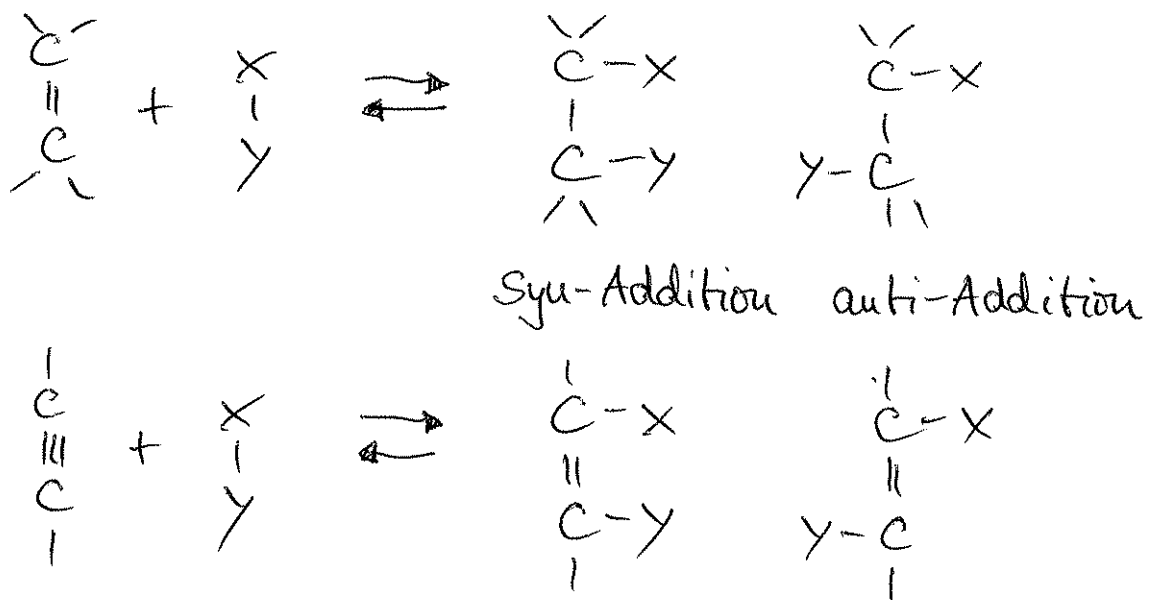


3. Addition

Addition ~~von~~ an nicht-aktivierte Doppel- und Dreifachbindung



Formal: Umkehrung der Eliminierung

Unterscheidung in

- a) elektrophile Addition (Ad_E)
- b) nukleophile Addition (Ad_N)
- c) radikalische Addition (Ad_R)

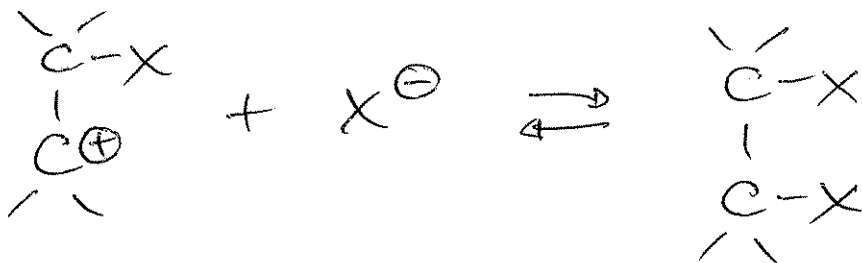
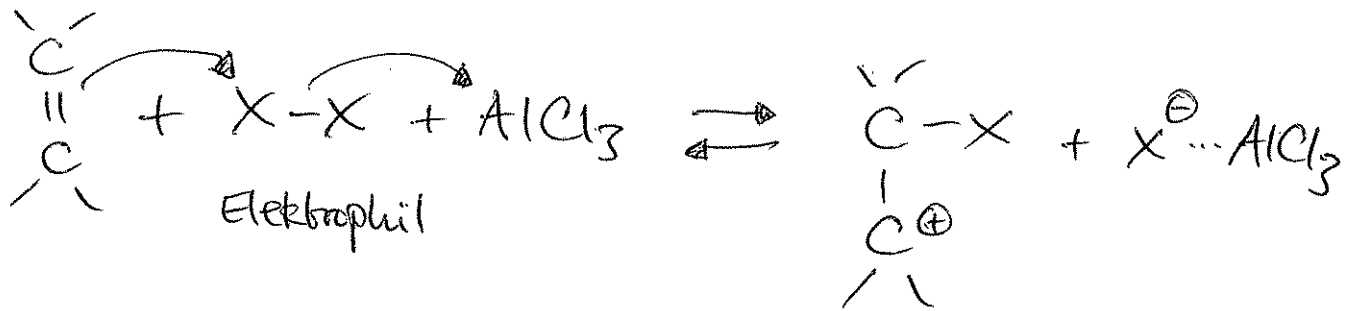
desweiteren:

- d) Cycloaddition
- e) Metall- und metallkomplextkatalysierte Umsetzungen

3a. Elektrophile Addition

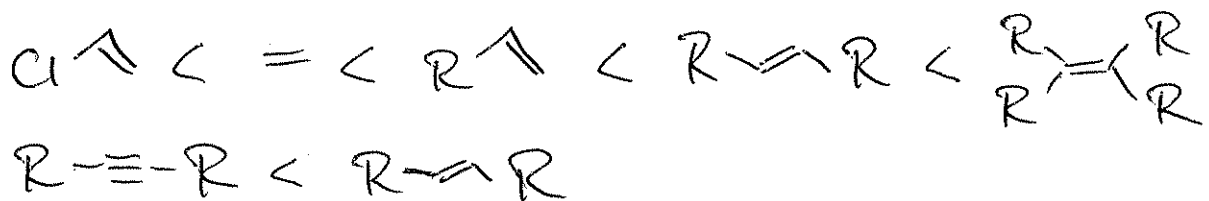
Vgl. elektrophile Substitution an Aromaten

Zweistufenmechanismus:

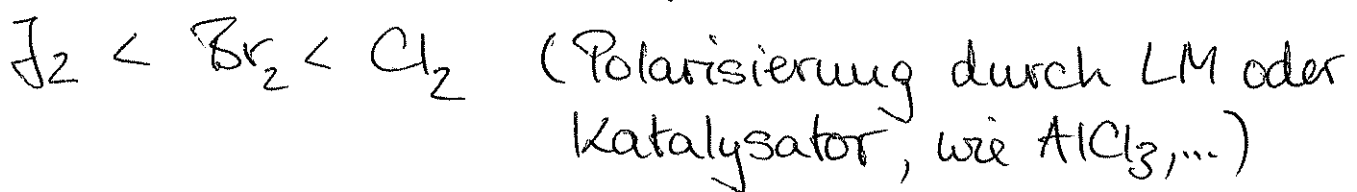


Reaktion ist umso leichter je basischer (nukleophiler) das Olefin / Acetylen und saurer (elektrophiler) das Reagenz.

