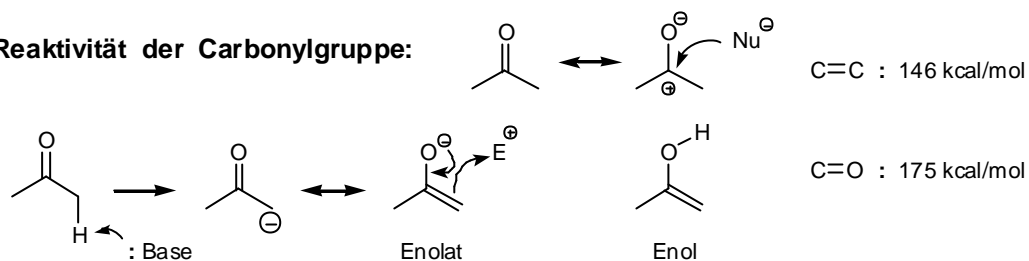
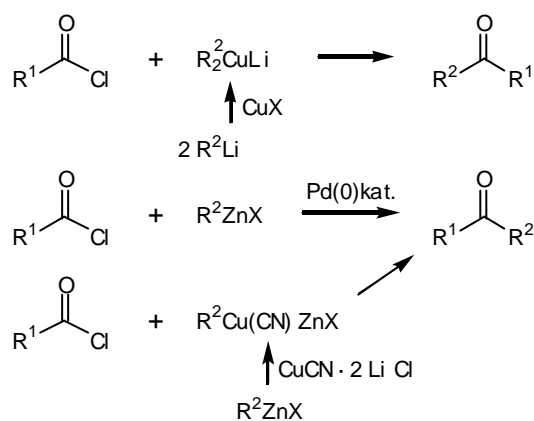


## 1) Darstellung von Aldehyden und Ketonen

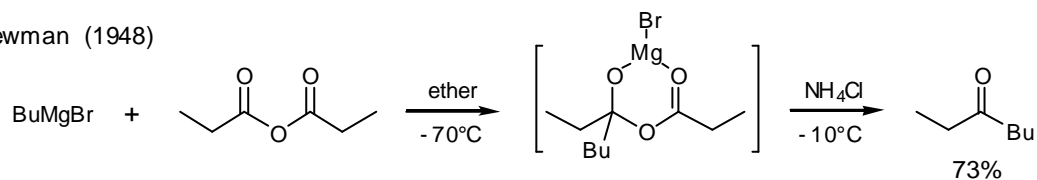
## 1.1. Reaktivität der Carbonylgruppe:



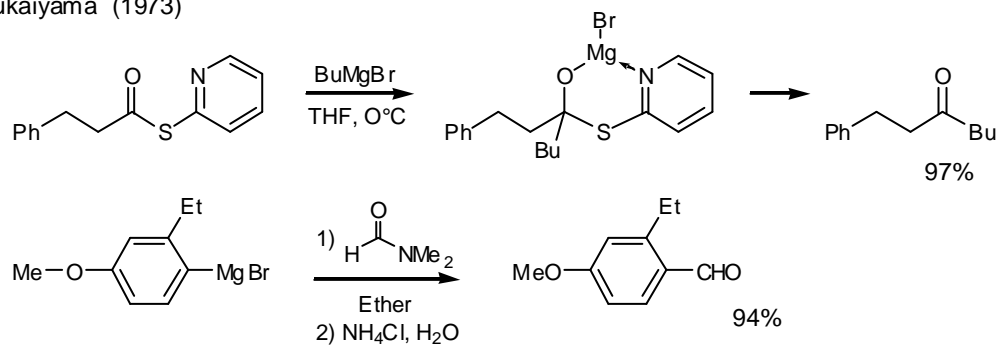
## 1.2. Metallorganische Synthese

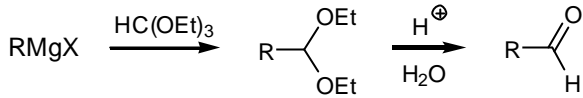
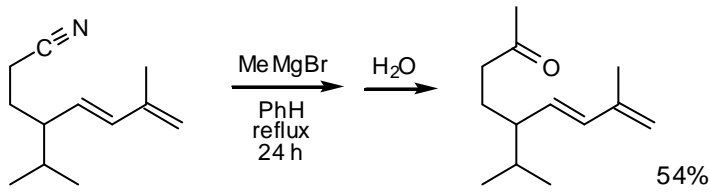


Newman (1948)



