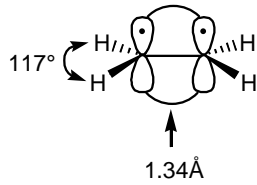


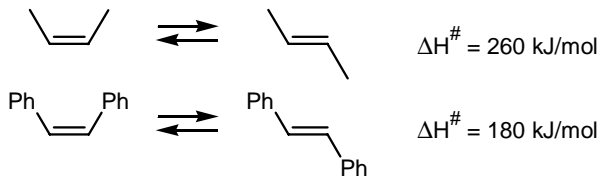
## 1) Alkene

### 1.1. Struktur und Isomerie der Alkene



C—C : 350 kJ/mol  
 C=C : 350 + 265 = 615 kJ/mol  
 Doppelbindungs-Anteil

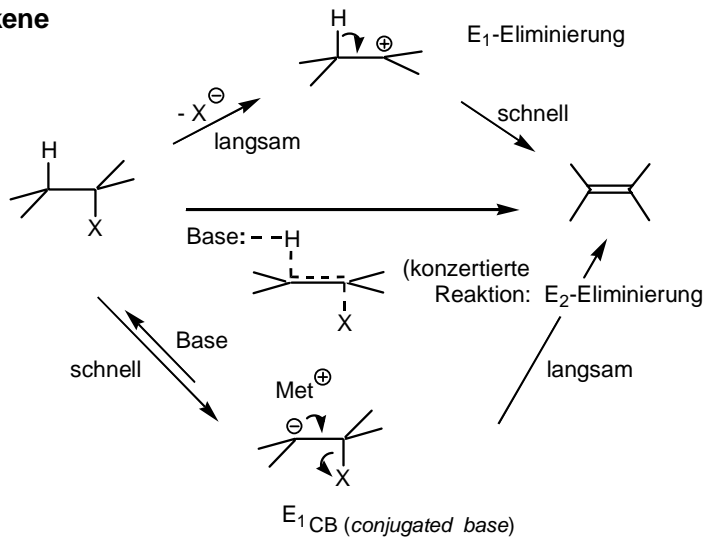
Isomerie



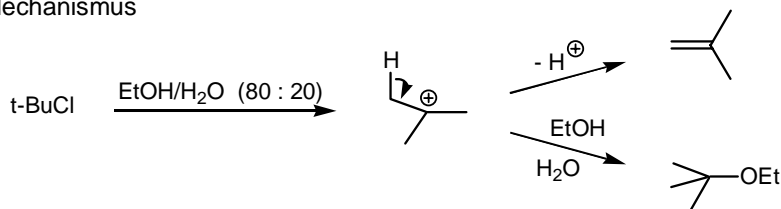
Saytzeff-Regel: Substituierte Doppelbindungen sind stabiler als endständige Doppelbindungen (Hyperkonjugation).

### 1.2. Darstellung der Alkene

#### 1.2.1. Mechanismen der Eliminierung von H-X

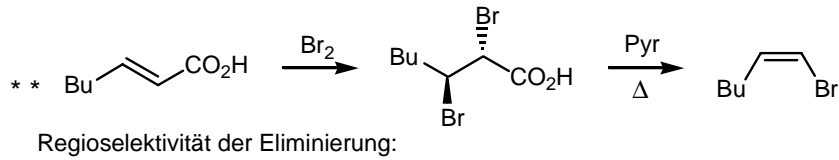
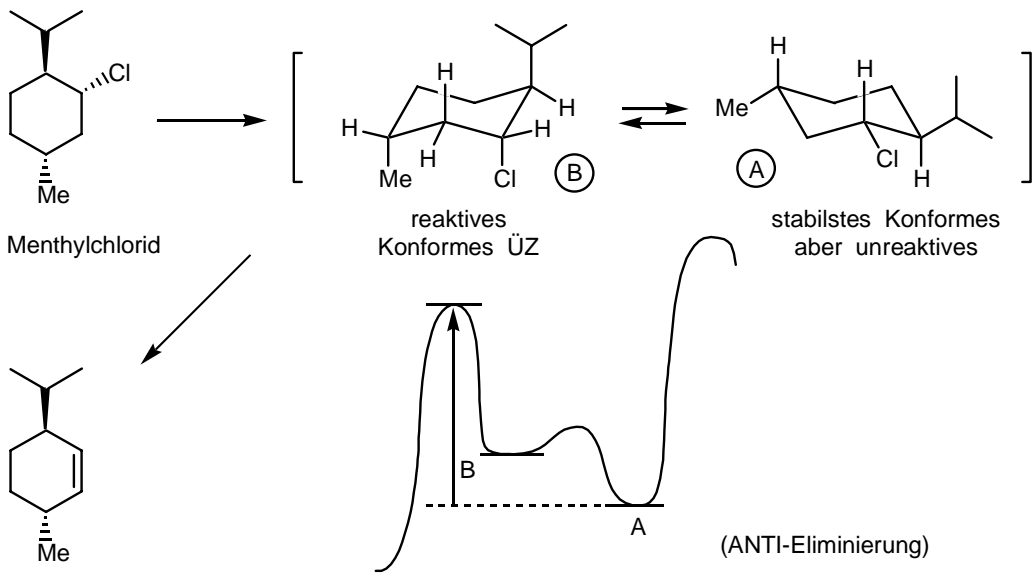
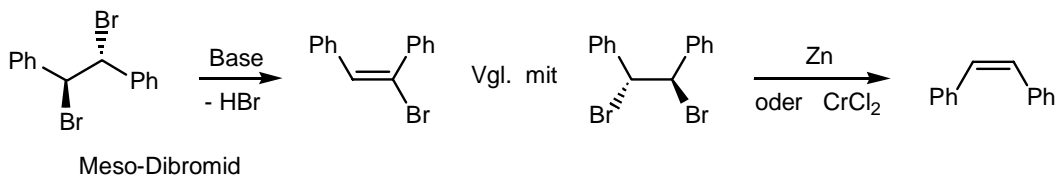
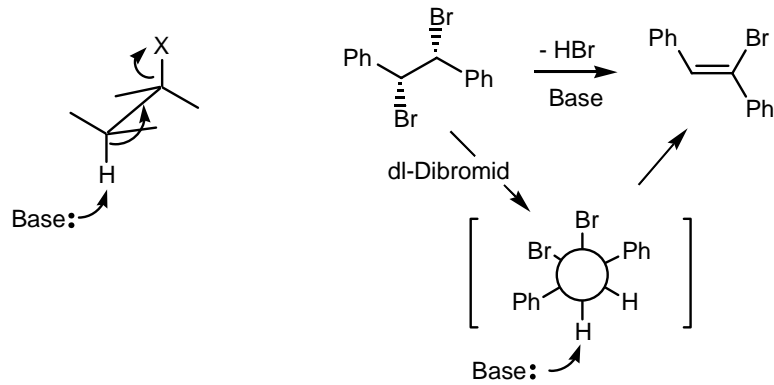


E<sub>1</sub>-Mechanismus



# 4. Gruppe: Alkene und Alkine

E<sub>2</sub>: Anti-Eliminierung

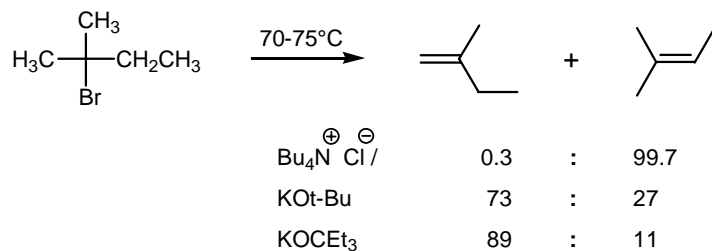


			Hofmann	Saytzeff
1875	$\text{H}_3\text{CH}_2\text{C}-\underset{\text{X}}{\overset{\text{H}}{\text{C}}}-\text{CH}_3$	$\xrightarrow[\text{EtOH}]{\text{KOAc}}$	$\text{H}_3\text{CH}_2\text{C}-\underset{\text{H}}{\text{C}}=\text{CH}_2$	$\text{H}_3\text{C}-\underset{\text{H}}{\text{C}}=\underset{\text{H}}{\text{C}}-\text{CH}_3$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

## 4. Gruppe: Alkene und Alkine

3

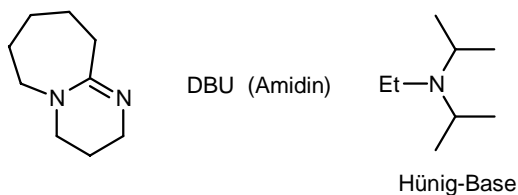
Base Stärke:



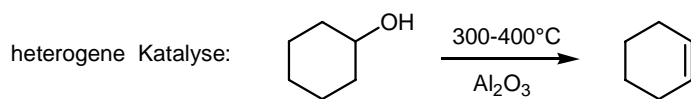
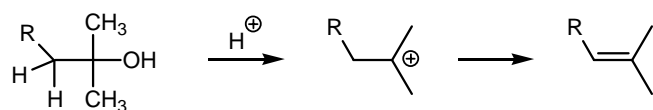
Elimin./Subst.

