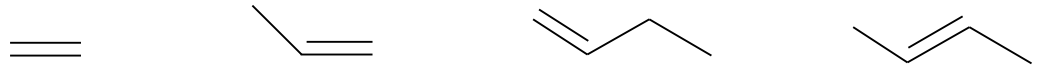
Alkene (Nomenklatur, Eigenschaften, Synthese, Reaktionen)

Merke: cis-trans-Isomere sind weder Konstitutions- noch Konformationsisomere. Sie sind Diastereomere.

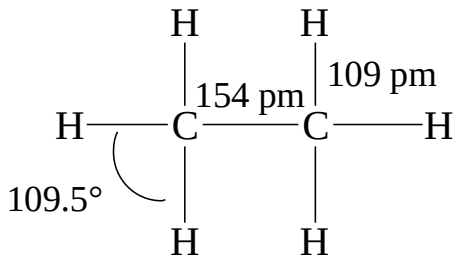
<u>Nomenklatur</u> Name = [Position Doppelbindung]-KW-Stamm + „en“



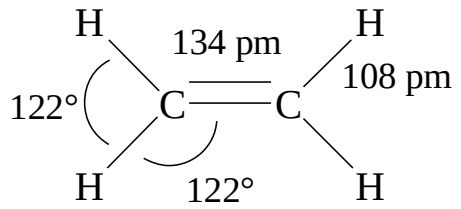
Ethen Propen 1-Buten 2-Buten

$=CH_2$ $H_2C=CH-$ $H_2C=CH-CH_2-$

Metylen- Vinyl- Allyl-

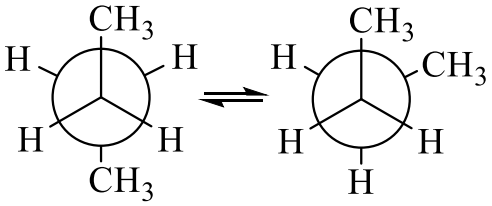


CC-Einfachbindung
ΔH = 335 kJ/mol

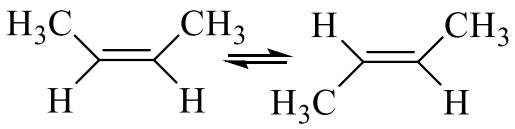


CC-Doppelbindung
ΔH = 595 kJ/mol

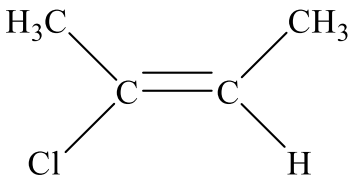
Cis-Trans-€-(Z)-Isomerie (Diastereomerie)



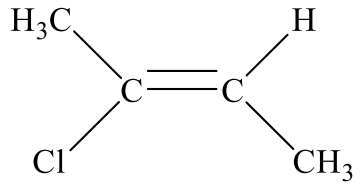
E_a = 14 kJ/mol



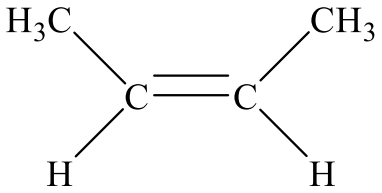
E_a = 150 kJ/mol



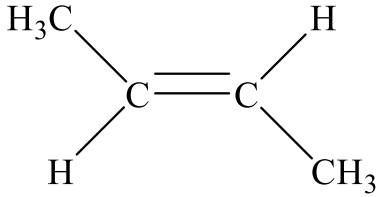
cis-2-Chlor-2-buten
(E)-2-Chlor-2-buten



trans-2-Chlor-2-buten
(Z)-2-Chlor-2-buten



cis-2-Buten
(Z)-2-Buten
Fp.: -139°C
Kp.: 3.7°C
ρ: 0.6213 g/L
n_D: 1.3931
μ > 0



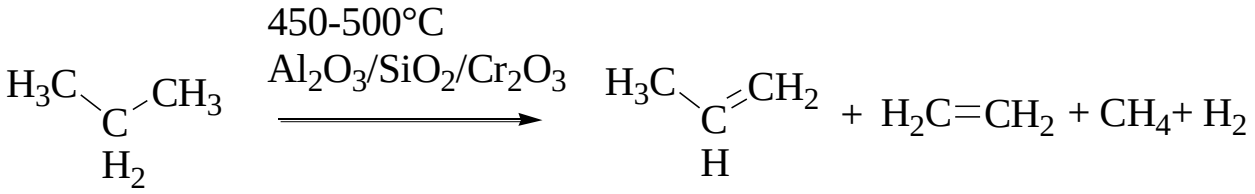
trans-2-Buten
(E)-2-Buten
Fp.: -106°C
Kp.: 1.0°C
ρ: 0.6042 g/L
n_D: 1.3848
μ = 0

