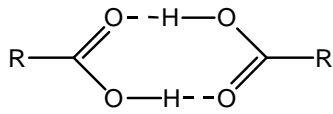


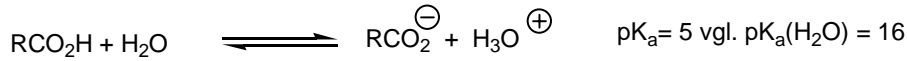
2. Gruppe: Carbonsäuren und Derivate

①

1) Eigenschaften der Carbonsäuren:

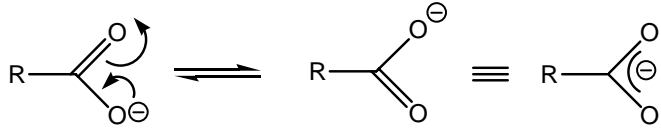


Carbonsäuren gehen Wasserstoffbrückenbindungen ein.



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

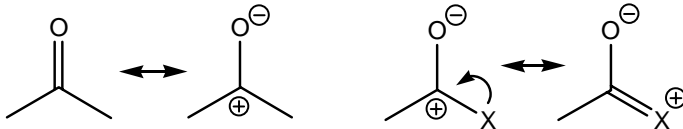
stabilisiert durch Mesomerie



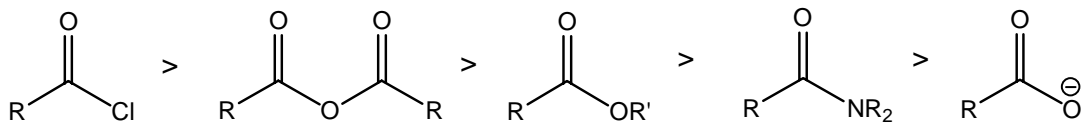
Bsp.:

Säure	CH ₃ CO ₂ H	ClCH ₂ CO ₂ H	Cl ₂ CHCO ₂ H	Cl ₃ CCO ₂ H	F ₃ CCO ₂ H	Pr-CO ₂ H	t-Bu-CO ₂ H
pK _a	4.76	2.86	1.29	0.65	-0.60	4.86	5.05

Reaktivität der Carbonylgruppe:

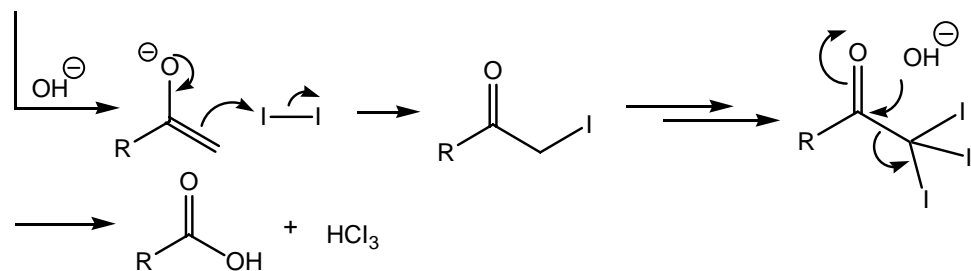
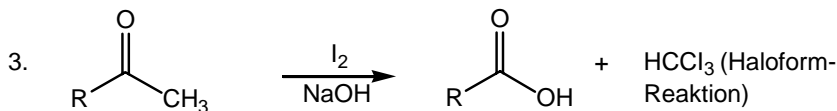
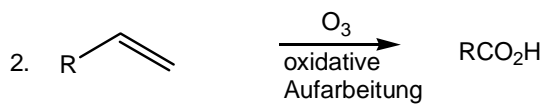
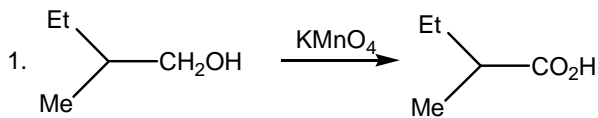


Reaktivitätsskala:



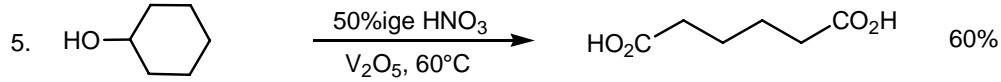
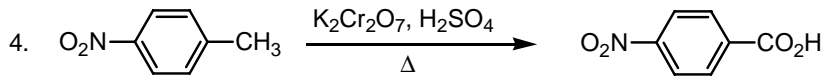
2) Synthesen von Carbonsäuren:

A) Oxidationsreaktionen:

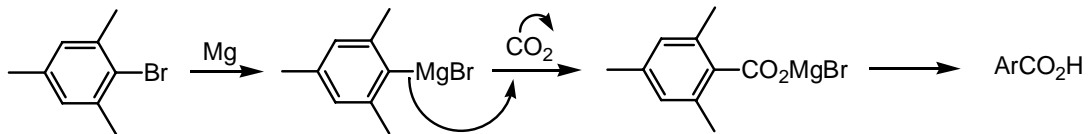
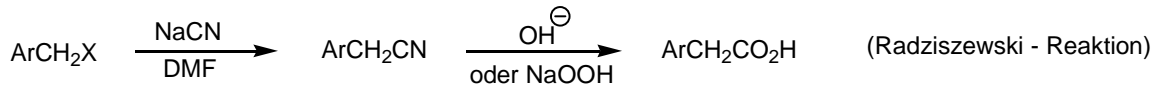