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

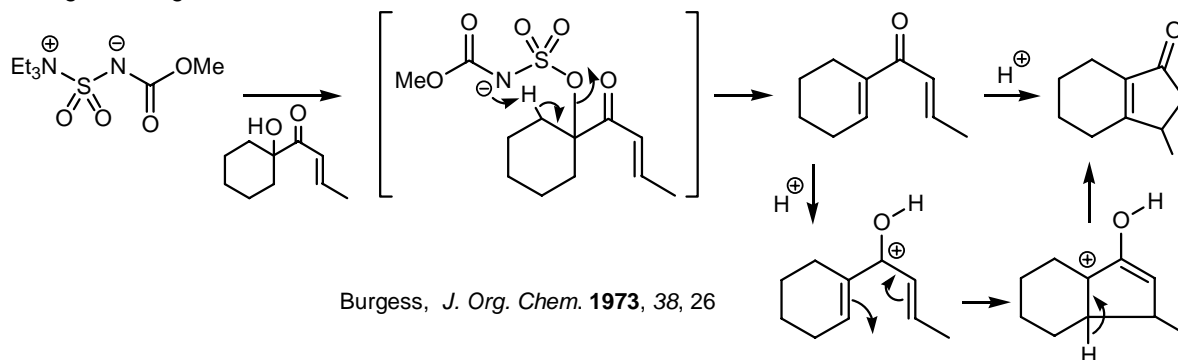
Base für Eliminierungen:



### 1.2.2. Dehydratisierung von Alkohole

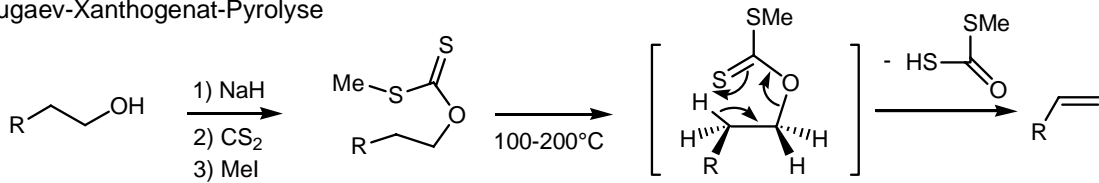


Burgess-Reagenz

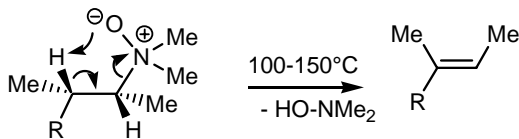


1.2.3. Syn-Eliminierung

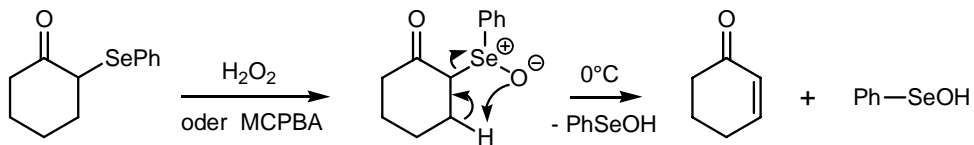
Chugaev-Xanthogenat-Pyrolyse



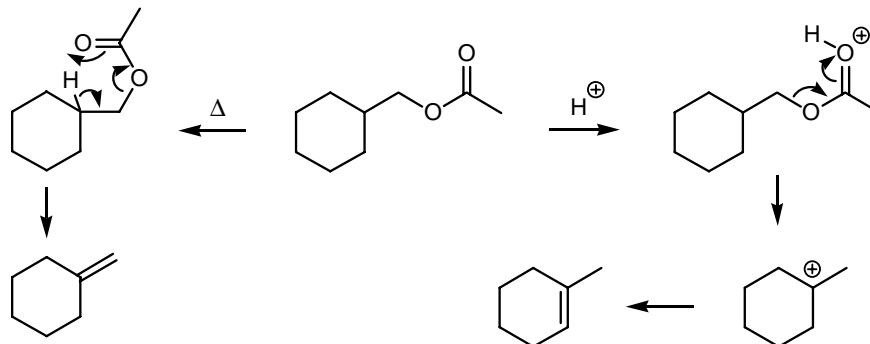
Cope-Eliminierung (Aminoxid-Pyrolyse)



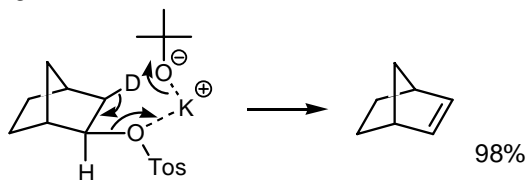
Selenoxid-Eliminierung



Ester-Pyrolyse

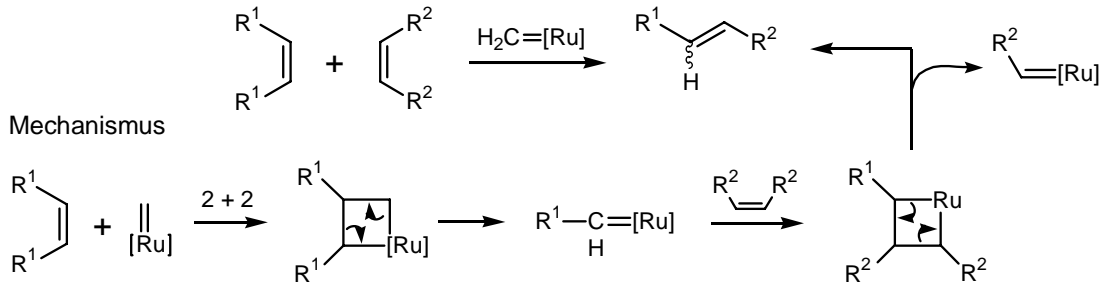


Syn-Eliminierung



1.2.4. Metathese von Olefinen

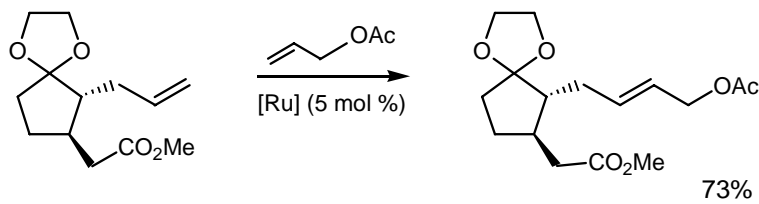
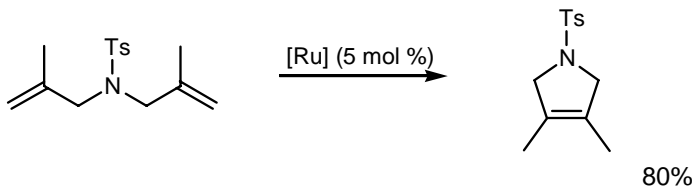
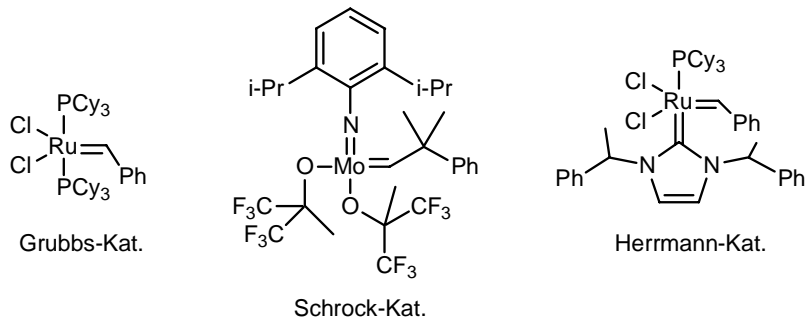
1990: Schrock, Grubbs