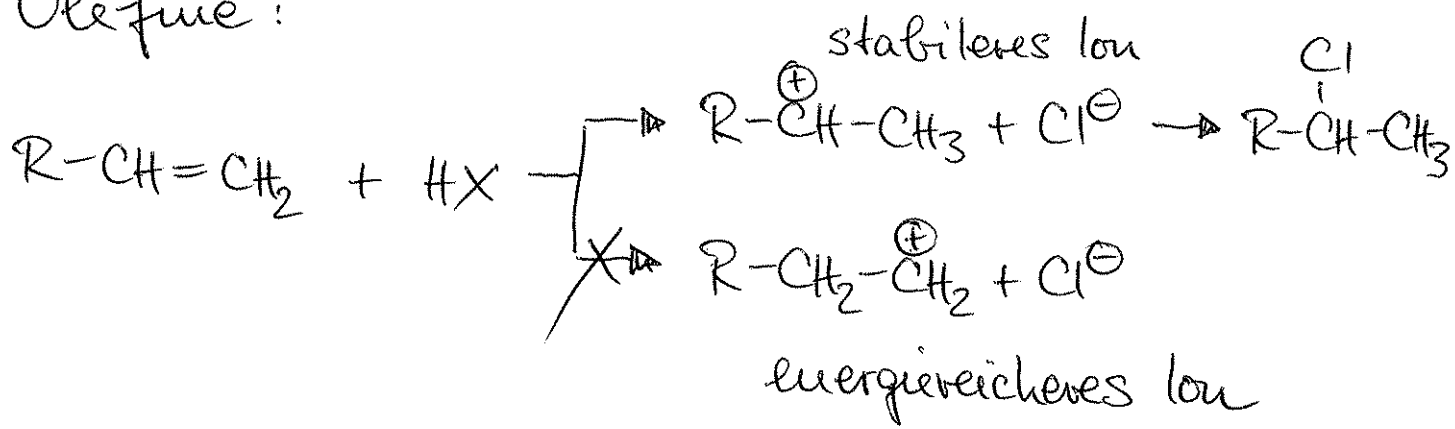
Olefin / Acetylen



Elektrophil

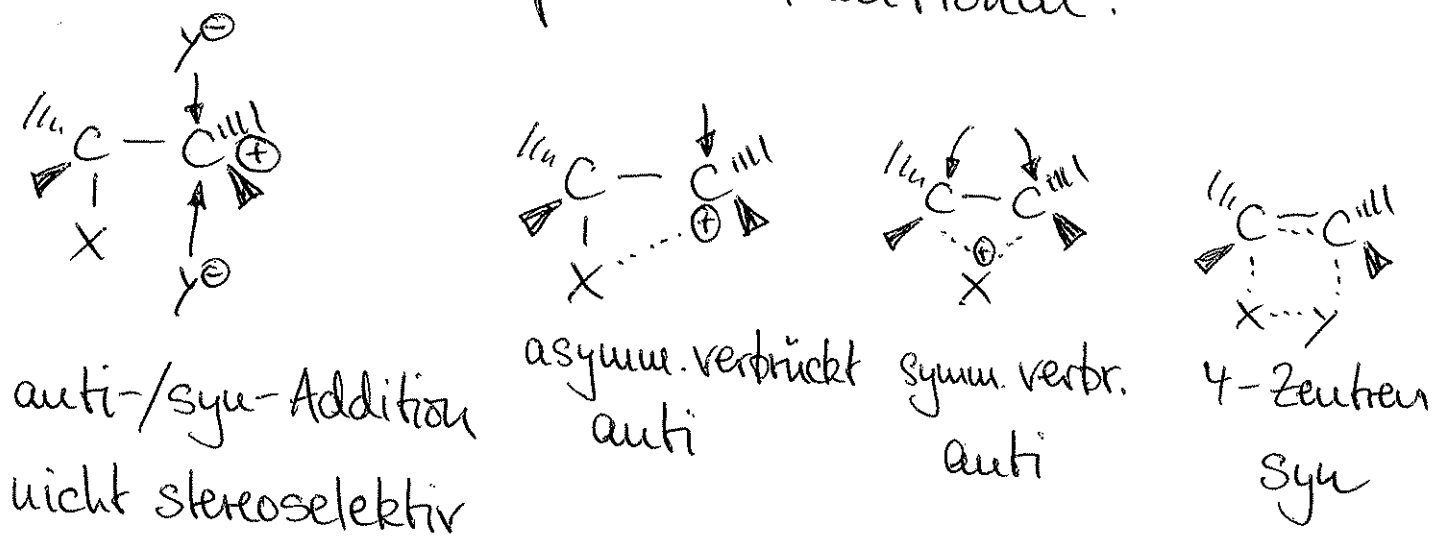


Addition unsymmetrischer Reagenzien (z.B. Protoneisäuren, HX) an unsymmetrische Olefine:



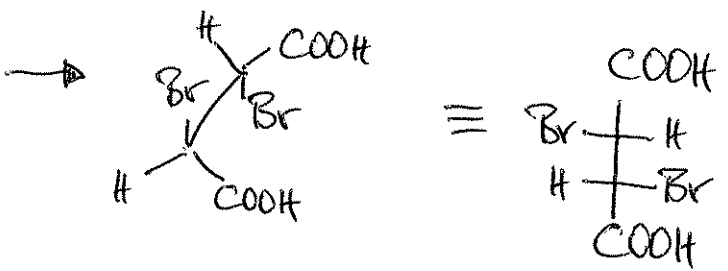
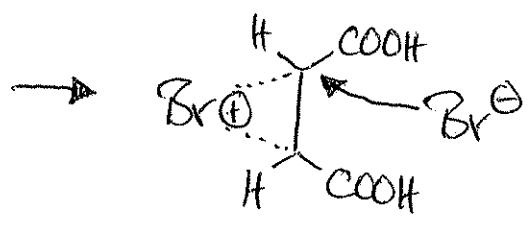
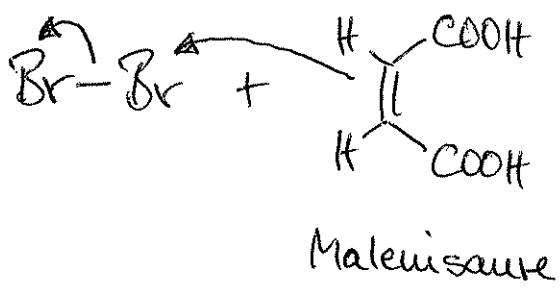
→ Regel von Markownikov: Bei der Ad_E an unsymmetrische Olefine tritt das H-Atom an das wasserstoffreichere Kohlenstoffatom der Doppelbindung (gilt nicht bei Ad_N und Ad_R).

1) Sterischer Verlauf von Additionen:

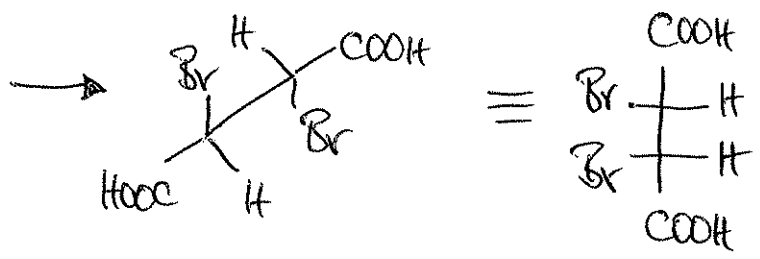
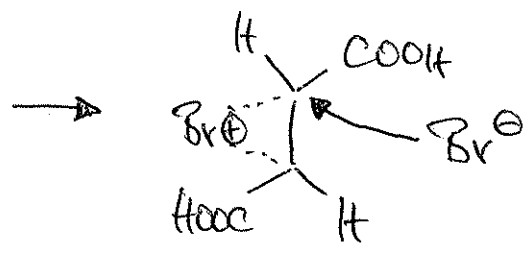
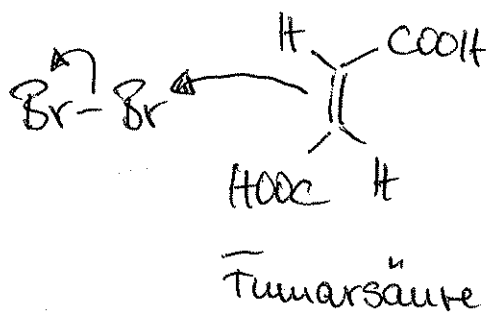


Bsp.: Addition von Brom

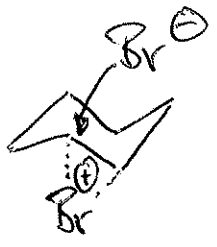
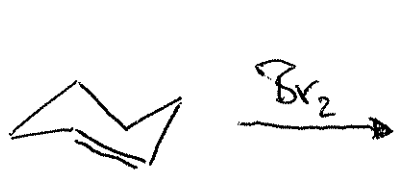
→ Verlauf über symmetrisch verbrücktes Ion