2. Gruppe: Carbonsäuren und Derivate

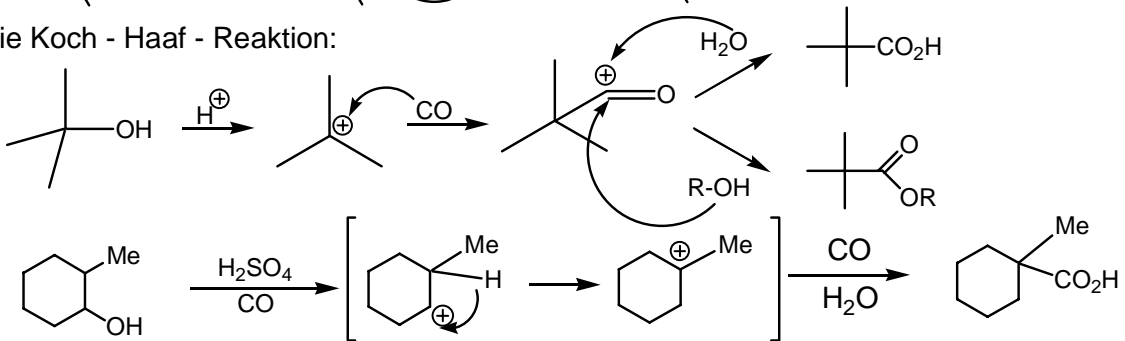
②



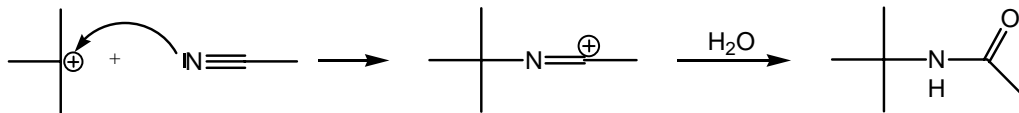
B) Substitutionsreaktionen



Die Koch - Haaf - Reaktion:



vgl. mit der Ritter - Reaktion:

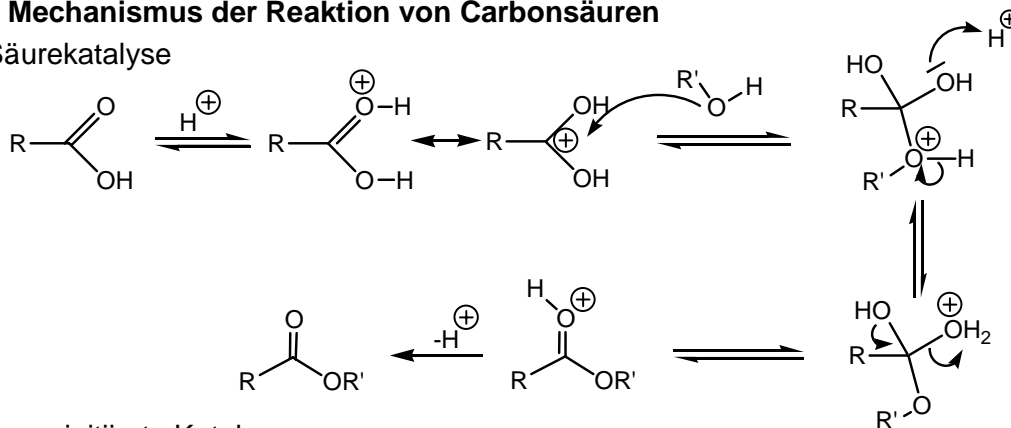


3 Reaktionen mit Nucleophilen

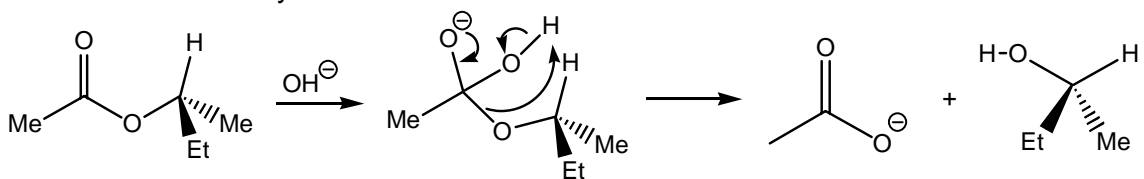
Synthese eines
tertiären Amids

3.1 Mechanismus der Reaktion von Carbonsäuren

Säurekatalyse



Baseninitiierte Katalyse



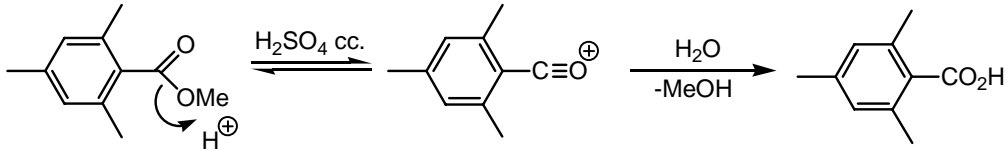
=> Verseifung

2. Gruppe: Carbonsäuren und Derivate

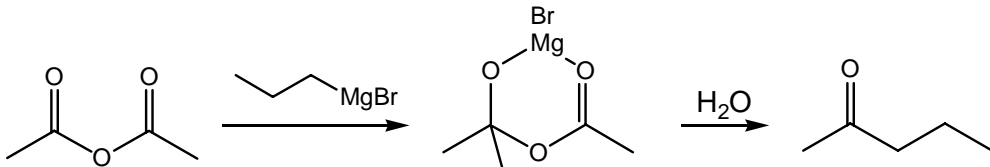
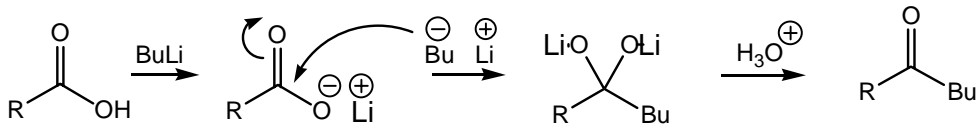
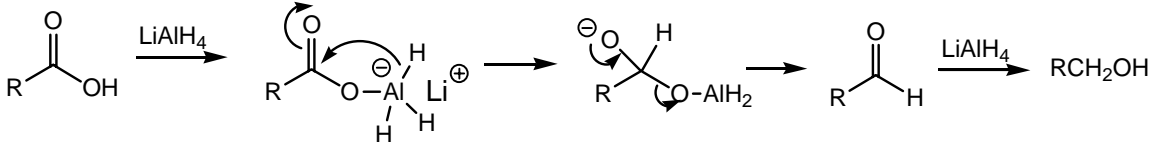
③