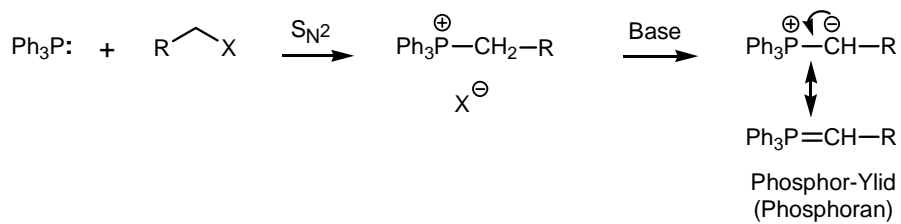
Beispiele:

Katalysatoren:

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



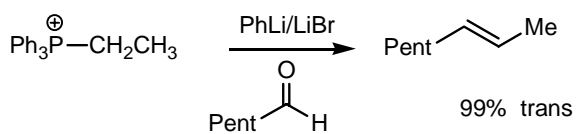
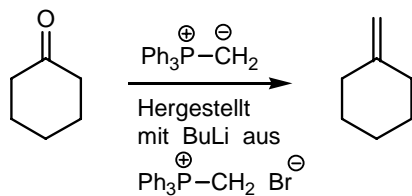
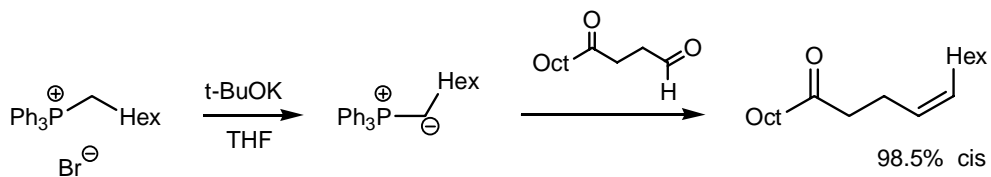
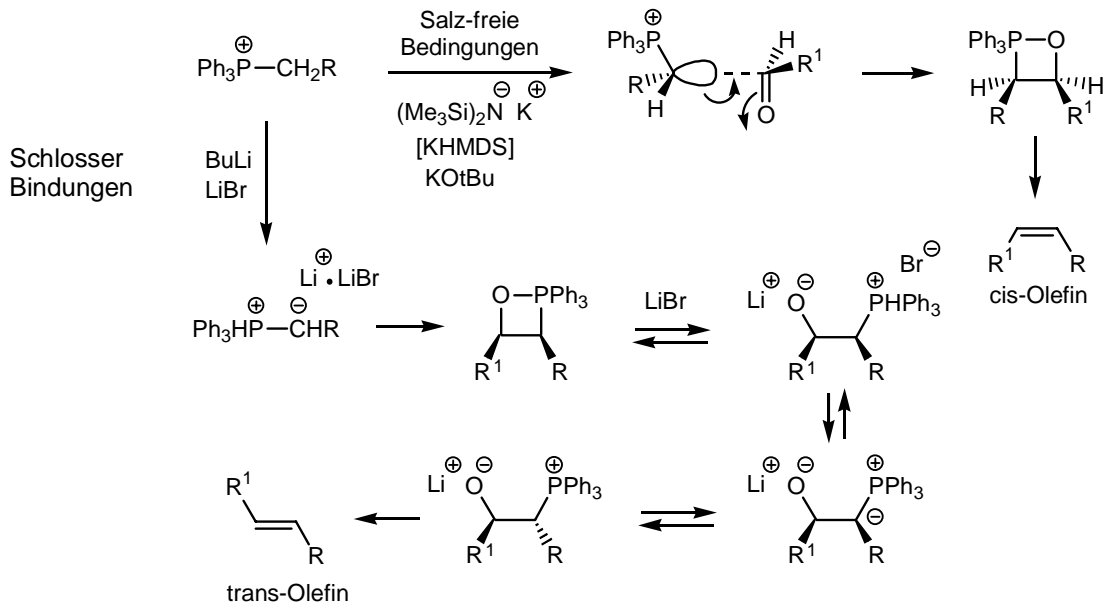
1.2.5. Wittig-Reaktion



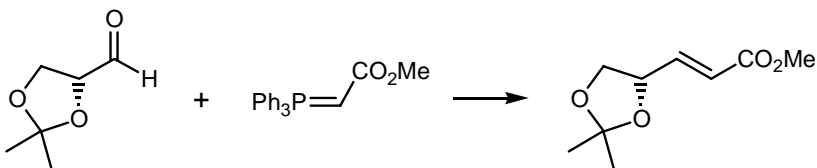
## 4. Gruppe: Alkene und Alkine

6

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



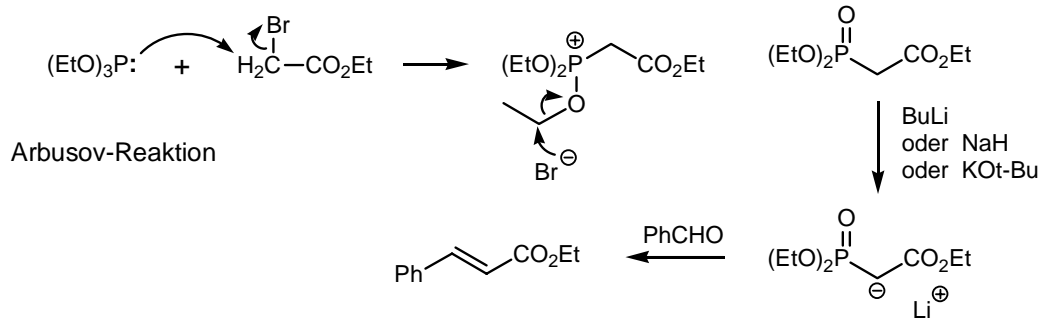
Stabilisierte Ylide geben die trans-Verbindung



