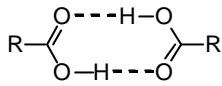
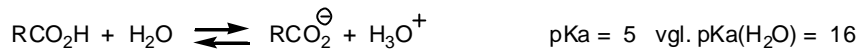


1) Eigenschaften der Carbonsäuren

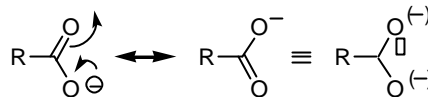


Carbonsäuren gehen Wasserstoffbrückenbindungen ein.



$$K_a = \frac{[\text{RCO}_2^-][\text{H}^+]}{[\text{RCO}_2\text{H}]}$$

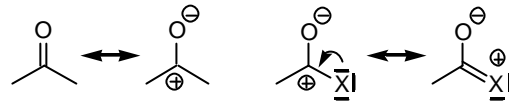
stabilisiert durch Mesomerie



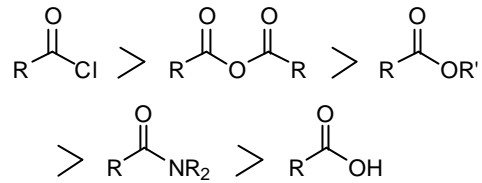
	$\text{CH}_3\text{CO}_2\text{H}$	$\text{ClCH}_2\text{CO}_2\text{H}$	$\text{Cl}_2\text{HC}-\text{CO}_2\text{H}$	$\text{CCl}_3\text{CO}_2\text{H}$	$\text{CF}_3\text{CO}_2\text{H}$
pKa	4.76	2.86	1.29	0.65	-0.6

	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$	$t\text{-Bu}-\text{CO}_2\text{H}$
pKa	4.86	5.05

Reaktivität der Carbonylgruppe

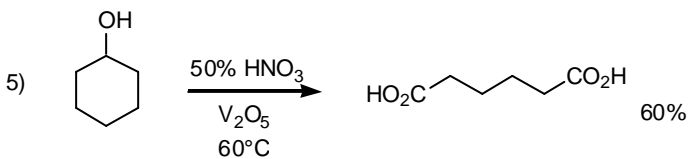
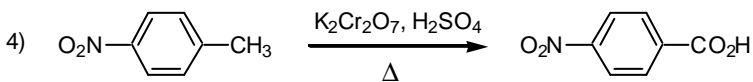
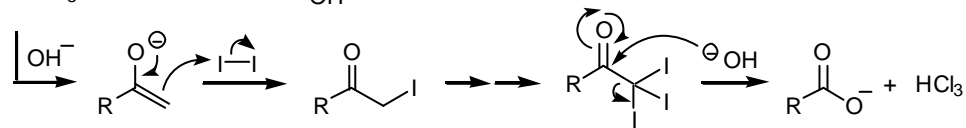
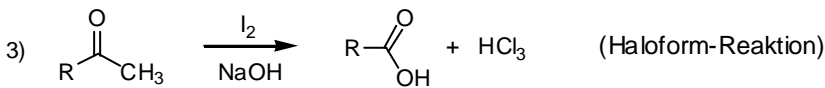
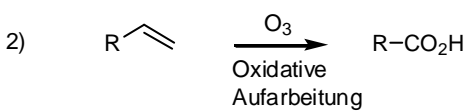
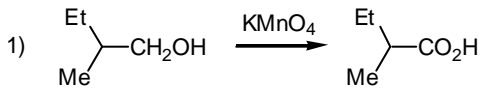


Reaktivitätskala

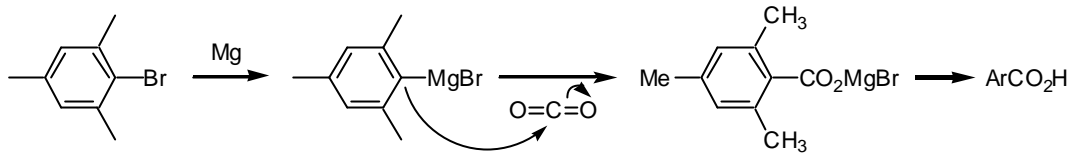
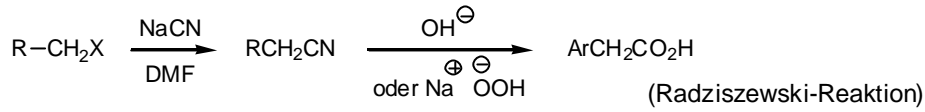


2) Synthesen von Carbonsäuren

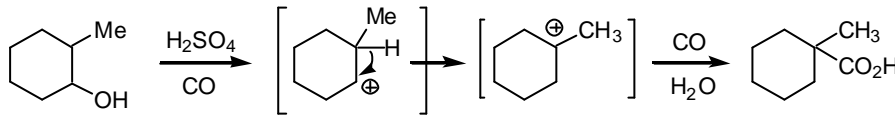
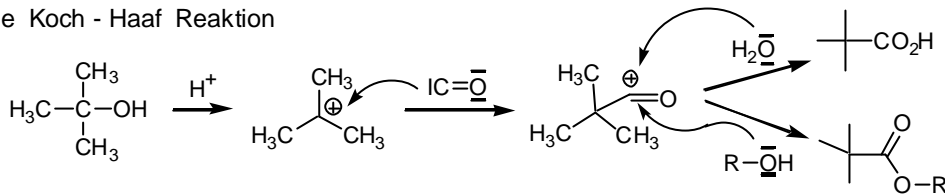
A) Oxidationsreaktionen



