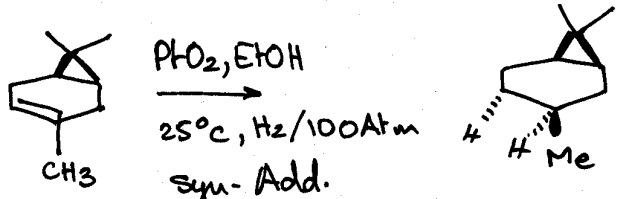
5. Gruppe Reduktions- und Oxidations-Reaktionen

1. Reduktion

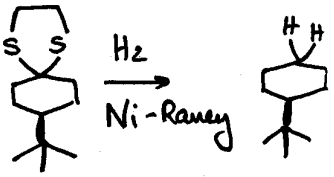
Reduktionsmittel

1.1 Katalytische Hydrierung

- Adams-Kat. $PtO_2 \xrightarrow{H_2} Pt$

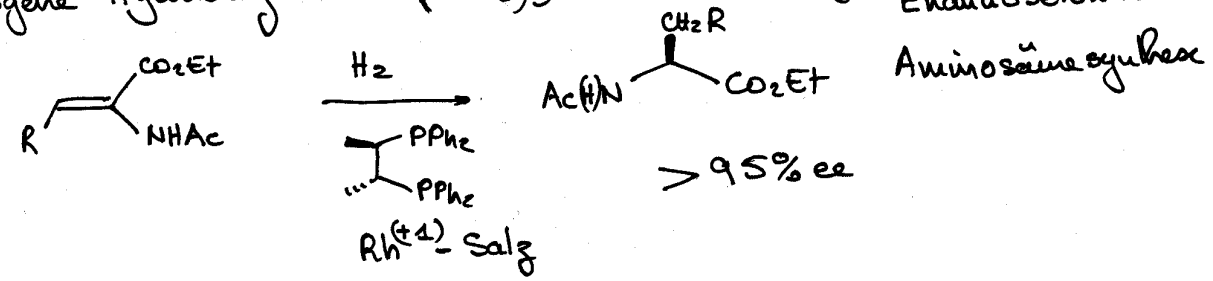


- Raney-Ni Ni/Al Legierung $\xrightarrow{NaOH}$ Ni + $Al(OH)_4^{\ominus}\ Na^{\oplus}$



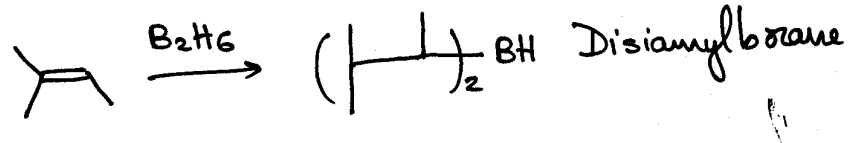
1.2. Homogene Hydrierung $ClRh(PPh_3)_3$ Wilkinson-Katalys.

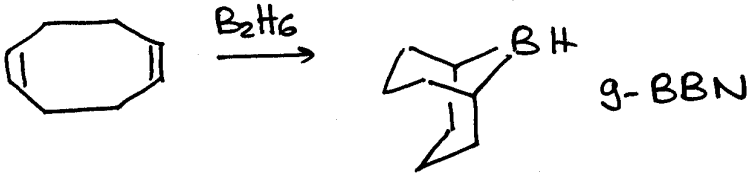
Enantioselektive Aminosäuresynthese

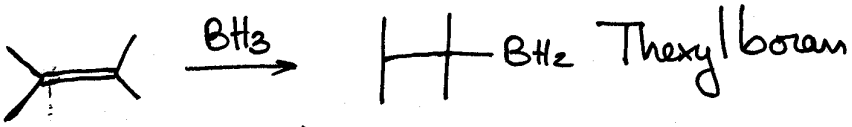


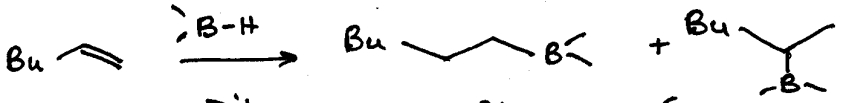
1.3. Reduktion mit Metalle, Metallhydride

$2\,BH_3 \rightleftarrows B_2H_6$ käuflich ($3\,NaBH_4 + 4\,BF_3 \longrightarrow 3\,NaBF_4 + 2\,B_2H_6$)