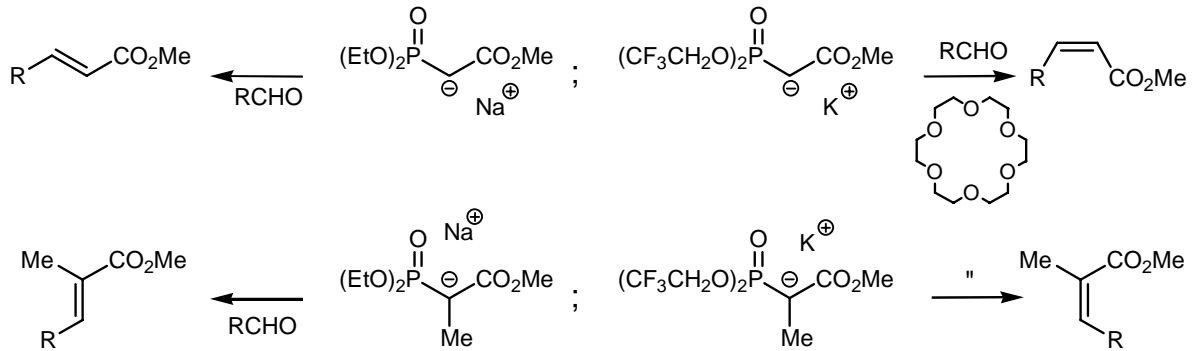
# 4. Gruppe: Alkene und Alkine

7

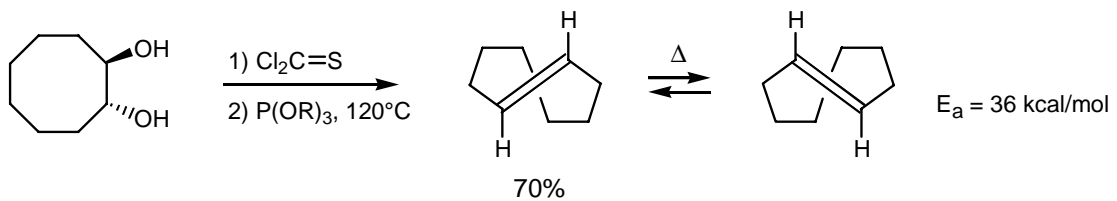
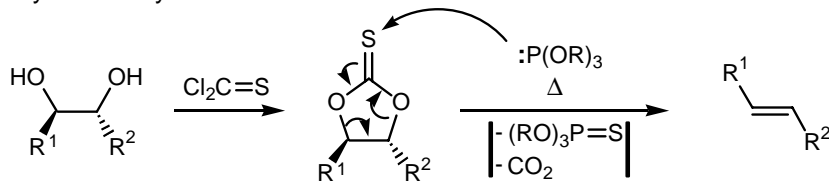
die Horner-Wadsworth-Emmons-Reaktion



Still-Gennari-Variante

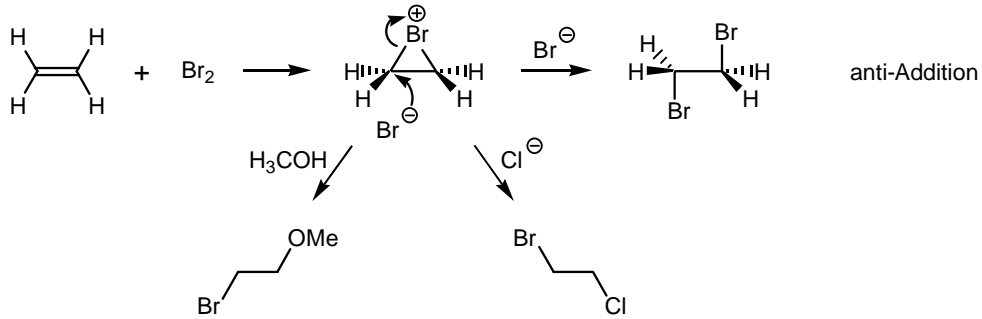


Corey-Winter-Synthese

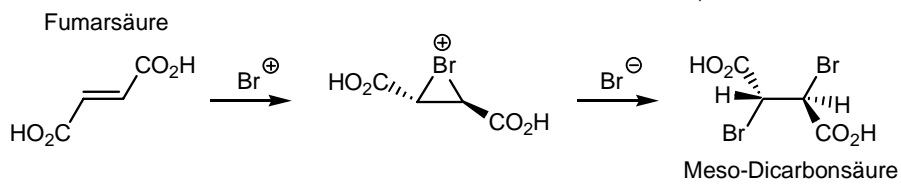
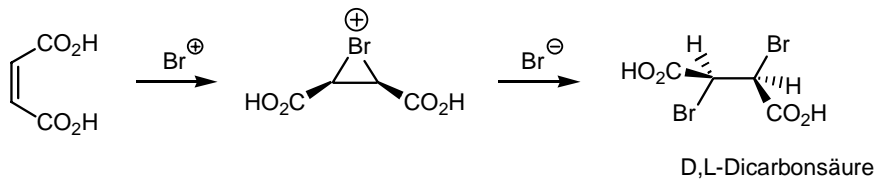


1.3. Reaktionen der Alkene

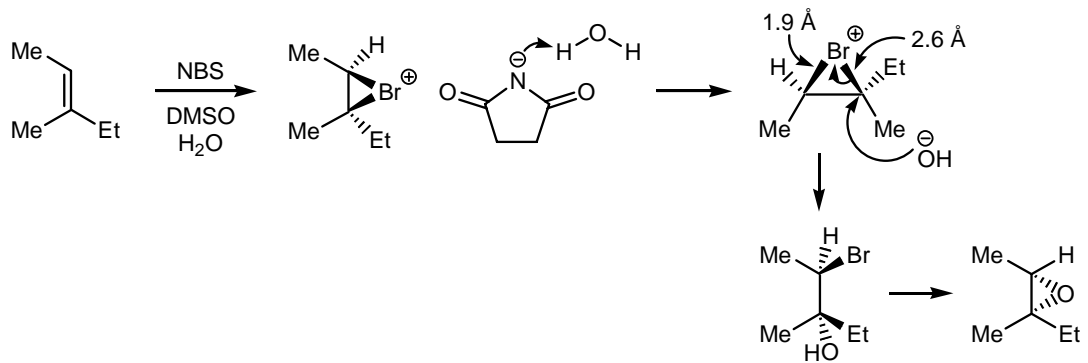
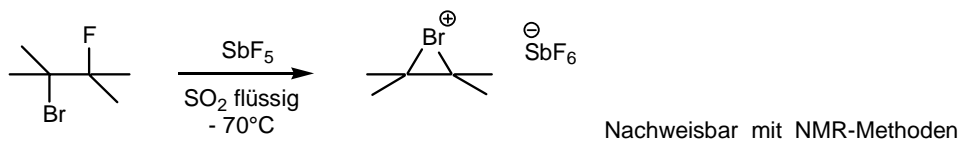
1.3.1. Halogen-Addition



Reaktion von Maleinsäure



Nachweis der Zwischenstufe mit NMR

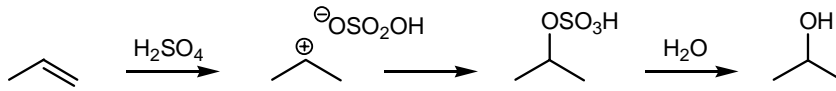




1.3.2. Addition von H-X

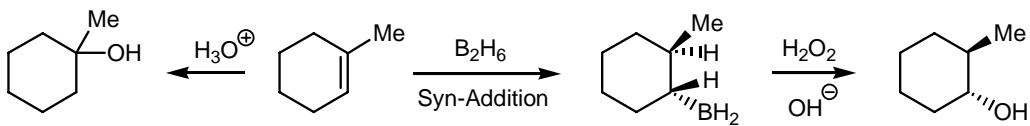
-ionische Addition: Markovnikov-Orientierung

-Radikal-Addition: anti-Markovnikov-Orientierung

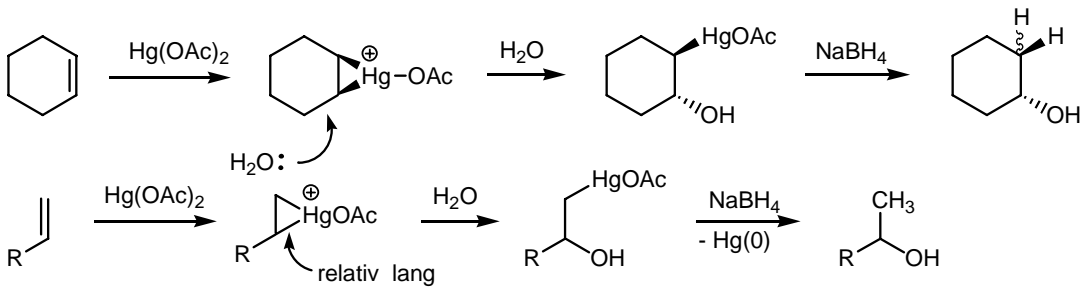


Reaktivität:  $\text{HI} > \text{HBr} > \text{HCl}$

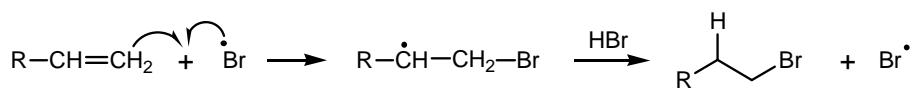
Addition von Wasser



Solvomercurierung von Olefinen

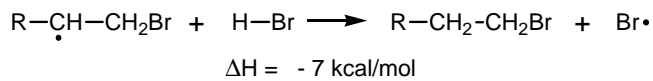
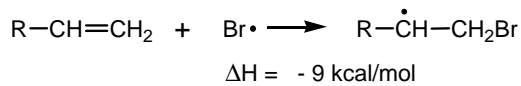