Cis/trans: nur C-Atome bestimmen Isomerie

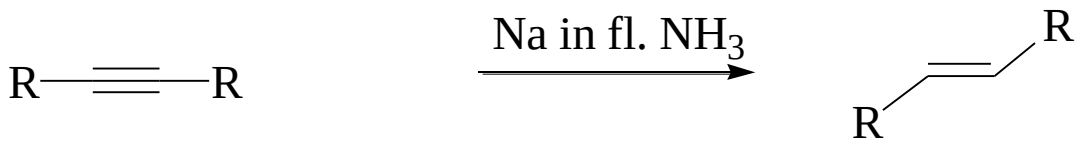
(E)/(Z): schwerste Atome bestimmen Isomerie

DARSTELLUNG der Alkene durch verschiedene chemische Reaktionen

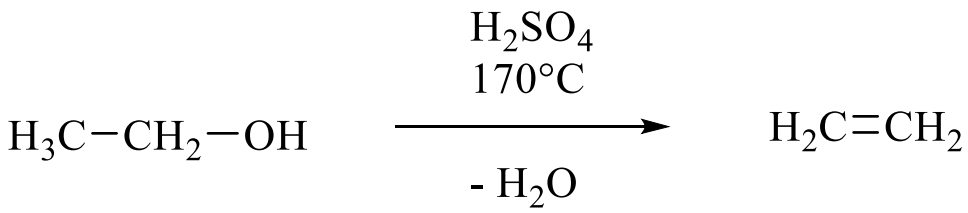
Cracking



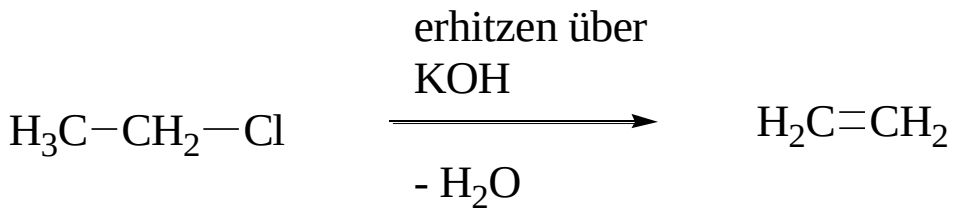
Hydrierung Von Alkinen



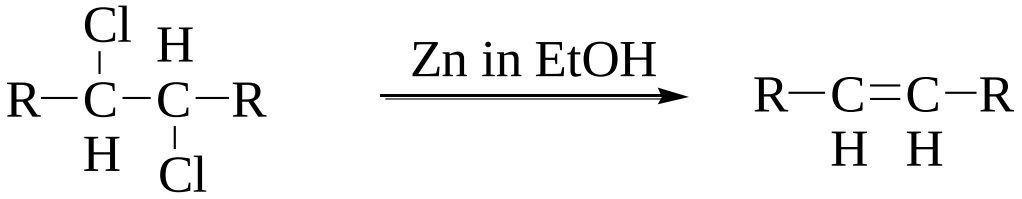
Dehydratisierung Von Alkoholen



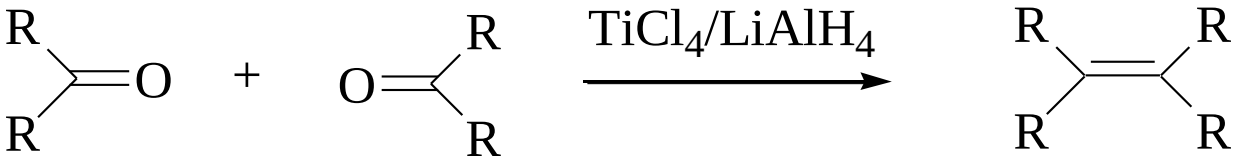
Dehydrohalogenierung von Halogenalkanen



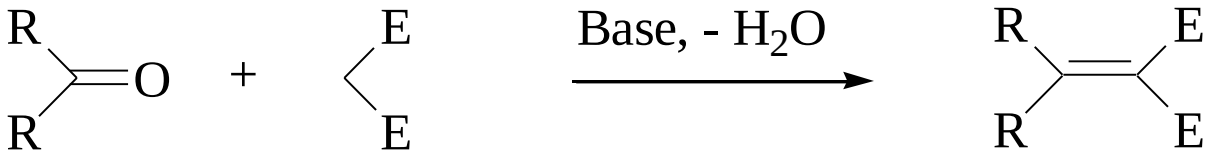
Dehalogenierung von 1,2-Dihalogenalkanen