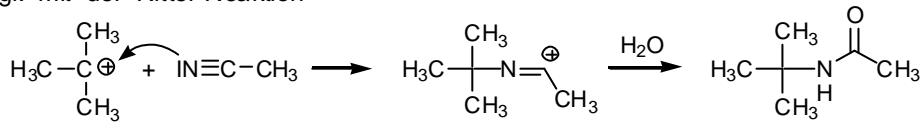
B) Substitutionsreaktionen



Die Koch - Haaf Reaktion



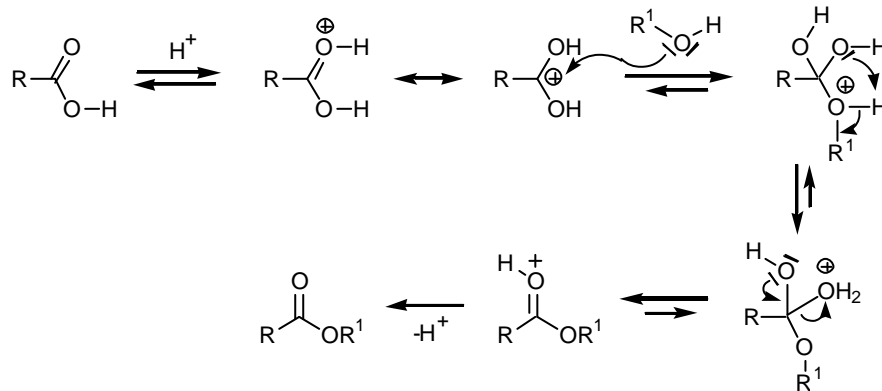
Vgl. mit der Ritter-Reaktion



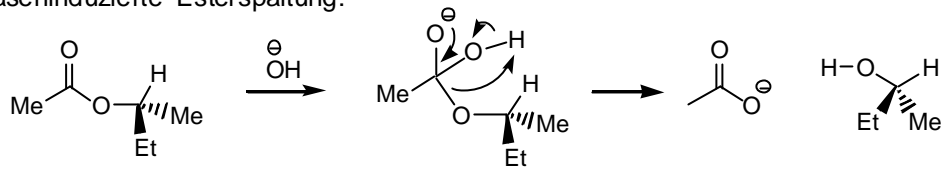
3) Reaktionen mit Nucleophilen

3.1. Mechanismen zu Reaktionen von Carbonsäuren:

Säurekatalysierte Esterkondensation und Esterspaltung

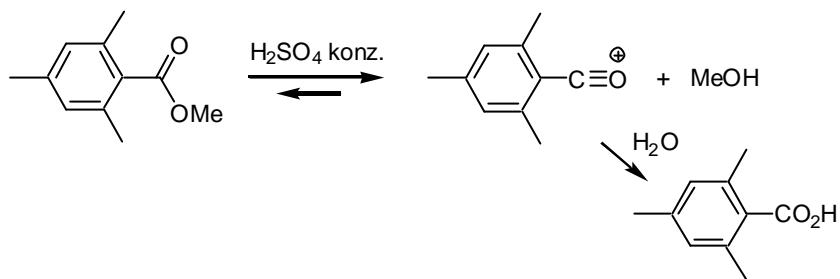


Baseninduzierte Esterspaltung:

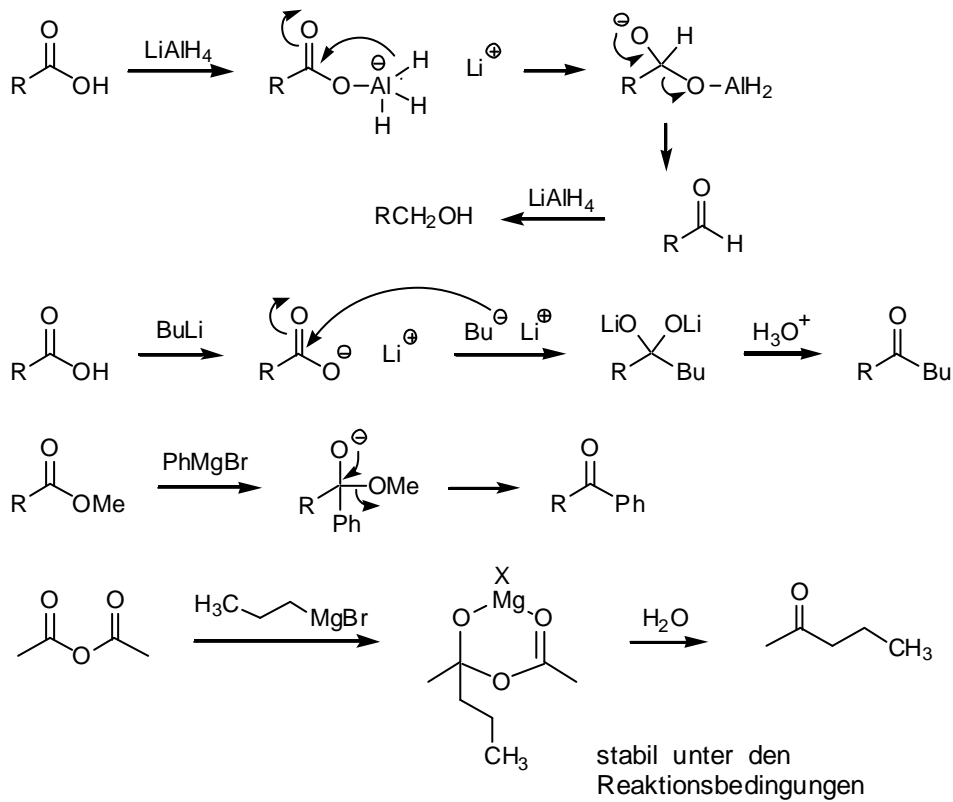


(Verseifung)

Spezieller Mechanismus bei sterisch gehinderten Estern:

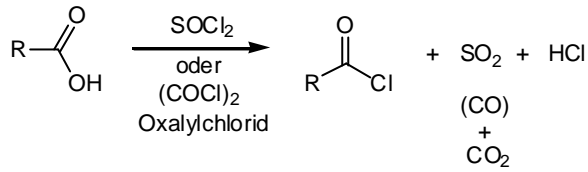


Andere nucleophile Additionen:

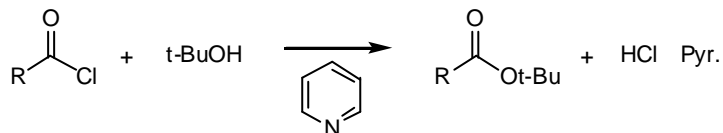
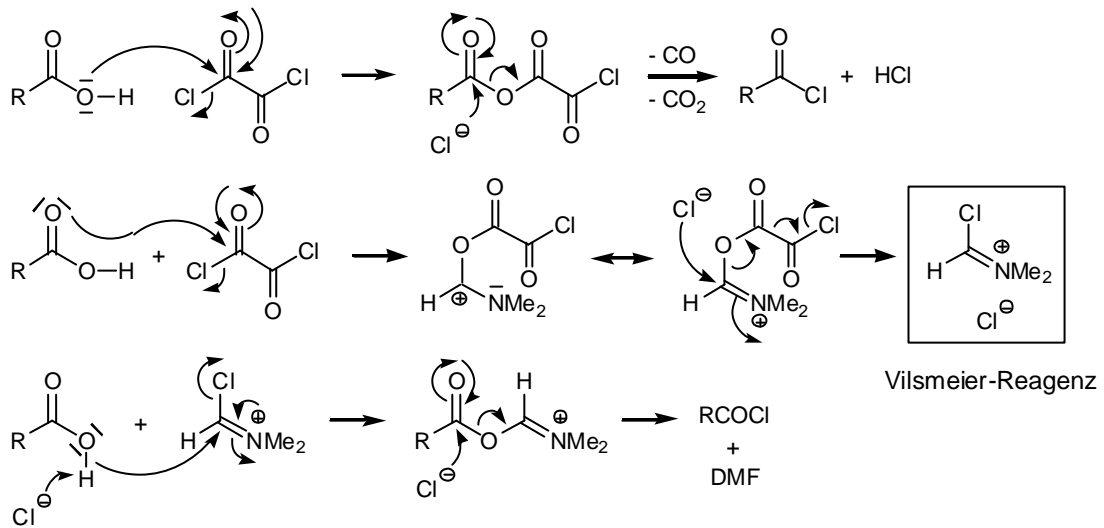


3.2. Reaktionen von Carbonsäurechloride

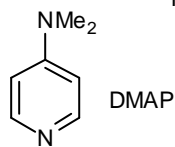
Darstellung mit Thionylchlorid



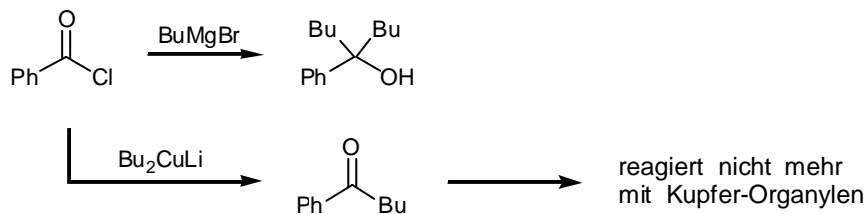
DMF kann als Katalysator für die Reaktion verwendet werden.



Katalyse mit

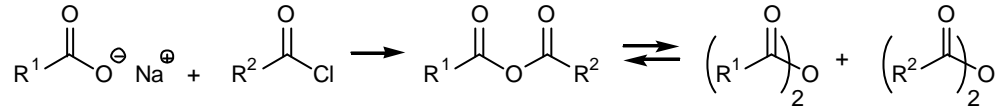
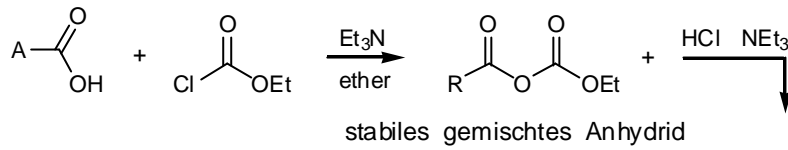
Säurechloride reagieren mit zahlreichen Nucleophilen: HNR_2 , HSR , $\text{H}_2\text{N}-\text{NH}_2$, ...