Radikal Reaktionen

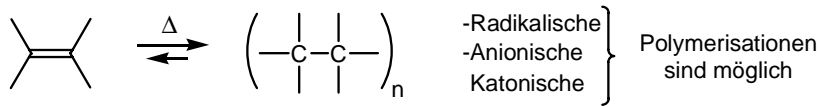


Kettenreaktion (Anti-Markovnikov Selektivität)

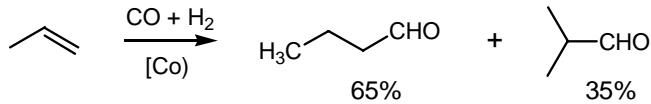
Nur HBr-Anlagerung ist radikalisch möglich



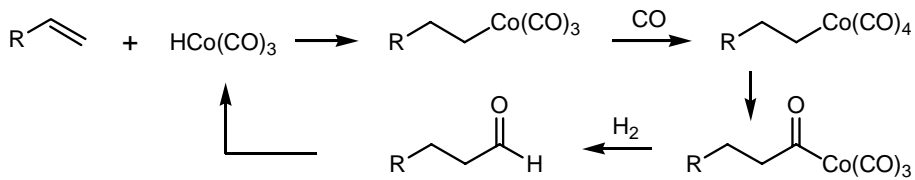
1.3.3. Polymerisation



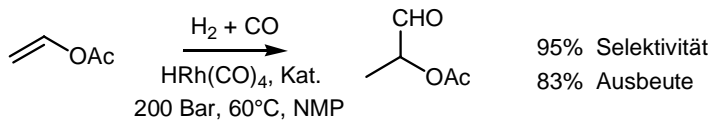
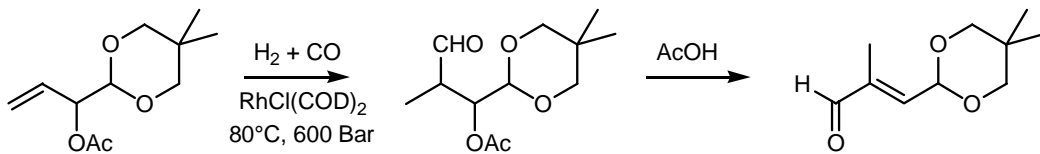
1.3.4. Oxo-Synthese (Hydroformylierungsreaktion)



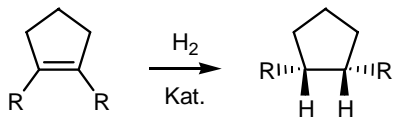
Kat:  $[\text{Co}(\text{CO})_4]_2$



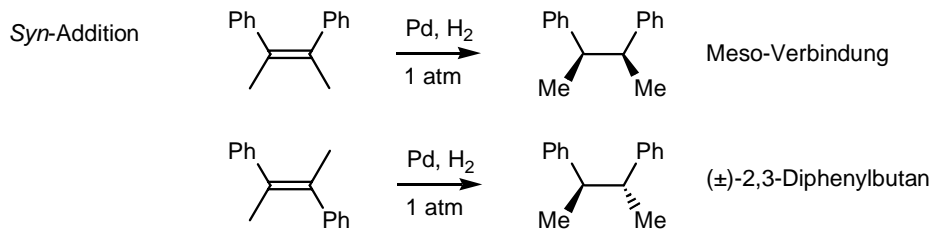
Moderne Hydroformylierung:



1.3.5. Katalytische Hydrierung

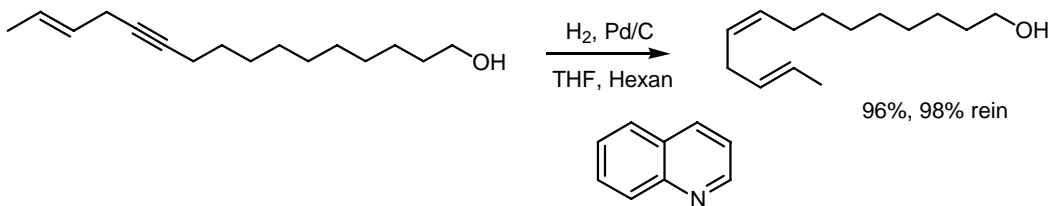


Heterogene Reduktion

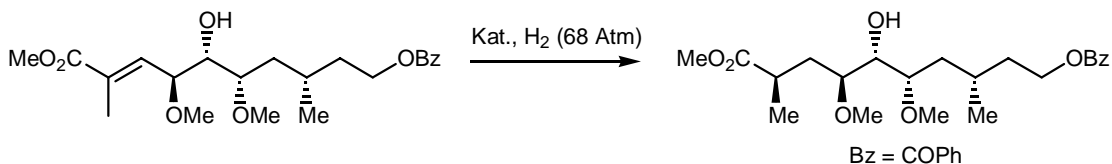
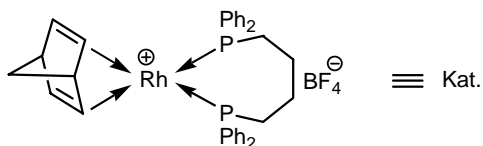
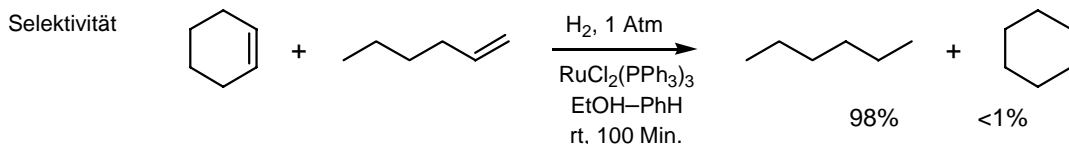


# 4. Gruppe: Alkene und Alkine

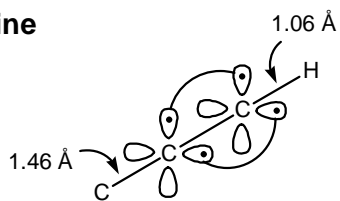
Lindlar-Reduktion von Alkine



Homogene Katalyse

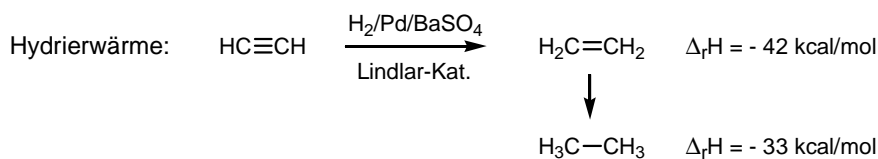


## 2) Alkine



### 2.1. Eigenschaften

Bindungsenergie:	C—C	C=C	C≡C	
	83	146	200	kcal/mol
			83	
			63	
			54	



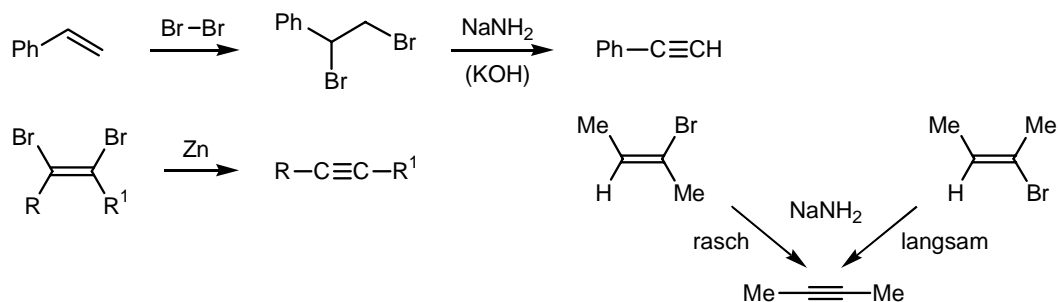
$\equiv\text{C}-\text{H} \leftarrow$  acide C—H Bindung

	pKa
$\text{H}_3\text{C}-\text{CH}_3$	60
$\text{H}_2\text{C}=\text{CH}_2$	> 46
$\text{HC}\equiv\text{CH}$	25