McMurry-Reaktion

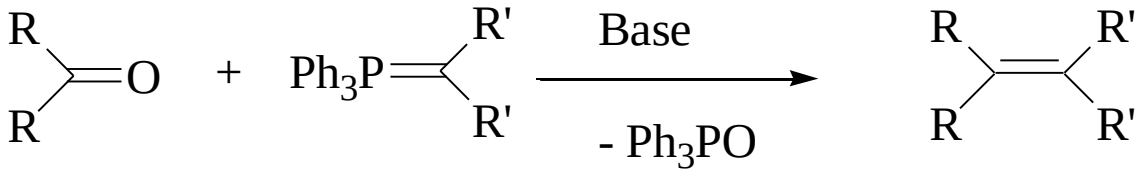


Knoevenagel-Reaktion



E = -COOR, -CN

Wittig-Reaktion

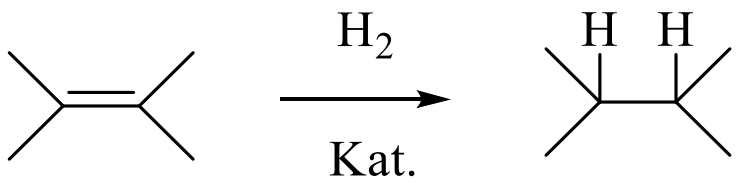


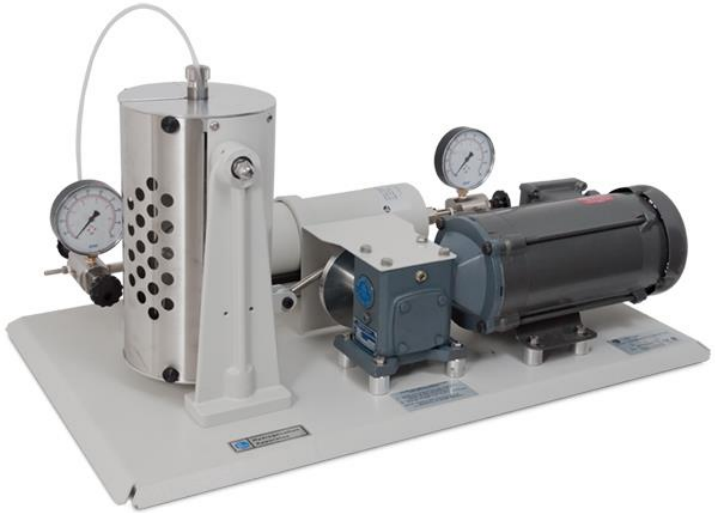
Reaktionen

Katalytische Hydrierung (siehe auch Darstellung von Alkanen)

Katalysatoren: Cu, Fe, Co, Pt, Pd, Ni (Raney-Ni), Rh-, Ru-Komplexe

Hydrierwärme pro Doppelbindung: $\Delta H = -125$ kJ/mol
cis-2-Buten: $\Delta H = -120$ kJ/mol;
trans-2-Buten: $\Delta H = -116$ kJ/mol

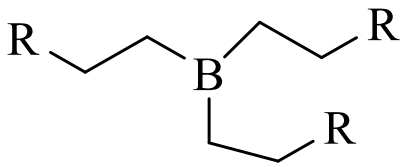




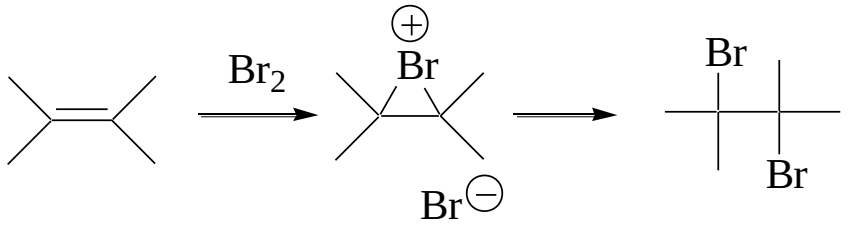
Hydroborierung

$$9\ R\text{-}CH{=}CH_2 + 3\ NaBH_4 + AlCl_3 \rightarrow 3\ (R\text{-}CH_2\text{-}CH_2)_3B$$

$$6\ R\text{-}CH{=}CH_2 + B_2H_6 \rightarrow 2\ (R\text{-}CH_2\text{-}CH_2)_3B$$



Halogenaddition



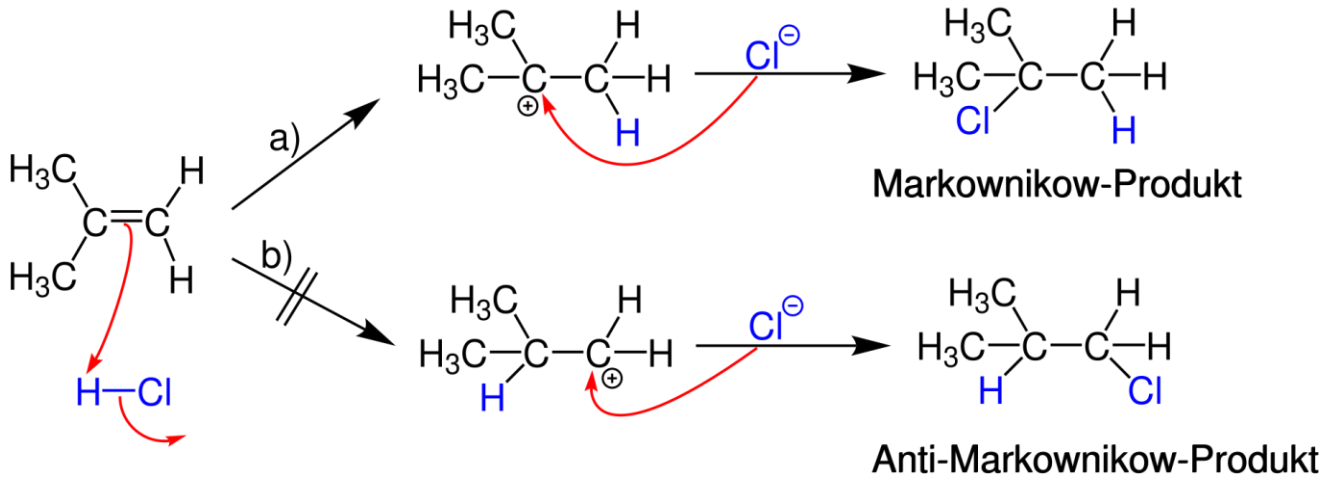
Halogenwasserstoffaddition / Hydratisierung