D,L-Dibrombernsteinsäure



meso-Dibrombernsteinsäure

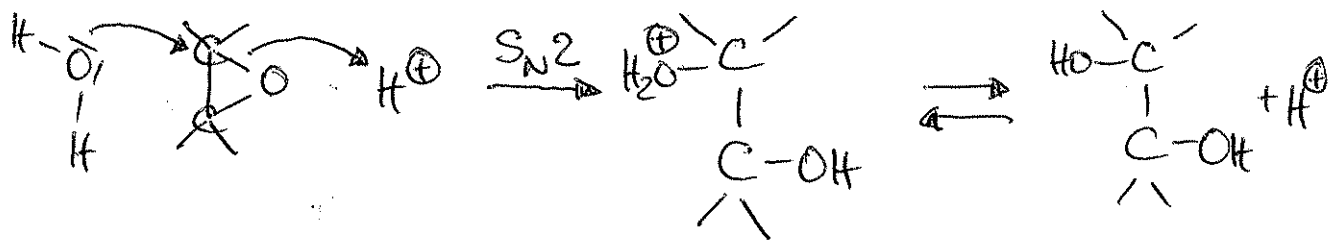
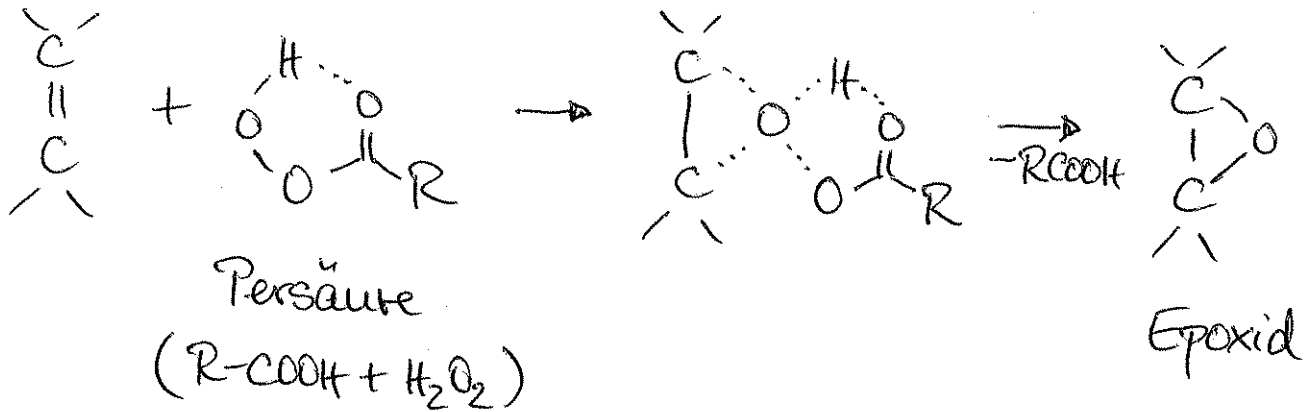