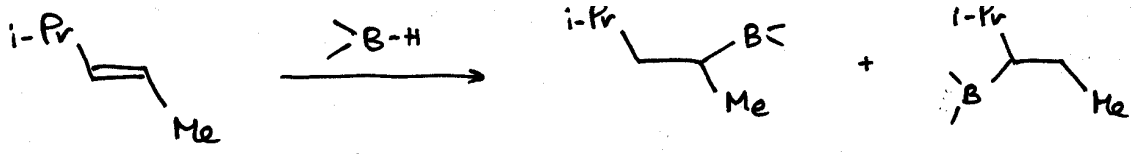




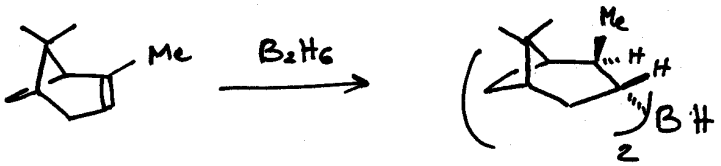




Diboran	94	:	6
Disiamylboran	99	:	1
9-BBN	99.9	:	0.1

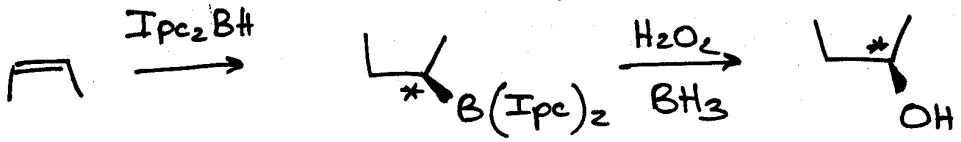


Diboran	57	43
Disiamylboran	97	3
9-BBN	99.8	0.2

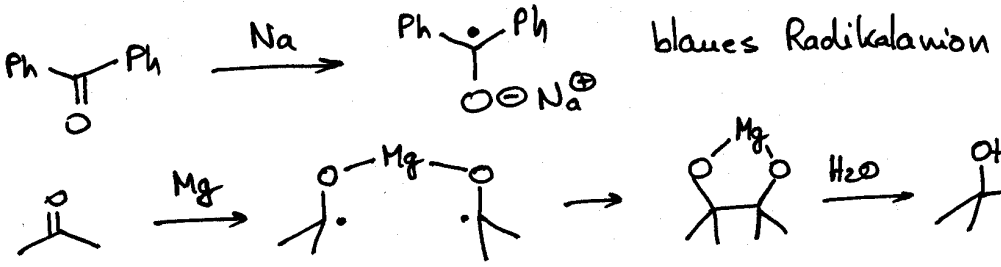


$(Ipc)_2BH$

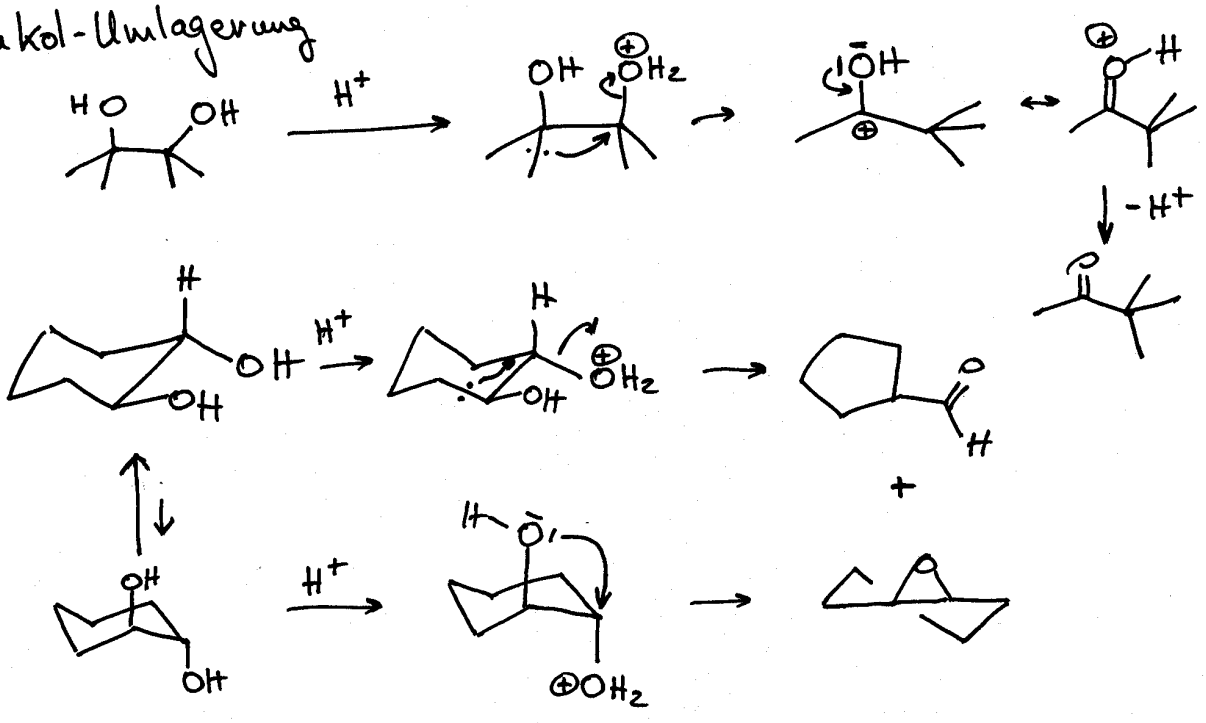
Bis-Isopinocampheylboran



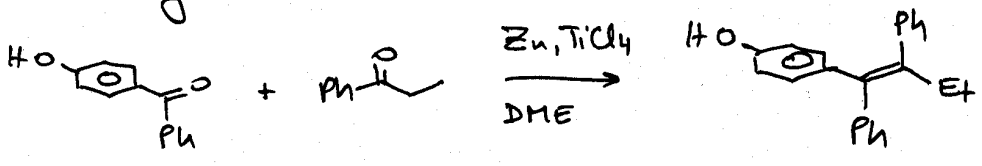
Reduktion mit Metalle

