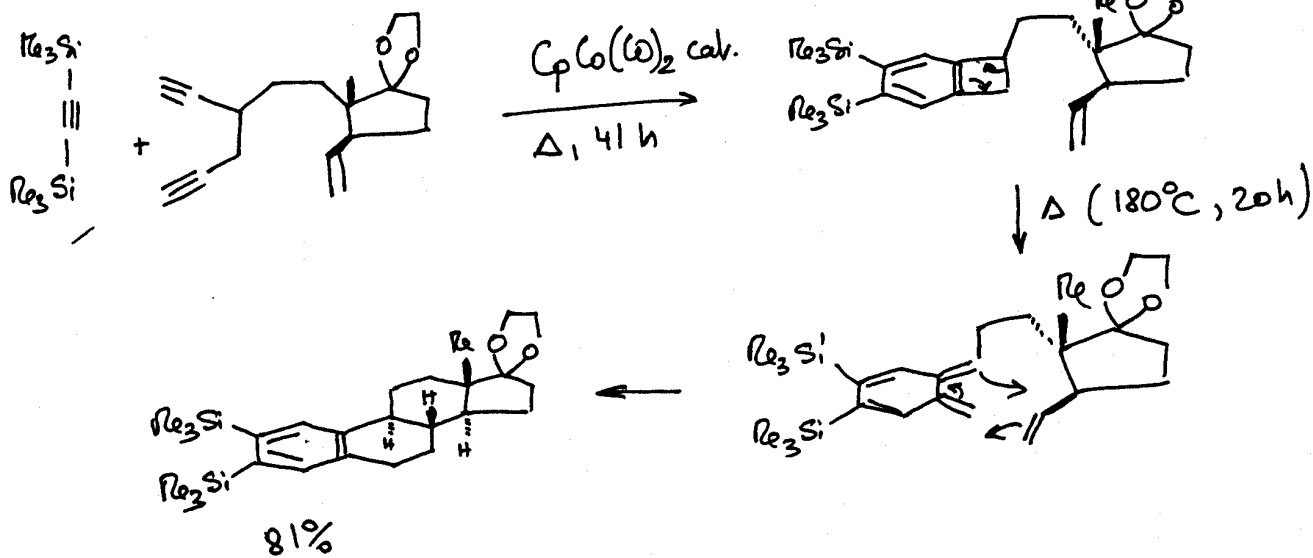
Oligomerisierung von Alkyläthylen



Paouan-Khan Reaktion



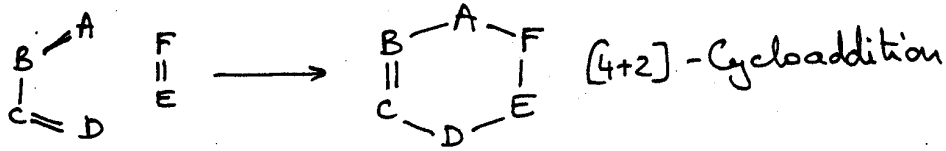
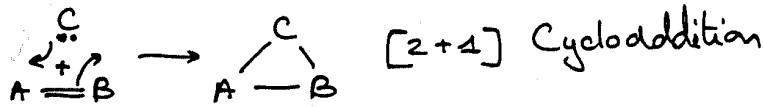
Reppe-Vollhardt-Reaktion



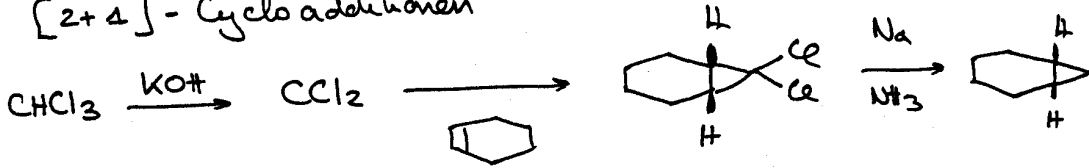
3. Cycloadditionen der Alkene und Alkine

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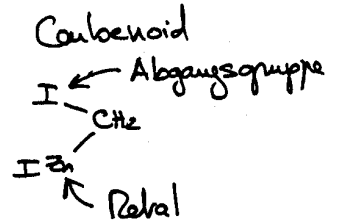
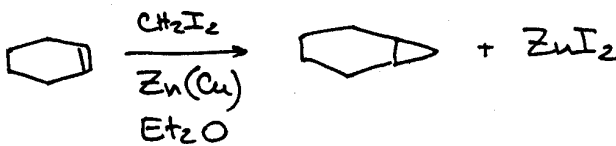
Definition: Zahl der an der Ringbildung beteiligte Atome



