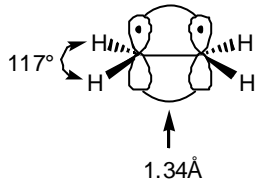


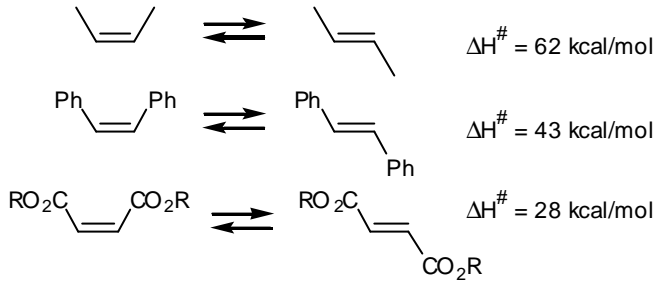
1) Alkene

1.1. Struktur und Isomerie der Alkene



C—C : 83 kcal/mol
 C=C : 83 + 63 = 146 kcal/mol
 Doppelbindung-Anteil

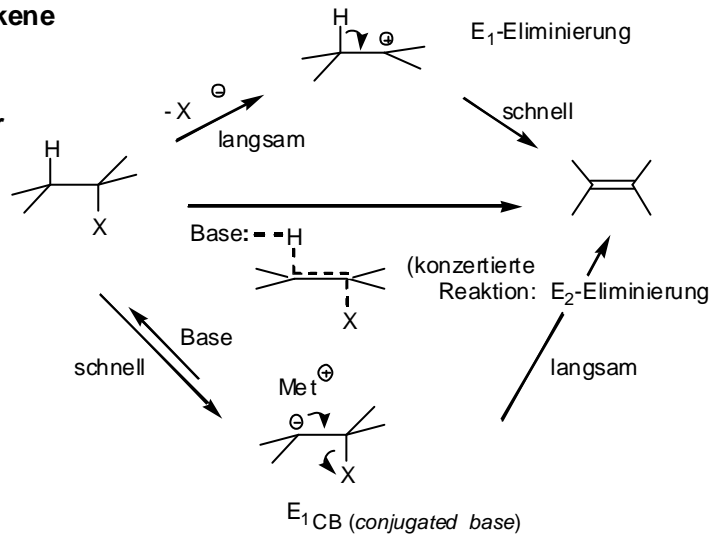
Isomerie



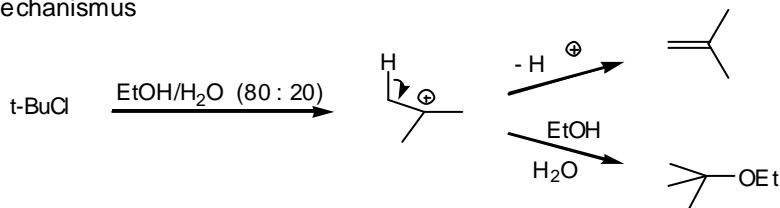
Saytzeff-Regel: Substituierte Doppelbindungen sind stabiler als endständige Doppelbindungen (Hyperkonjugation).

1.2. Darstellung der Alkene

1.2.1. Mechanismen der Eliminierung von H-X

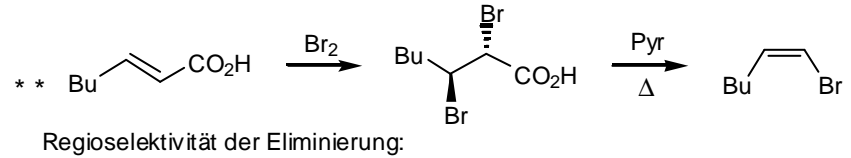
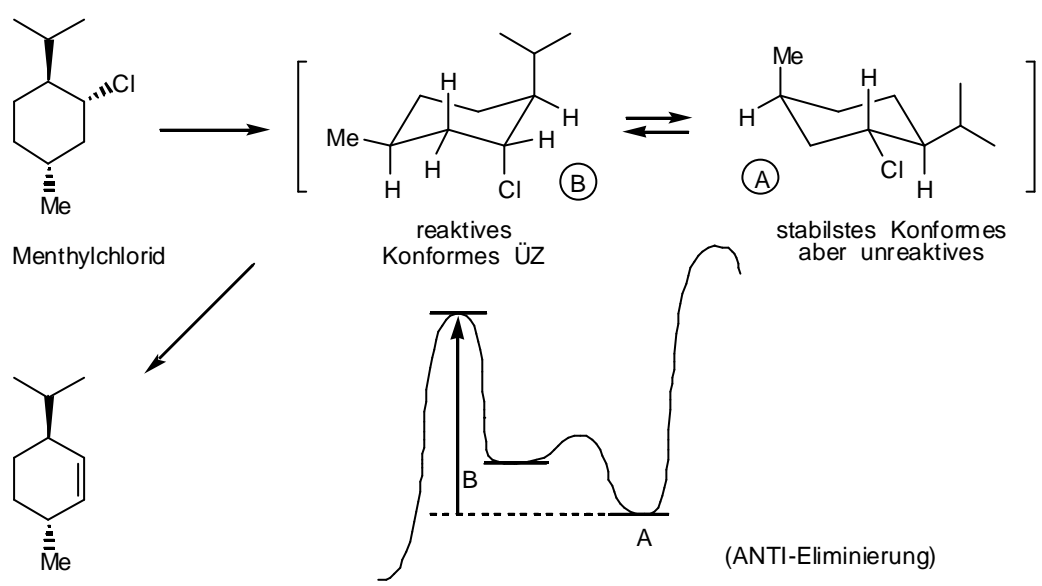
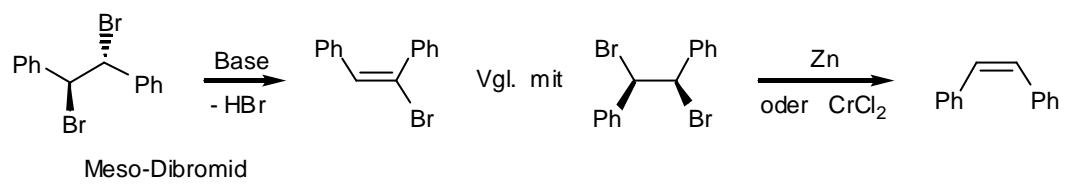
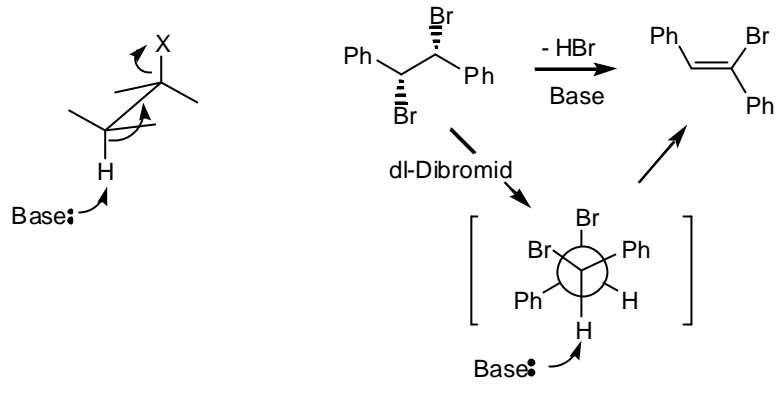


E₁-Mechanismus



4. Gruppe: Alkene und Alkine

E₂: Anti-Eliminierung

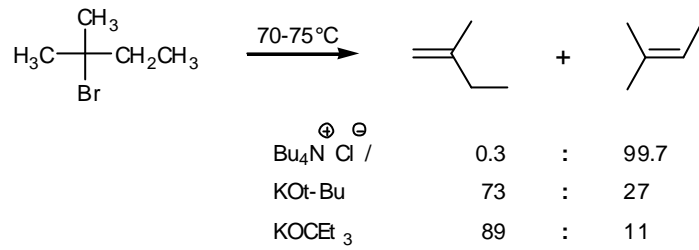


1875	$\text{H}_3\text{CH}_2\text{C}-\overset{\text{H}}{\underset{\text{X}}{\text{C}}}-\text{CH}_3$	$\xrightarrow[\text{EtOH}]{\text{KOAc}}$	Hofmann $\text{H}_3\text{CH}_2\text{C}-\overset{\text{H}}{\text{C}}=\text{CH}_2$	Saytzeff $\text{H}_3\text{C}-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}-\text{CH}_3$
	X = I		30	70
	X = NMe ₃ ⁺		98	2
	X = SMe ₂ ⁺		87	13

4. Gruppe: Alkene und Alkine

③

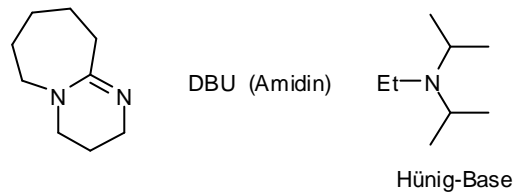
Base Stärke:



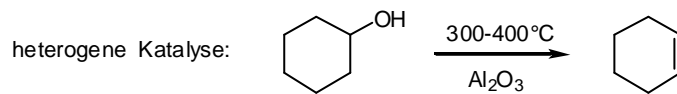
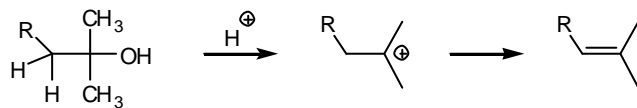
Elimin./Subst.