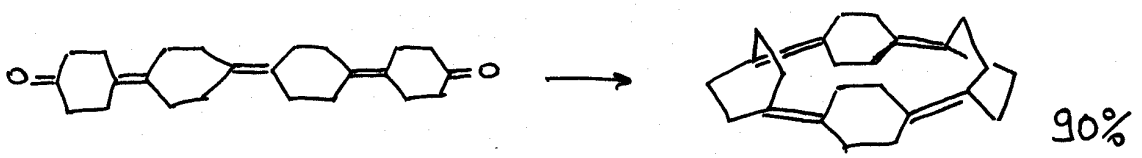


Pinakol-Umlagerung



1.4. McMurry - Reduktion

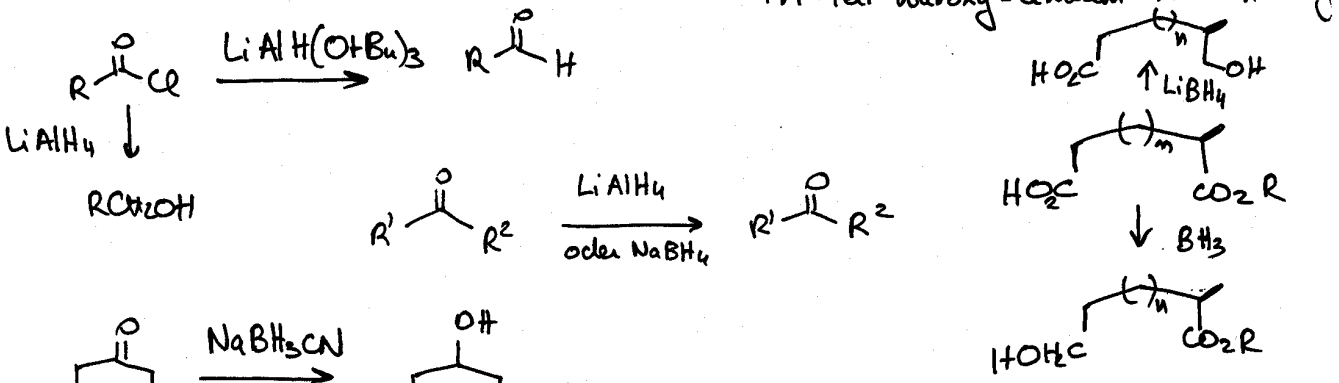


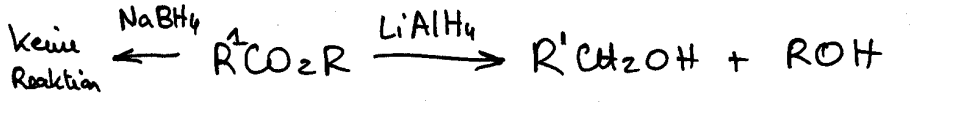


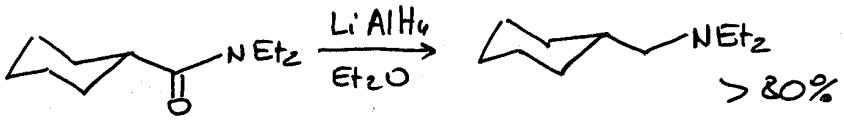
Reduktion mit $LiAlH_4$ und andere komplexe Hydride

Milderes, selektives Reduktionsmittel: $LiAlH(Ot\text{-}Bu)_3$

Tri-tert-butoxy-Lithium-Aluminiumhydrid

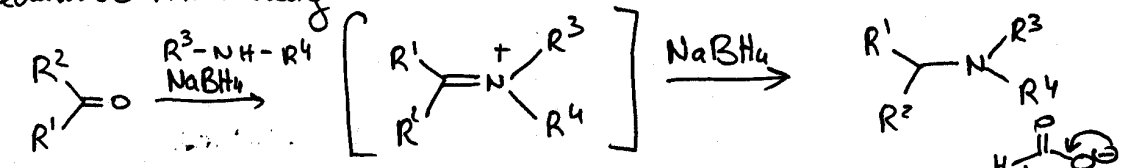






(Siehe Tabelle)

