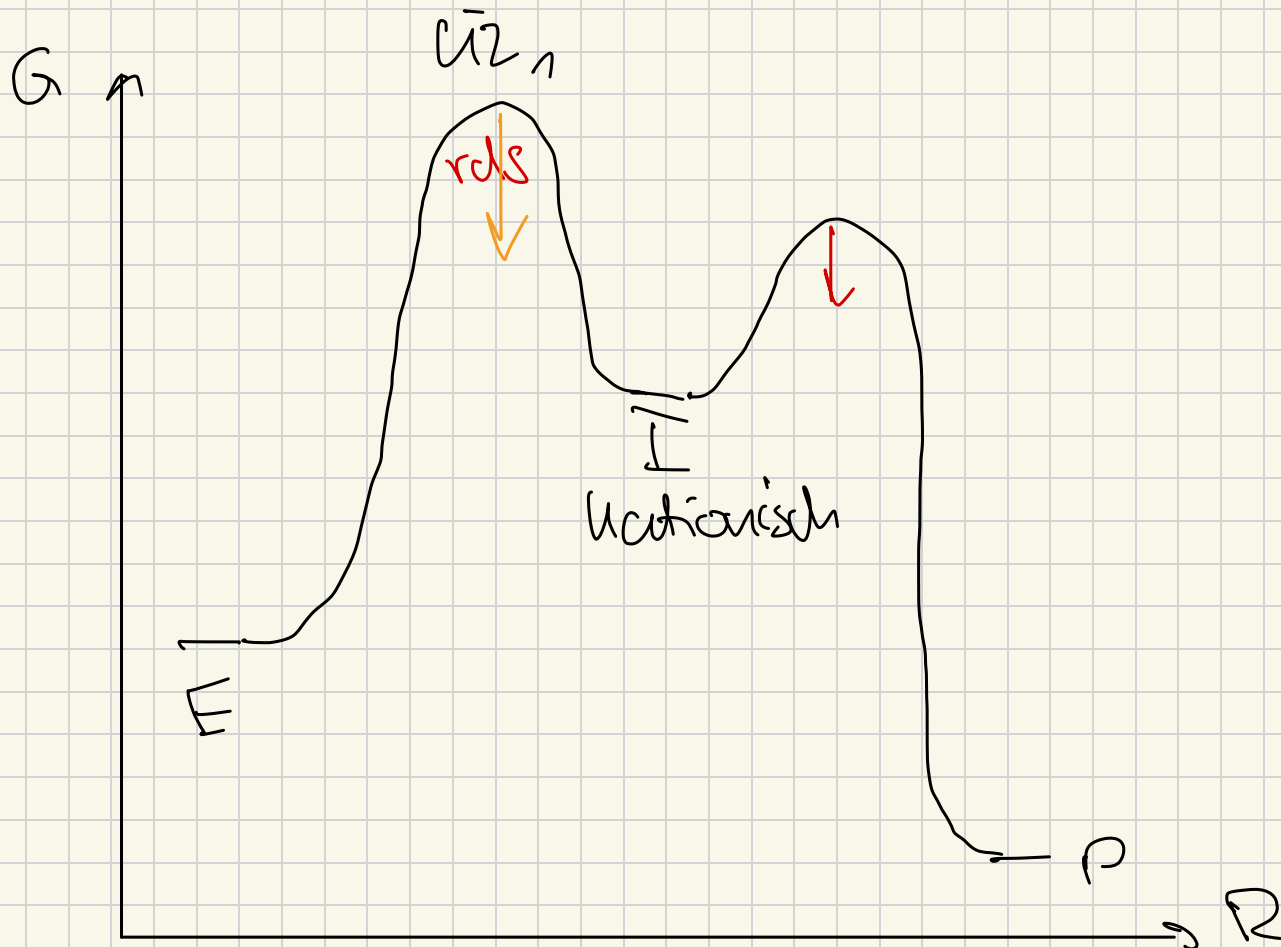
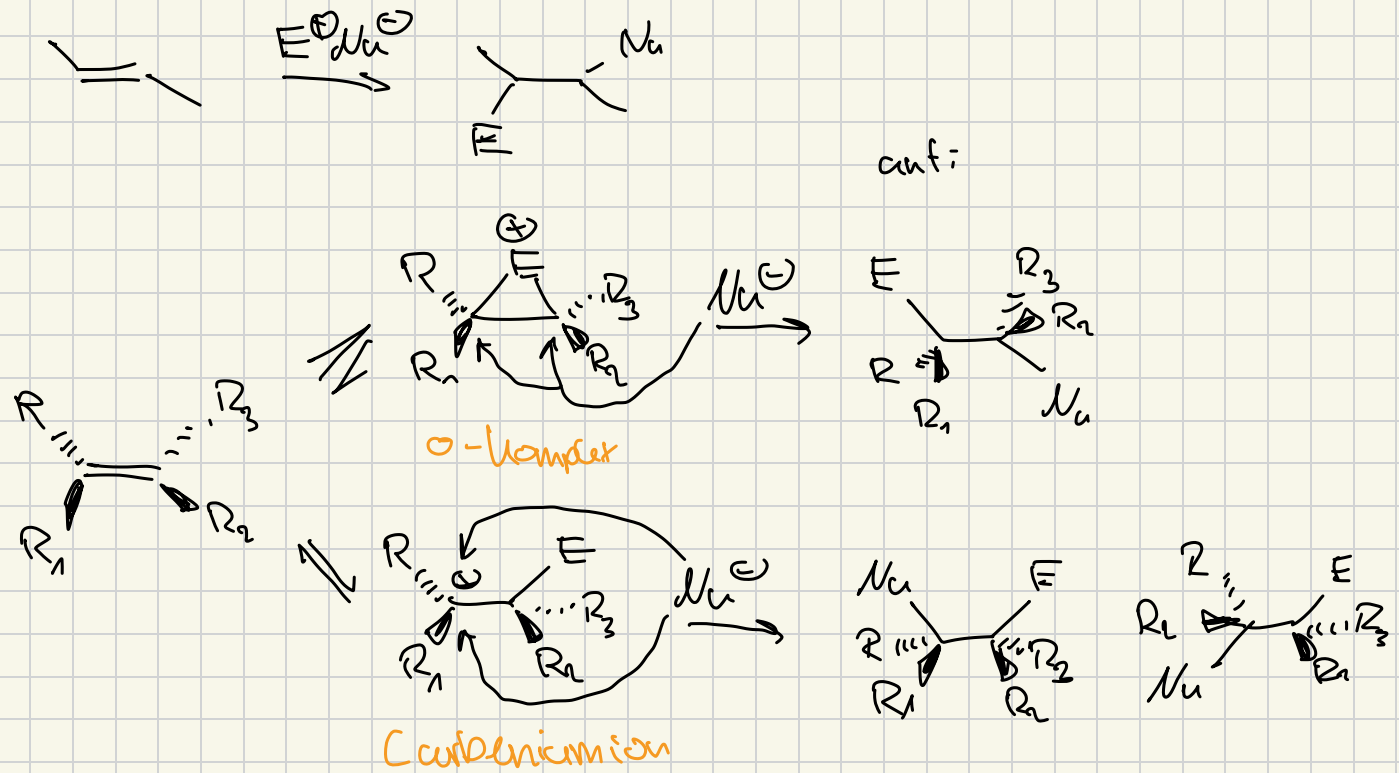