		% Eliminierung
<chem>CC(C)(C)Br</chem>	$\text{NBu}_4^{\oplus} \text{Cl}^{\ominus}$	96%
	EtONa/EtOH	100%
<chem>CC(C)Br</chem>	$\text{NBu}_4^{\oplus} \text{Cl}^{\ominus}$	0%
	NaOEt	75%
<chem>CCBr</chem>	$\text{NBu}_4^{\oplus} \text{Cl}^{\ominus}$	0%
	NaOEt	10%

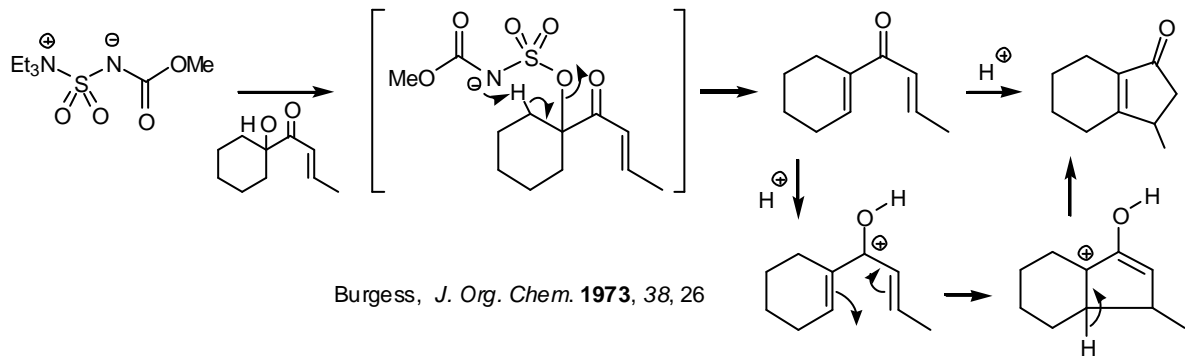
Base für Eliminierungen:



1.2.2. Dehydratisierung von Alkohole

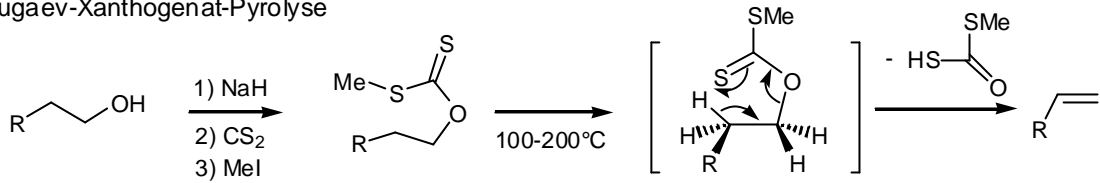


Burgess-Reagenz

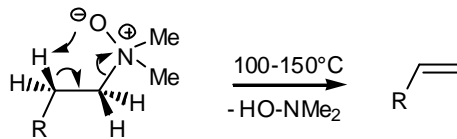


1.2.3. Syn-Eliminierung

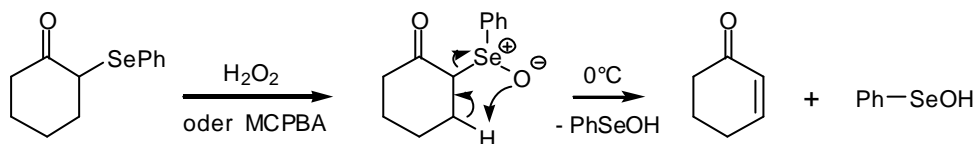
Chugaev-Xanthogenat-Pyrolyse



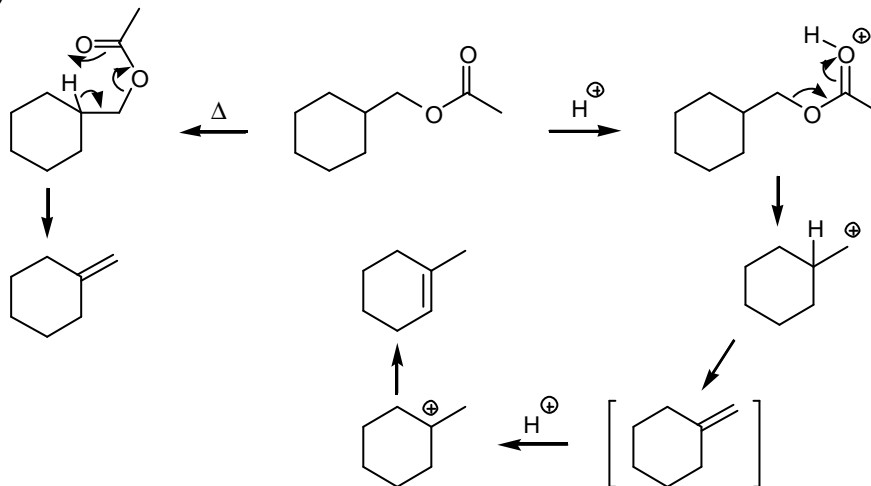
Cope-Eliminierung (Aminoxid-Pyrolyse)