Spezielle Mechanismen:

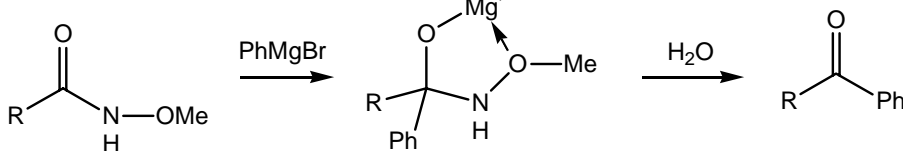
sterisch gehinderte Ester



Andere nucleophile Additionen

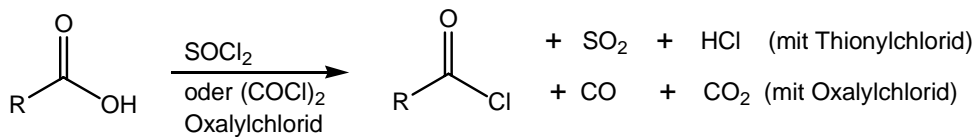


unter den Reaktionsbedingungen ist das tetraedrische Intermediat stabil

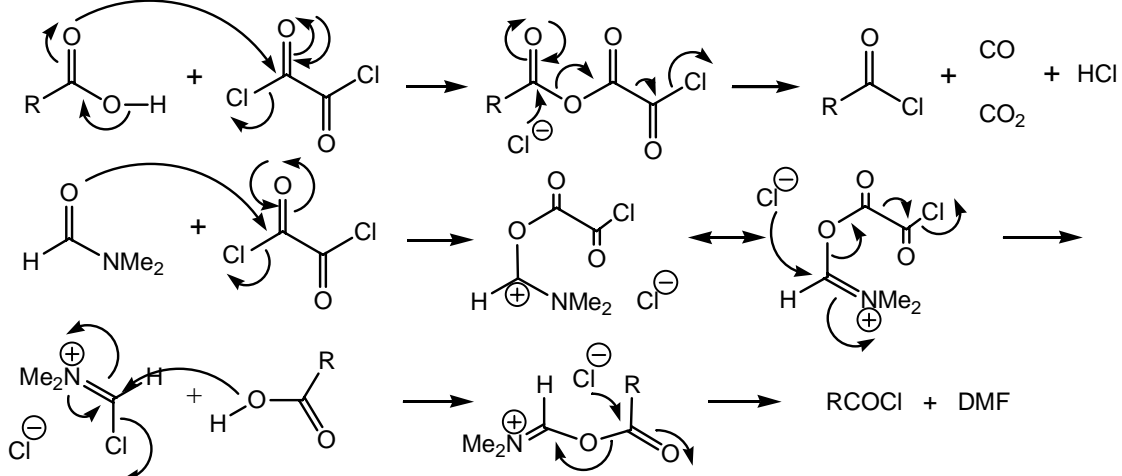


3.2 Reaktionen von Carbonsäurechloriden

Darstellung von Carbonsäurechloriden:

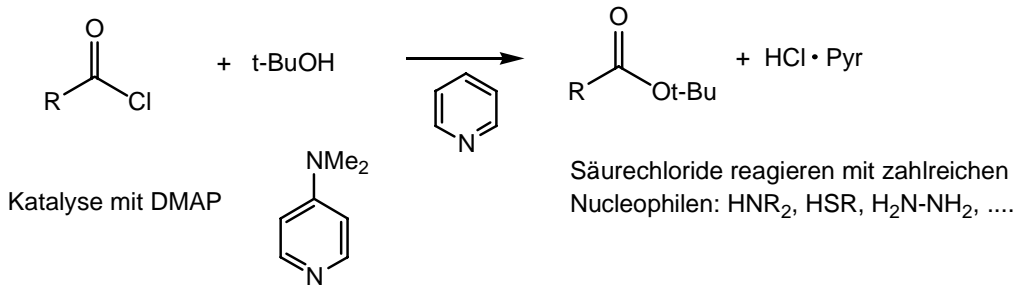


DMF kann als Katalysator für die Reaktion verwendet werden : Vilsmeier - Reagenz:

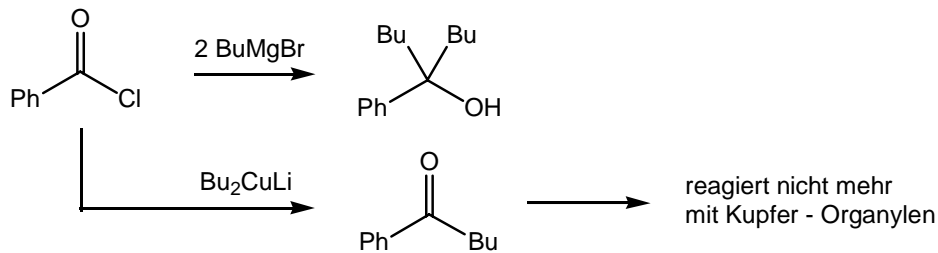


2. Gruppe: Carbonsäuren und Derivate

4

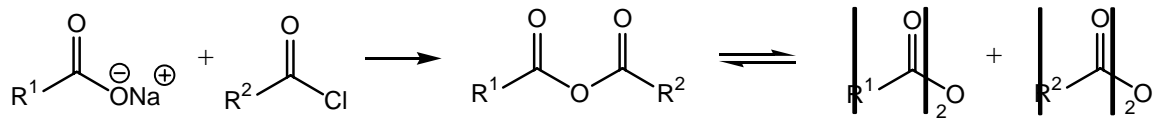


Reaktion von Säurechloriden mit metallorganischen Reagenzien

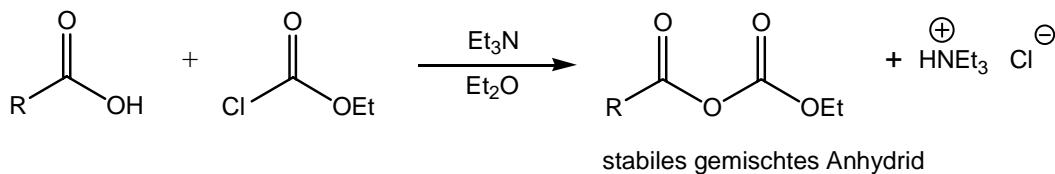


3.3 Reaktionen der Carbonsäureanhydride

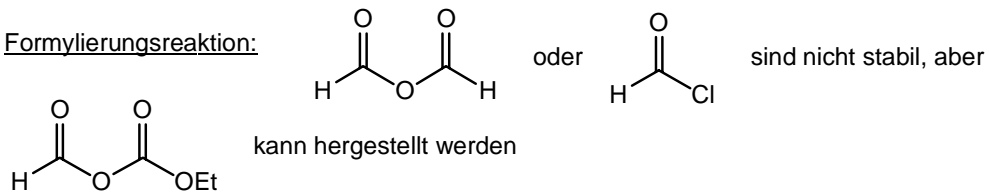
Darstellung



Synthese von gemischten Anhydriden:



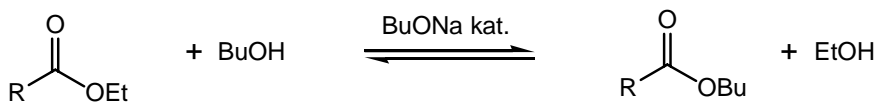
Formylierungsreaktion:



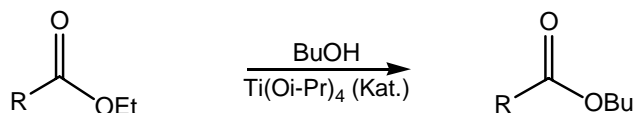
3.4 Carbonsäureester

Carbonsäureester sind schwache Elektrophile

Umesterung:



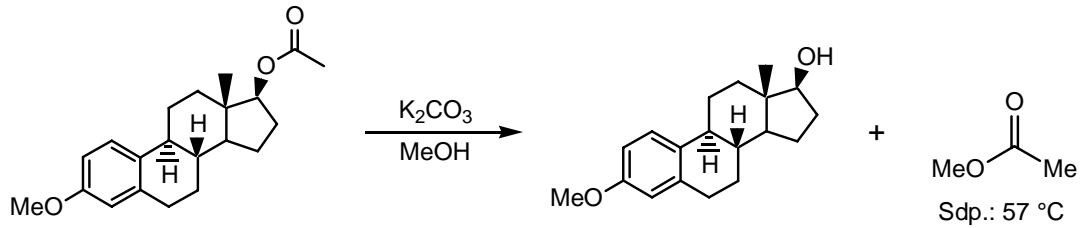
Verwendung in der Synthese:



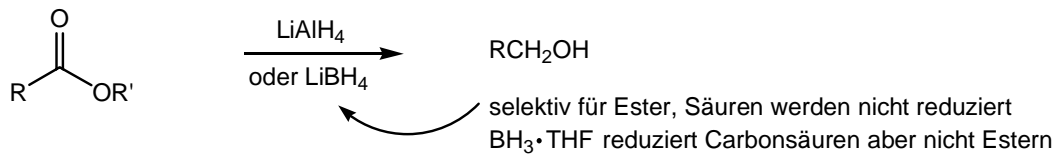
2. Gruppe: Carbonsäuren und Derivate

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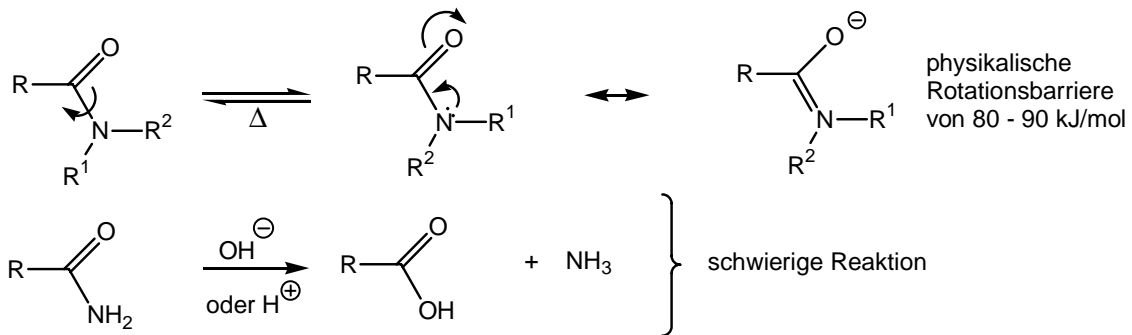
Ester können auch als Schutzgruppe verwendet werden:



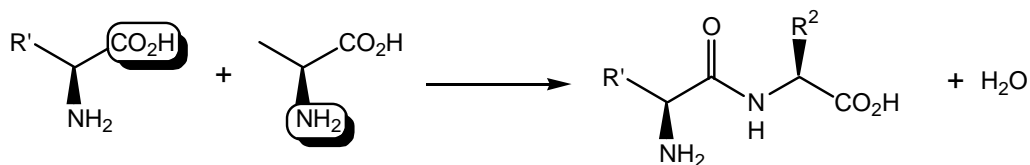
Reduktion von Estern:



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

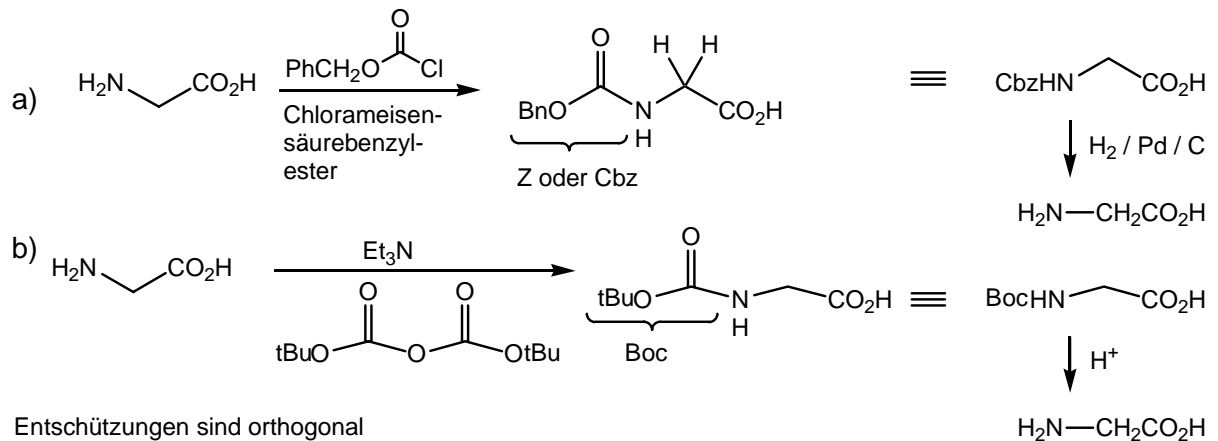


Peptidsynthese: Problem: Unselektivität bei der Amidbildung und Racemisierung



Die Verwendung von Schutzgruppen ist notwendig:

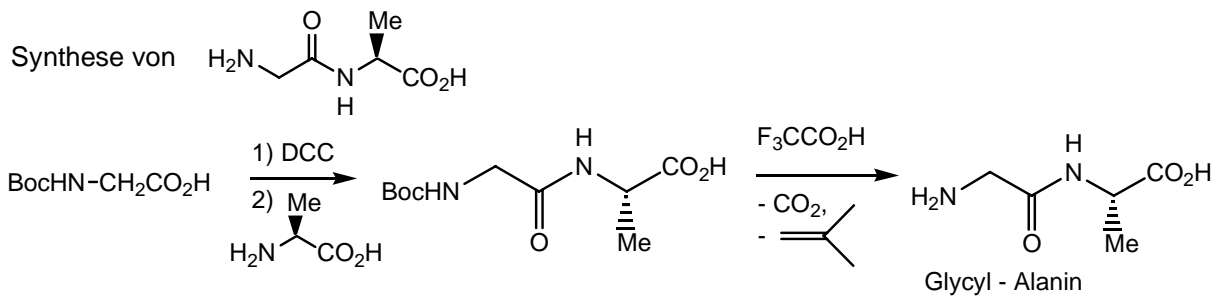
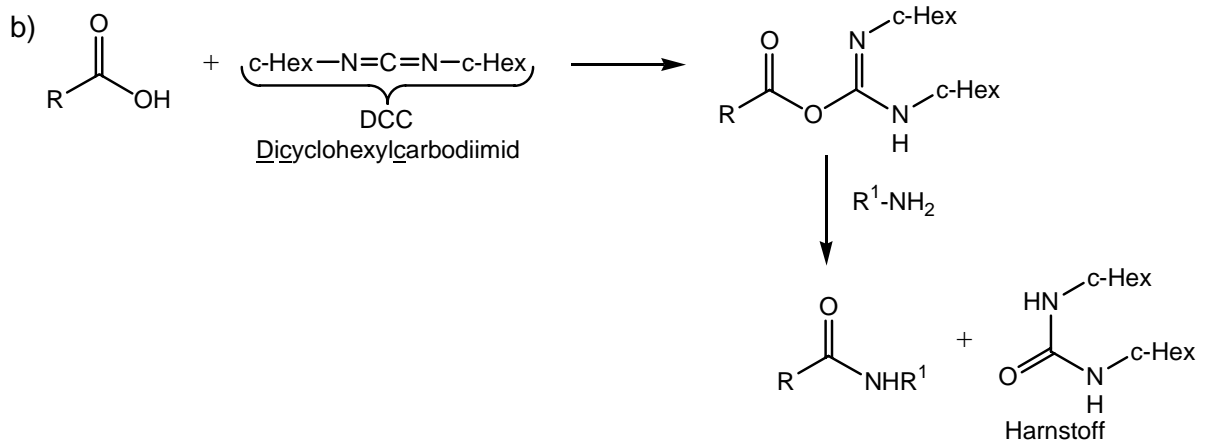
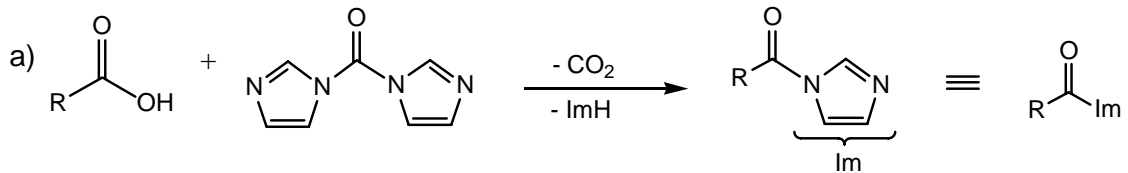
Schützung der Aminfunktion:



2. Gruppe: Carbonsäuren und Derivate

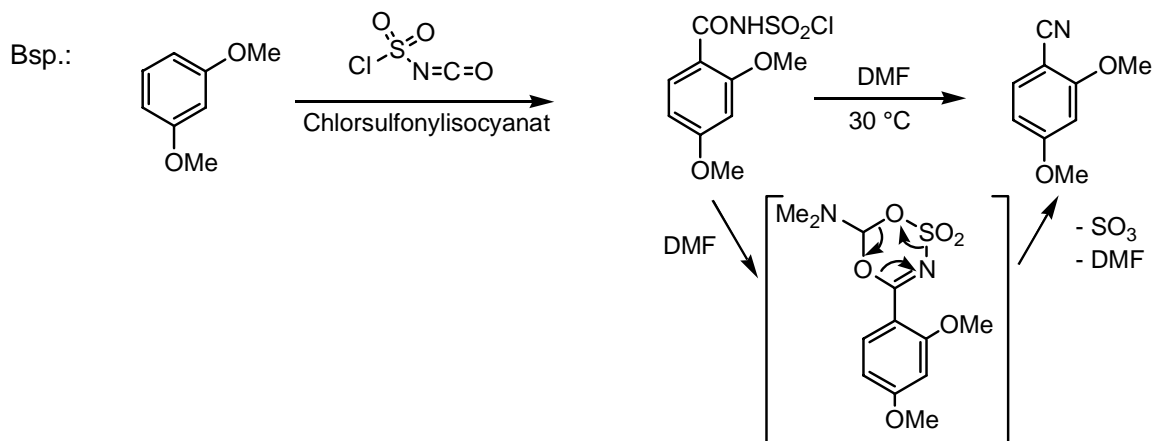
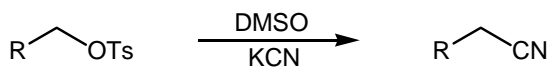
⑥

Aktivierung der Carbonylgruppe von Carbonsäuren:



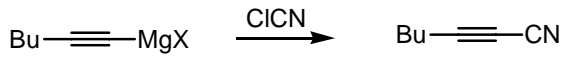
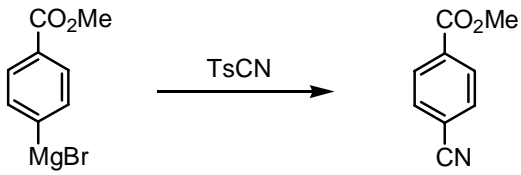
3.6 Reaktionen der Carbonitrile

Darstellung (Nitrile sind auch durch Dehydratisierung von Carbonsäureamiden zugänglich):