ALOC II PVK Tag 2

• Elektrophilic Addition



σ -Komplex

Carbeniumion

• Halogene

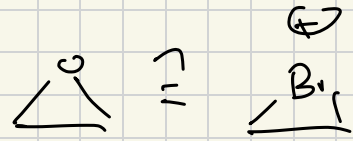
CM

apolar

polar

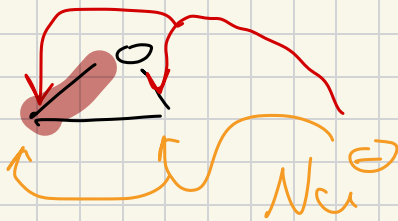
σ -Komplex offen

• auch gültig für Epoxide

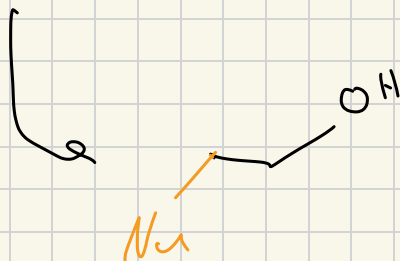


• freie

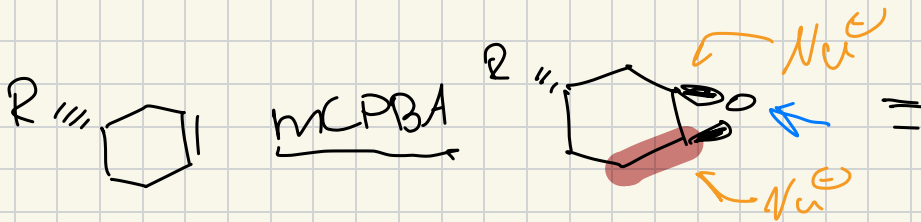
anti angriff



obligator anti angriff

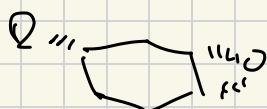
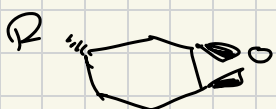


• σ -Komplex am 6 Ring: Firstposition



oben

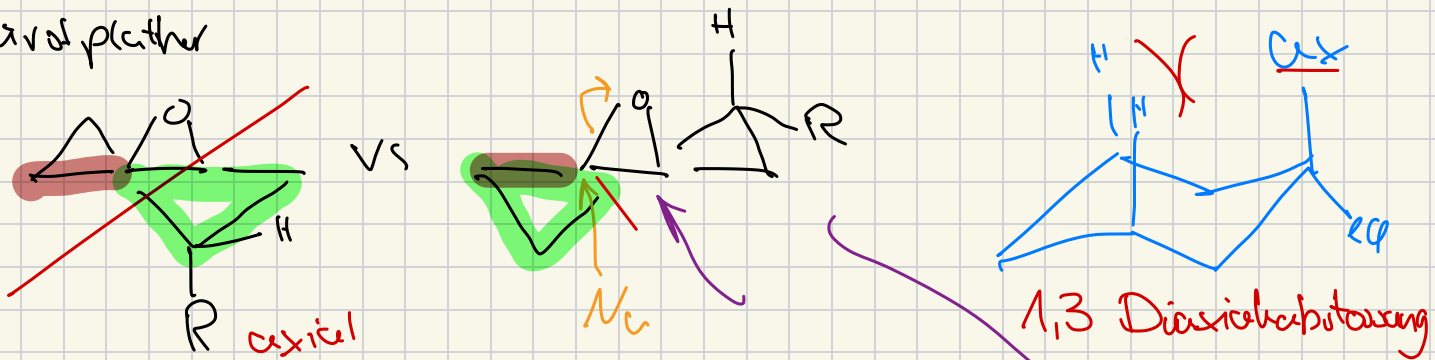
unten



=> von oben

bevorzugt aufgrund der Sterik

Fürsplechter

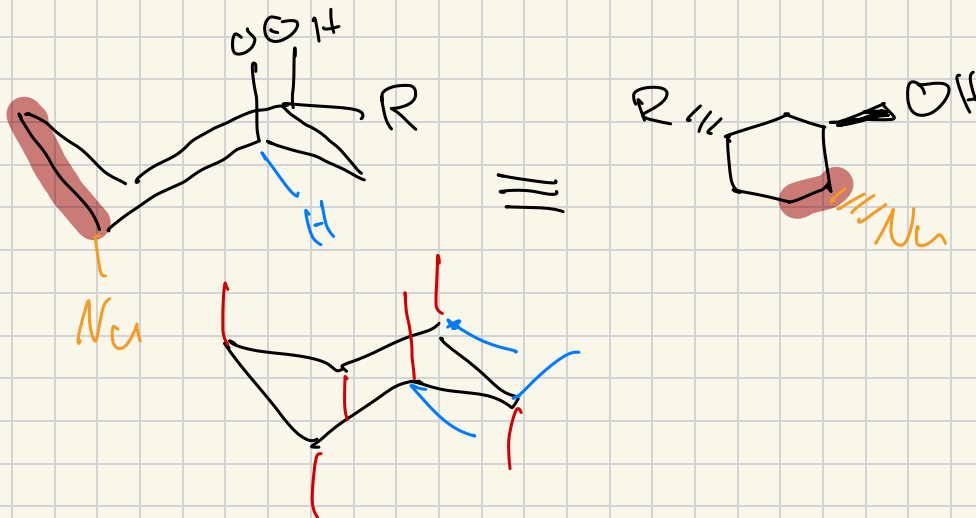


1) Welcher Halbsessel ist am stabilsten?