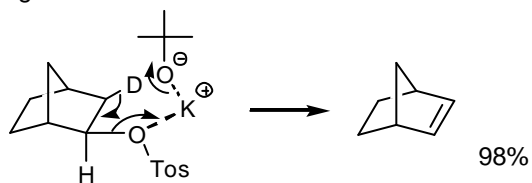
Selenoxid-Eliminierung



Ester-Pyrolyse

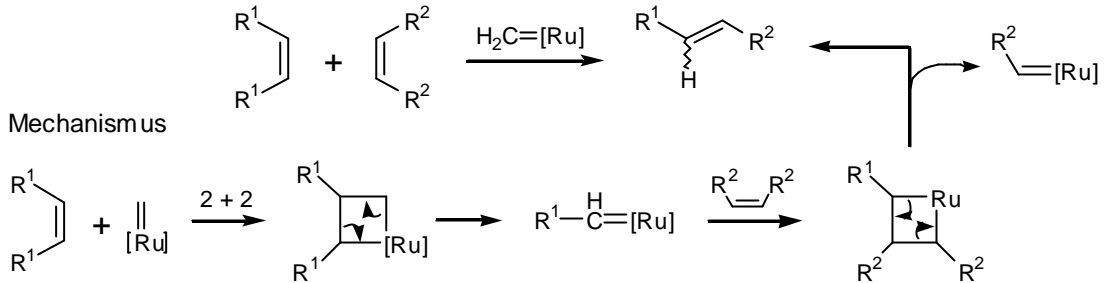


Syn-Eliminierung



1.2.4. Metathese von Olefinen

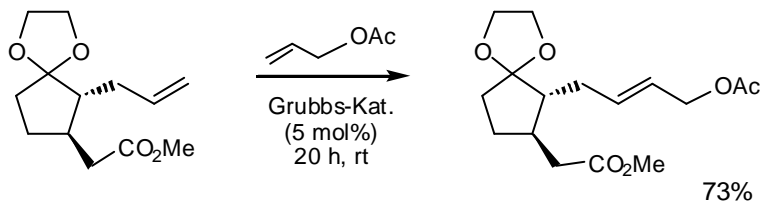
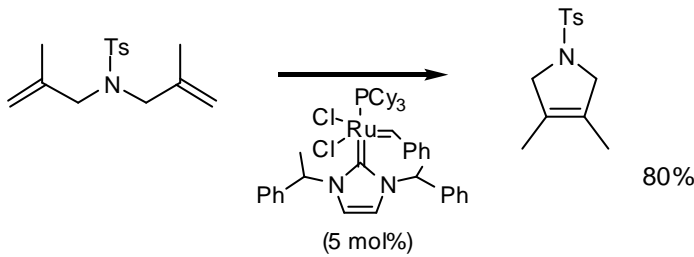
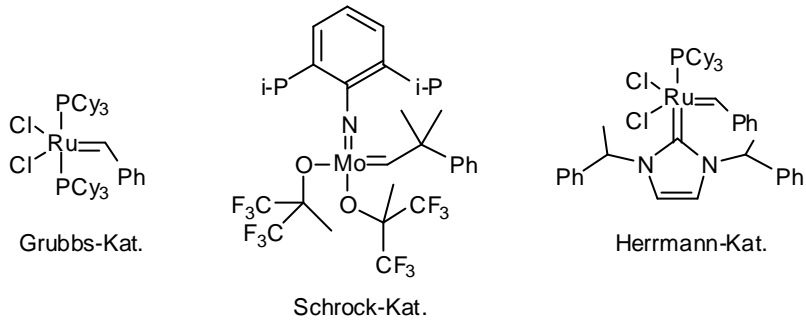
1990: Schrock, Grubbs



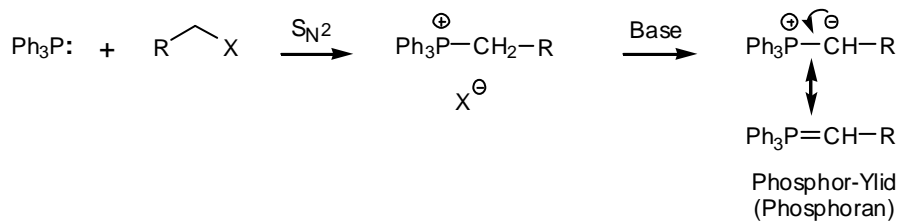
Beispiele:

Katalysatoren:

Übersicht:
Maier,
Angew. Chem.
Int. Ed.
2000, 39, 2073

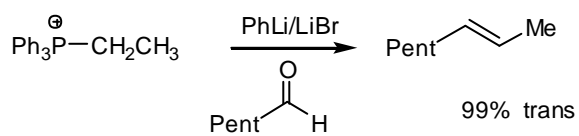
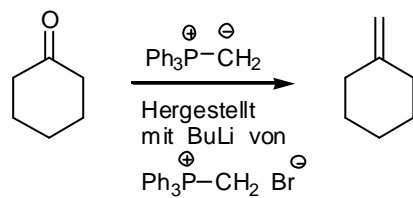
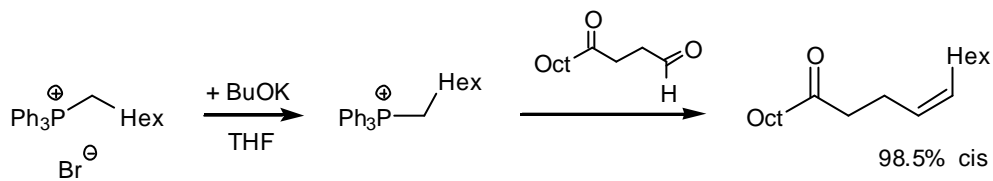
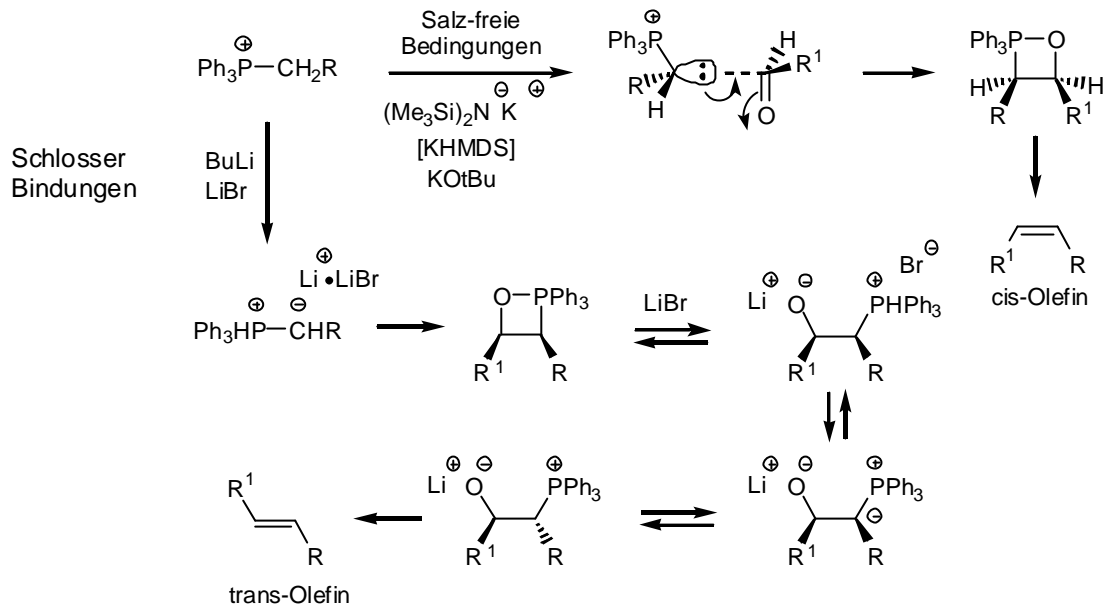


1.2.5. Wittig-Reaktion

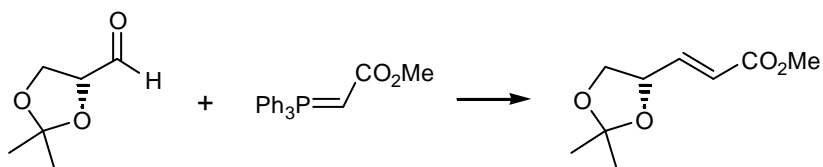


4. Gruppe: Alkene und Alkine

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



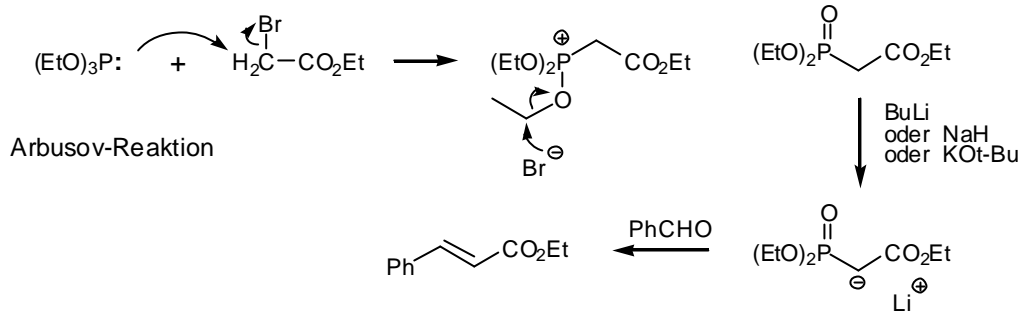
Stabilisierte Ylid geben die trans-Verbindung