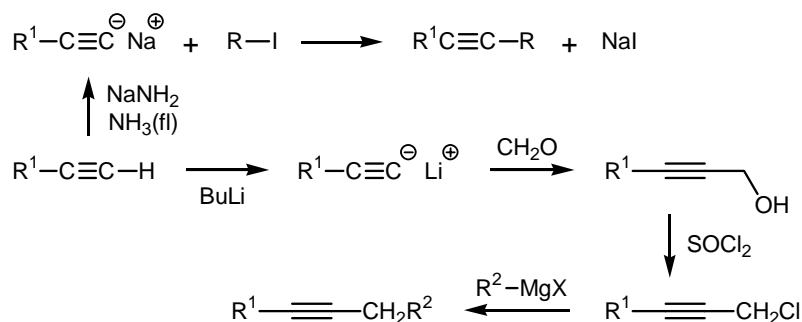
Acetylen ist eine besonders endotherme Verbindung:

	$\Delta_f H$ (kcal/mol)
$\text{C} + \text{H}_2 \longrightarrow \text{HC}\equiv\text{CH}$	54
$\text{C} + 2\text{H}_2 \longrightarrow \text{H}_2\text{C}=\text{CH}_2$	12
$\text{C} + 3\text{H}_2 \longrightarrow \text{H}_3\text{C}-\text{CH}_3$	-20

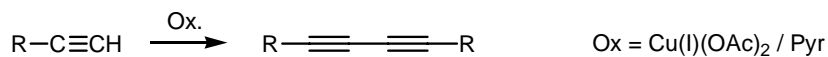
## 2.2. Darstellung



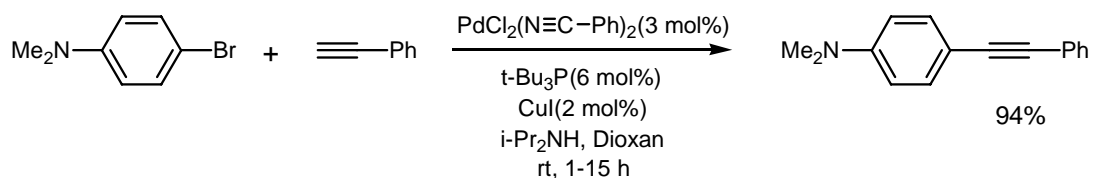
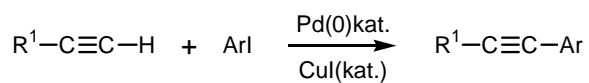
## Alkylierung des Acetylid-Anions



## Oxidative Kupplung

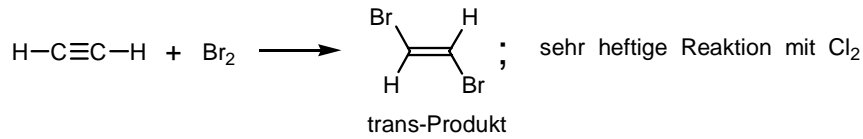


## Sonogashira-Kreuzkupplung

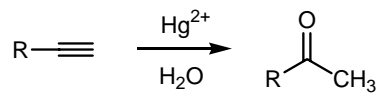
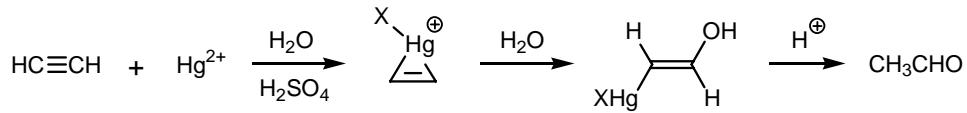


2.3. Darstellung

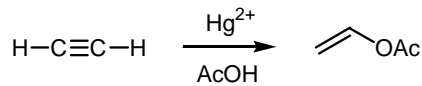
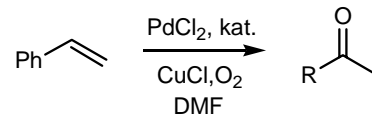
2.3.1 Elektrophile Additionen



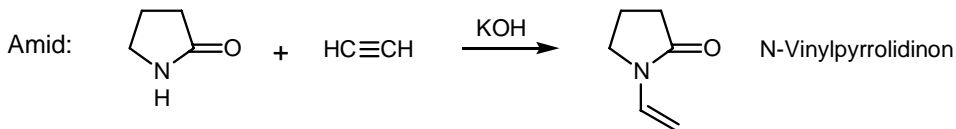
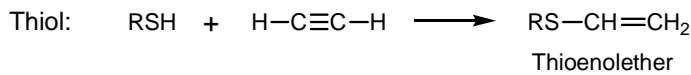
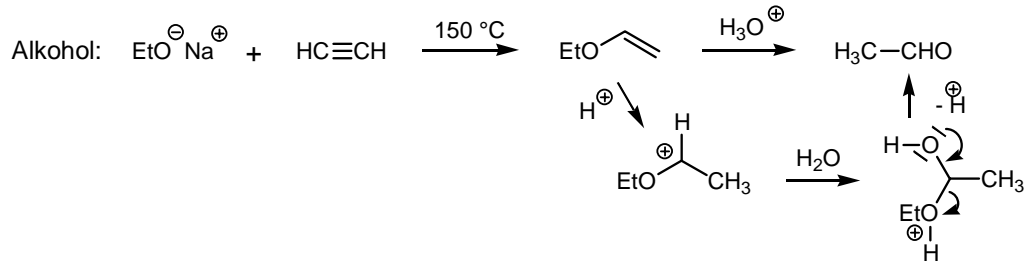
Elektrophile Addition von Halogenen an Alkine ist langsamer als an Alkene



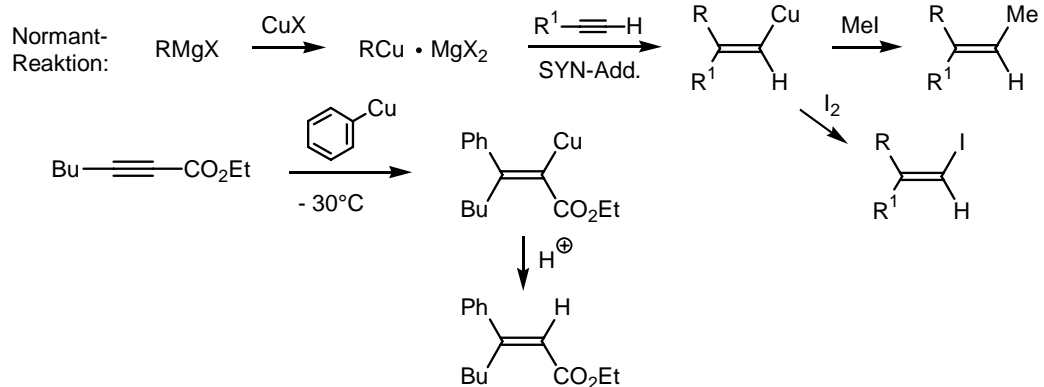
Vgl. mit der Wacker-Reaktion:



2.3.2 Nucleophile Addition (Alkine addieren Nucleophile leichter als Olefine)

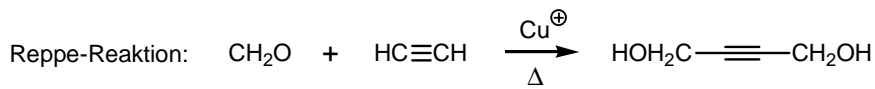
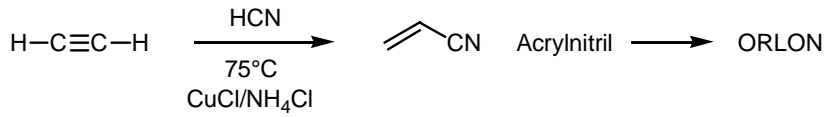
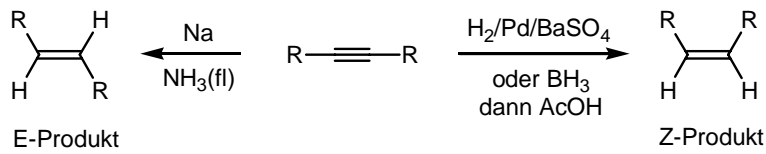