- links axial \Rightarrow schlecht.

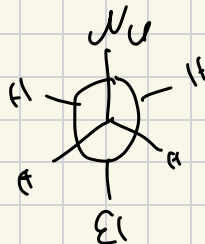
2) Angriff über den Berg

3) wie kommen zurück zur 2D Darstellung

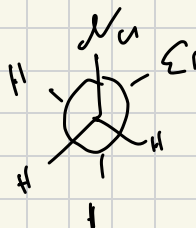


Syn & anti

• Newman

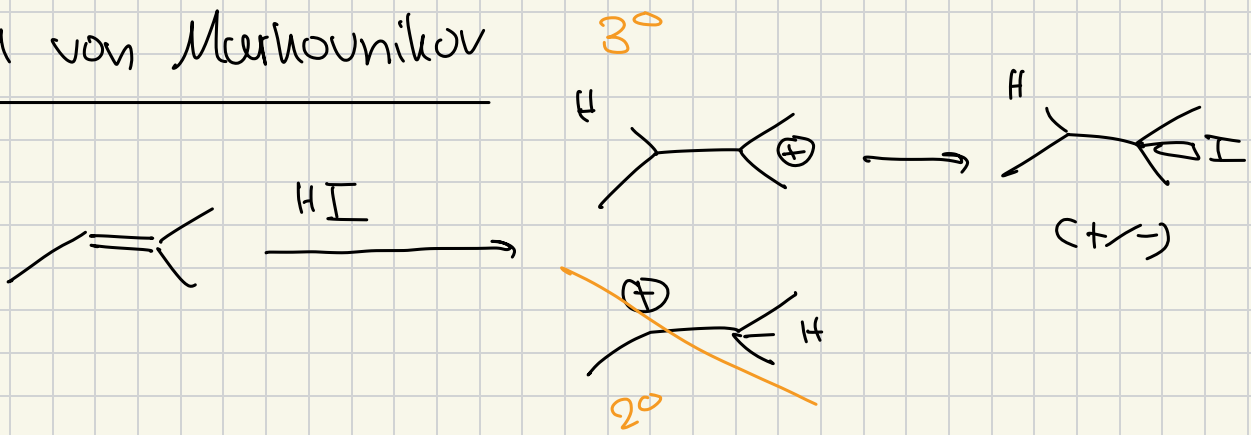


anti;



syn

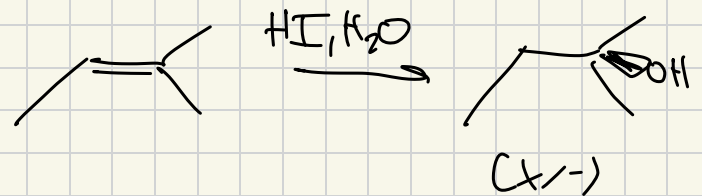
Regel von Markownikow



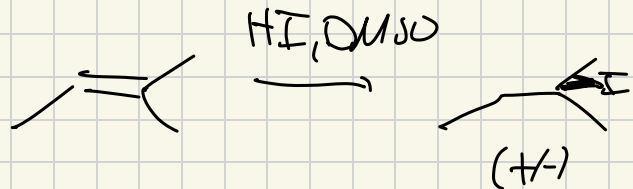
- so angreifen, dass der stabilere Kation entsteht

Lösungsmiteleinfluss

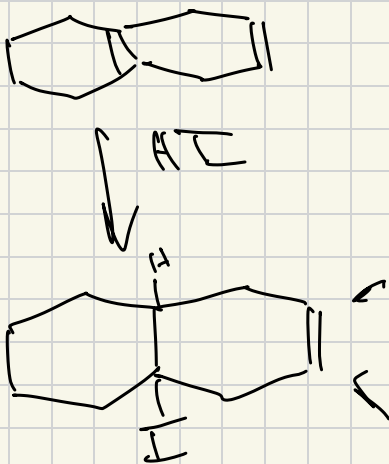
- LM ein Nucleophil ist
- Problem 2 Nucleophile
- I^- stärker



- H_2O mehr vorhanden



Regioselektivität

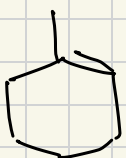
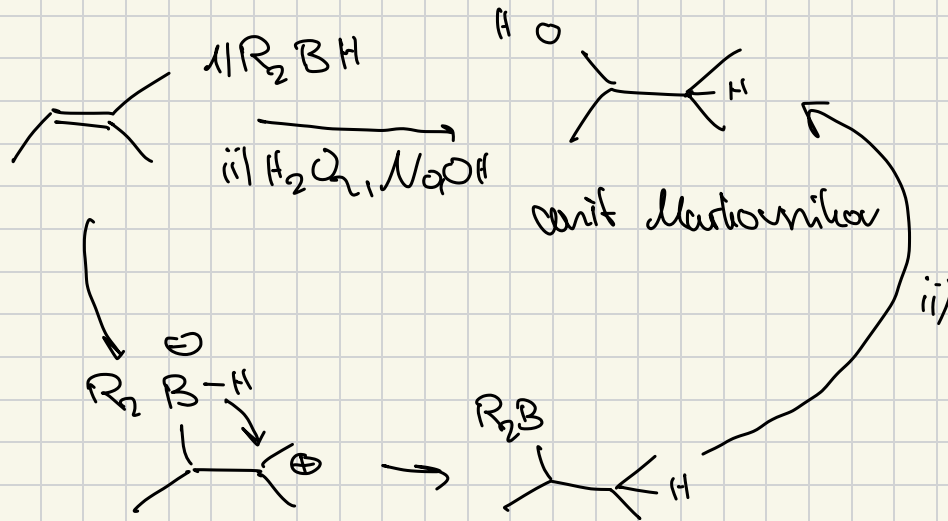