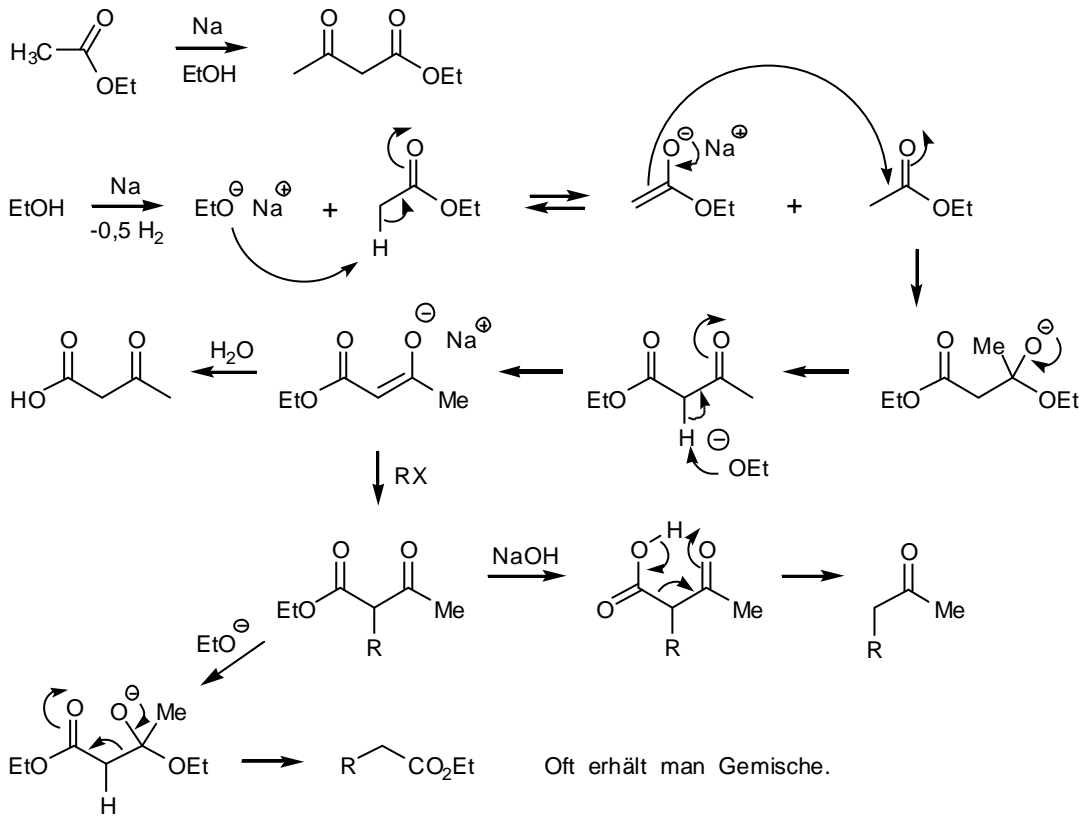
Mukaiyama (1973)