Metallorganische Reagenzien:



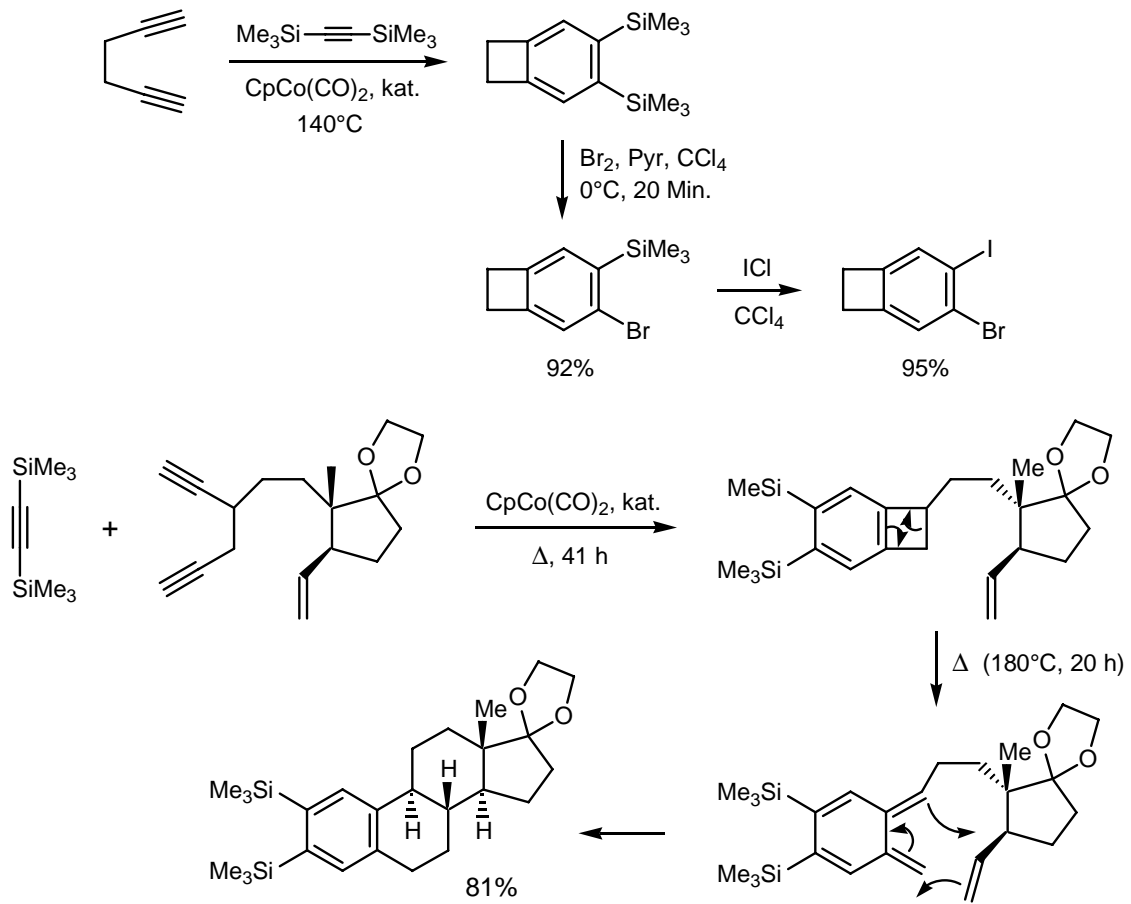
# 4. Gruppe: Alkene und Alkine

## Selektive Reduktion



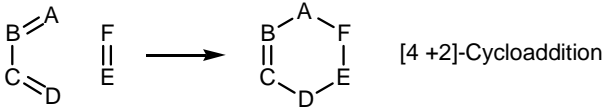
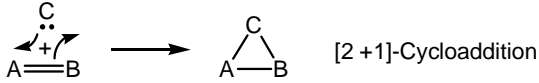
## Trimerisierung von Alkinen

Reppe-Vollhardt-Reaktion:

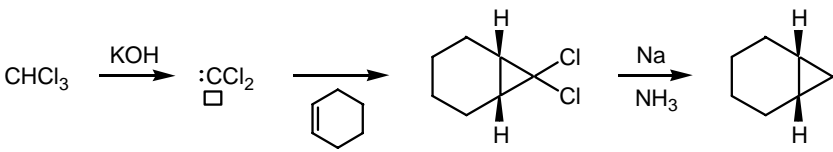


3) Cycloadditionen der Alkene und der Alkine

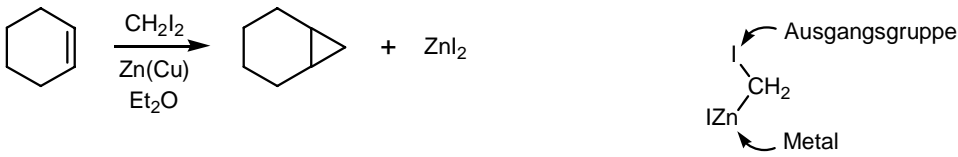
Ringgrößen - Klassifizierung: Zahl der an der Ringbildung beteiligten Atome



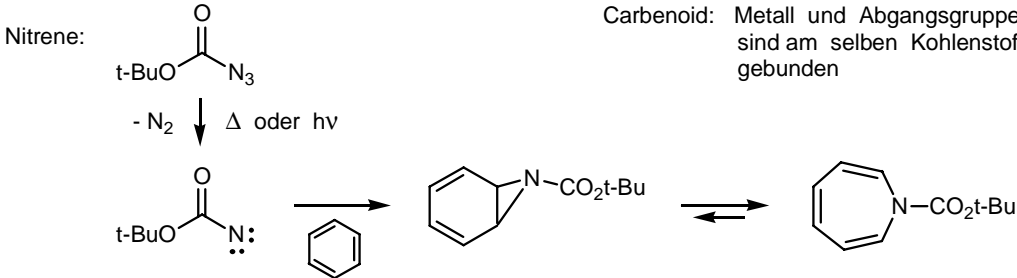
3.1. [2 + 1]-Cycloadditionen



Simmons-Smith-Reaktion: IH2C-I + Zn  $\xrightarrow[\text{oder Ether}]{\text{THF}}$  IH2C-ZnI Carbenoid

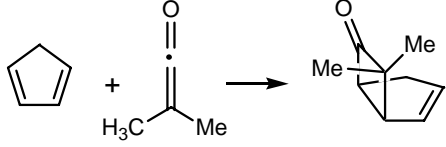
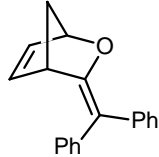
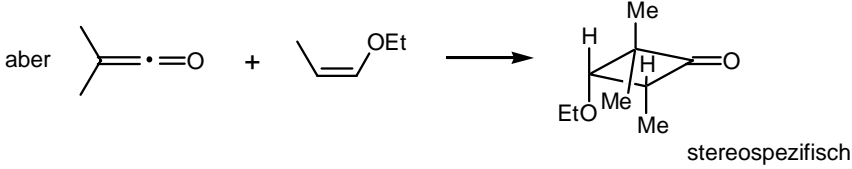