$$R\text{-}CH{=}CH_2 + HX \rightarrow R\text{-}CHX\text{-}CH_3$$

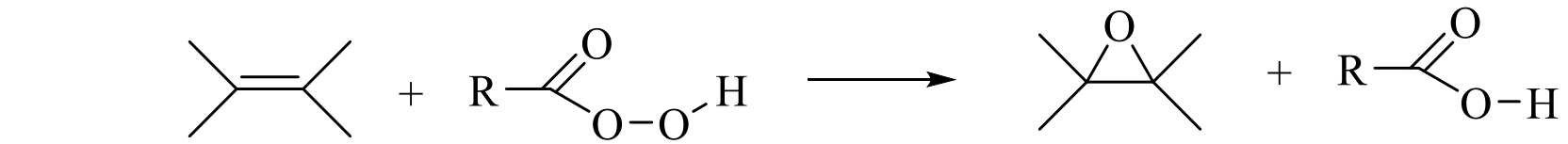
X=Hal, OH

Wladimir Wassiljewitsch Markownikow (1837-1904)

Markovinkov-Regel: Der Wasserstoff geht an das wasserstoffreichere C-Atom

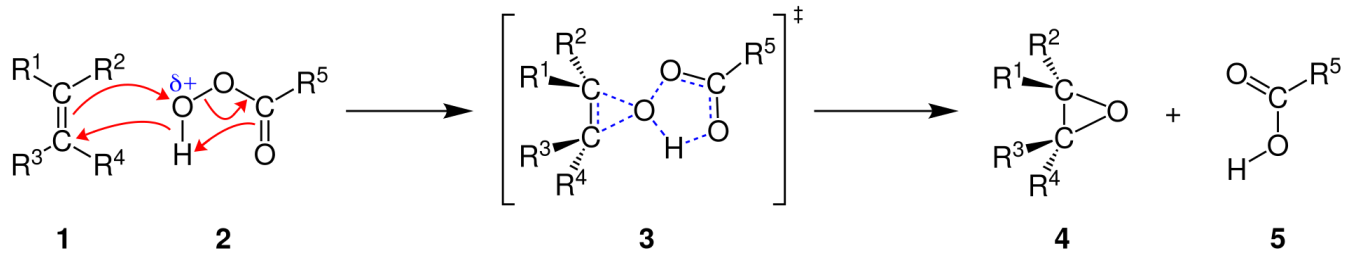


Prins-Reaktion

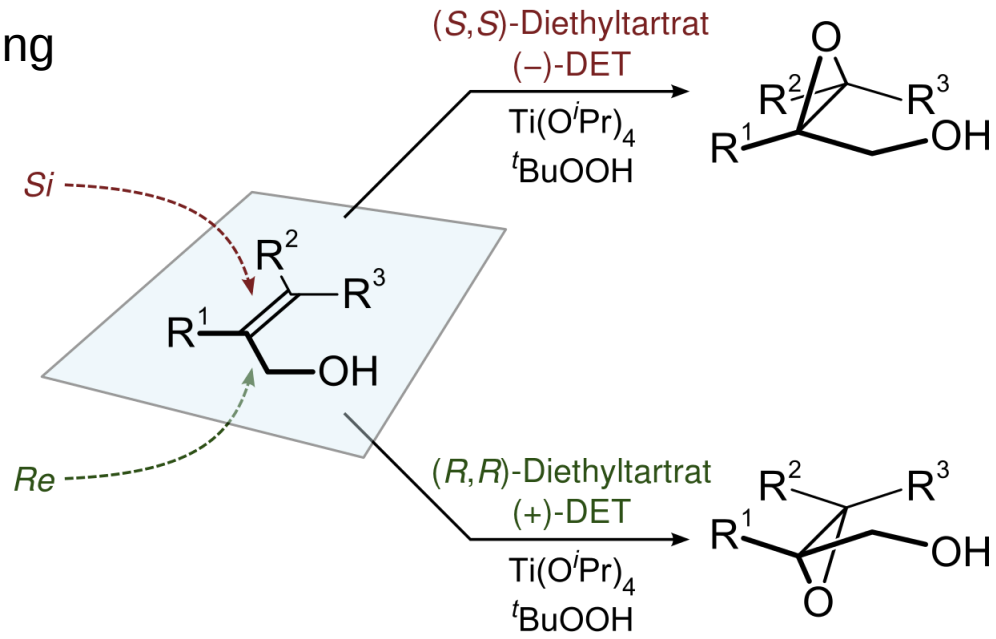


Epoxidierung

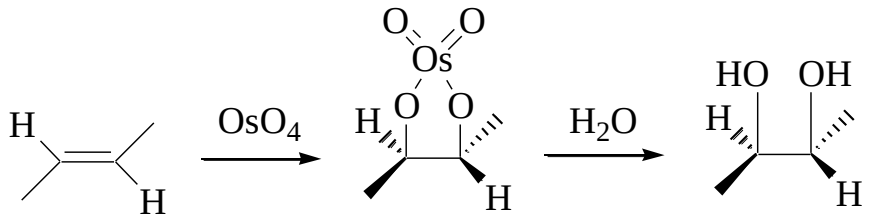
Prileschajew-Reaktion



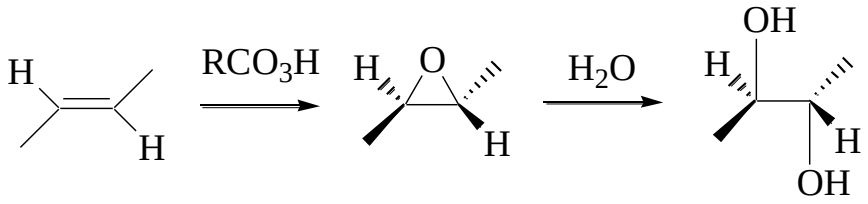
Sharpless-Epoxidierung



Dihydroxylierung