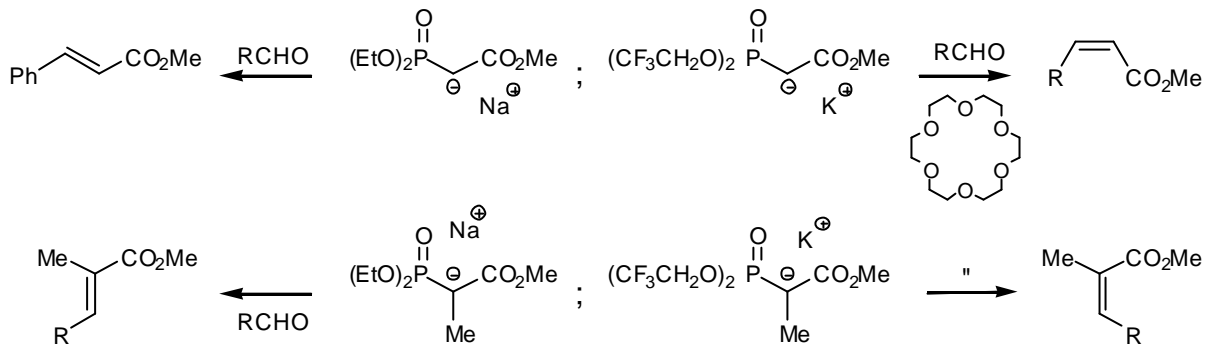
4. Gruppe: Alkene und Alkine

7

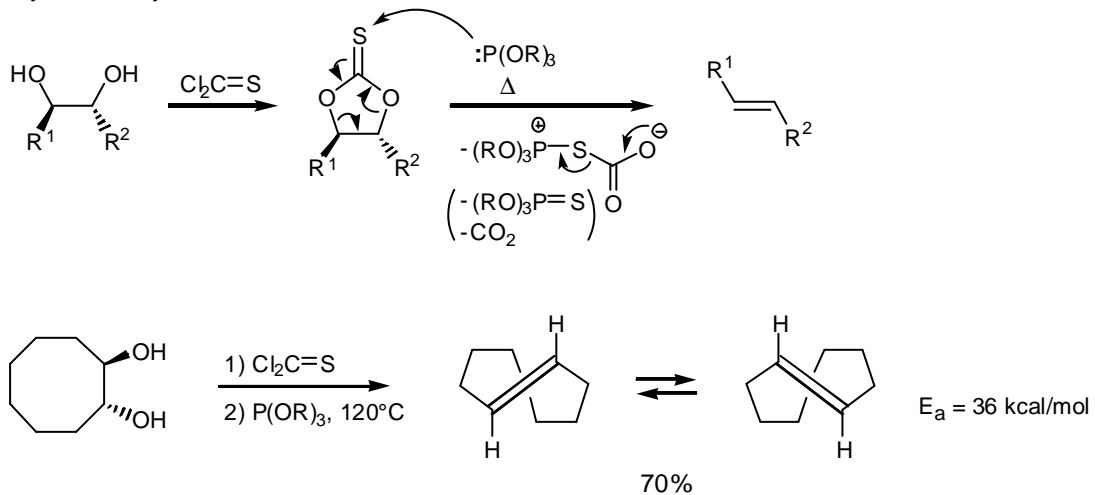
die Horner-Wadsworth-Emmons-Reaktion



Still-Gennari-Variante

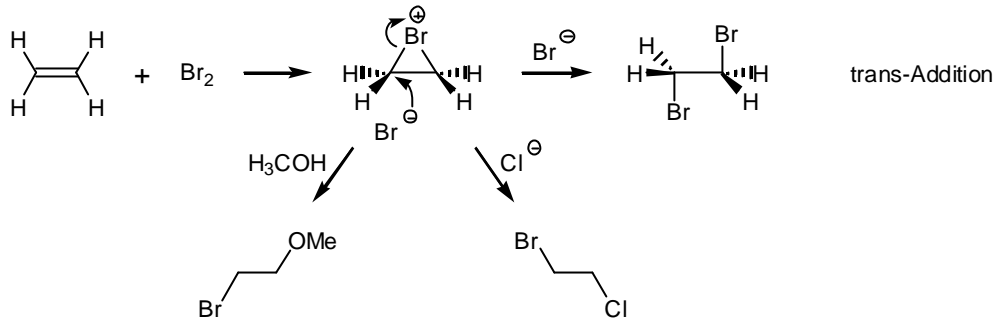


Corey-Winter-Synthese

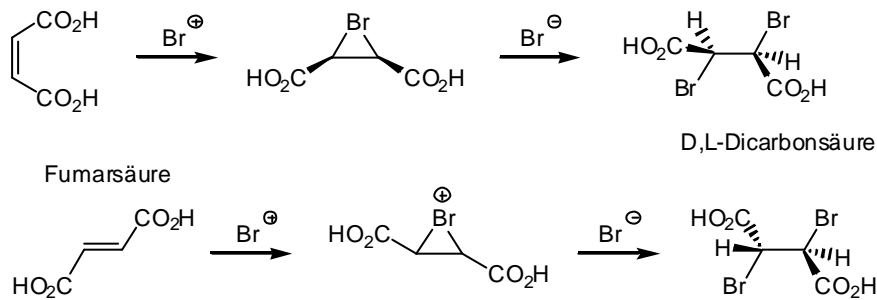


1.3. Reaktionen der Alkene

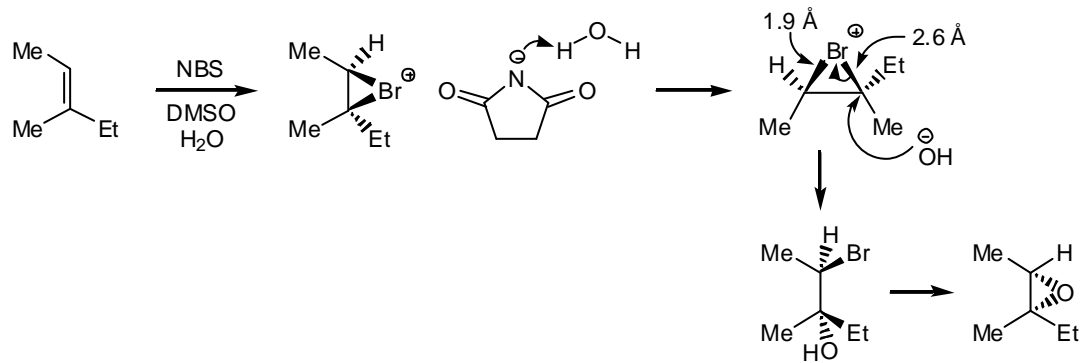
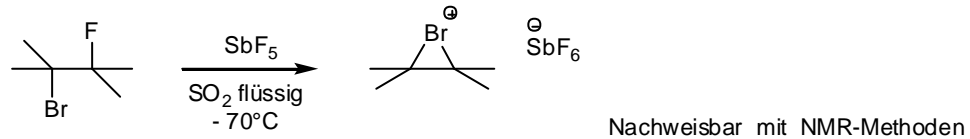
1.3.1. Halogen-Addition



Reaktion von Maleinsäure



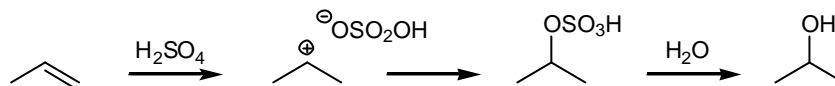
Nachweis der Zwischenstufe mit NMR



1.3.2. Addition von H-X

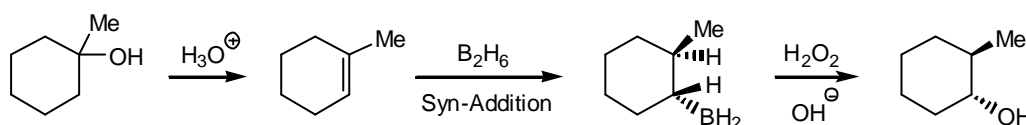
-ionische Addition: Markovnikov-Orientierung

-Radikal-Addition: anti-Markovnikov-Orientierung

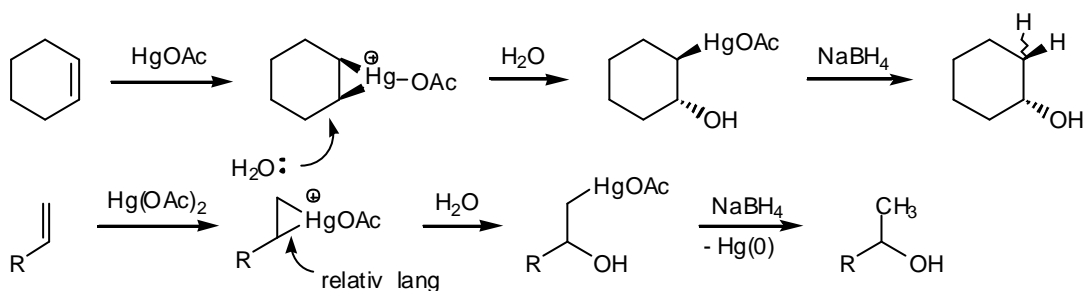


Reaktivität: HI > HBR > HCl

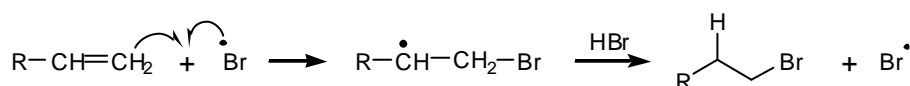
Addition von Wasser



Solvomercurierung von Olefinen

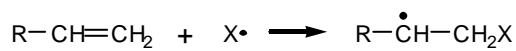


Radikale Reaktionen



Kettenreaktion (Anti-Markovnikov Selektivität)