Carbenoid: Metall und Abgangsgruppe sind am selben Kohlenstoff gebunden



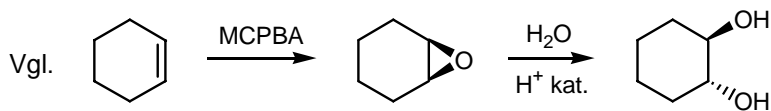
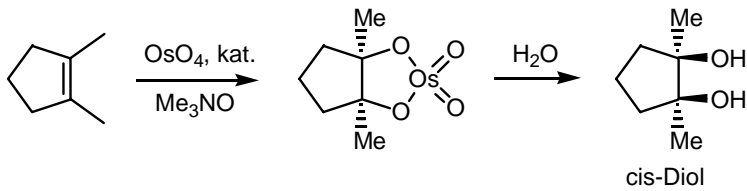
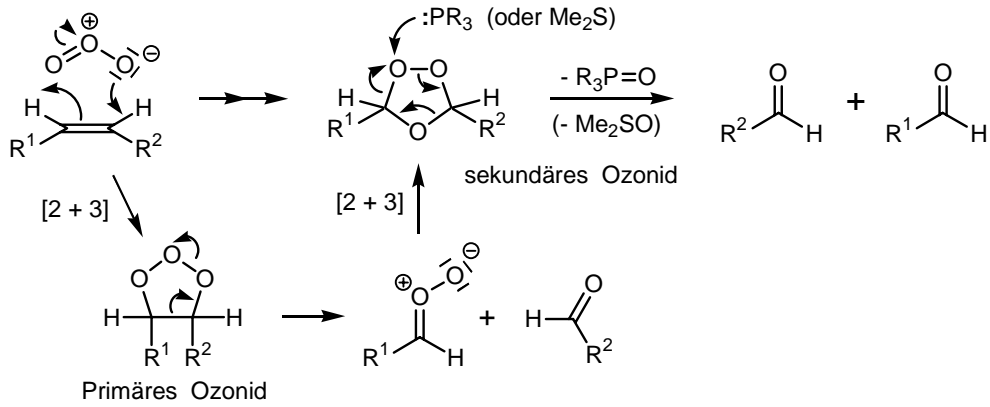
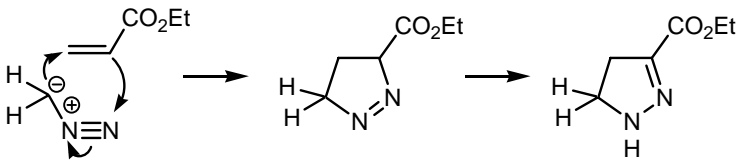
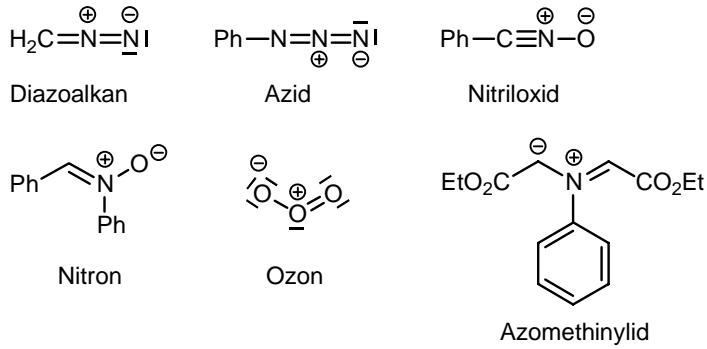
3.2. [2 + 2]-Cycloadditionen

in der Regel zweistufig meist nicht stereospezifisch



# 4. Gruppe: Alkene und Alkine

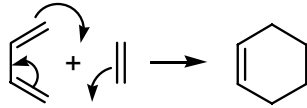
[3+2]-Cycloaddition: 1,3-Dipolare Cycloadditionen



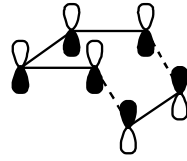


3.4. [4 + 2]-Cycloadditionen

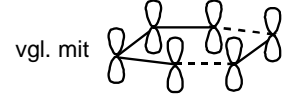
Diels-Alder-Reaktion



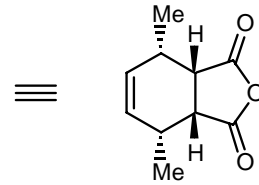
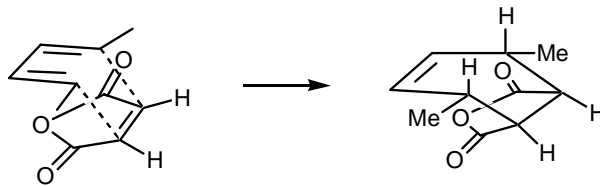
konzertierte  
Reaktion



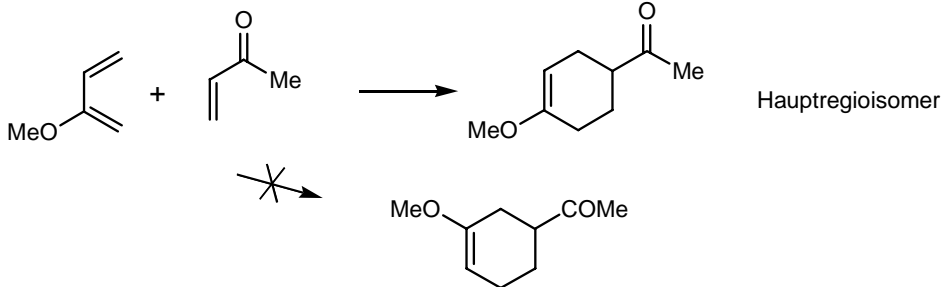
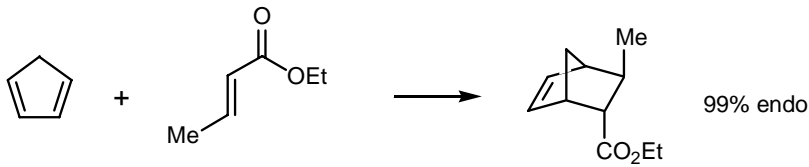
aromatischer ÜZ



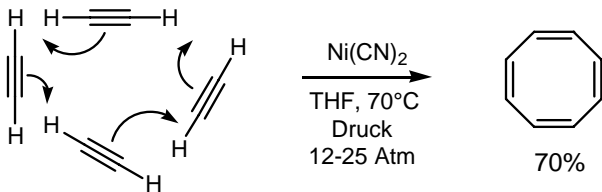
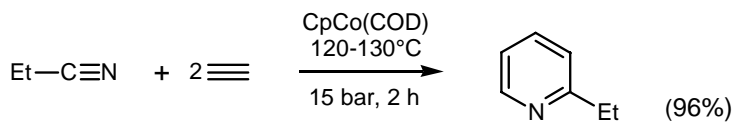
*Benzol*



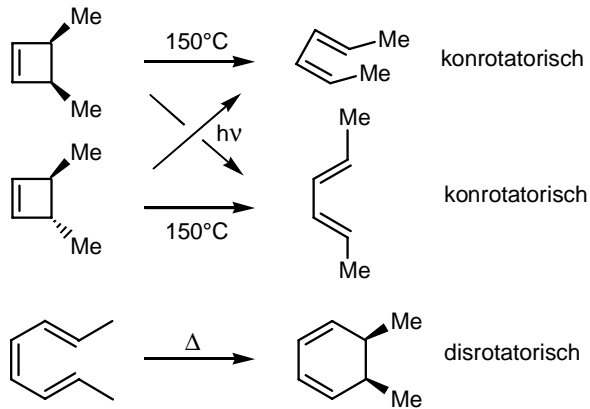
die relative Stereochemie  
von 4 Zentren ist  
kontrolliert



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



4) Elektrocyclische Reaktionen



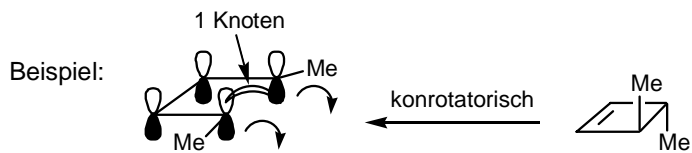
Woodward-Hoffmann Regeln

Aromatischer ÜZ ist erlaubt

Antiaromatische ÜZ sind verboten

Aromatisch:  $4n + 2 e^\ominus$  ohne Phasensprung !

Antiaromatisch:  $4n e^\ominus$  ohne Phasensprung !



$4 e^\ominus \Rightarrow$  antiaromatisch aber + 1 Phasensprung = aromatisch (erlaubt)