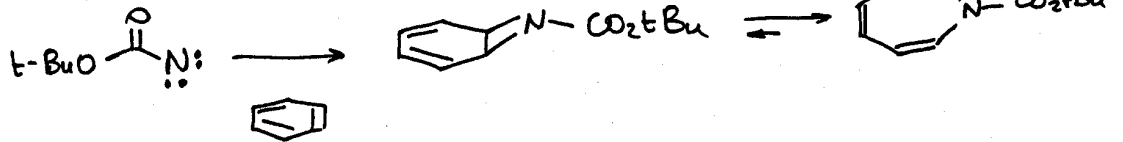
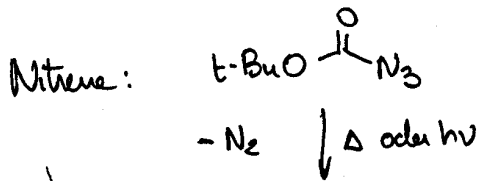
3.1. [2+4]-Cycloadditionen



Simmons-Smith-Reaktion: $\text{ICH}_2\text{-I} + \text{Zn} \xrightarrow[\text{ether}]{\text{THF}}$ $\text{ICH}_2\text{-ZnI}$

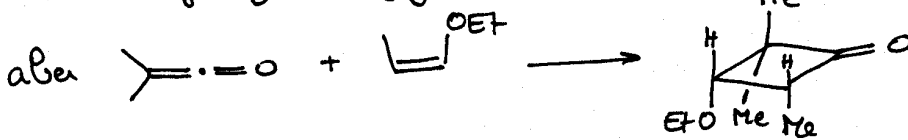


Carbenoid: Rehal und Abgangsgruppe am selben Kohlenstoff

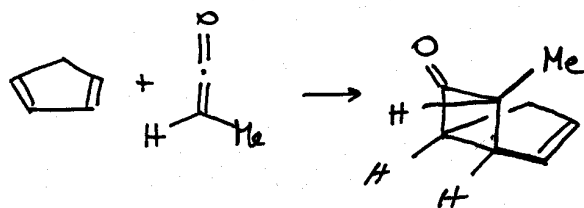


3.2. [2+2]-Cycloadditionen

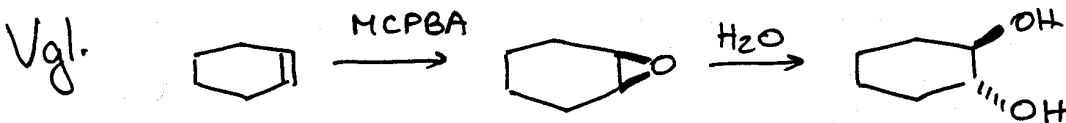
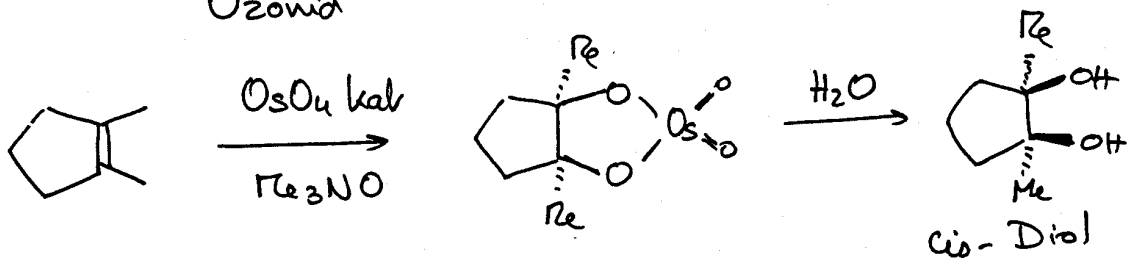
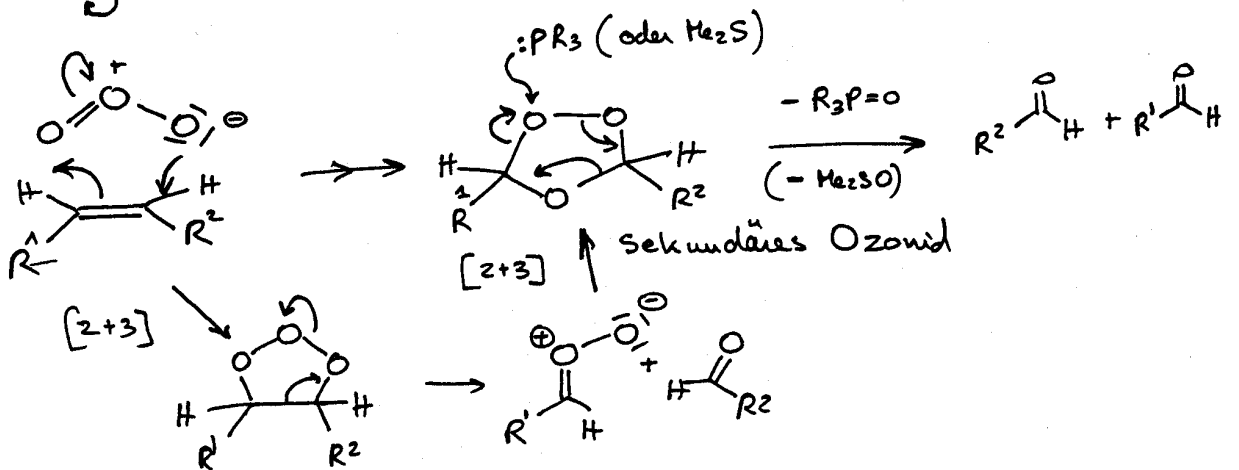