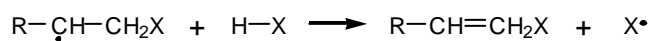
Nur HBr-Anlagerung ist radikalisch möglich



$$X = Cl \quad \Delta H = -30 \text{ kcal/mol} \checkmark$$

$$X = Br \quad \Delta H = -9 \text{ kcal/mol} \checkmark$$

$$X = I \quad \Delta H = +3 \text{ kcal/mol}$$



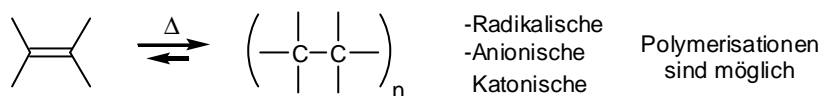
$$X = Cl \quad \Delta H = +9 \text{ kcal/mol}$$

$$X = Br \quad \Delta H = -7 \text{ kcal/mol} \checkmark$$

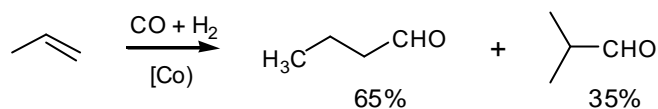
$$X = I \quad \Delta H = -23 \text{ kcal/mol} \checkmark$$

Beide Schlüsselschritte
der Kettenreaktion
sind exotherm

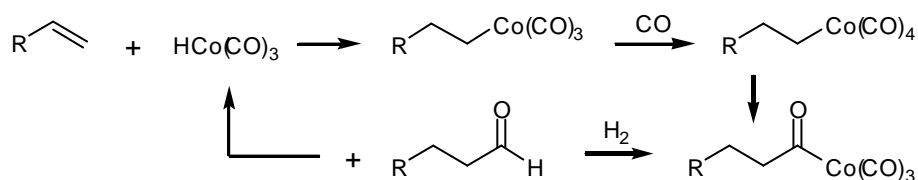
1.3.3. Polymerisation



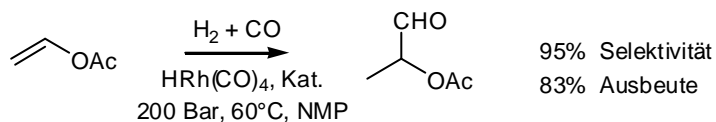
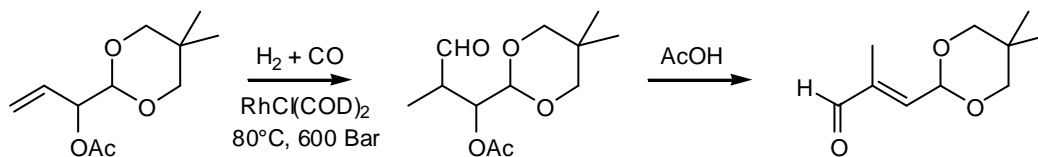
1.3.4. Oxo-Synthese (Hydroformylierungsreaktion)



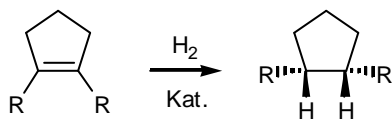
Kat: $[\text{Co}(\text{CO})_4]_2$



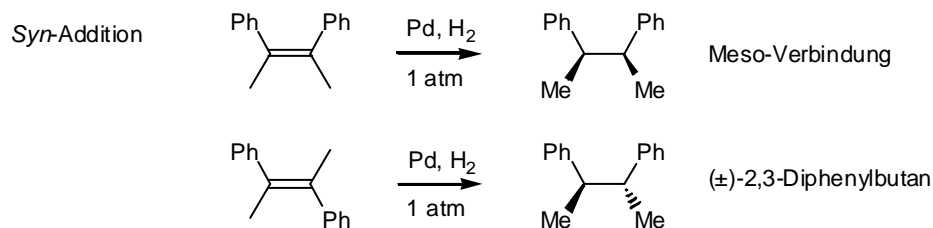
Moderne Hydroformylierung:



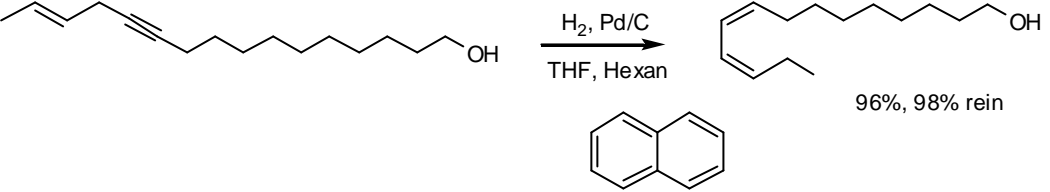
1.3.5. Katalytische Hydrierung



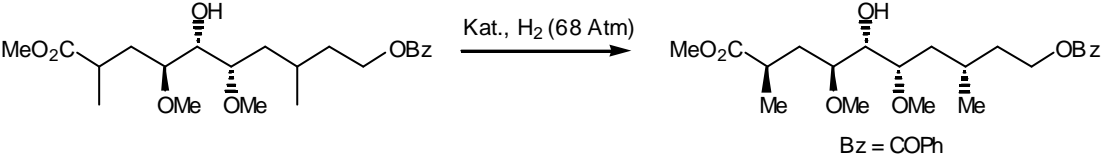
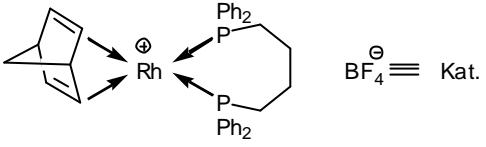
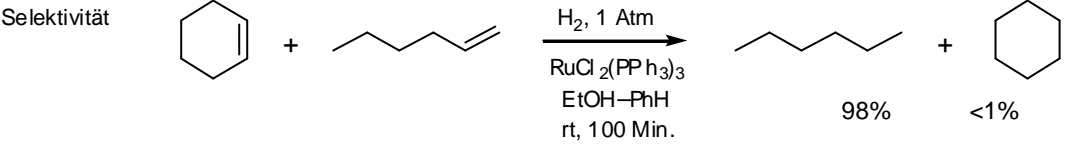
Heterogene Reduktion



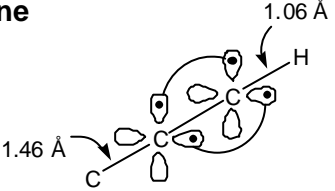
Lindlar-Reduktion von Alkyne



Homogene Katalyse



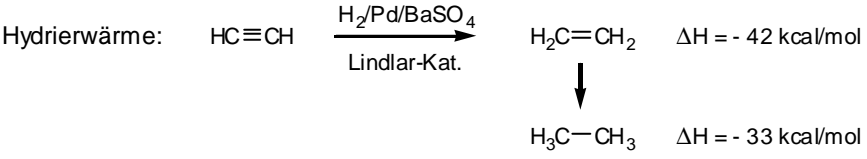
2) Alkine



2.1. Eigenschaften

Bindungsenergie:

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



≡C-H ← acide C-H Bindung

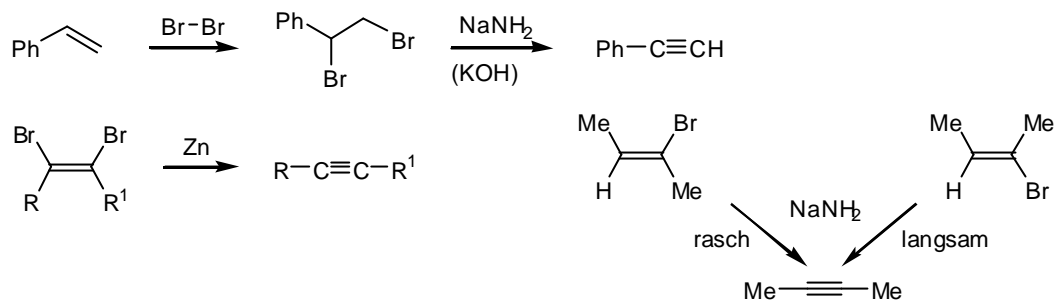
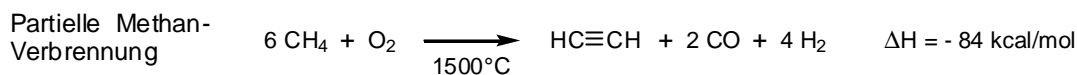
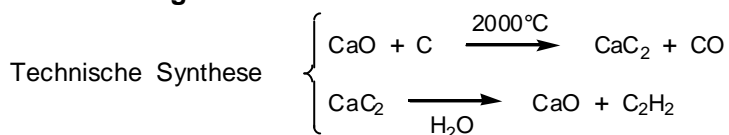
	pKa
H ₃ C-CH ₃	60
H ₂ C=CH ₂	> 46
HC≡CH	25