~~→~~

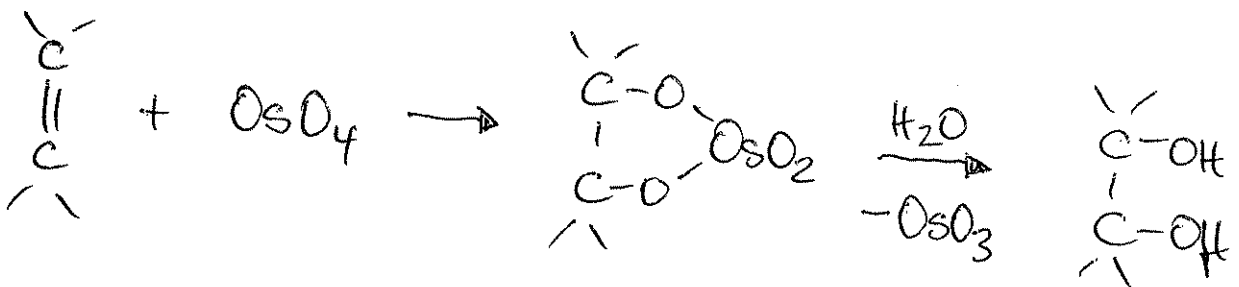
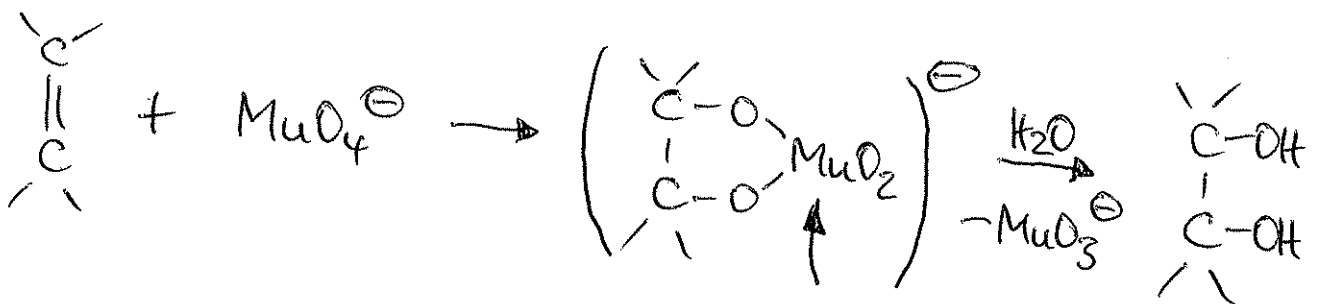


Bsp.: Hydroxilierung von Olefinen

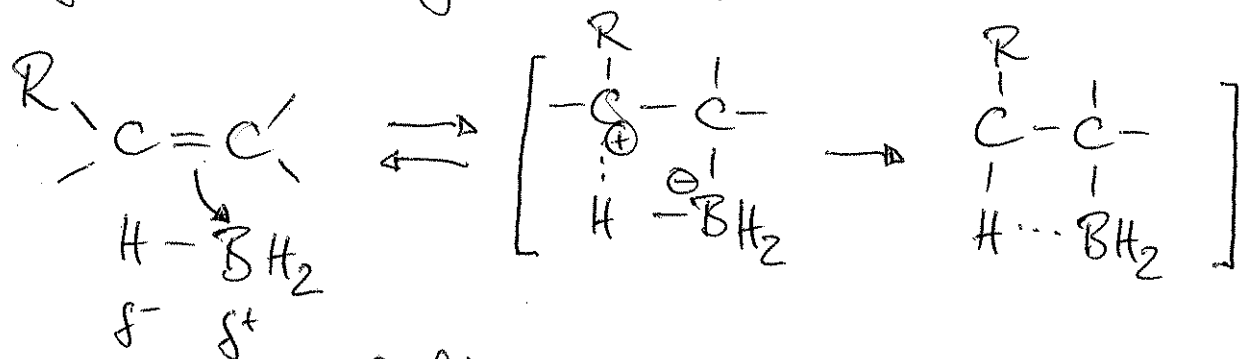
Epoxidierung \rightarrow trans-Diole



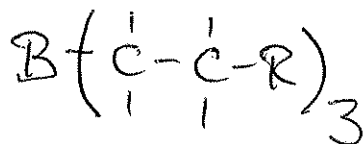
Umsetzung mit Kaliumpermanganat oder Osmiumtetroxid \rightarrow cis-Diole



Hydroborierung (Nobelpreis 1979, H.C. Brown):

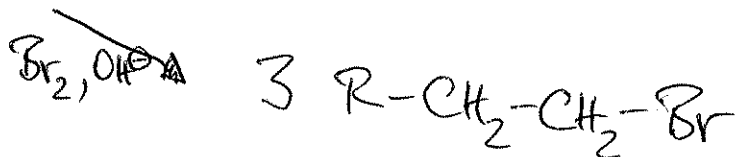
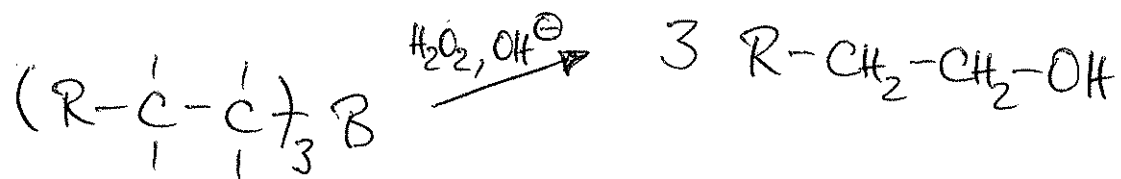