1.5. Reduktive Aminierung

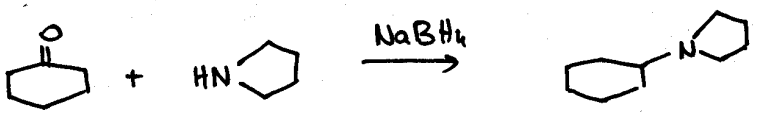


Eschweiler-Clark N-Methylierung: $R_2NH \xrightarrow[HCO_2H]{CH_2O} R_2N^{\oplus}=CH_2 \longrightarrow R_2N\text{-}CH_3$

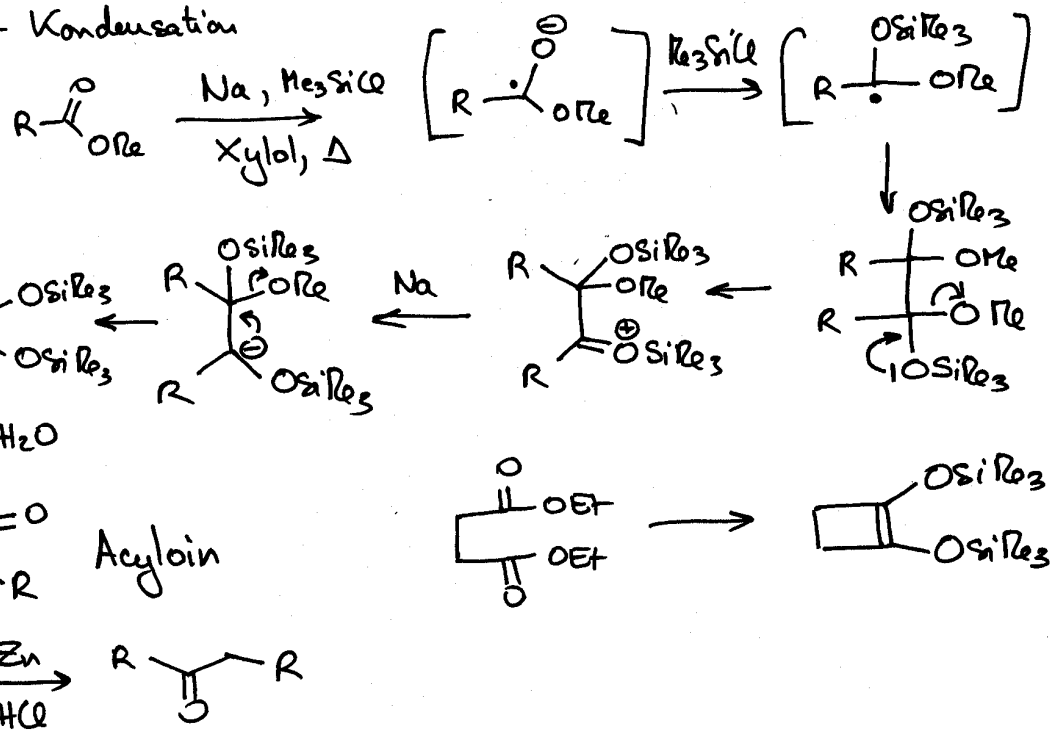
Tabelle 2.5. Selektivität der Reduktionsmittel [67]

	$LiAlH_4$	$NaAlH_4$	Red-Al[1]	$LiBH_4$	$NaBH_4$	$NaBH_3CN$	$Li(t\text{-}BuO)_3AlH$	B_2H_6	$BH_3 \cdot NR_3$	$(iBu)_2BH$	AlH_3	$(iBu)_2AlH$
R—CHO	+	+	+	+	+	+[2]	+	+	+	+	+	+
>C=O	+	+	+	+	+	+[2]	+	+	+	+	+	+
R—CO—Cl	+	+	+	+	+	–	+[3]	–	+	–	+	
Lactone	+	+	+	+	(+)[4]	–	–	–		+[5]	+	+[5]
>C(—O—)C<	+	+	+	+	(+)[4]	–	–	+		–	+	
$R^1—CO_2R^2$	+	+[6]	+	+	(+)[4]	–	+[7]	–	–	–	+	+[3]
$R—CO_2H$	+	+	+	–	–	–	–	+	–	–	+	–
$R—CO_2^{\ominus}M^{\oplus}$	+	+	+	–	–	–	–	–		–	+	–
R—CO—N<	+	+	+	–	–	–	–	+		+[3]	+	+[3]
$R—C\equiv N$	+	+	–		–	–	–	+	–	–	+	+[3]
$R—NO_2$	+	+		–	–	–	–	–		–	–	–
>C=C<	–	–	–	–	–	–	–	+	+	+	–	–
R—Hal	+	+	+	–	–	+	–	–	–		–	–
$>C=N^{\oplus}—$	+			+		+						

i-Bu: iso-Butyl; t-Bu: tert.-Butyl
+: wird reduziert; –: wird nicht reduziert
[1] Red-Al = $NaAl(OCH_2CH_2OCH_3)_2H_2$
[2] in saurer Lösung reduziert, pH 3 bis 4
[3] Produkt: Aldehyd
[4] Reaktion sehr langsam
[5] Produkt: Lactol
[6] Reaktionen bei –78°C, Produkt: R^1CHO
[7] wenn R^2-Phenyl, Produkt: R^1CHO



1.6. Acyloin-Kondensation

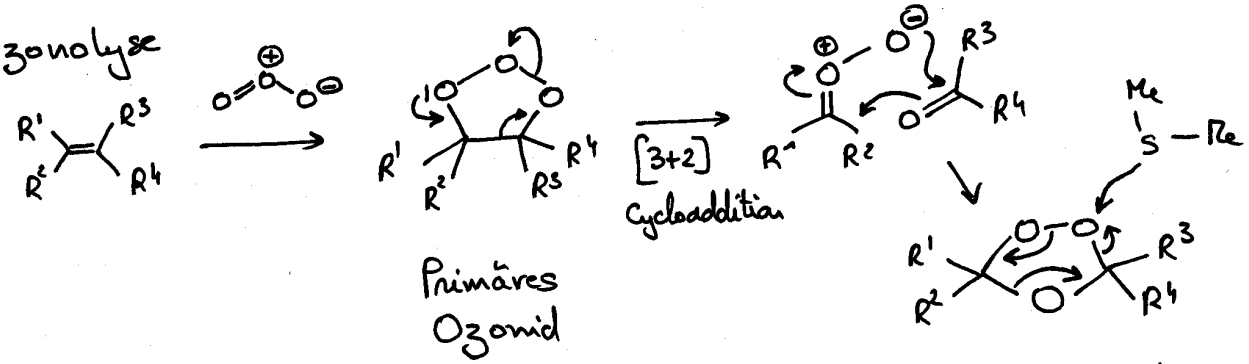


Acyloin

2. Oxidations-Reaktionen

2.1. Oxidation von Alkenen

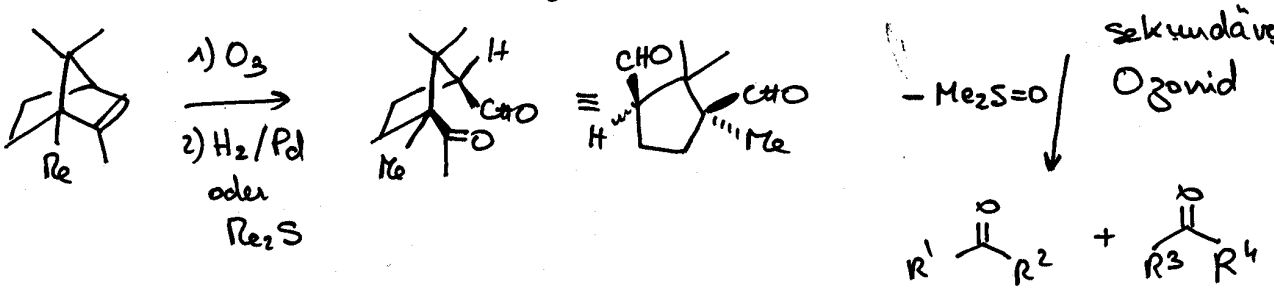
2.1.1. Ozonolyse



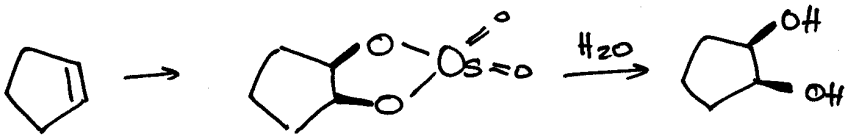
Primäres Ozonid

[3+2] Cycloaddition

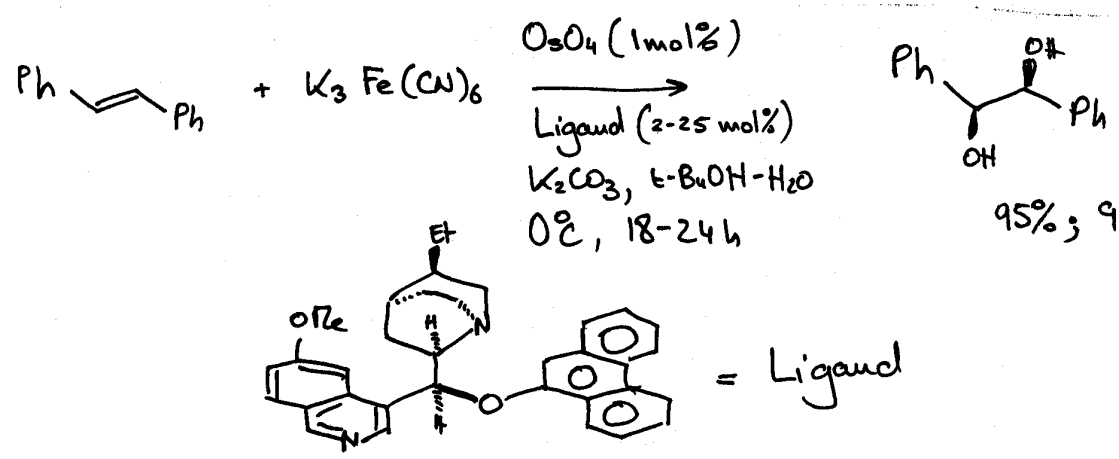
Sekundäres Ozonid



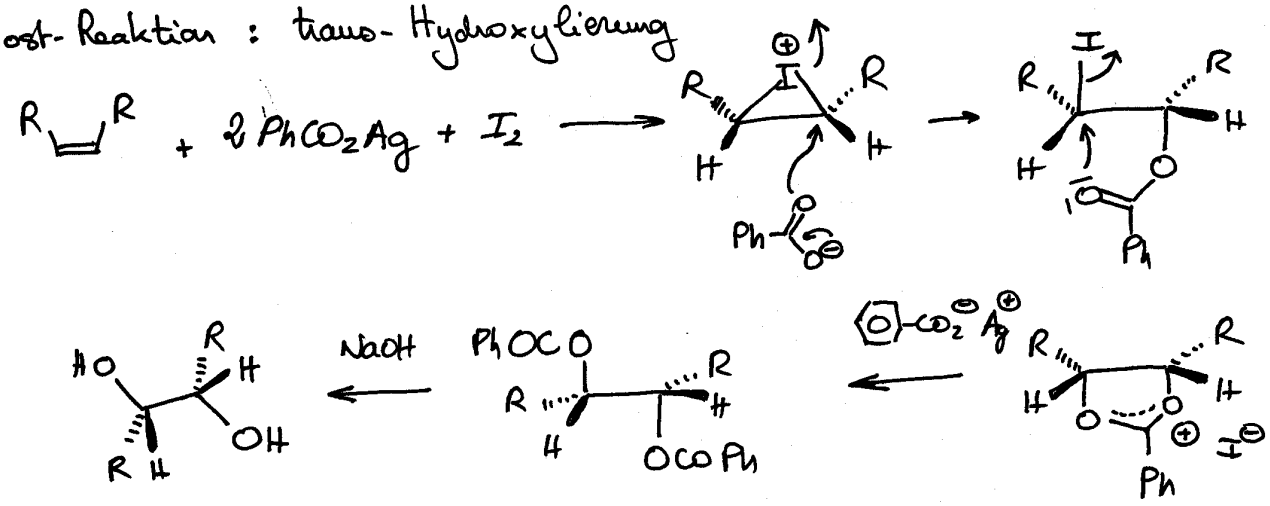
2.1.2. OsO_4 - Oxidation



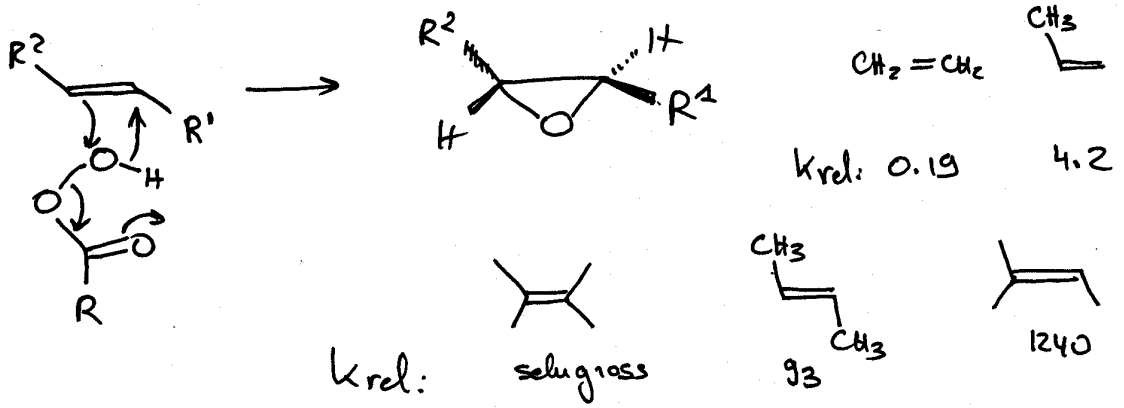
Asymmetische Variante von Sharpless:

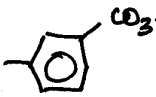


.1.3. Prevost-Reaktion: trans-Hydroxylierung

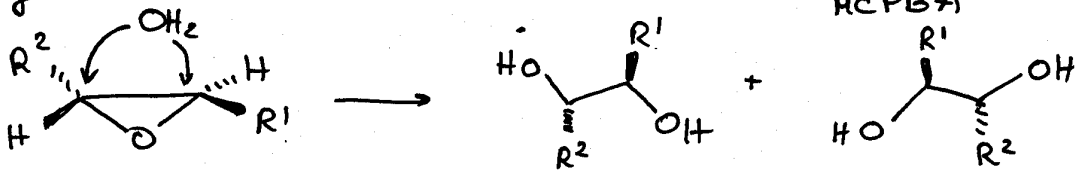


.1.4. Epoxidation

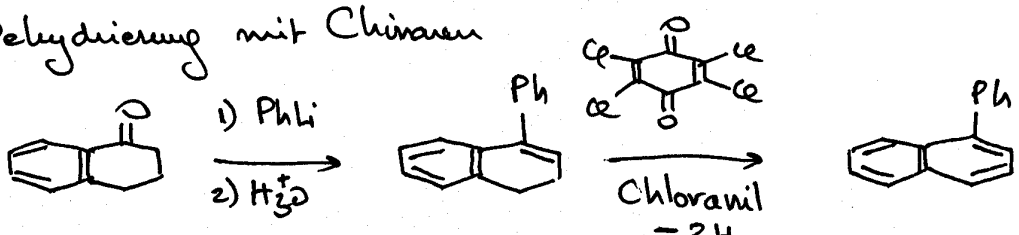


Epoxidierungsaktivität: $CF_3CO_3H > HCO_3H >$  $> CH_3CO_3H$

Ringöffnung



2.1.5. Dehydrierung mit Chinonen



2.1.6 Wacker-Oxidation

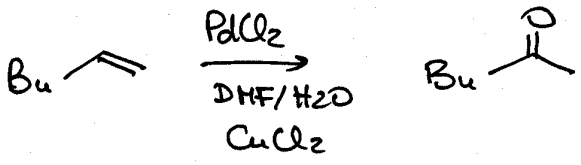
$$H_2C{=}CH_2 \xrightarrow[O_2/CuCl_2]{PdCl_2,\ HCl} CH_3CHO$$

$$CH_2{=}CH_2 + \cancel{H_2O} + \cancel{PdCl_2} \longrightarrow CH_3CHO + \cancel{2HCl} + \cancel{Pd(0)}$$

$$\cancel{Pd(0)} + \cancel{2CuCl_2} \longrightarrow \cancel{PdCl_2} + \cancel{2CuCl}$$

$$\cancel{2HCl} + \cancel{2CuCl} + \tfrac{1}{2}O_2 \longrightarrow 2CuCl_2 + \cancel{H_2O}$$

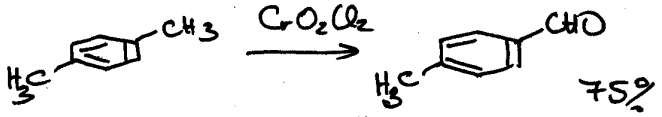
$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 \longrightarrow CH_3CHO$$

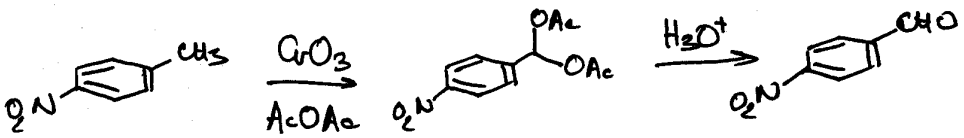


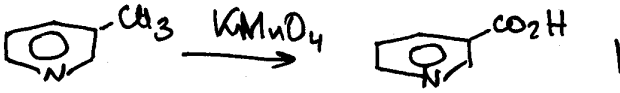
Synthese von Methylketonen

2.2. Oxidation von Aromaten

Etard-Reaktion



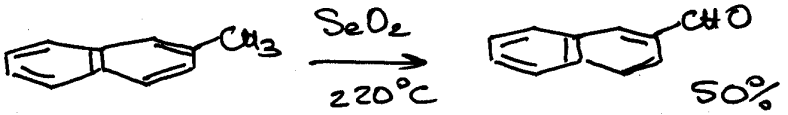


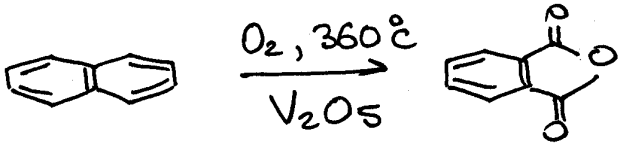


Nicotinsäure

Phthalsäure

Selektivität mit SeO_2

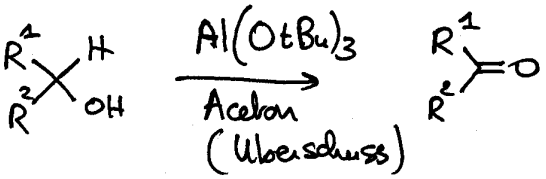




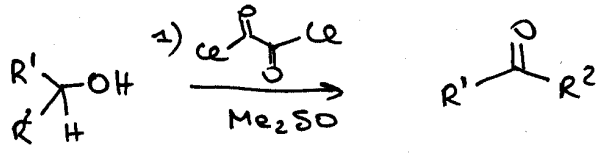
Phthalsäure-Anhydrid

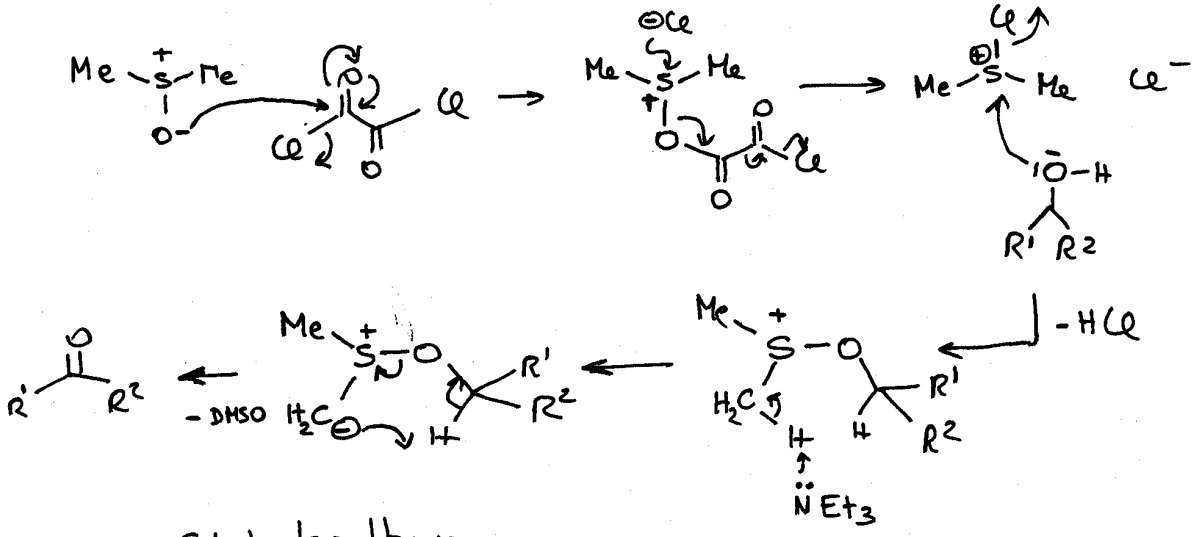
2.3. Oxidation von Alkohole

2.3.1. Oppenauer-Oxidation

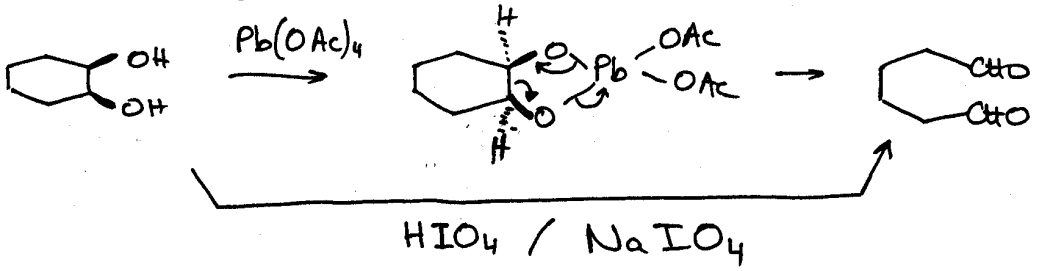


2.3.2. Swern-Oxidation





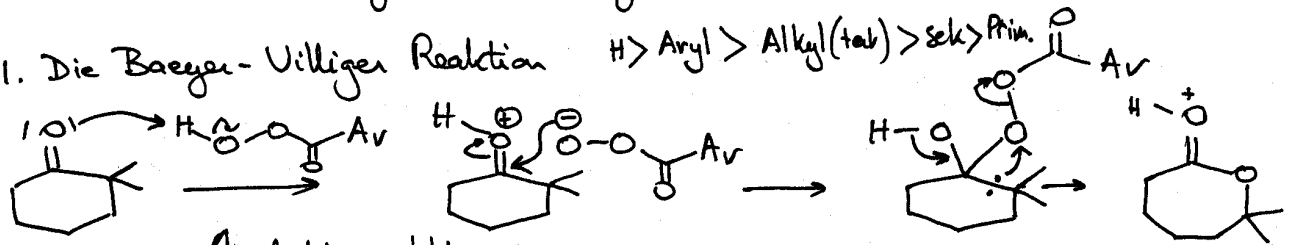
2.3.3. Glykolspaltung



2.4. Oxidation von Carbonyl-Verbindungen

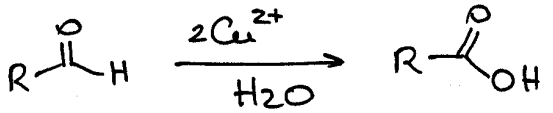
2.4.1. Die Baeyer-Villiger Reaktion

H > Aryl > Alkyl(tert) > sek > Prim.



2.4.2. Verschiedene Oxidationsreaktionen

Aldehyde können unter sehr milde Bedingungen oxidiert werden. Fehling Test



Tollens-Reagenz