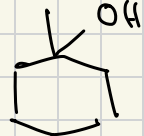
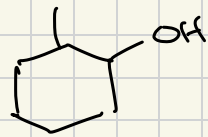
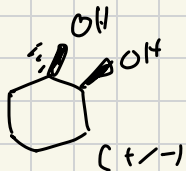
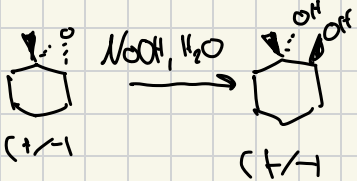
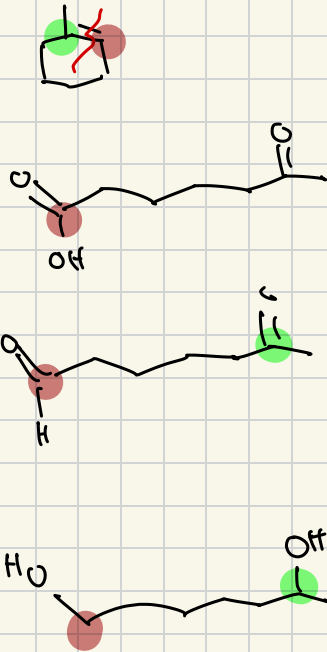
- klassischer Elektrophiler Addition:

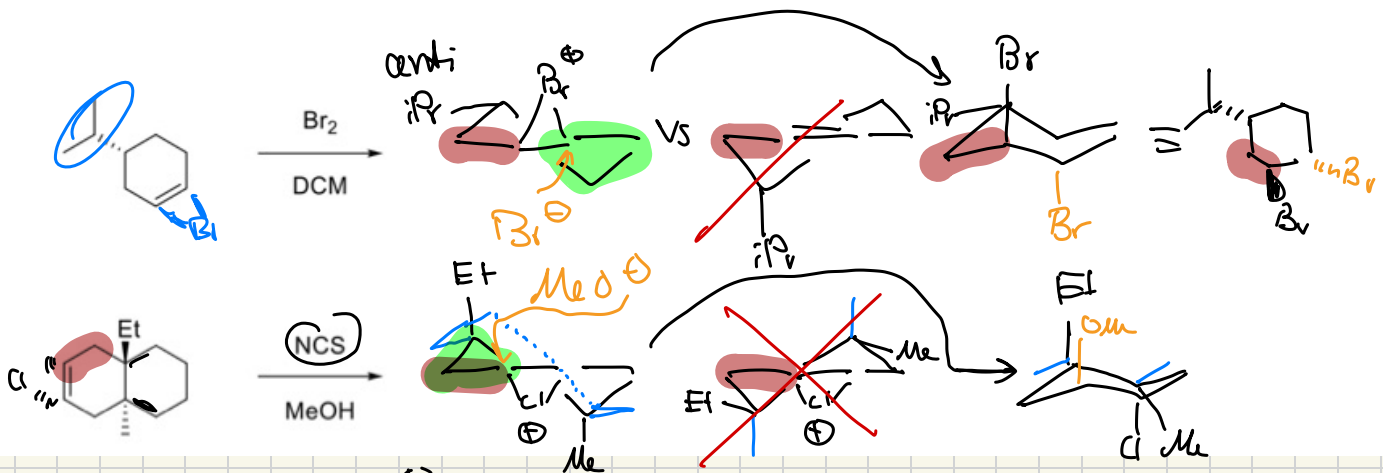
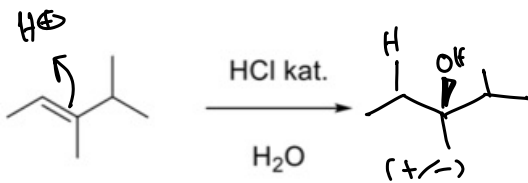
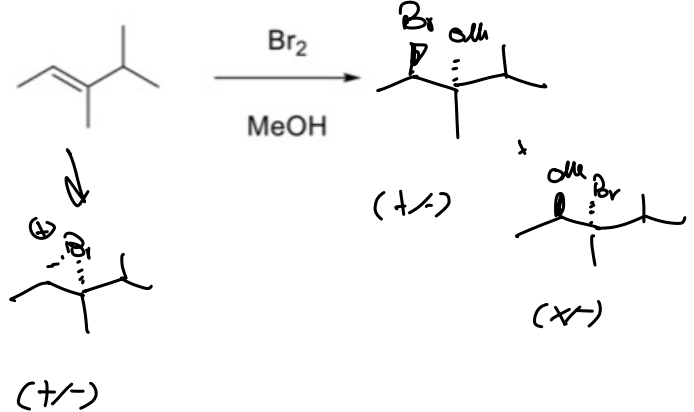
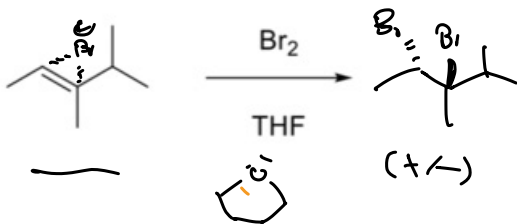
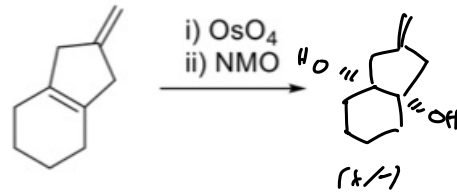
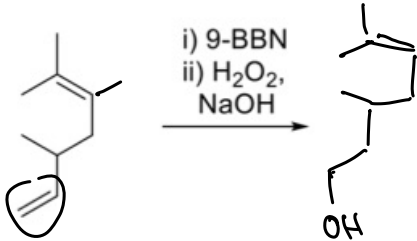
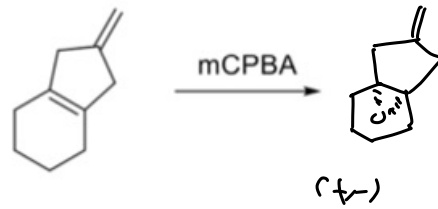
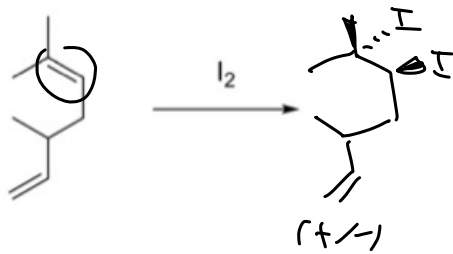
- höher Substituierte DB
- reagiert schneller

Anti Markovnikov

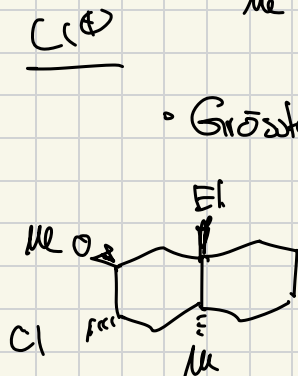
- umgekehrte Regioselektivität:
- Radikalische Reaktionen
- Hydroborierung



Reaktion	Bedingungen	Produkte	Bemerkungen
Halogenierung	X_2		Exo-addition
Hydrohalogenierung	HX		Markownikow
Hydratisierung	H^+, H_2O		Markownikow
Hydrobromierung	1) HBR_2, THF 2) $H_2O_2, NaOH$		anti Markownikow
Dihydroxylierung	$OsO_4, H_2S / NMO$ $KMnO_4, NaOH$	 (+/-)	cis/syn
Epoxidierung	mCPBA	 (+/-) $\xrightarrow{NaOH, H_2O}$ (+/-)	anti Öffnung Exo/anti
Ozonolyse	1) $O_3, DCM, -78^\circ C$ 2) Aufarbeitung a) $H_2O_2, NaOH$ (oxidativ) b) $Zn, AcOH$ (reduktiv) c) $NaBH_4$ (reduktiv)		a) CrO_3 b) $Mg, S / H_2, Pd$

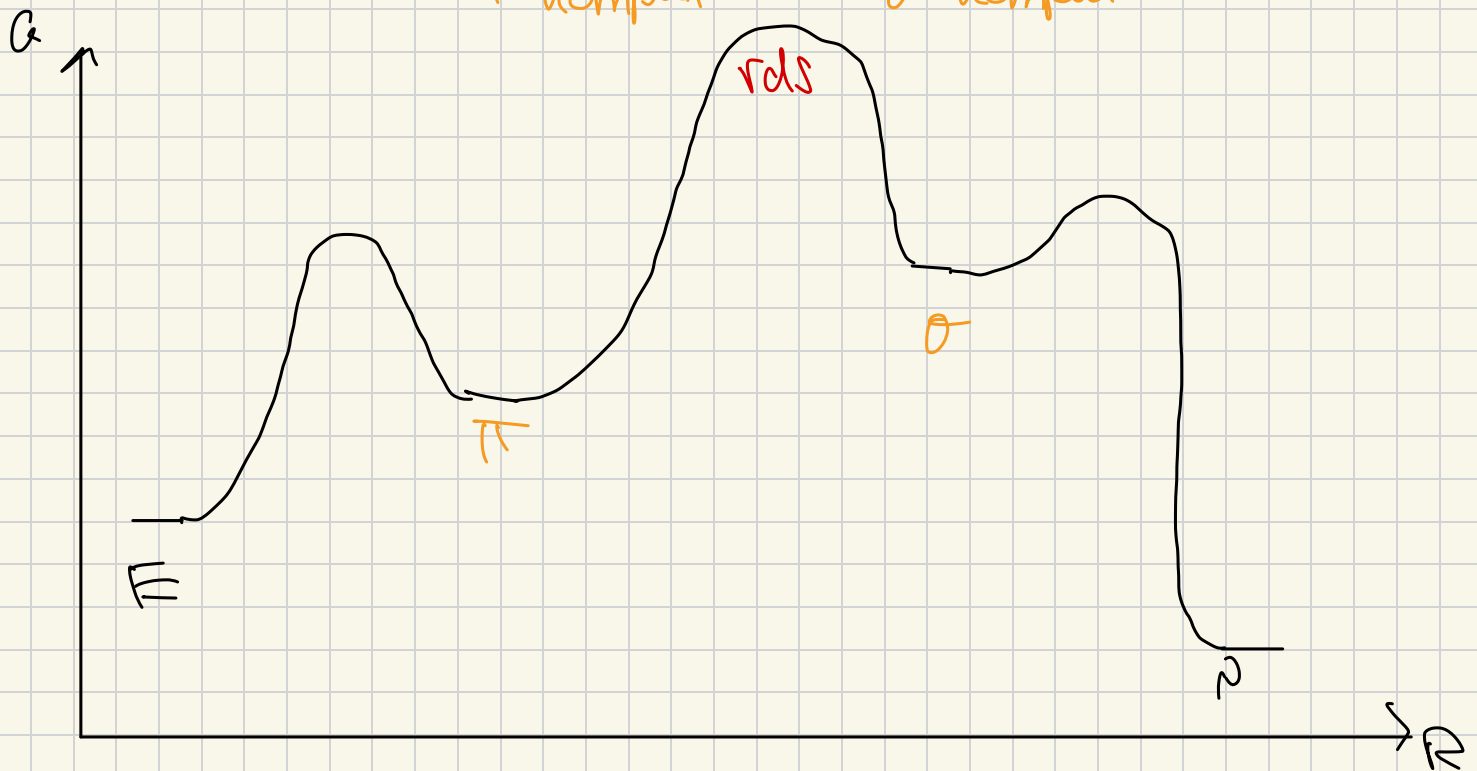
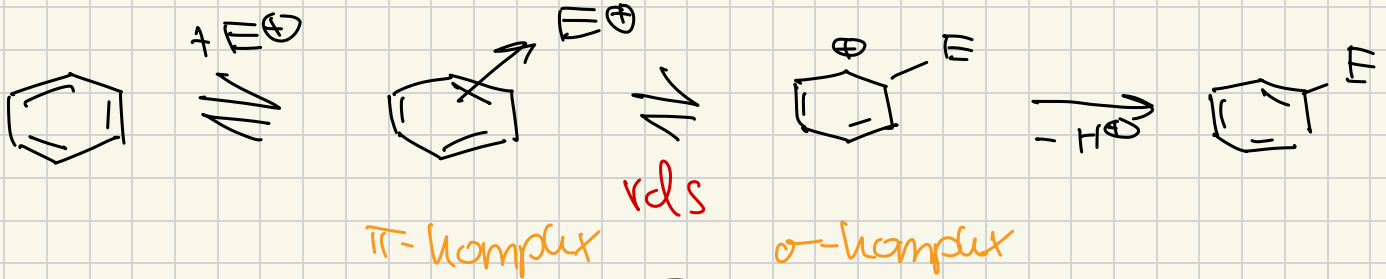
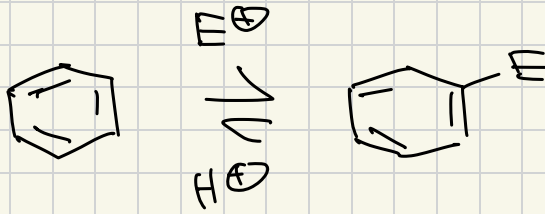


Cl⁻
 ↓
 ABU
 DBPO



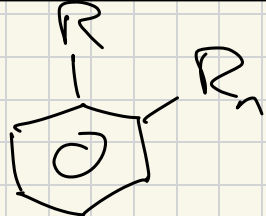
• Größter Substituent muss äquatorial

Elektrophile Aromatische Substitution (S_EAr)

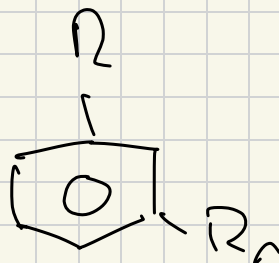


! Regiospezifität

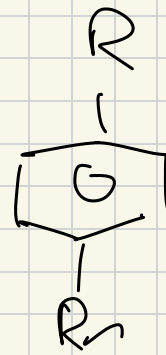
Nomenklatur



ortho



meta

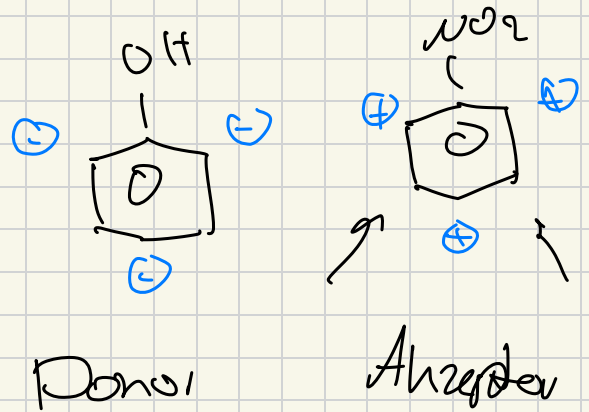


para

• Zweitsubstitution

• Regioselektivität

- Donor: ortho/para
- Akzeptoren: meta
- $\pi > \sigma$
- Halogenen
 - Desaktivierend
 - o/p



• Donoren

2 x ortho
Statistisch
bevorzugt

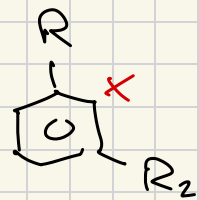
1 x para
Sterisch
bevorzugt

\Rightarrow

Me und
größer

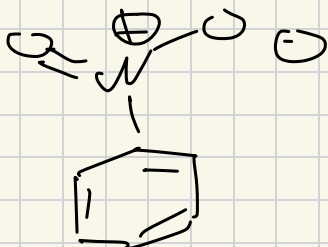
• Drittsubstitution

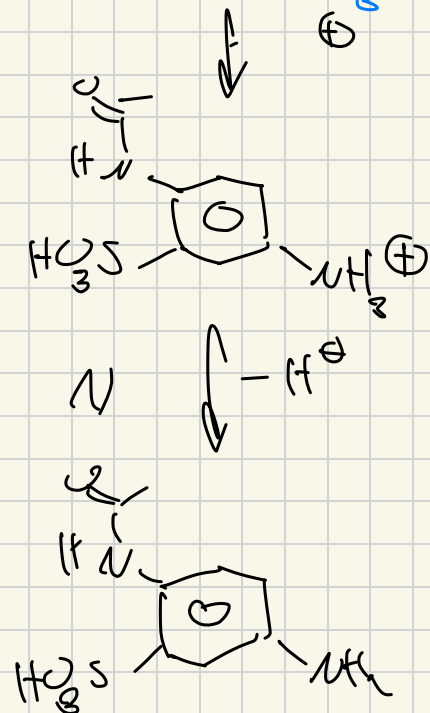
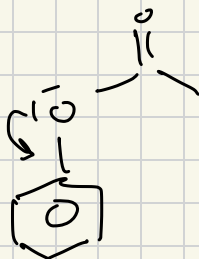
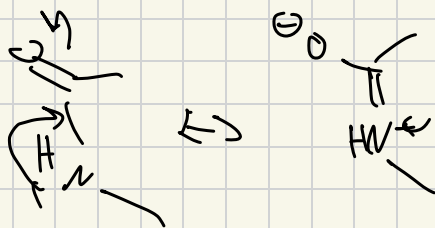
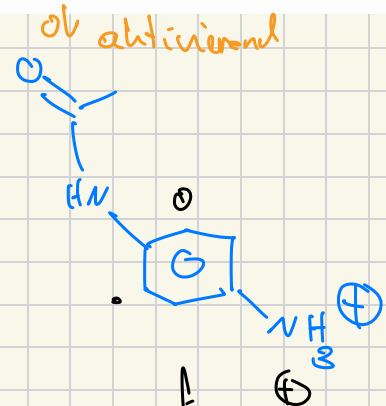
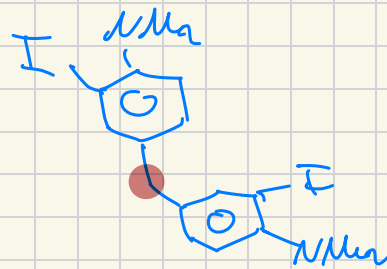
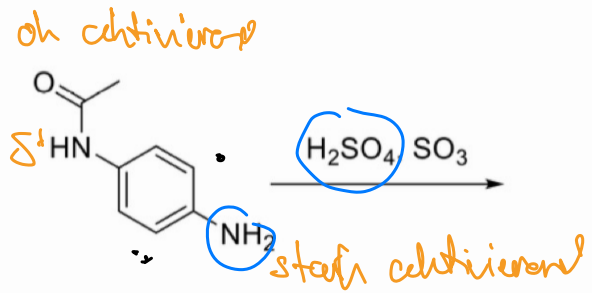
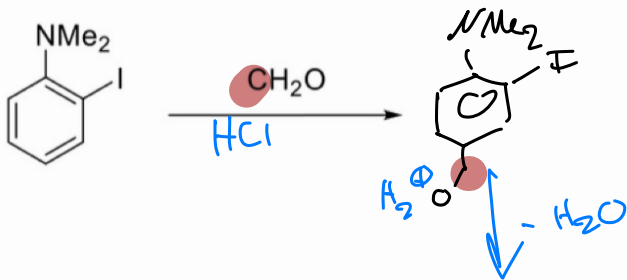
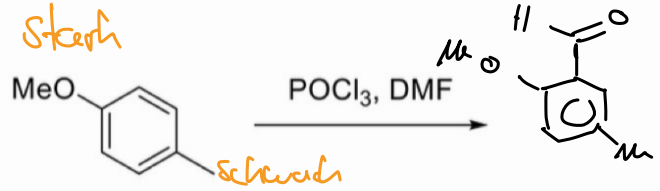
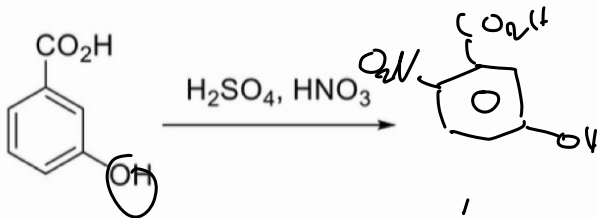
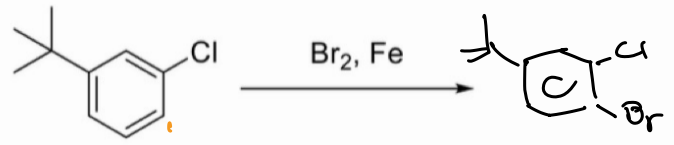
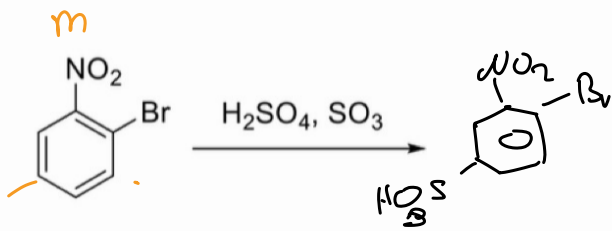
- Stärkste aktivierende Gruppe dirigiert
- Wahrscheinlichkeit zwischen zwei meta ständigen Substituenten zu landen gering



- 2 meta Subs.: 1 aktivierend 1 desaktivierend

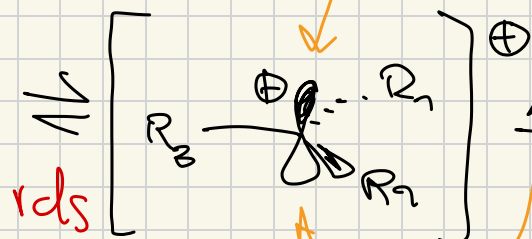
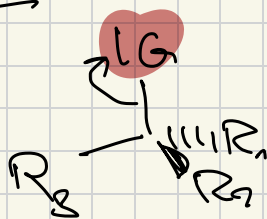
\Rightarrow lieber para zur aktivierenden Gruppe





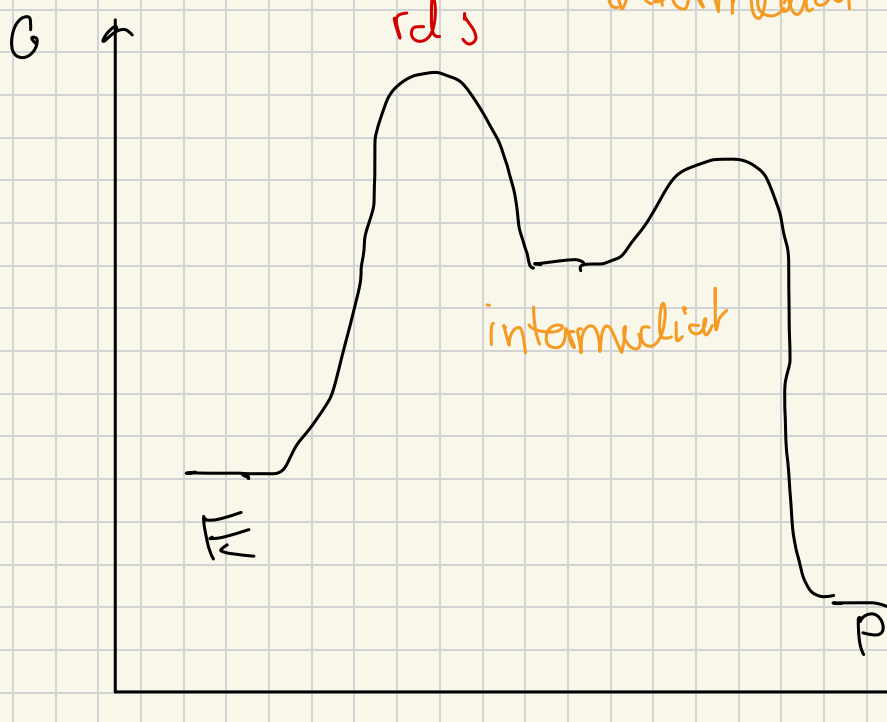
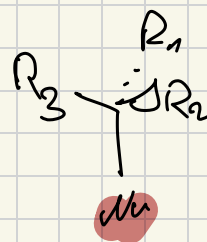
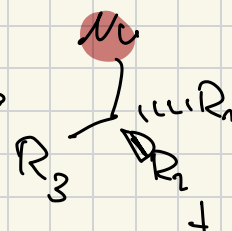
Nucleophilic Substitution