olefin

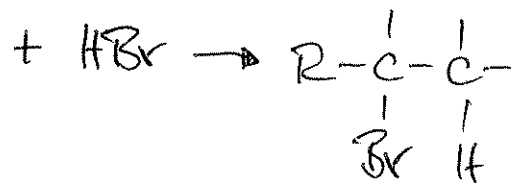
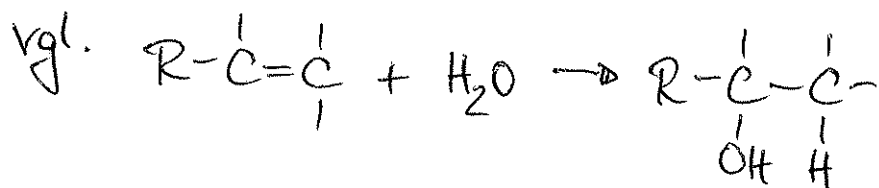


Trialkylboran (dimer)

Folgereaktionen, u.a.

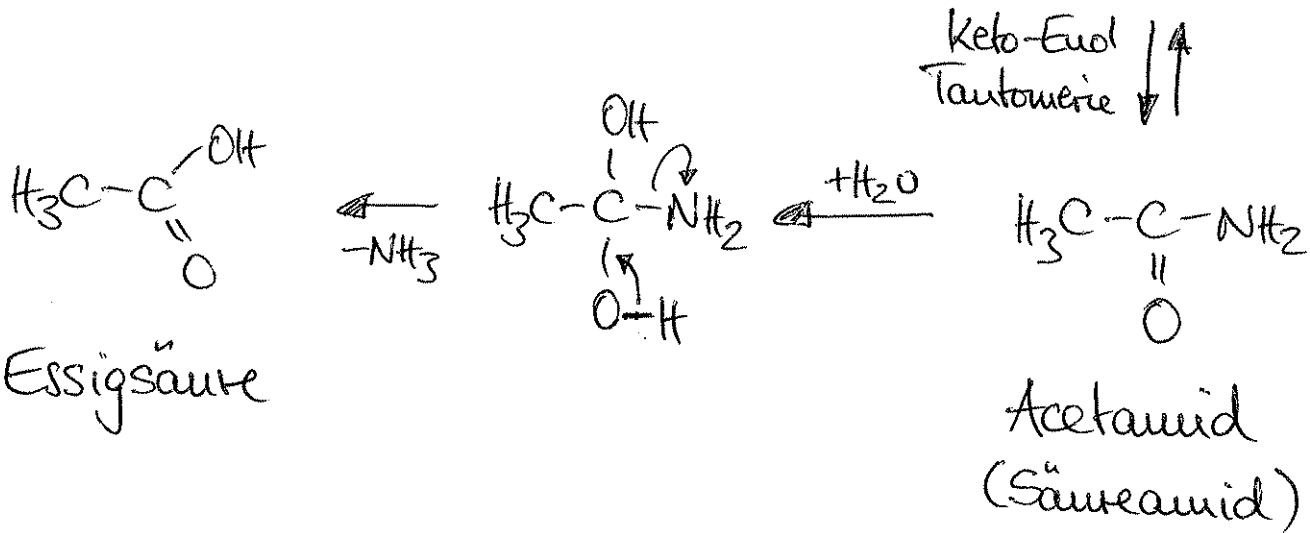
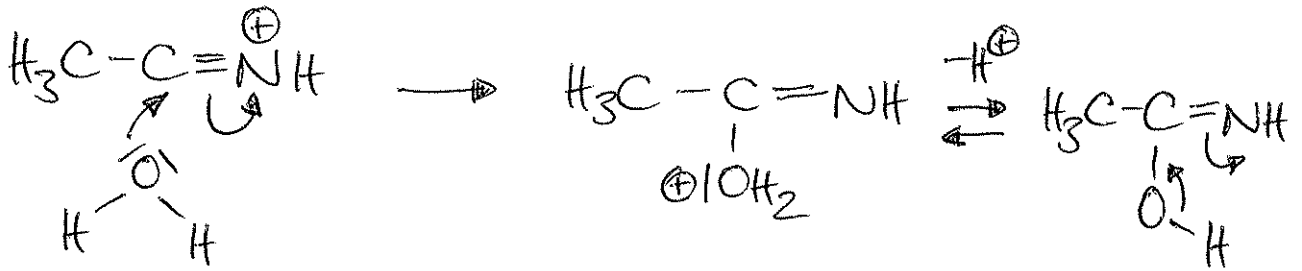
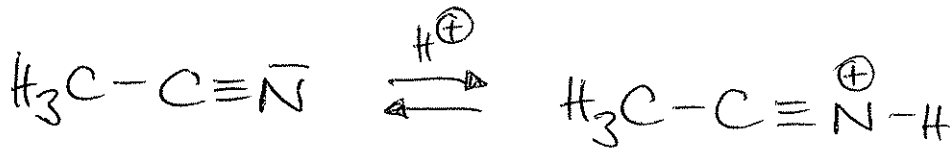