Acetylen ist eine endotherme Verbindung:

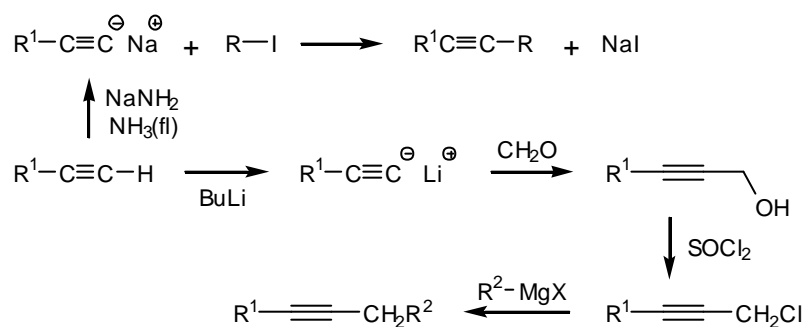
C + H ₂	→	HC≡CH	54
C + 2H ₂	→	H ₂ C=CH ₂	12
C + 3H ₂	→	H ₃ C-CH ₃	-20

ΔH_f (kcal/mol)

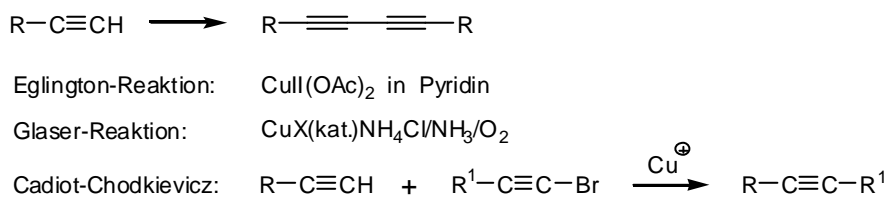
2.2. Darstellung



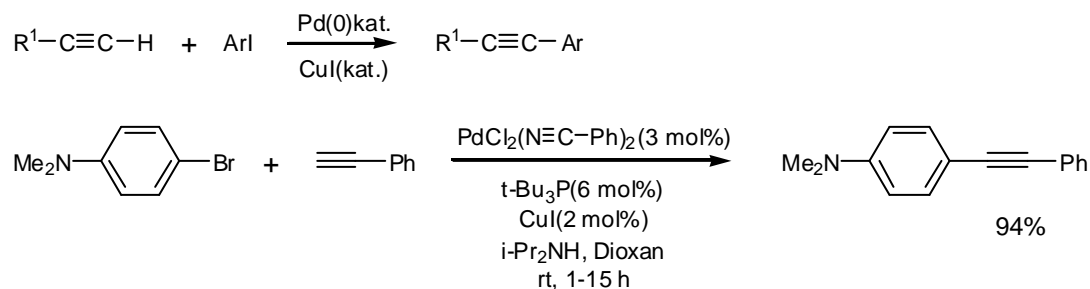
Alkylierung des Acetylid-Anions



Oxidative Kupplung

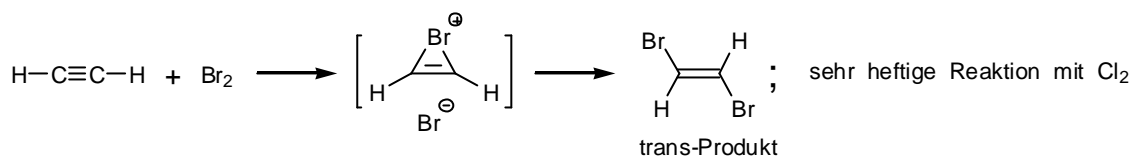


Sonogashira-Kreuzkupplung

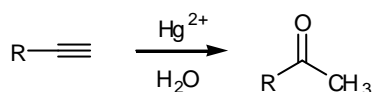
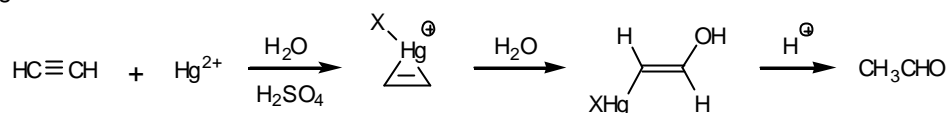


2.3. Darstellung

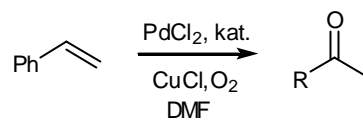
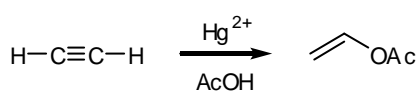
2.3.1 Elektrophile Additionen



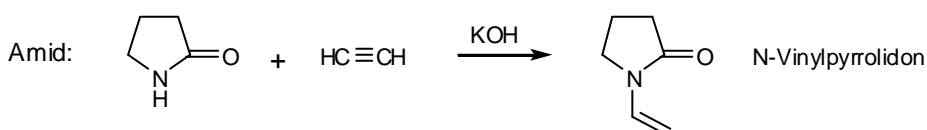
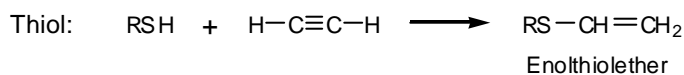
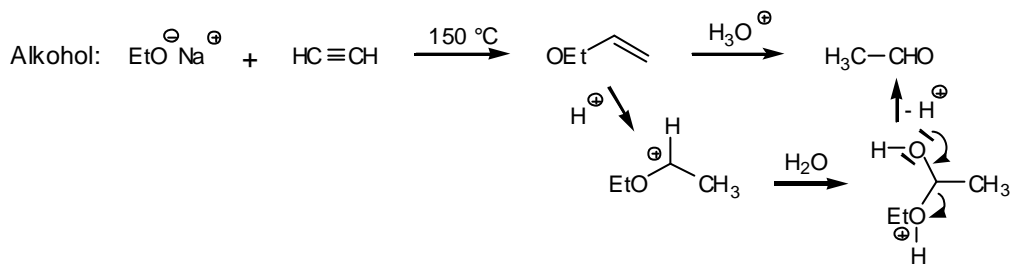
Elektrophile Addition an Alkine sind langsamer als an Alkene



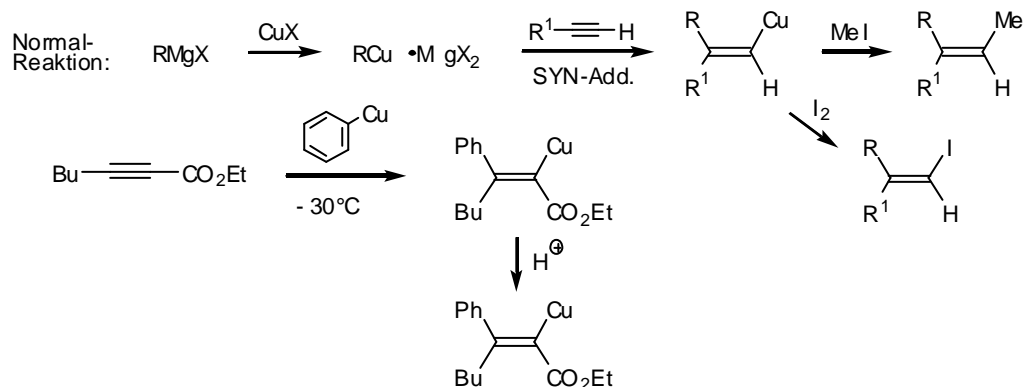
Vgl. mit der Wacker-Reaktion:



2.3.2 Nucleophile Addition (an Alkyne sind leichter als bei Olefinen)

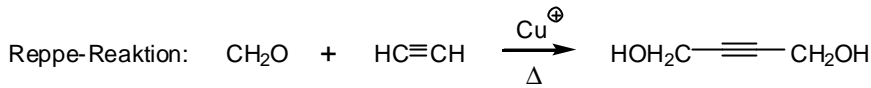
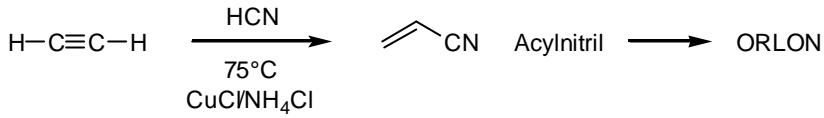
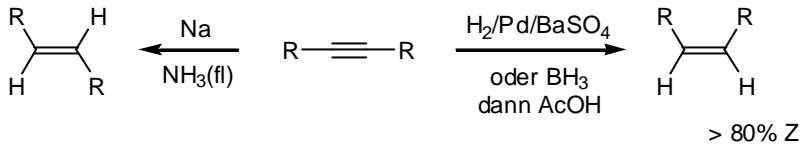


Metallorganische Reagenzien:



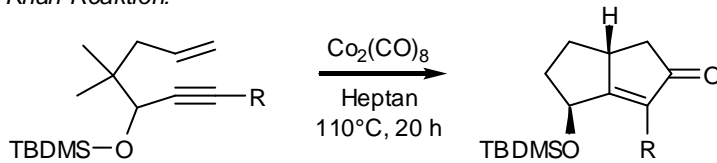
4. Gruppe: Alkene und Alkine

Selektive Reduktion

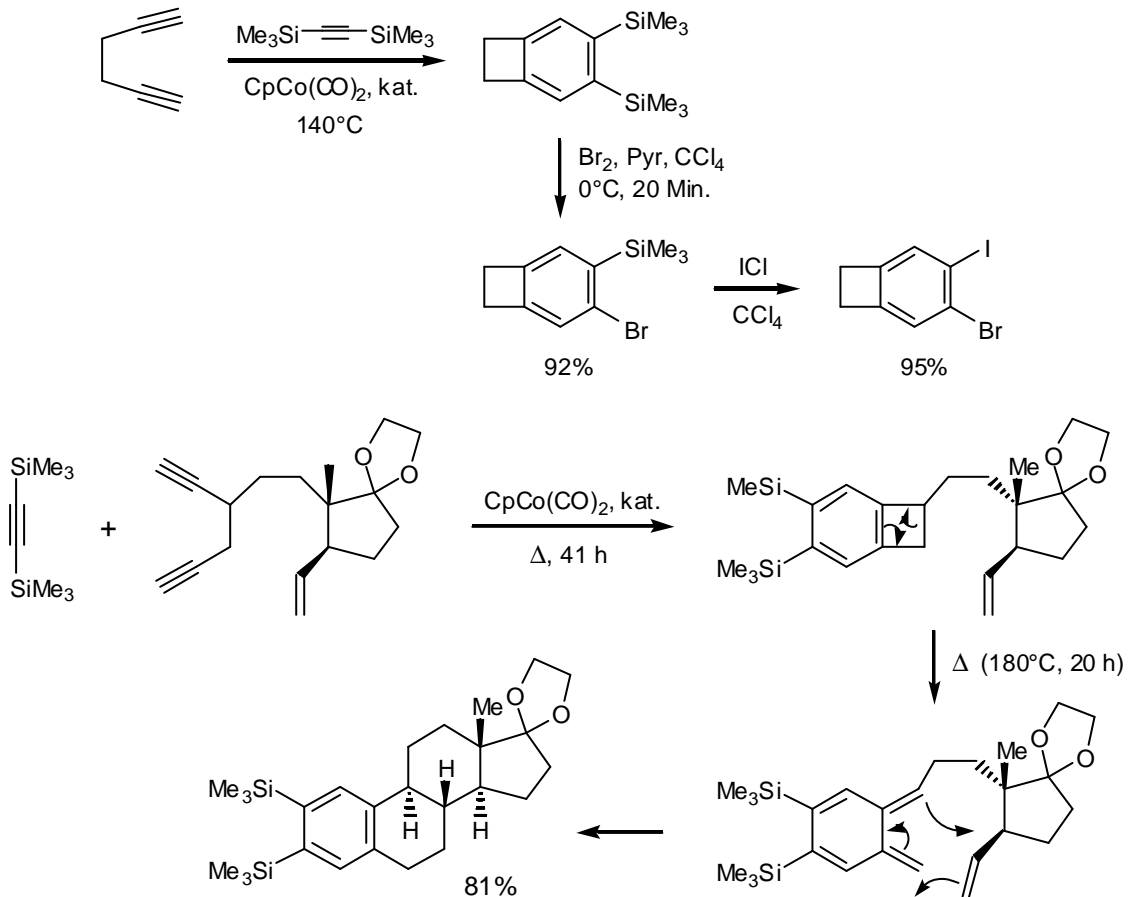


Oligomerisierung von Alkyne

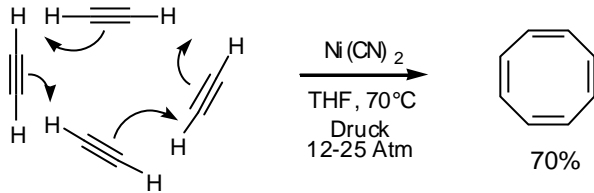
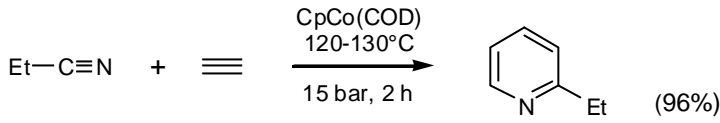
Pauson-Khan-Reaktion:



Repe-Vollhardt-Reaktion:

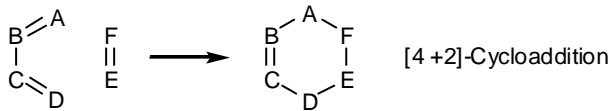
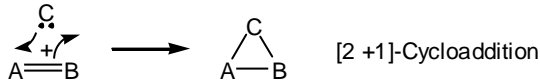


4. Gruppe: Alkene und Alkine

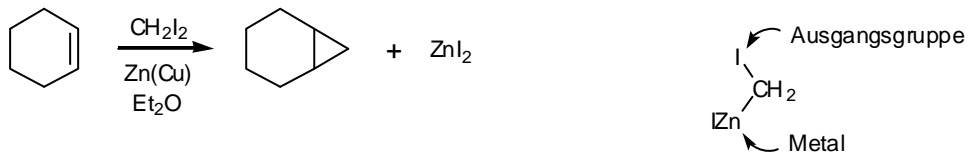
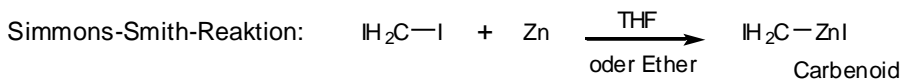
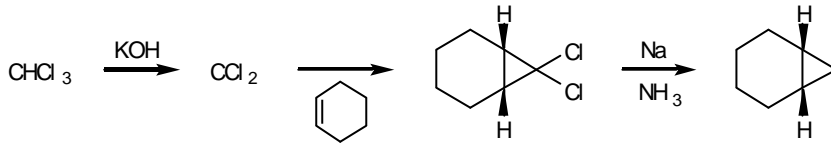


3) Cycloaddition der Alkene und der Alkine

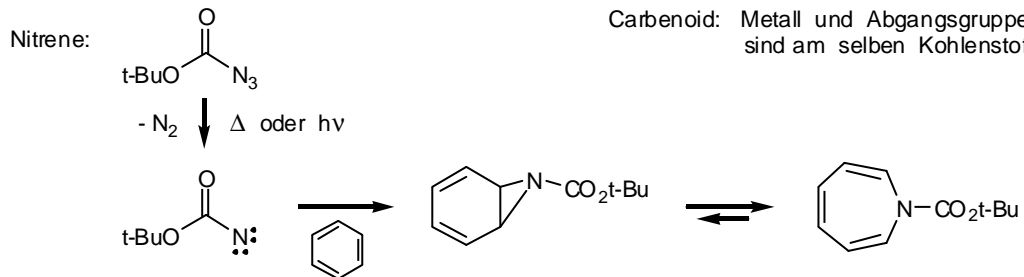
Definition: Zahl der an der Ringbildung beteiligten Atome



3.1. [2 + 4]-Cycloadditionen

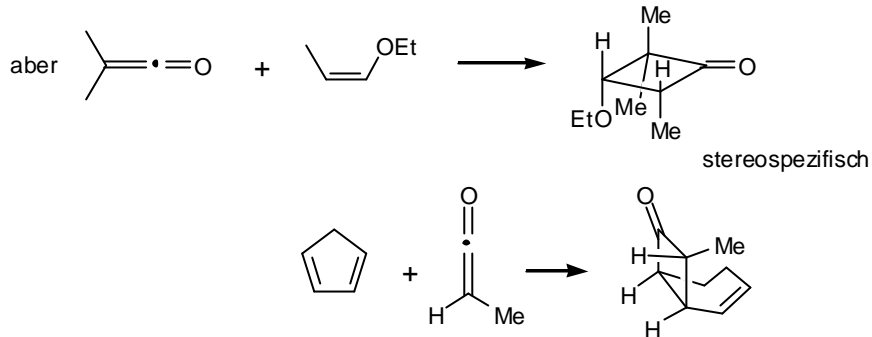


Carbenoid: Metall und Abgangsgruppe sind am selben Kohlenstoff

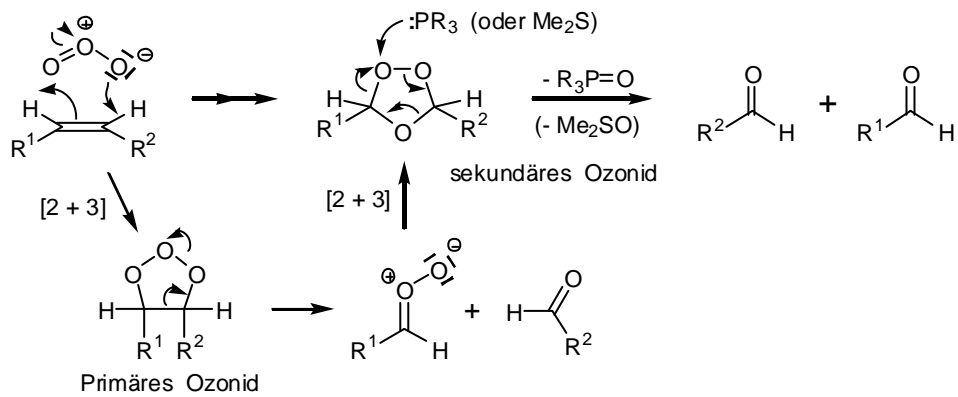
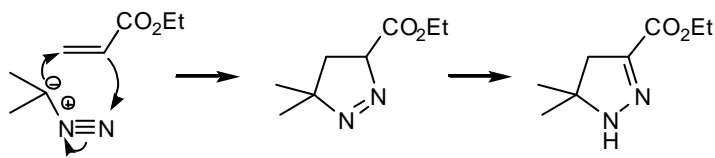
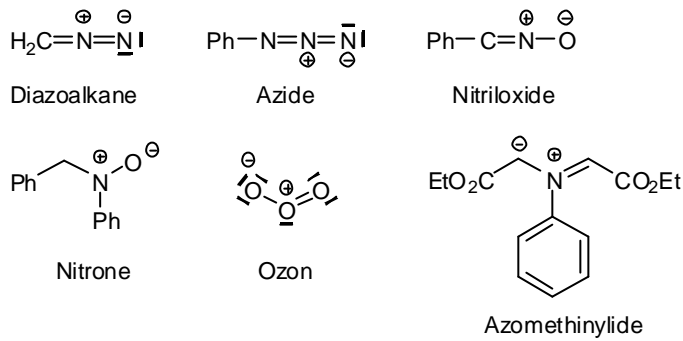


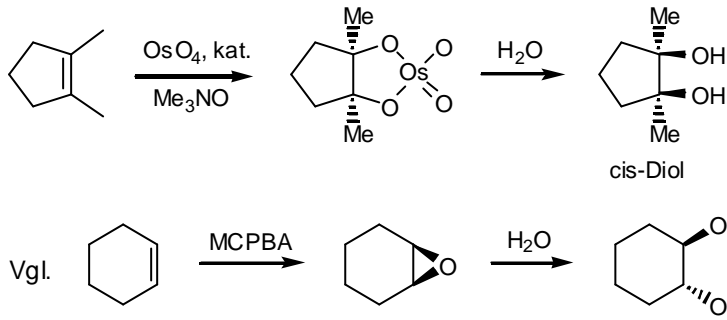
3.2. [2 + 2]-Cycloadditionen

in der Regel zweistufig meist nicht stereospezifisch



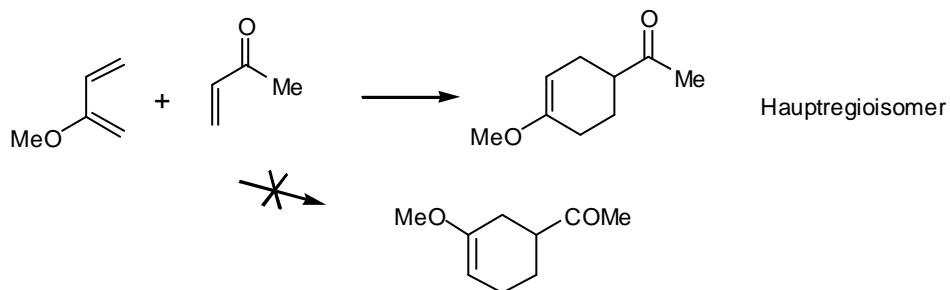
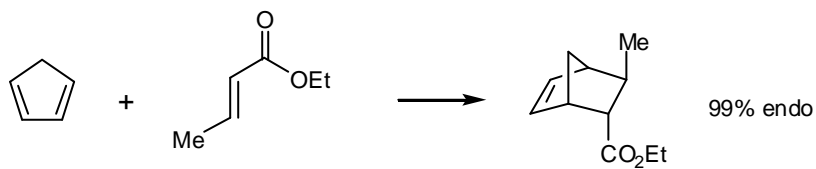
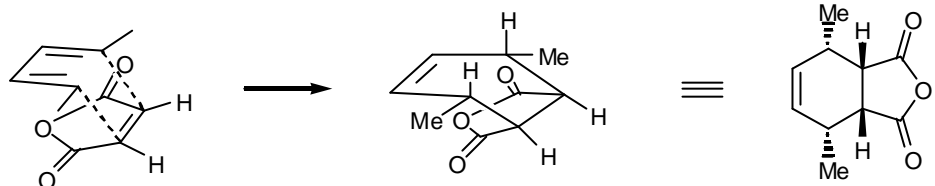
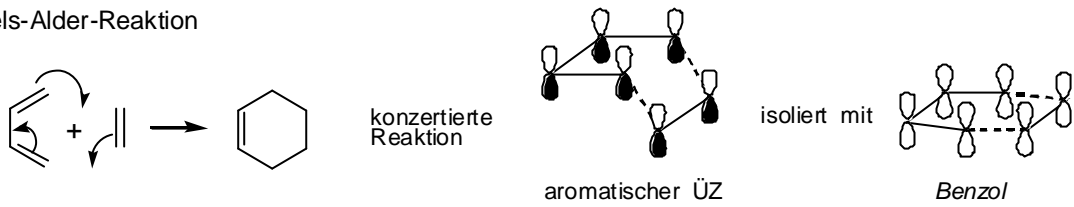
(3+2)-Cycloaddition: 1,3-Dipolare Cycloadditionen





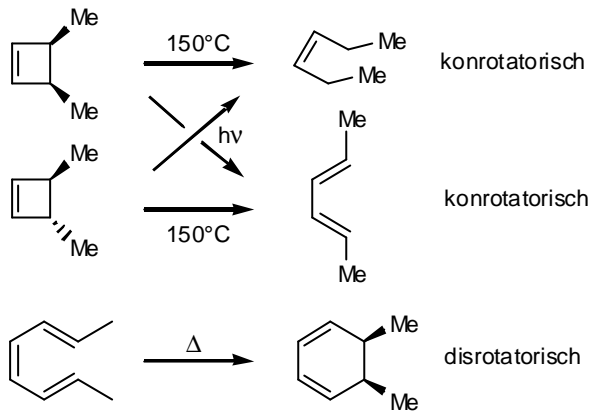
3.4. [4 + 2]-Cycloadditionen

Diels-Alder-Reaktion



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

4) Erhaltung der Orbitalsymmetrie



Woodward-Hoffmann Regeln

Aromatischer ÜZ ist erlaubt

Antiaromatische ÜZ sind verboten

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

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