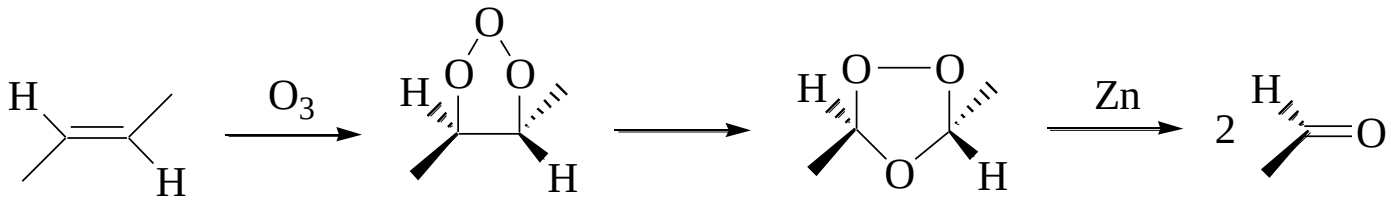


cis-Dihydroxylierung

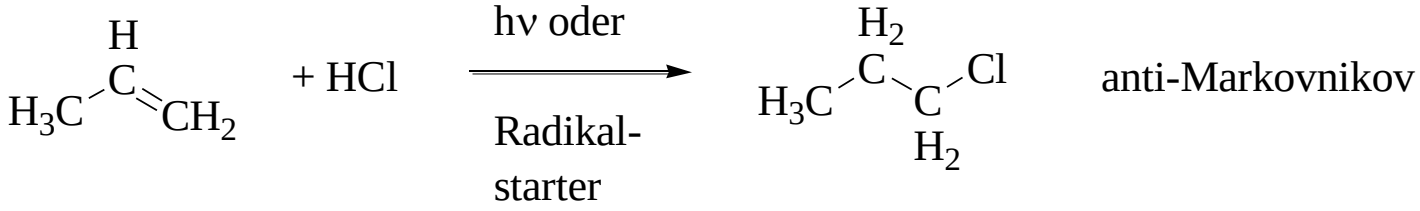


trans-Dihydroxylierung

Ozonolyse

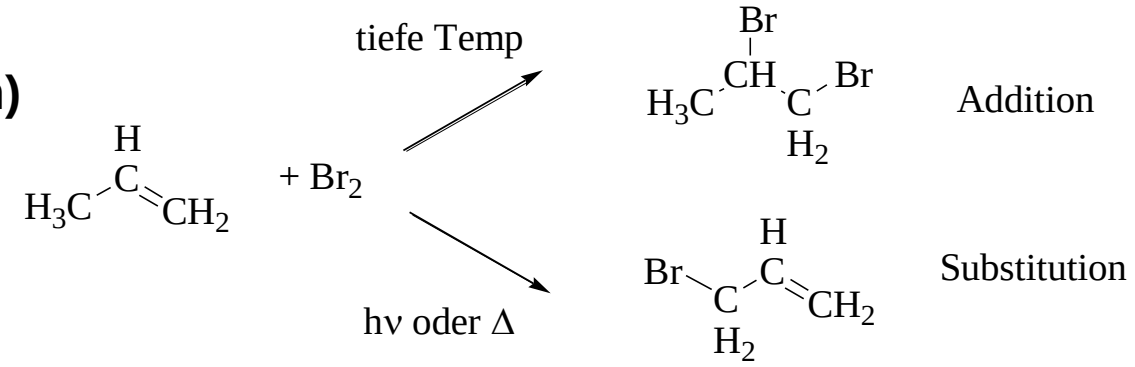


Radikalische Addition

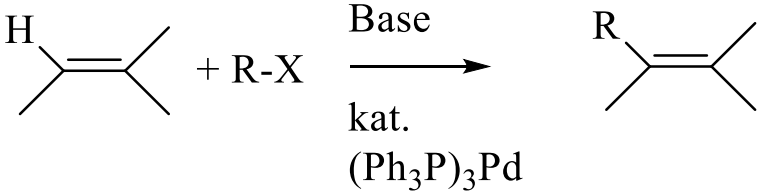


anti-Markovnikov

Radikalische Substitution (Allylposition)

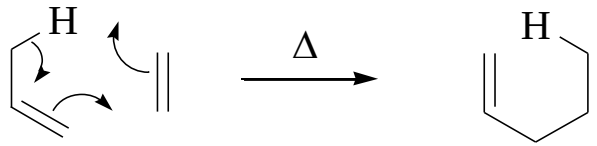


Heck-Reaktion

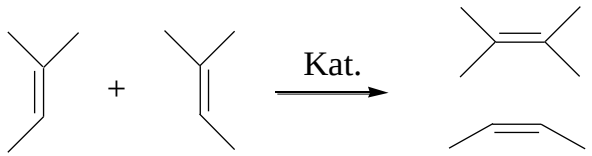


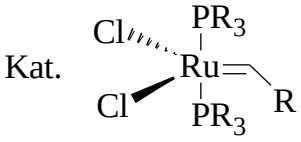
R= Alkyl ohne ß-H, Alkenyl, Aryl
X= Br, I

En-Reaktion

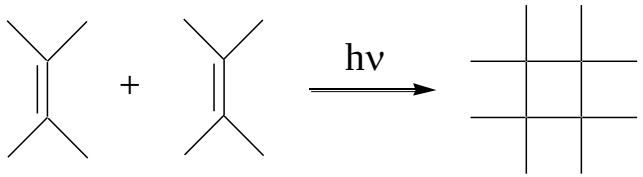


Metathese-Reaktion

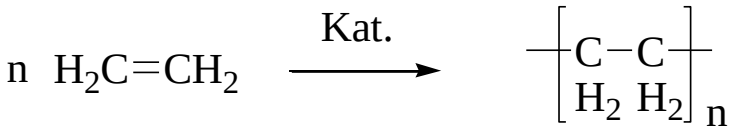




Photodimerisierung



Polymerisation

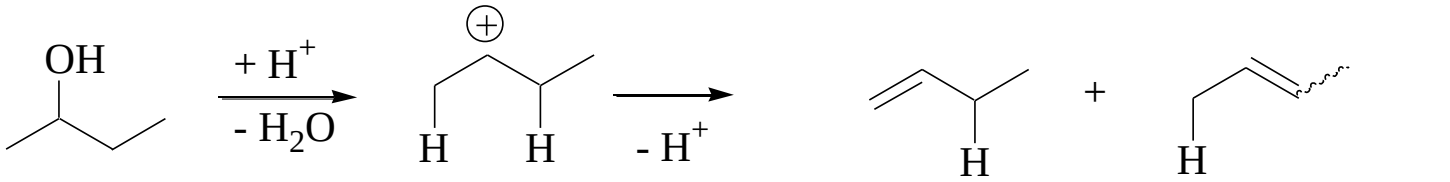


Eliminierung

Die **ELIMINIERUNG** kann über verschiedene **REAKTIONSMECHANISMEN** ablaufen und zu verschiedenen Produkten (Alkene) führen.

Die **E_1-ELIMINIERUNG** erfolgt **MONOMOLEKULAR** mit der Reaktionsordnung 1
Die **E_2-ELIMINIERUNG** erfolgt **BIMOLEKULAR** mit der Reaktionsordnung 2
Die **E_{1CB}-ELIMINIERUNG** erfolgt über die **KONJUGIERTE BASE**