anti-Markovnikov Produkte

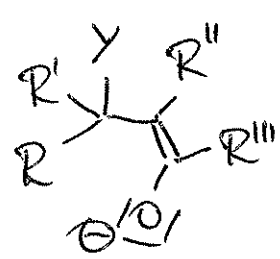
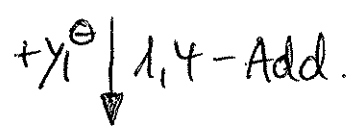
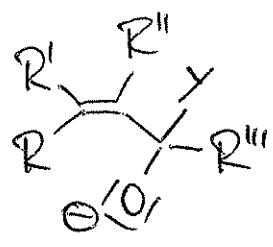
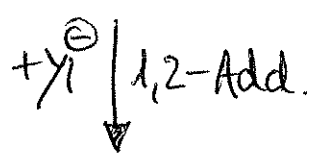
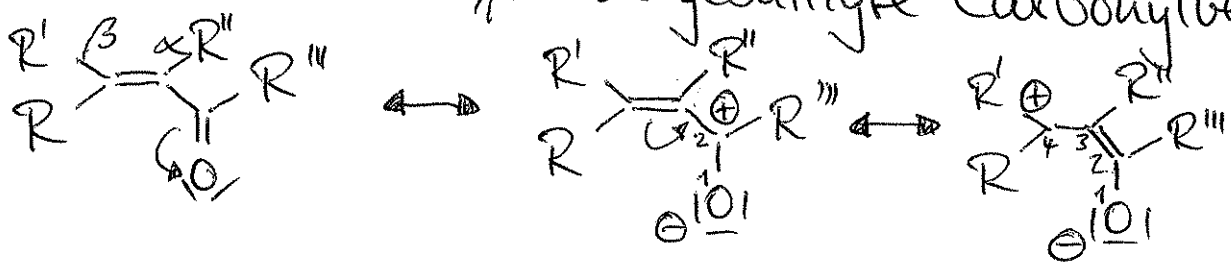


Analog: Addition an $-C \equiv N$

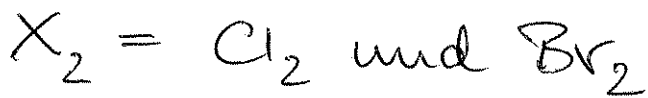
Bsp.: Hydrolyse von Acetonitril



o Addition an α, β -ungesättigte Carbonylverb.:



3c. Radikalische Addition



auch: HBr , $CHBr_3$, $CHCl_3$, CCl_4 , $R-SH$, etc.

Addition von HBr an unsymmetrische Olefine:

