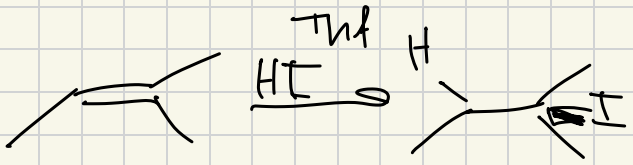
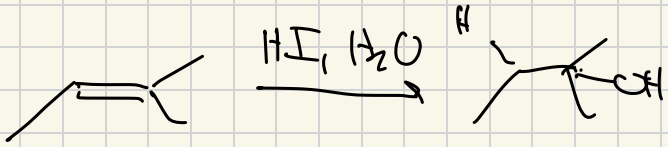
Elektrophiler Addition

- Lösungsmitteleinfluss

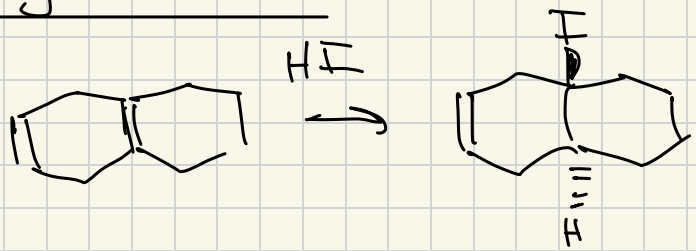


  - Wenn LM ein Nucleophil ist, reagiert das eher mit dem Elektrophil
    ⇒ Konzentration



oder MeOH

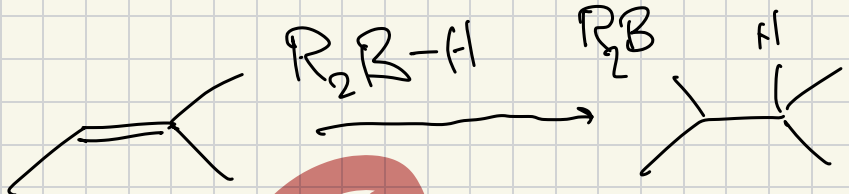
- Regioselektivität

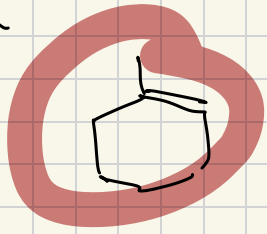


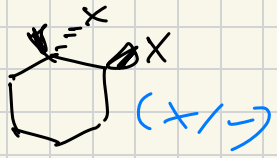
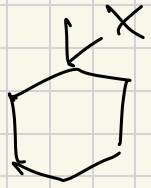
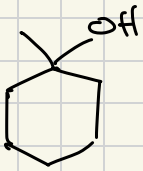
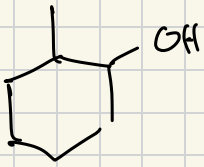
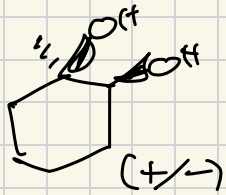
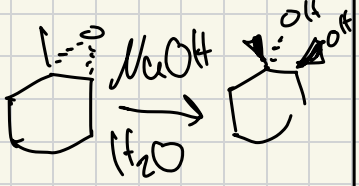
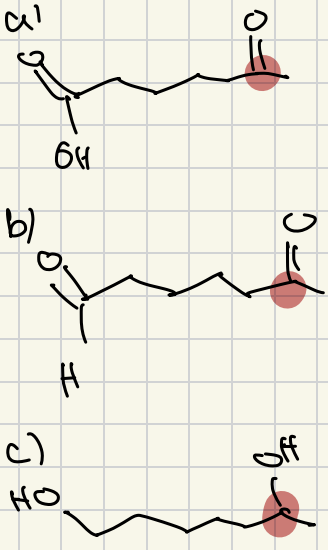
  - höher substituierte DB reagiert eher

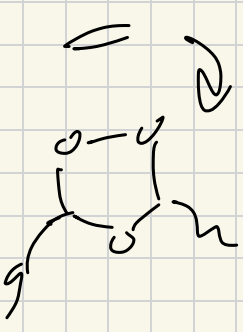
- Anti Markovnikov

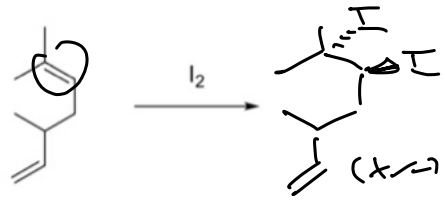
  - DB die niedriger substituiert ist
  - Ort des Nucleophils ist invertiert
  - Wenn man ich darauf achten:
    - Radicalreactions
    - Hydroborierung

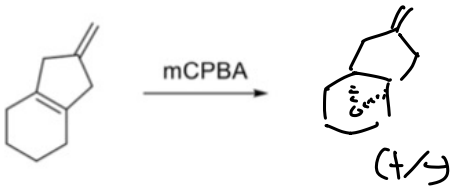


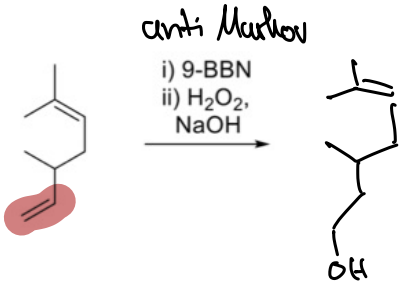


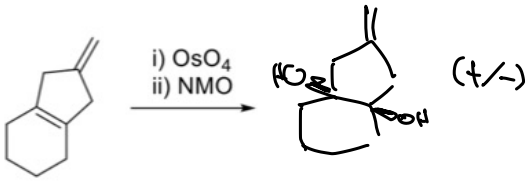
Reaktion	Bedingung	Produkt	Bemerkung
Halogenierung	X_2		Trans-Addition
Hydrogen-halogenierung	HX		Markovnikov
Hydratisierung	$H^{\oplus}$, H_2O		Markovnikov
Hydroborierung	1) HBR_2, THF 2) H_2O_2, NaOH		anti-Markovnikov
Dihydroxylierung	OsO_4, H_2S / NMO $KMnO_4$, NaOH		cis-Dihydroxy
Epoxidierung	mCPBA		anti-Dihydroxy anderes Nuc ist möglich
Ozonolyse	1) O_3, DCM, -78°C 2) Aufarbeitung a) H_2O_2, NaOH (oxidativ) b) Zn, AcOH (reduktiv) c) $NaBH_4$ reduktiv		σ-Bindung nicht brechen a) CrO_3 b) Me_2S oder H_2, Pt

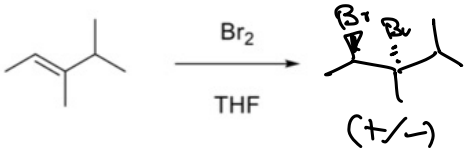


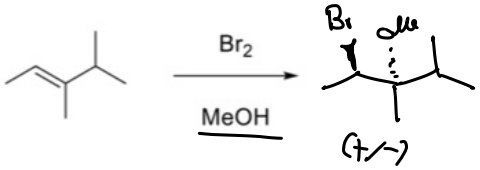

I_2
(+/-)

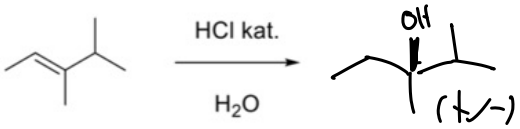

mCPBA
(+/-)

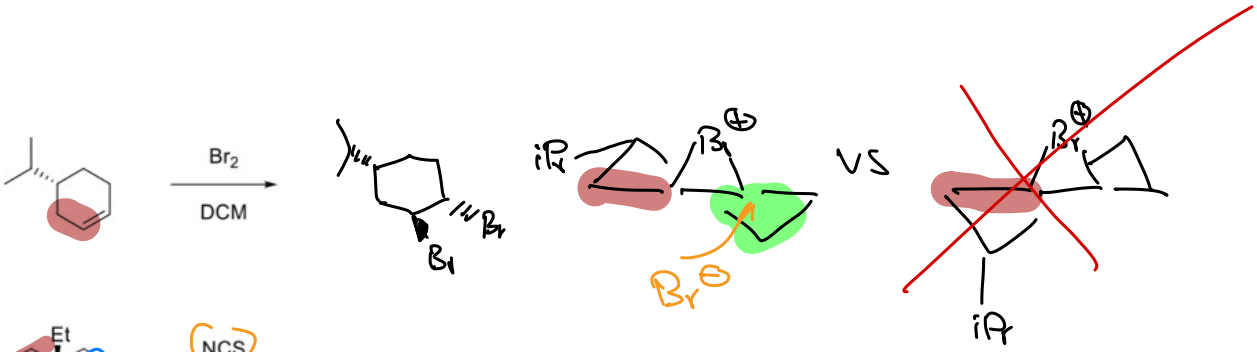

anti Markov
i) 9-BBN
ii) H_2O_2, NaOH
OH

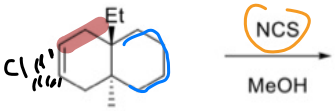

i) OsO_4
ii) NMO
(+/-)

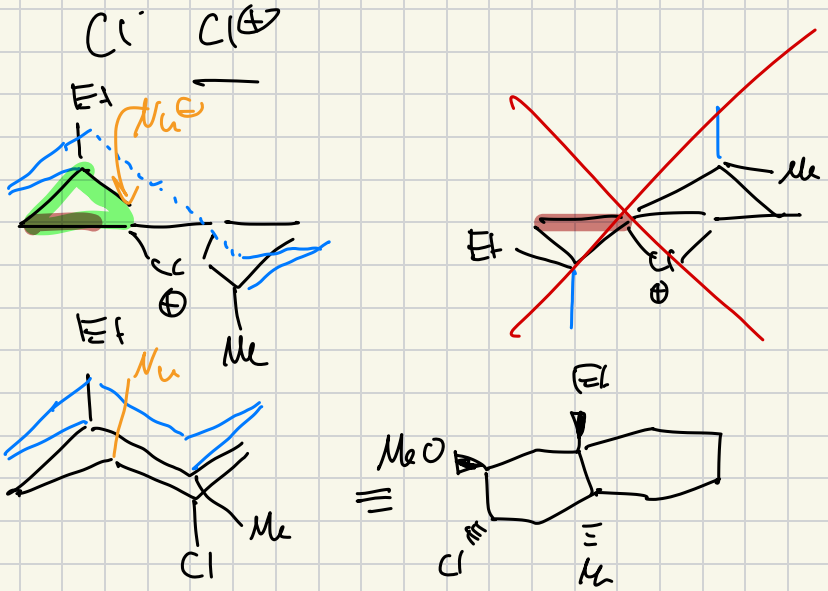

Br_2
THF
(+/-)


Br_2
MeOH
(+/-)

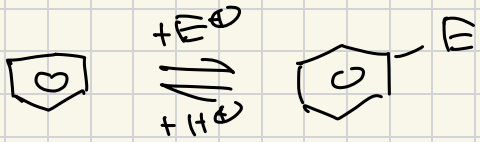

HCl kat.
H_2O
OH
(+/-)

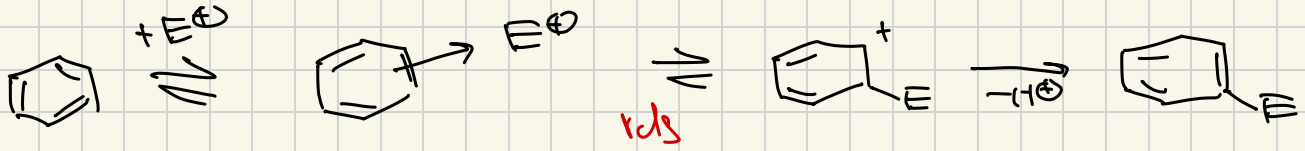

Br_2
DCM
vs
iA

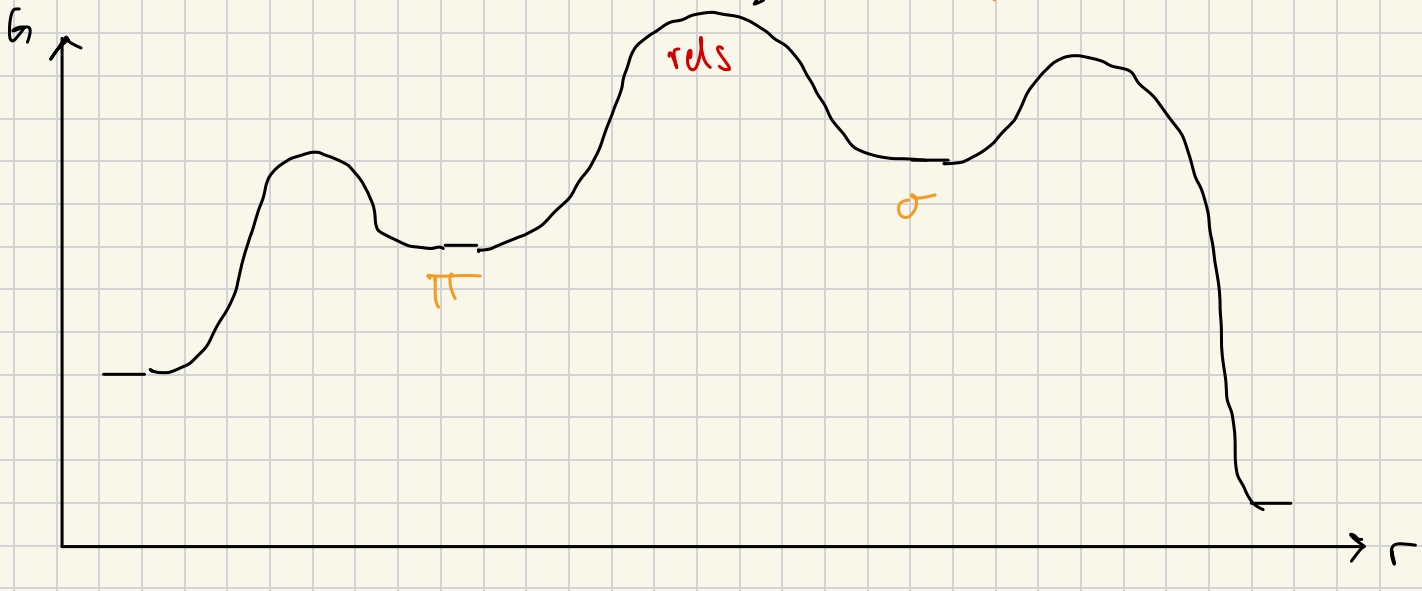

Et
NCS
MeOH


Et
Me
Cl
MeO
=

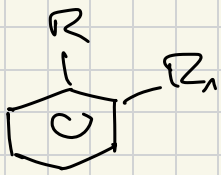
Elektrophile Aromatische Substitution S_EAr

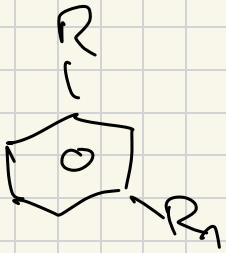


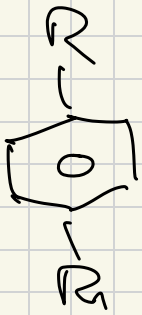




Nomenklatur





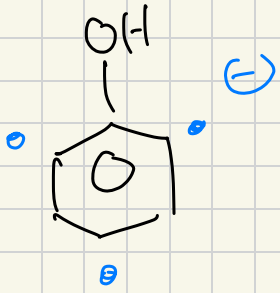


2x ortho 2x meta para

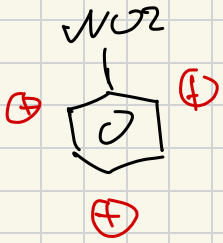
Statistisch bevorzugt

Sterisch bevorzugt

- Zweitsubstitution
  - Regioselektivität ist relevant
  - Donoren: ortho, para
  - Akzeptor: meta
  - $\pi > \sigma$
  - Halogene sind Akzeptoren
    → desaktivierend
    → ortho, para

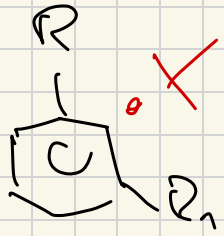


Donor

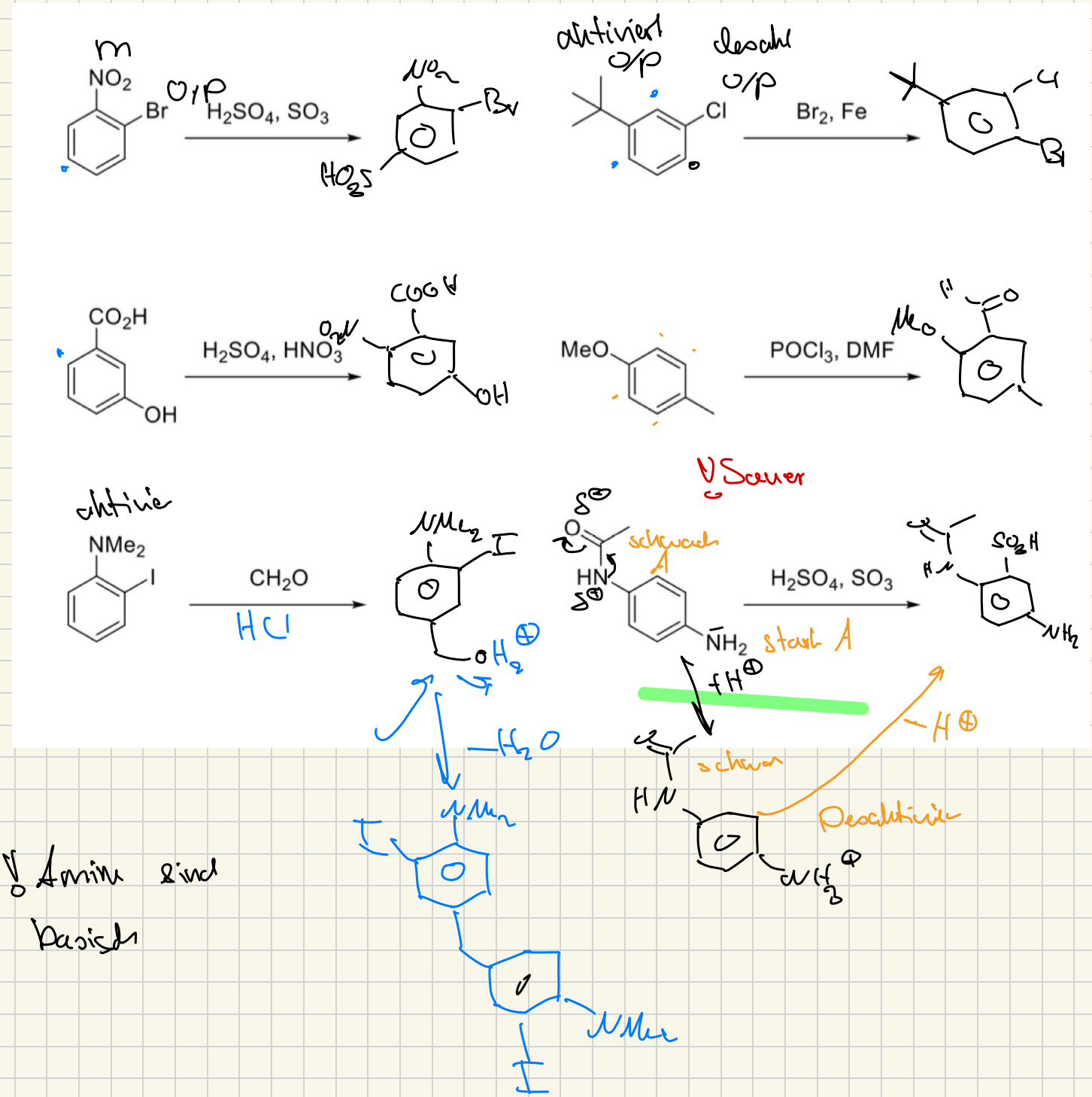


Akzeptoren

- Drittsubstitution
  - was ist am stärksten aktivierend?
    → dirigiert



  - W'keit zwischen 2 meta ständigen Substituenten zu landen ist gering
  - 1,2,3 ungünstig wegen sterik
  - 2 meta: 1 aktivierend der andere desaktivierend
    ⇒ para zum aktivierenden

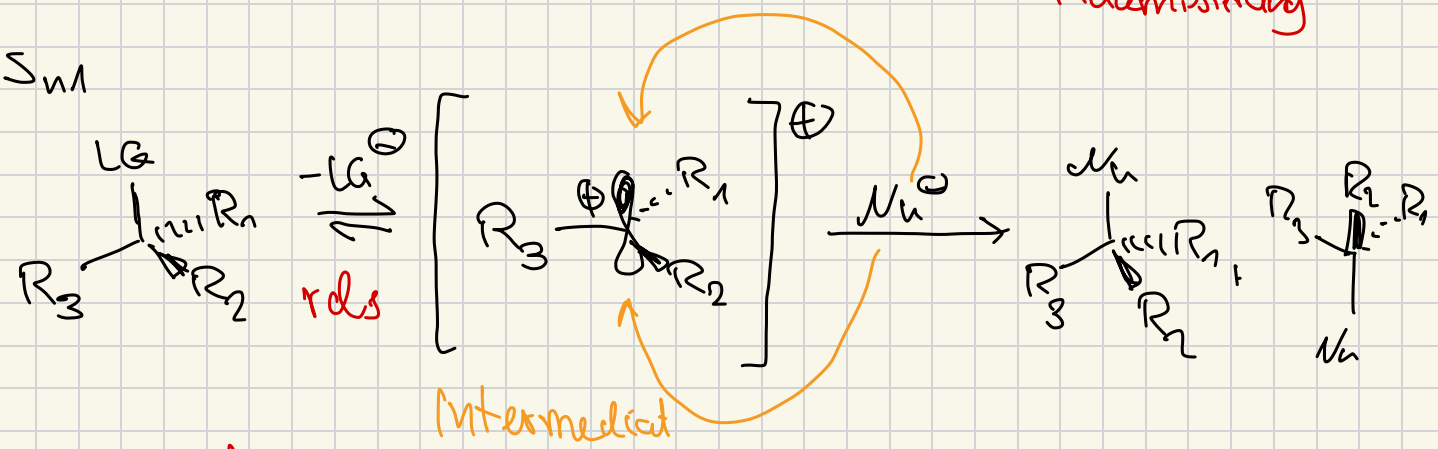


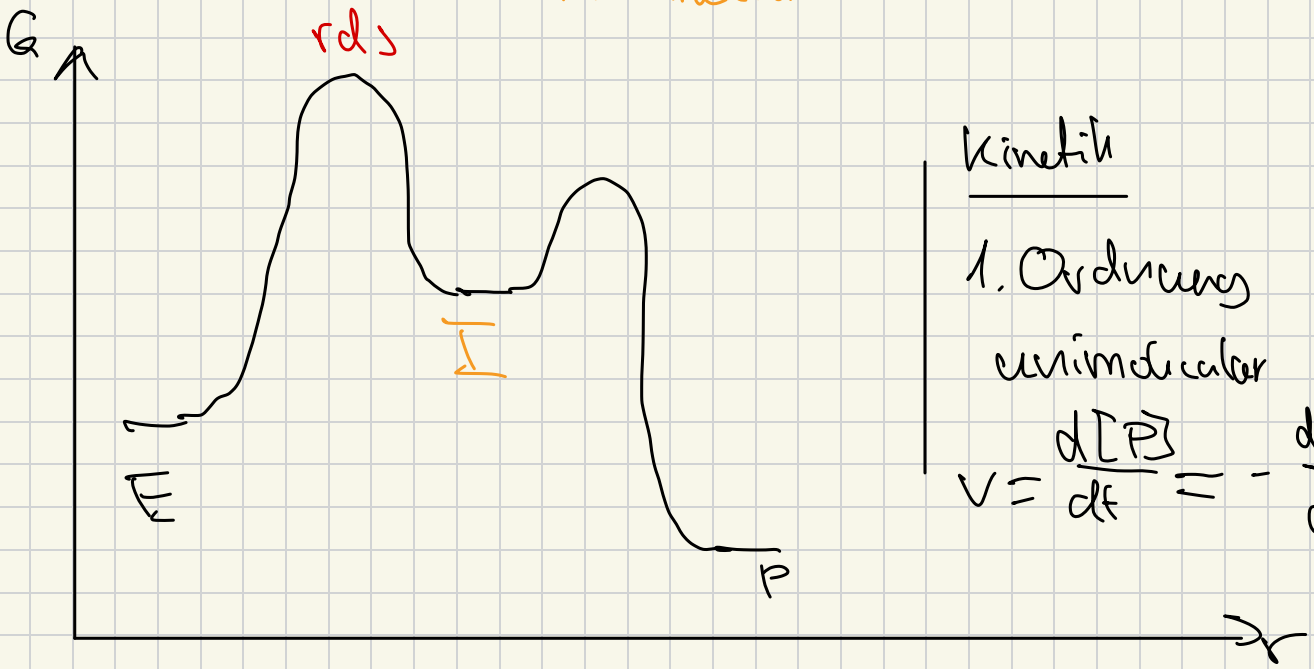
V Amine sind basisch

Nucleophile Substitution

- S_N1

Racemisierung





Kinetik

1. Ordnung

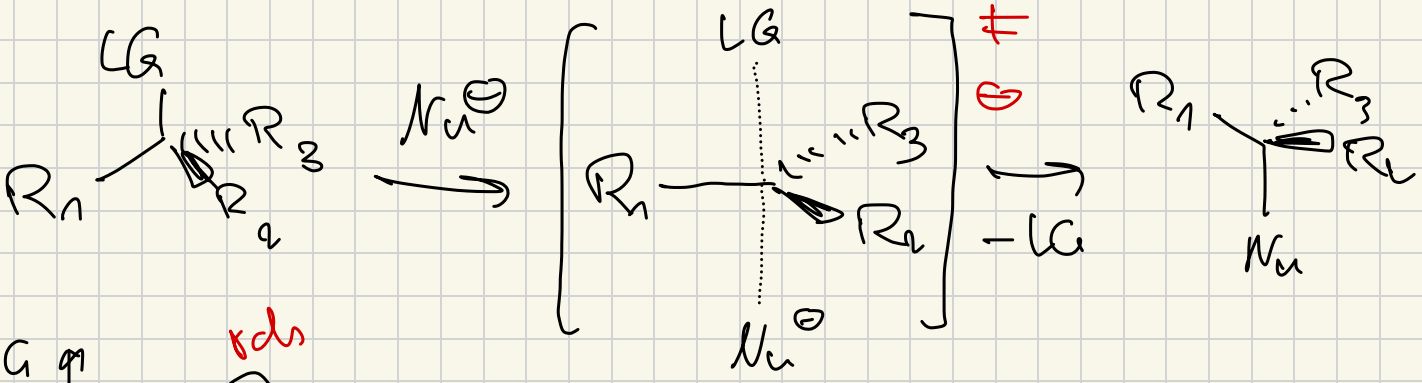
unimolecular

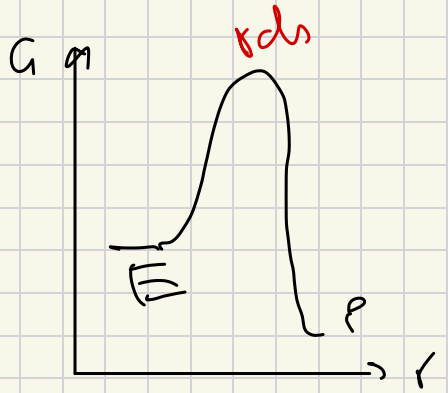
$$v = \frac{d[P]}{dt} = -\frac{d[E]}{dt} = k[\text{Edukt}]$$

- S_N2

rds

Stereoinversion





Kinetik

2. Ordnung · Bimolecular

$$v = \frac{d[P]}{dt} = -\frac{d[E]}{dt} = k[\text{Edukt}][Nu]$$

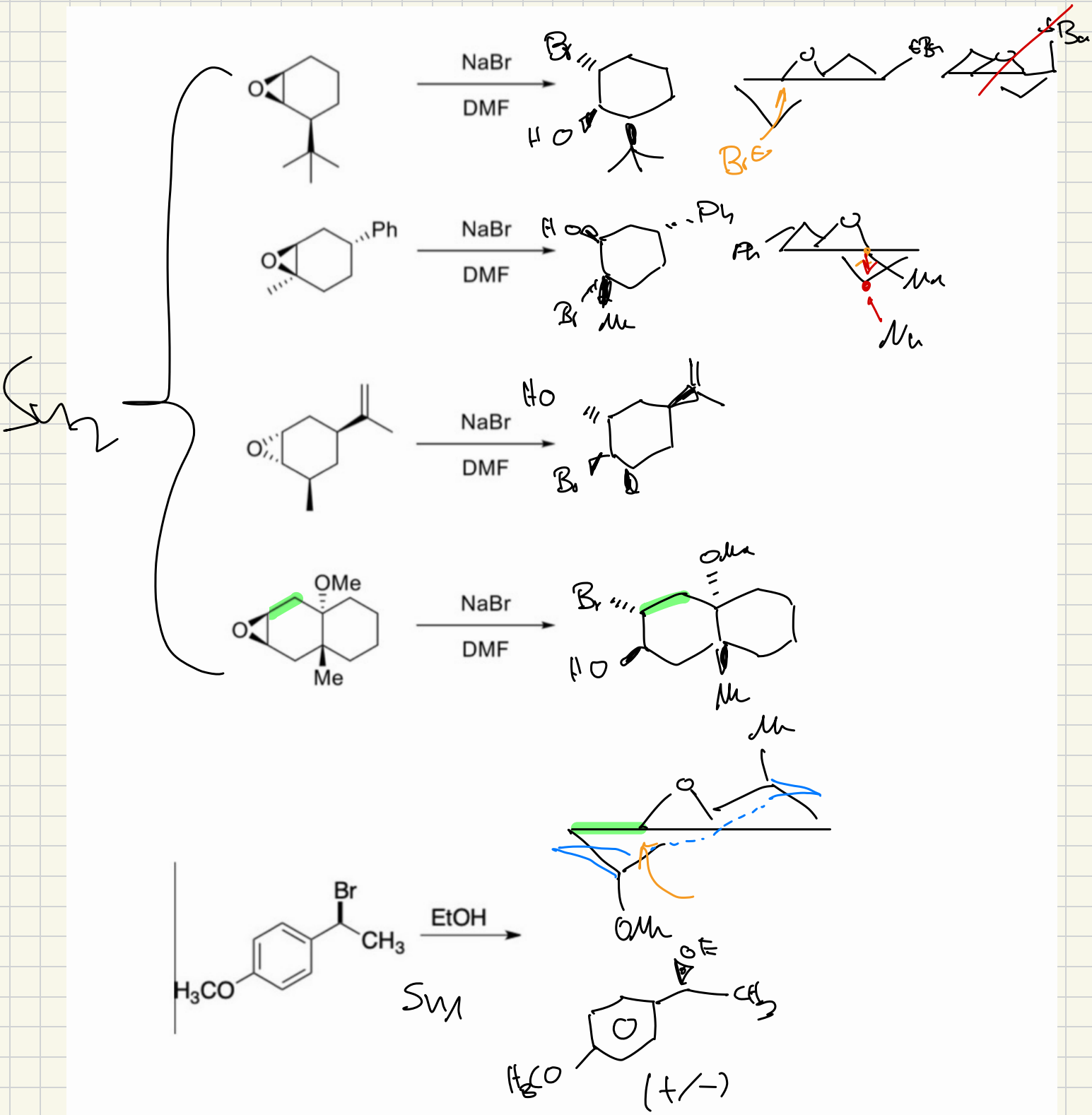
- **Abgangsgruppen**

$-N_2^+ > -OTf > -OMs \approx -OTs \approx -I > -Br \approx -OH_2^{\oplus} > -Cl > -SR_2^{\oplus}$

- **Nucleophil**

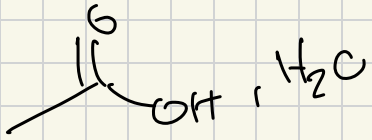
$PhS^{\ominus} > Et_3P \gg Ph_3P > SCN^{\ominus} \gg PhO^{\ominus} > NH_3 \gg F^{\ominus}$

	SN1	SN2
Kinetik	1. Ordnung	2. Ordnung
Stereoinfo.	Racemisierung	Stereoinversion
Zwischenstufe	Carbokation	Übergangszustand $\delta^{\ominus}$
Substituenten einfluss	stabiles Kation wichtig $\rightarrow 3^{\circ} > 2^{\circ} > 1^{\circ}$	$1^{\circ} > 2^{\circ} > 3^{\circ}$
Sterik Edukt	Brückenkopf schnell V. Bredt'sche Regel	Brückenkopf unmöglich → Rückseite blockiert
Lösungsmittel	polar, protisch	polar, aprotisch
Abgangsgruppe	LG stabilisiert wichtig → parallel pKa → kleiner pKa ⇒ gute LG	weiche LG LG nicht auf Solvatisierung angewiesen
Nucleophil		weich Nuc $PhS^{\ominus}$


NaBr
DMF
Ph
NaBr
DMF
NaBr
DMF
OMe
Me
NaBr
DMF
Br
CH3
H3CO
EtOH
Sn1
(+/−)

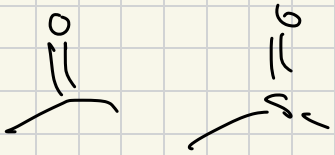
protisch:

H abgeben

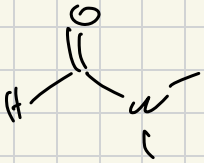


aprotisch:

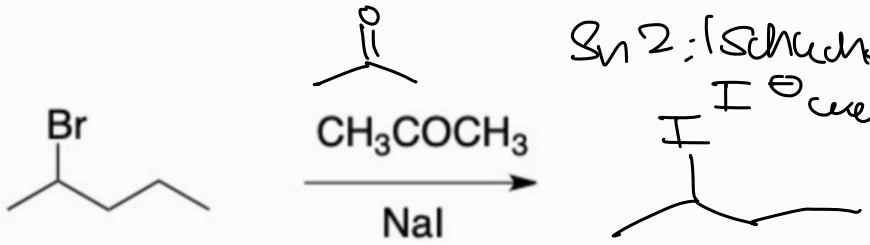
kein H abgeben



DMSO



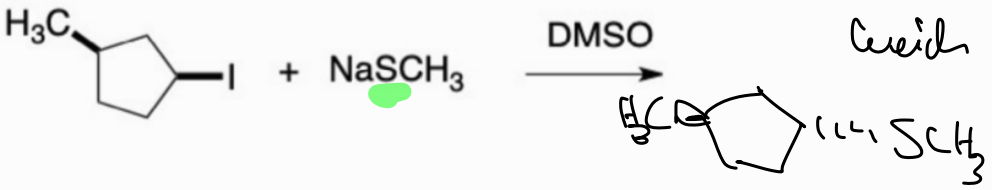
DMF

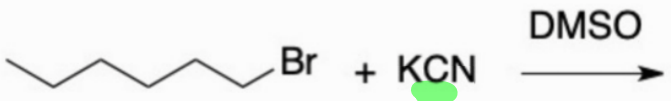


Sn2: (schlecht) LG, LM
$I^{\ominus}$ zweid

Sn2: 1°, schlechte LG
S zweid

Sn2: LM, gute LG
zweid





Sn2: LM, CN, 1°