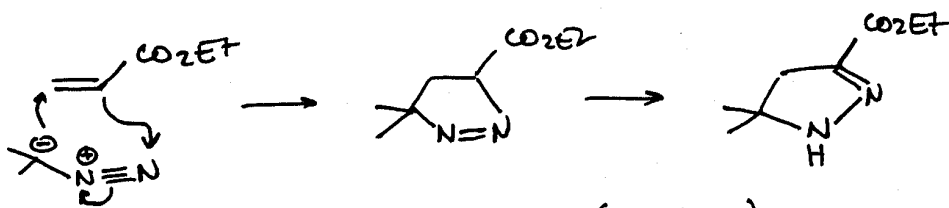
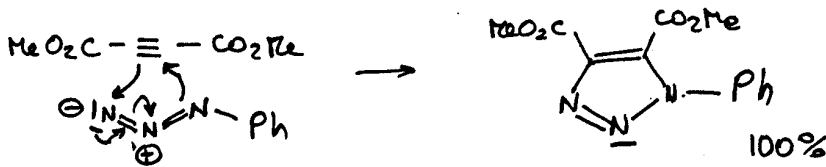
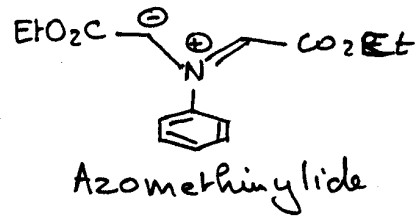
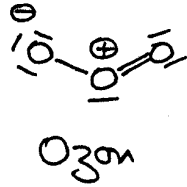
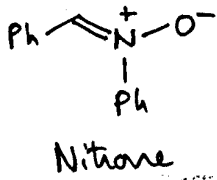
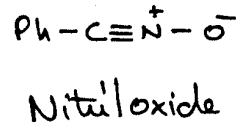
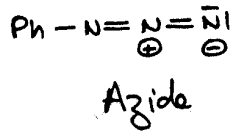
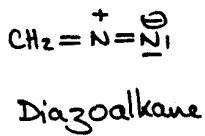
in der Regel zweistufig, meist nicht stereospezifisch



stereospezifisch



(3+2)-Cycloadditionen : 1,3-Dipolare Cycloadditionen

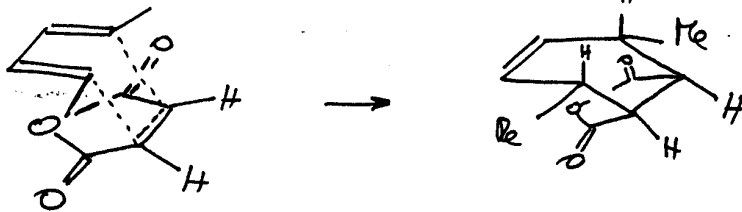
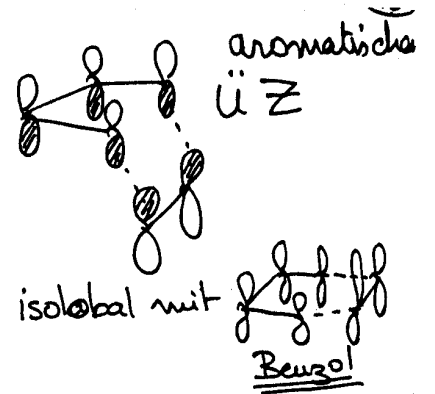


3.4. [4+2]- Cycloadditionen

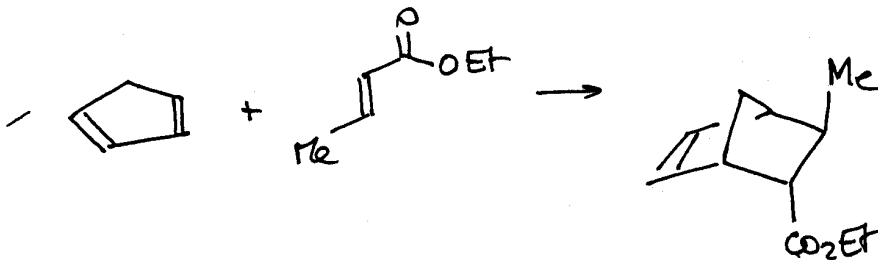
Diels-Alder Reaktion



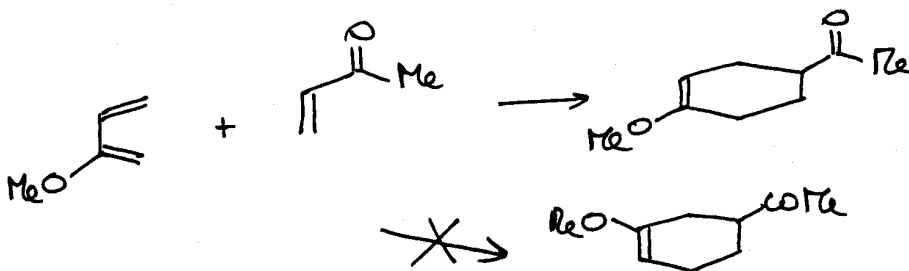
Konzertierte
Reaktion



die relative Stereochemie
von 4 Zentren wird
kontrolliert



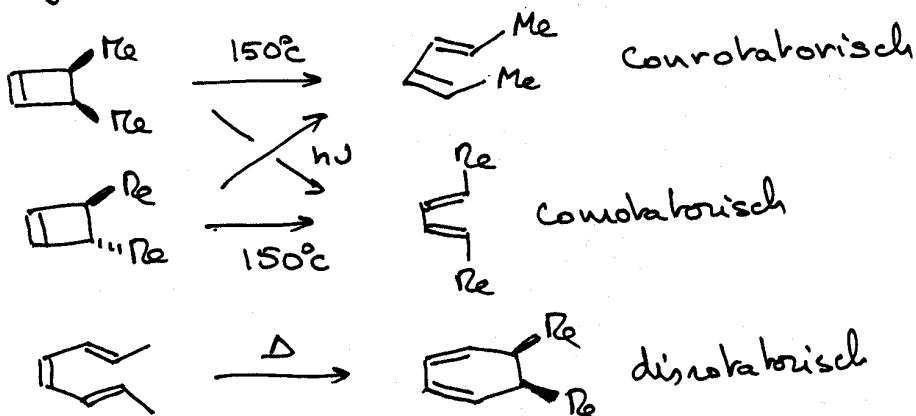
99% Endo



Hauptregioisomer

Eine Lewis-Säure-Katalyse beschleunigt Diels-Alder-Reaktionen mit ungesättigte Carbonylverbindungen

4. Erhaltung der Orbital-symmetrie



Woodward-Hoffmann Regeln

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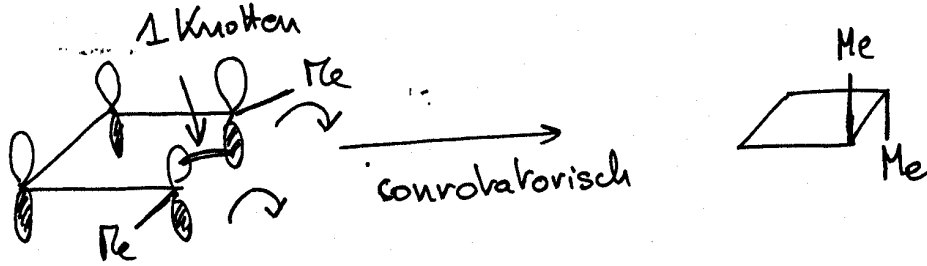
Aromatische π Z ist erlaubt

Antiaromatische π Z sind verboten

Aromatisch: $4n+2 e^-$ ohne Knoten!

Antiaromatisch: $4n e^-$ ohne Knoten!

Beispiel:



$4e^- \Rightarrow$ antiaromatisch aber + 1 Knoten

\Rightarrow aromatisch
wird