Reaktion von Säurechloriden mit metallorganischen Reagenzien



3.3. Reaktionen der Carbonsäureanhydride

Darstellung

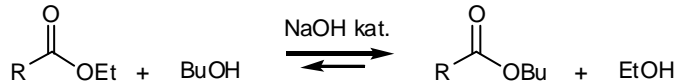
Synthese von gemischten Anhydriden:

Formylierungsreaktion: $H-\overset{\text{O}}{\parallel}{C}-O-\overset{\text{O}}{\parallel}{C}-H$ oder $H-\overset{\text{O}}{\parallel}{C}-Cl$ sind nicht stabil,
 aber $H-\overset{\text{O}}{\parallel}{C}-O-\overset{\text{O}}{\parallel}{C}-OEt$ kann hergestellt werden

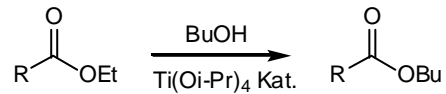
3.4. Carbonsäureester

Carbonsäureester sind schwache Elektrophile.

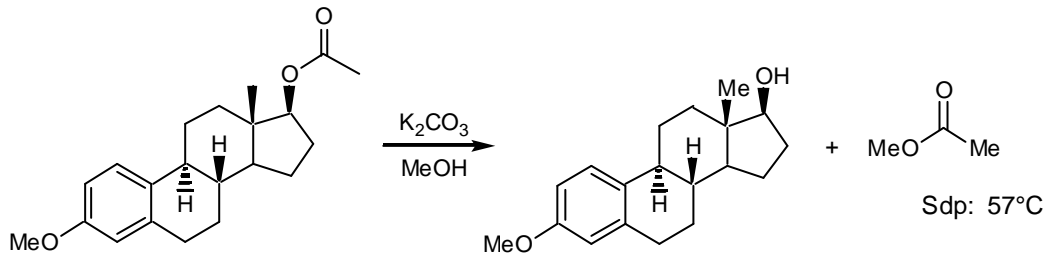
Umesterung



Verwendung in der Synthese



Ester können als Schutzgruppe verwendet werden.

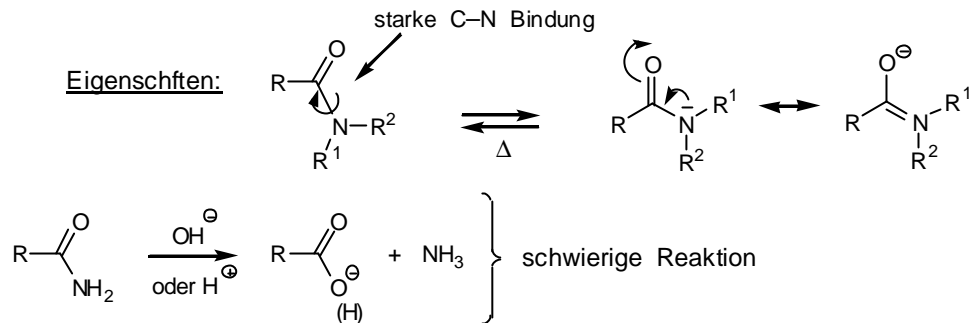


2. Gruppe: Carbonsäuren und deren Derivate

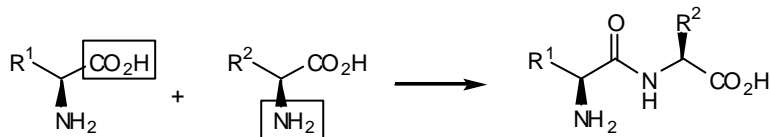
⑥

3.5. Carbonsäureamide (Proteine, Peptide, Nylon, Perlon, ...)

Rotationsbarriere von ~ 22 kcal/mol

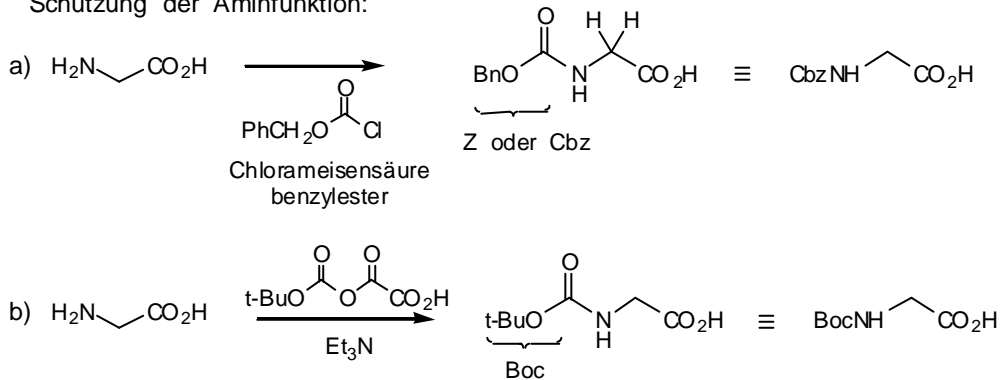


Peptid-Synthese Probleme: Unselektivität in der Amidbildung und Racemisierung

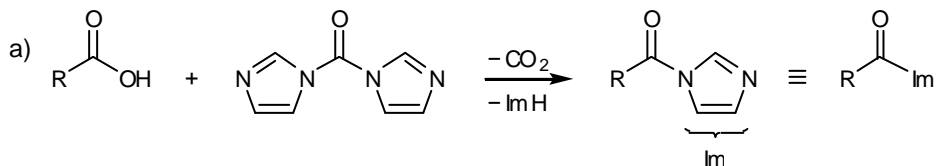


Die Verwendung von Schutzgruppen ist notwendig.