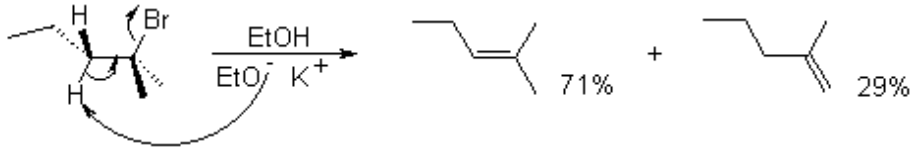
Regioselektivität



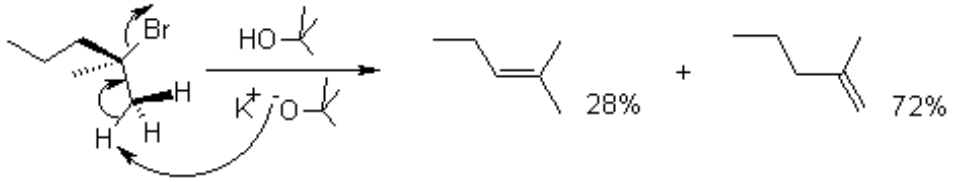
Hofmann- Saytzeff-Produkt

Saytzeff-Regel

Die Saytzeff-Regel besagt, dass basenkatalysierte Eliminierungen nach E_2 (sogenannte bimolekulare Eliminierungen, d.h. zwei Moleküle sind an der Reaktion beteiligt) so ablaufen, dass die thermodynamisch günstigere Doppelbindung entsteht - also die höher substituierte.

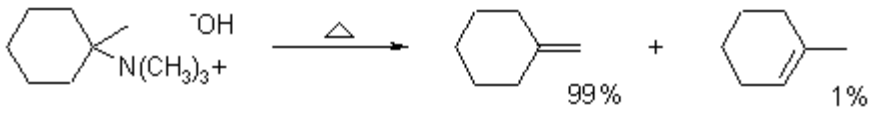


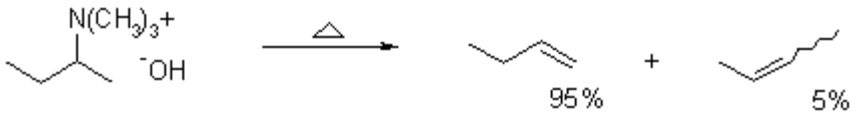
Beim Einsatz von sterisch gehinderten Basen ist die Aktivierungsenergie-Barriere für die Reaktion an den zugänglicheren Protonen merklich niedriger:



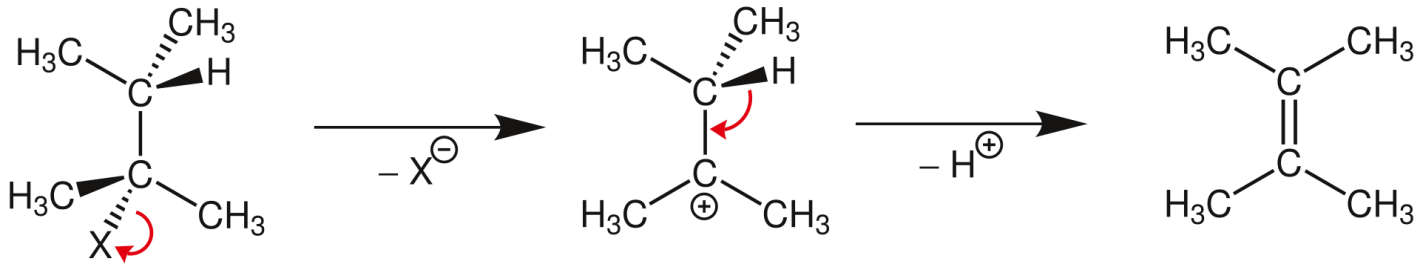
Hofmann-Regel

Sterische Effekte sind ausschlaggebend bei Eliminierungen. Eine β-H-Elimierung erfolgt an der zugänglicheren Stelle. Es gilt: $-CH_3 > -CH_2-R > -CH(R_2)$. Es entstehen bervorzugt weniger hoch substituierte Alkene (im Gegensatz zur Saytzeff-Regel)