• S_N1



Racemate

(+/-)



Kinetic:

1. Ordnung

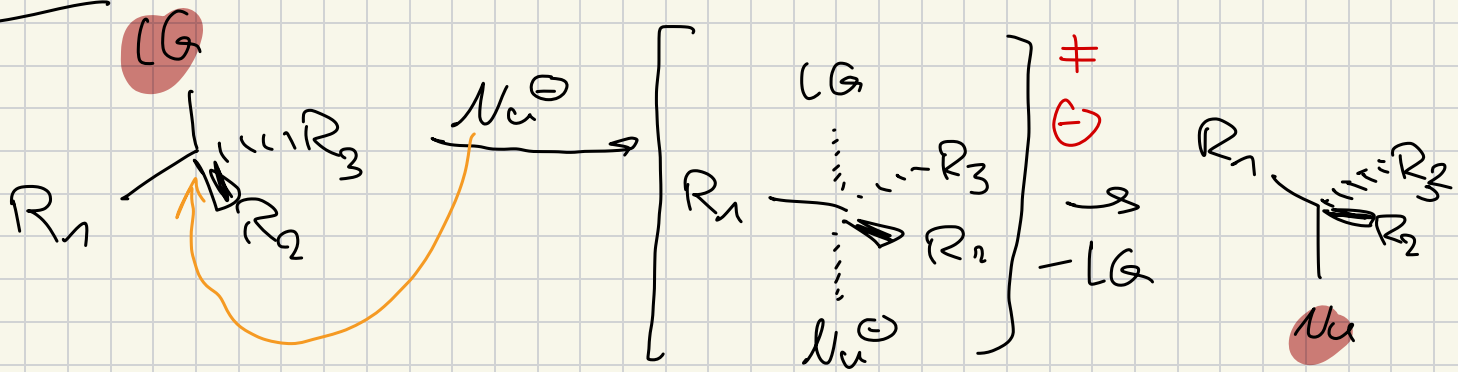
unimolecular

$$v = \frac{d[P]}{dt} = - \frac{d[E]}{dt}$$

$$= k [E_{aktiv}]$$

S_N2

||||

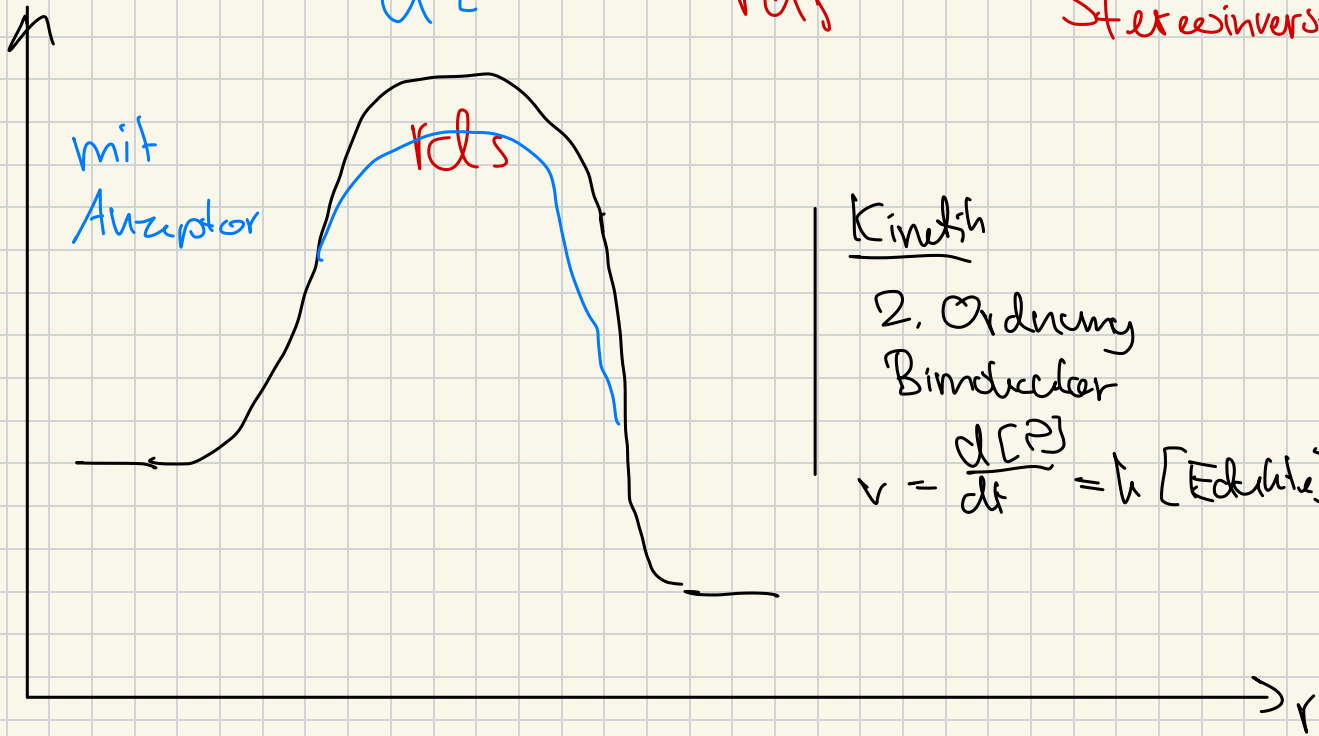


G

G 2 \ominus

rd, s

Stereoisomerie

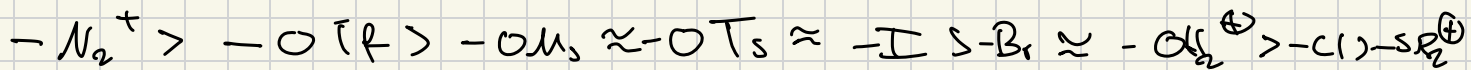


Kinetik

2. Ordnung
Bimolekular

$$v = \frac{d[P]}{dt} = k [\text{Edukte}] [\text{Nu}]$$

Abgangsgruppen



Nukrophilie