Schützung der Aminfunktion:

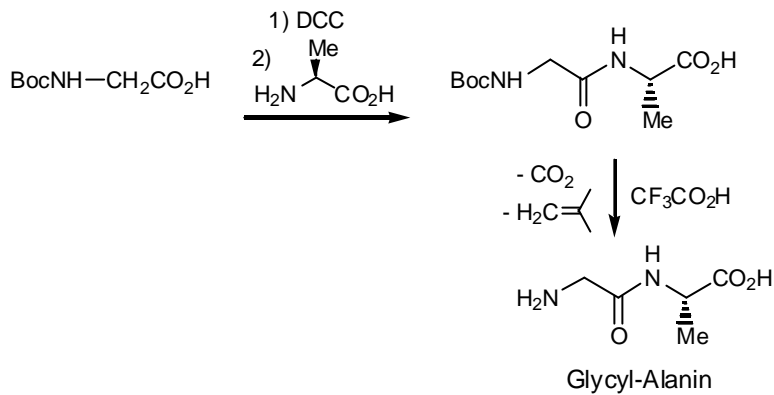
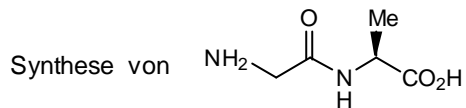
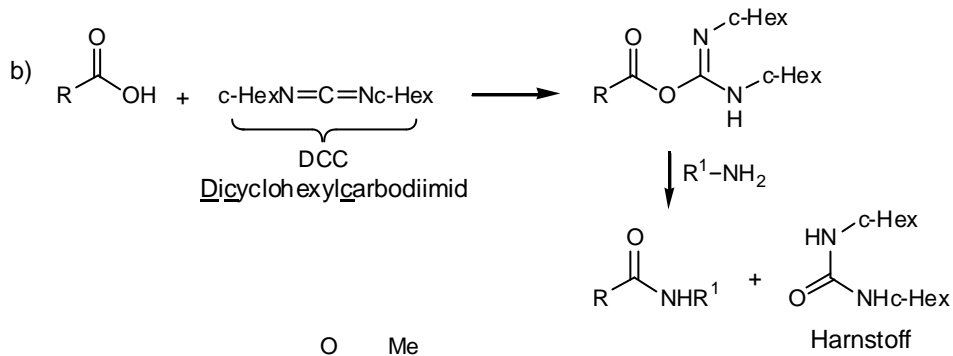


Aktivierung der Carbonylgruppe der Carbonsäure:



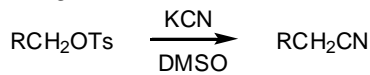
2. Gruppe: Carbonsäuren und deren Derivate

7

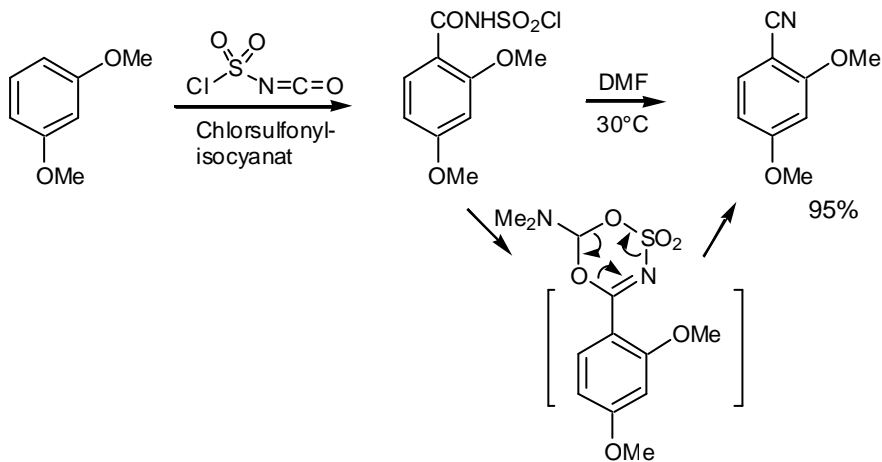
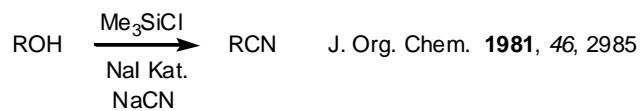


3.6. Reaktionen der Carbonitrile

Darstellung



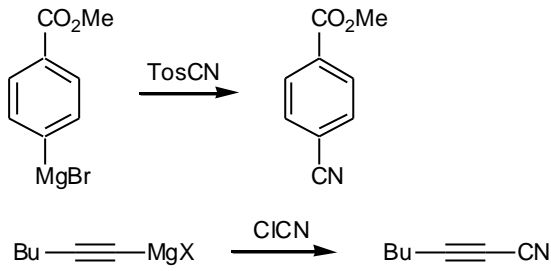
Generelle Methode



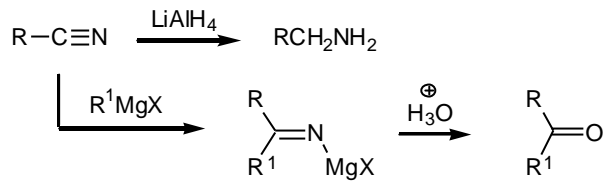
Org. Synth.
Coll. Vol. VI
Seite 465 (1988)

2. Gruppe: Carbonsäuren und deren Derivate

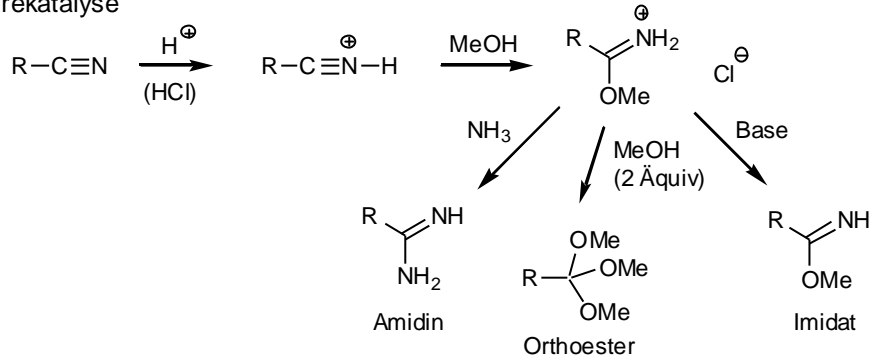
8



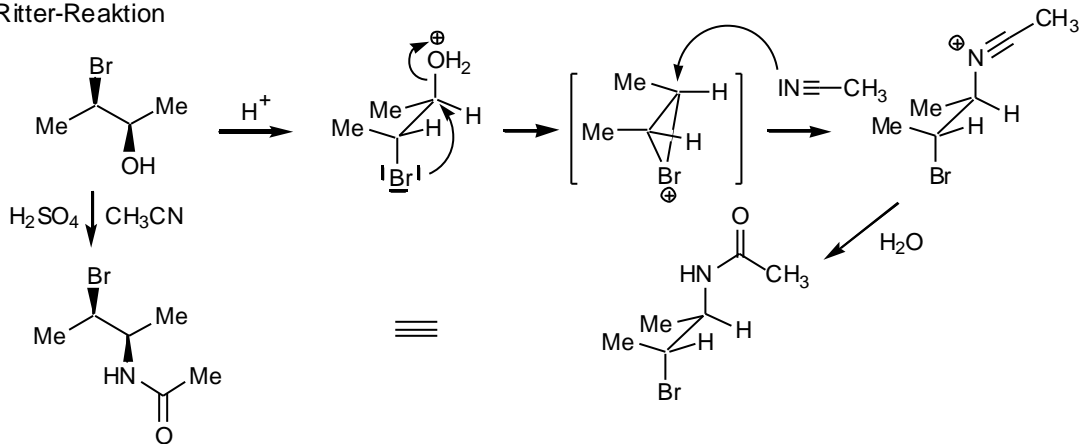
Reaktionen



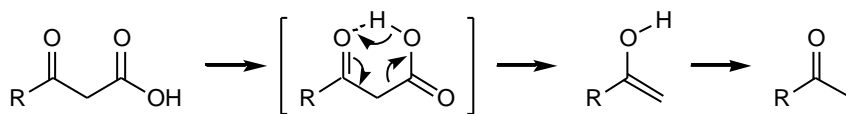
Säurekatalyse



Ritter-Reaktion

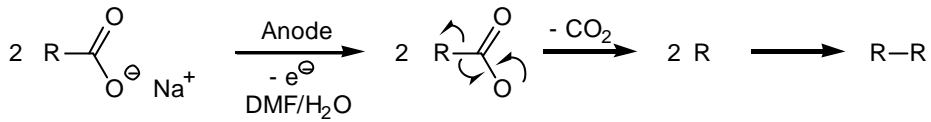
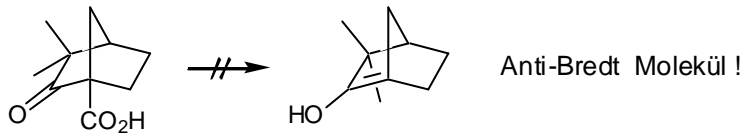


4) Abbau der Carbonylgruppe

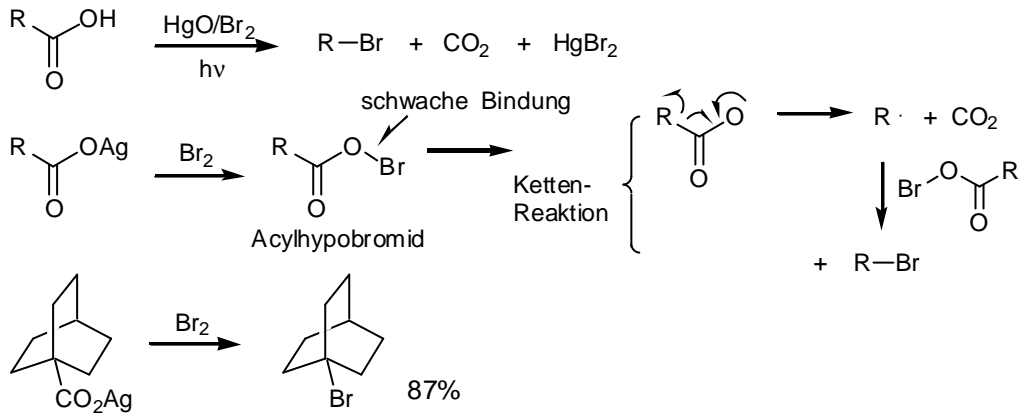


2. Gruppe: Carbonsäure und Derivate

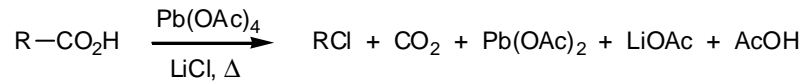
9



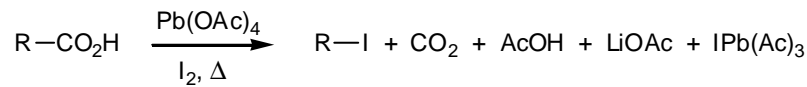
Hunsdiecker-Reaktion



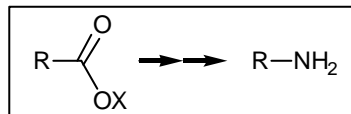
Kochi - Reaktion



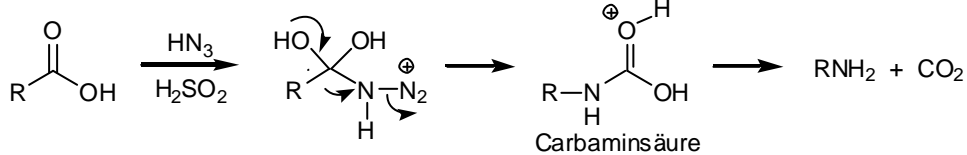
Barton - Reaktion



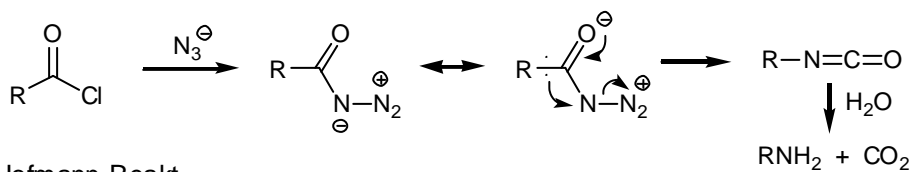
Schmidt-, Curtius-, Hofmann-Abbau



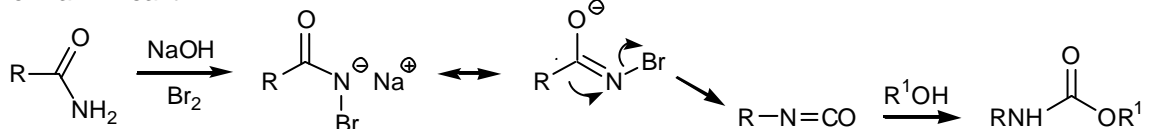
Schmidt-Reakt.



Curtius-Reakt.



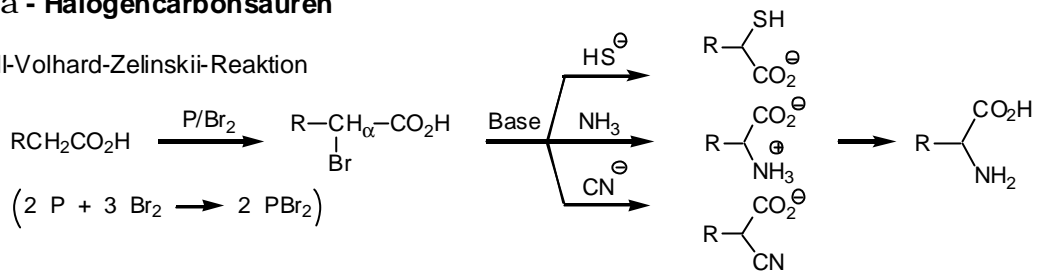
Hofmann-Reakt.