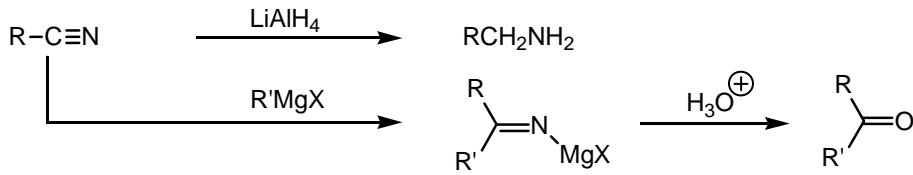


2. Gruppe: Carbonsäuren und Derivate

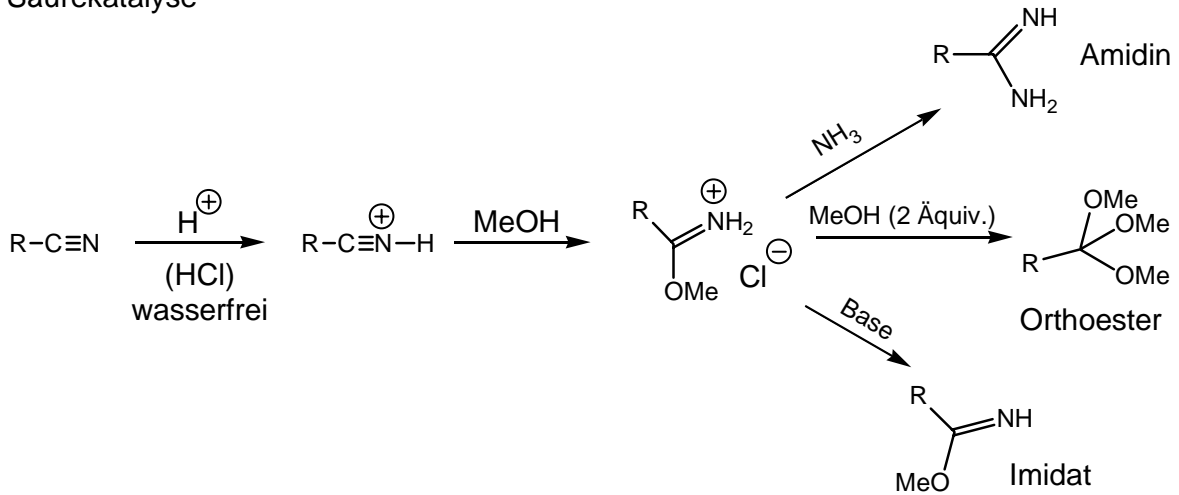
⑦



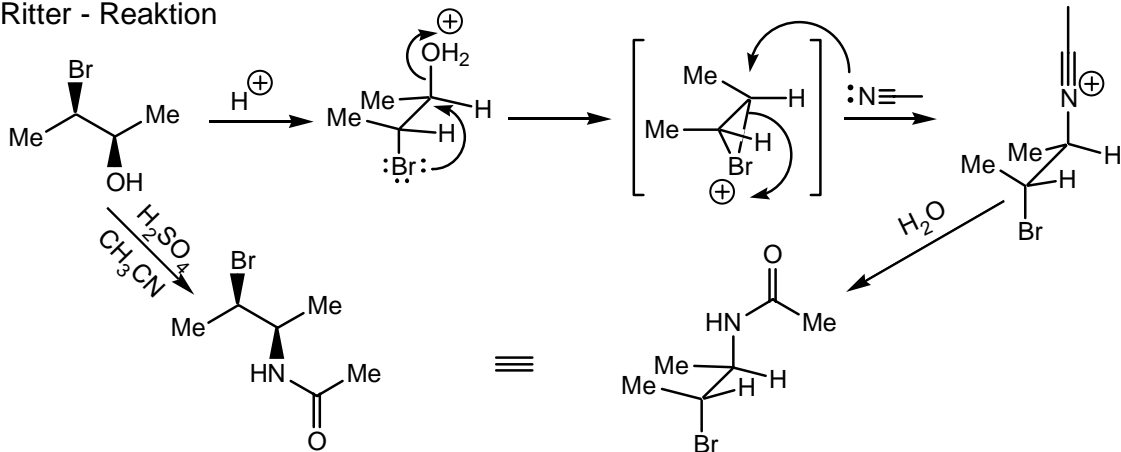
Reaktionen



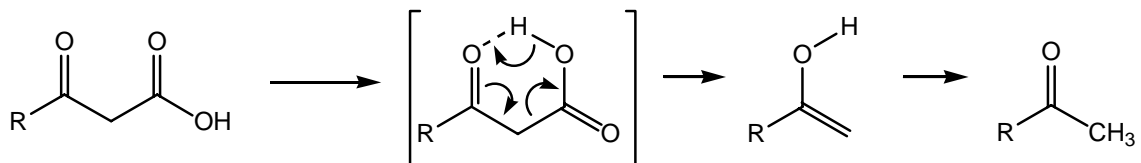
Säurekatalyse



Ritter - Reaktion



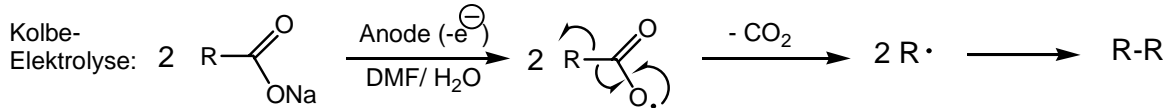
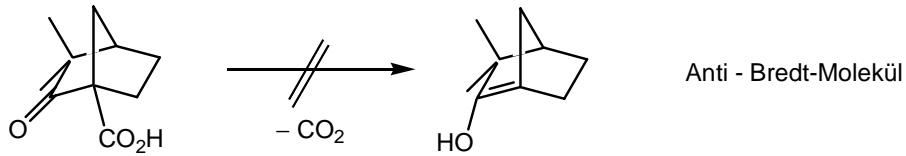
4. Abbau der Carbonylgruppe



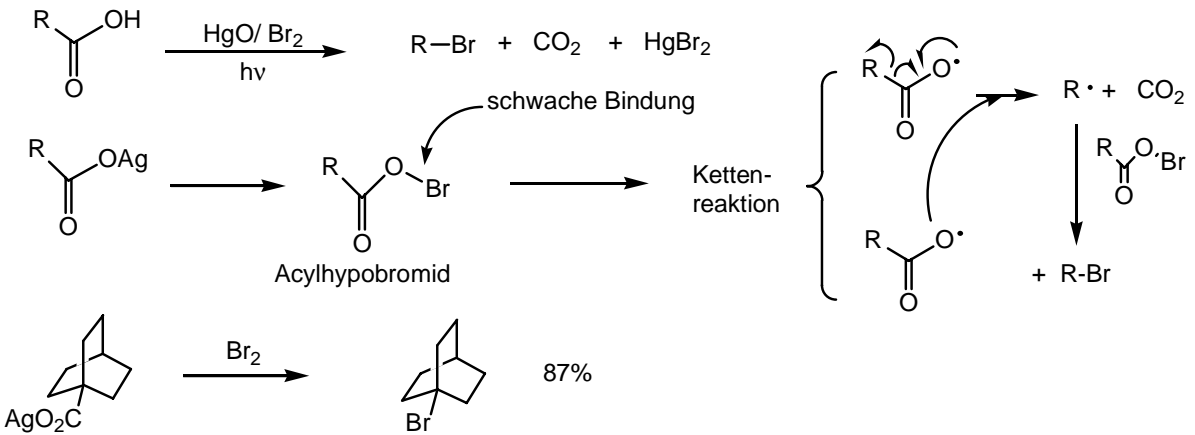
2. Gruppe: Carbonsäuren und Derivate

8

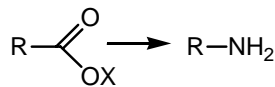
Bredt - Regel: Doppelbindungen am Brückenkopf sind instabil



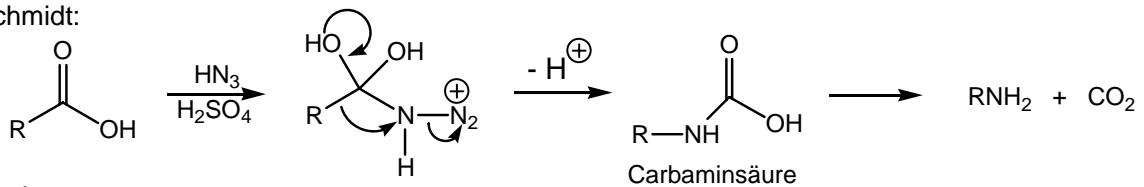
Hundsdiecker - Reaktion:



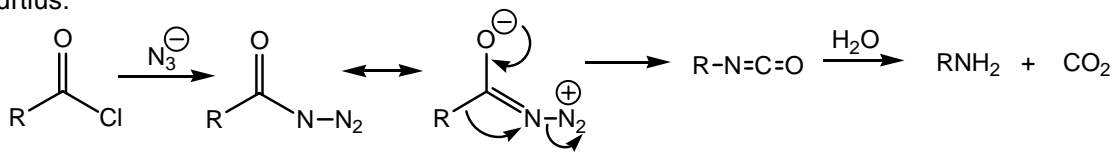
Schmidt, Curtius, Hofmann - Abbau:



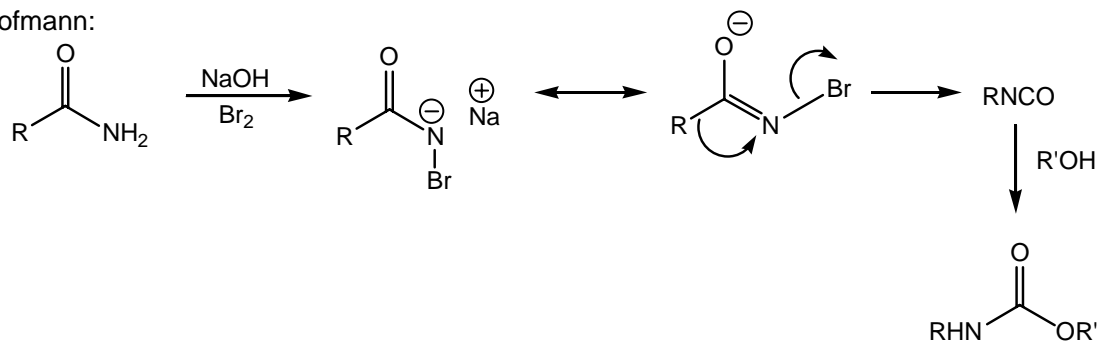
Schmidt:



Curtius:



Hofmann:



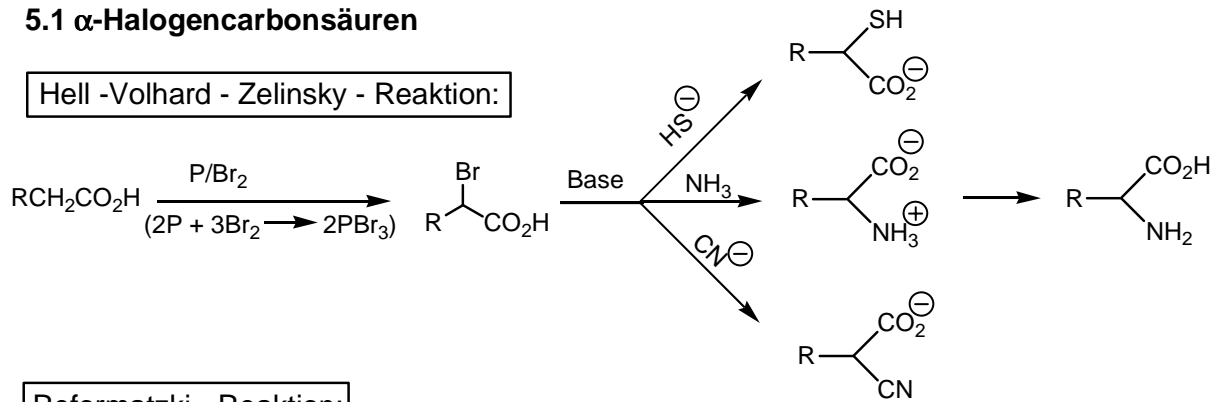
2. Gruppe: Carbonsäuren und Derivate

⑨

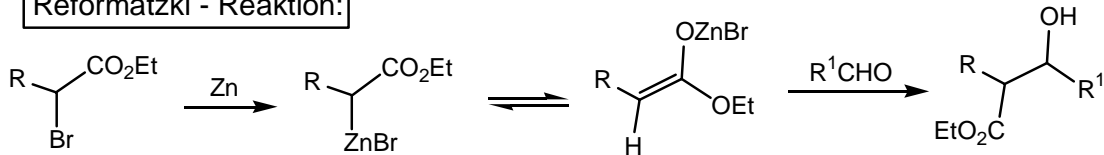
5. Reaktionen in der Seitenkette

5.1 α -Halogencarbonsäuren

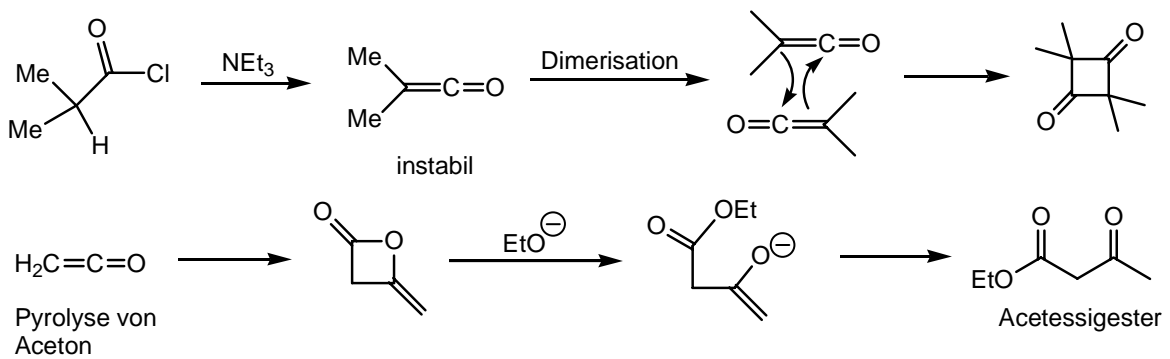
Hell -Volhard - Zelinsky - Reaktion:



Reformatski - Reaktion:

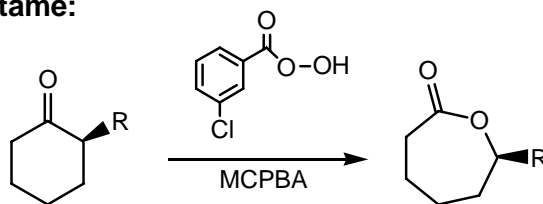


5.2 Ketene:



5.3 Lactone und Lactame:

Baeyer - Villiger -
Synthese



Beckmann -
Umlagerung