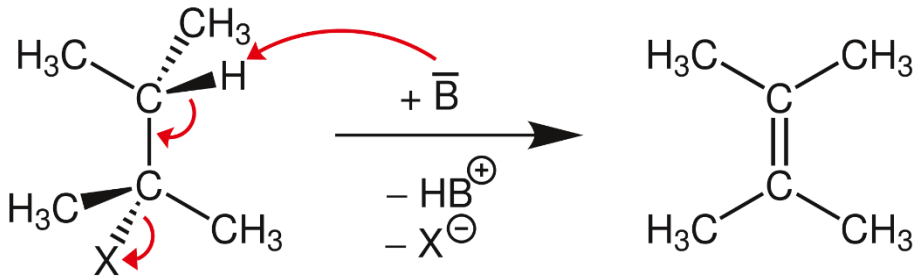


E_1-ELIMINIERUNG



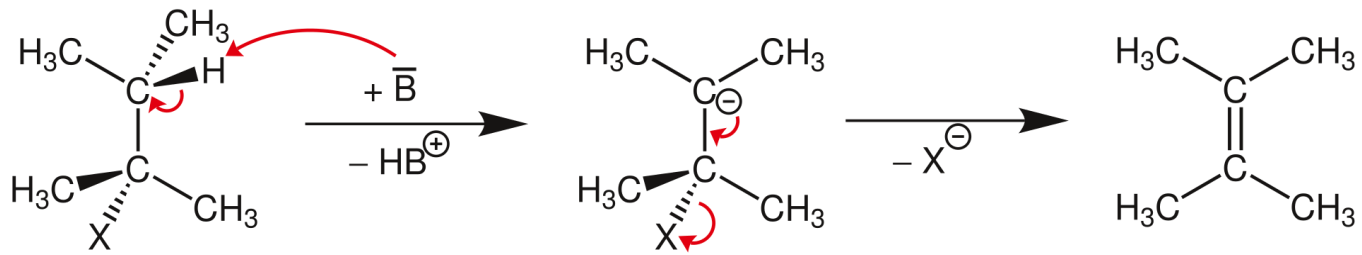
v=k[Substrat]

E_2-ELIMINIERUNG



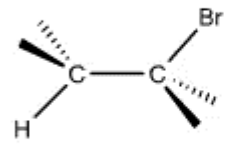
v=k[Substrat][Base]

E_{1CB}-ELIMINIERUNG



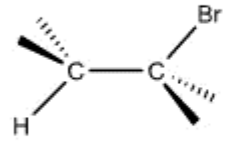
v=k[Substrat]

E_1-ELIMINIERUNG



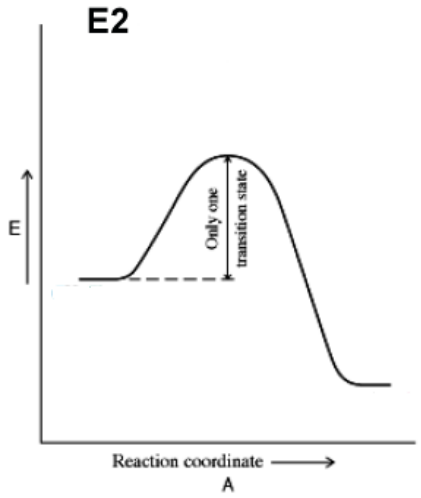
Bromalkan

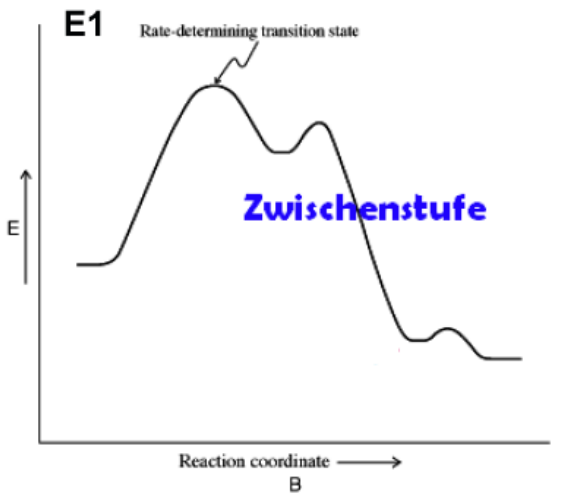
E_2-ELIMINIERUNG



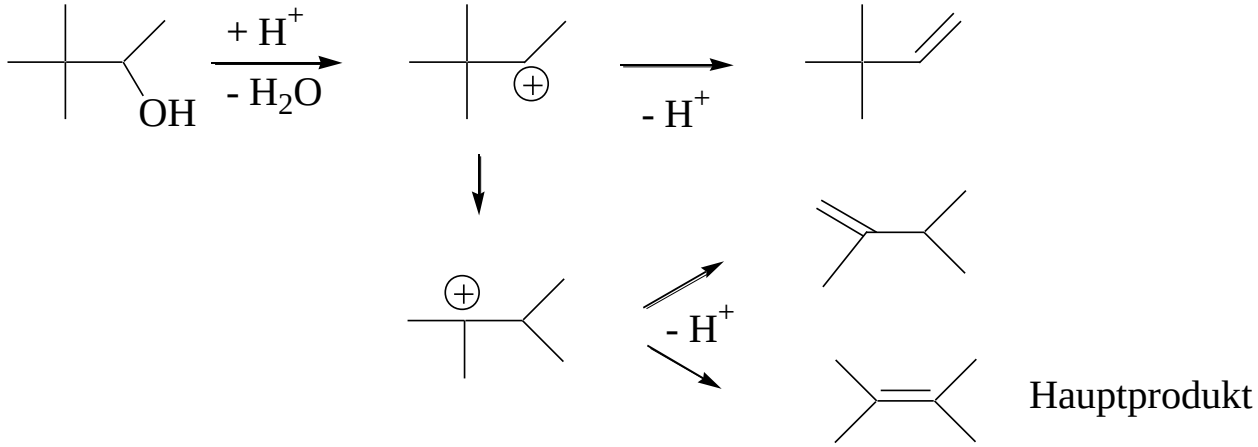
$I_B^{\ominus}$

Bromalkan





Wagner-Meerwein-Umlagerung



Beispiel: Wagner-Meerwein-Umlagerung von Borneol zu Camphen.