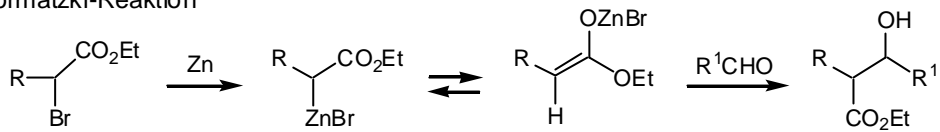
5) Reaktionen in der Seitenkette

5.1. α -Halogen-carbonsäuren

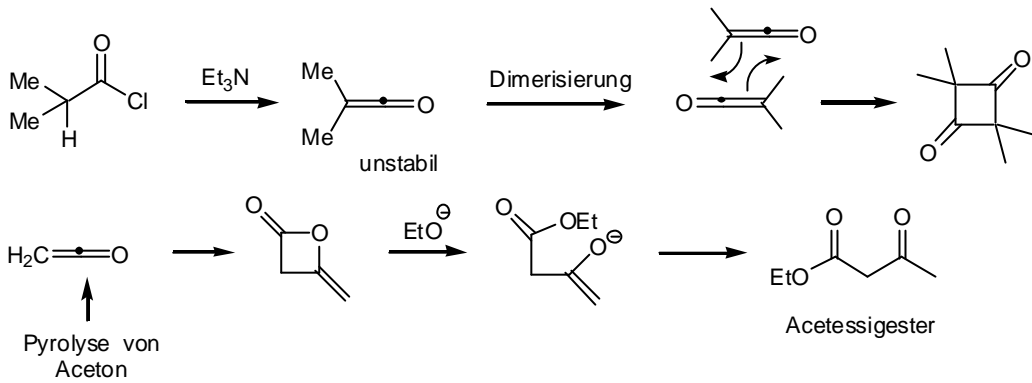
Hell-Volhard-Zelinskii-Reaktion



Reformatski-Reaktion

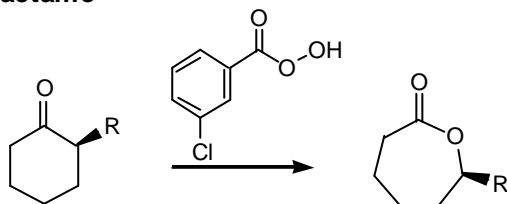


5.2. Ketene

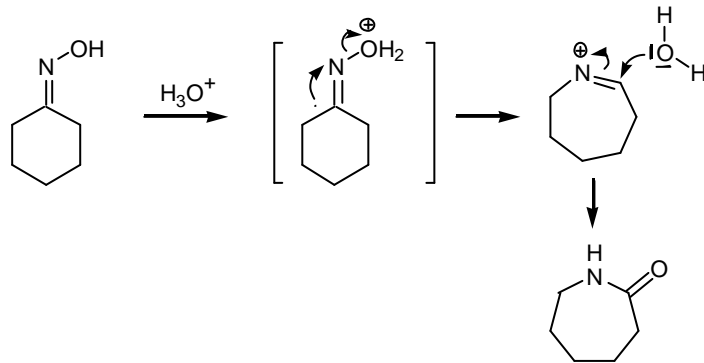


5.3. Lactone, Lactame

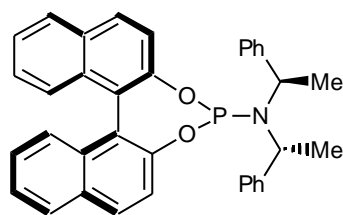
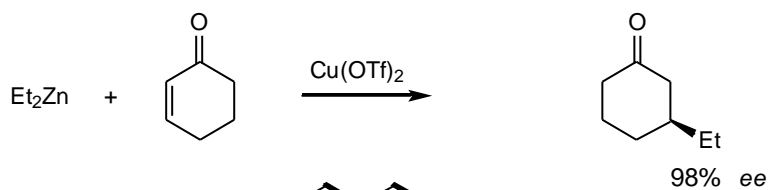
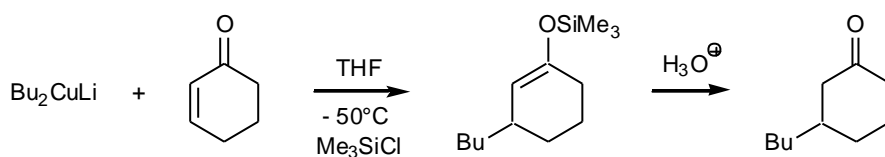
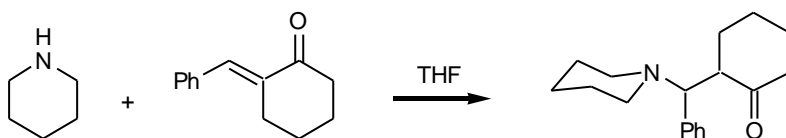
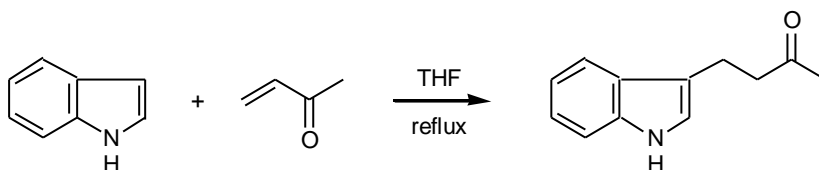
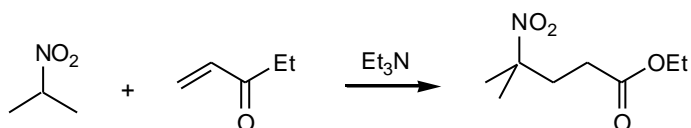
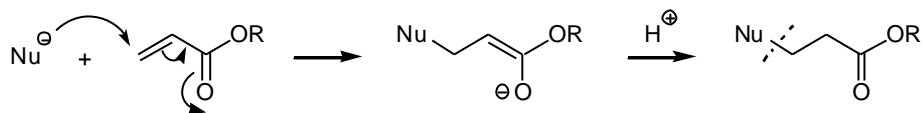
Baeyer-Villiger-Synthese



Beckmann-Umlagerung



5.4. Michael-Addition



Feringa (1998)

Kat.