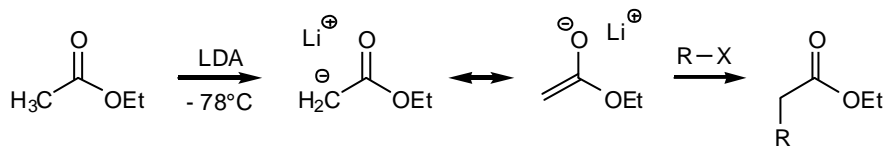


### 1.3. Enolat-Chemie

Claisen-Kondensation



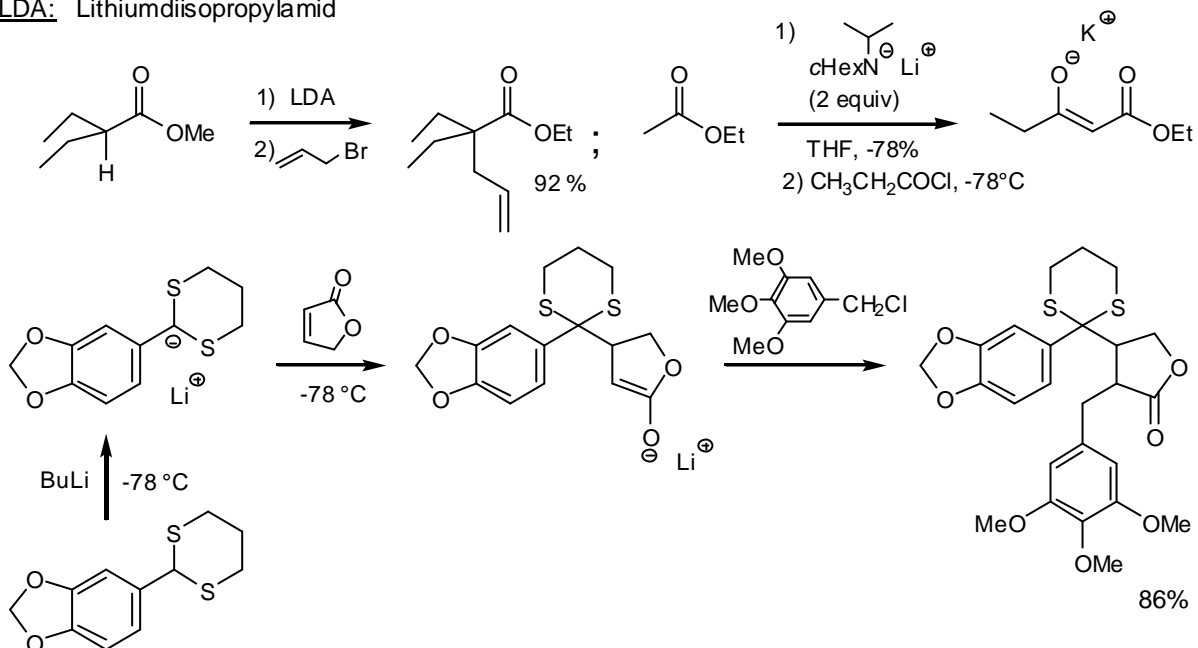
Moderne Methode: Stöchiometrische Bildung des Lithium-Enolats



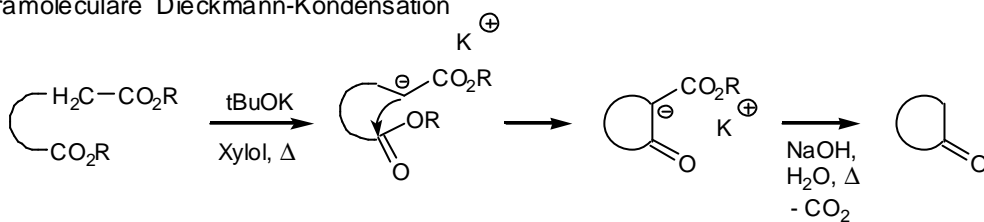
## 6. Gruppe: Carbonylverbindungen

③

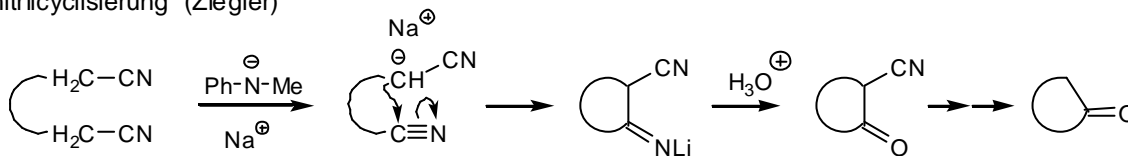
**LDA:** Lithiumdiisopropylamid



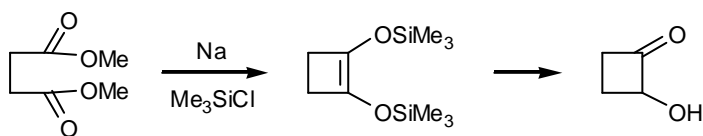
**Intramolekulare Dieckmann-Kondensation**



**Dinitrilsyclisierung (Ziegler)**

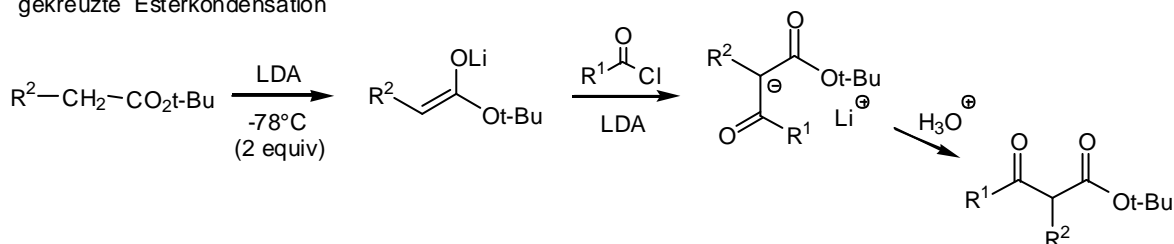


**Acyloinkondensation**



Ausbeute: 9- bzw. 10-Ringe: 30-42%; größere Ringe: > 90%

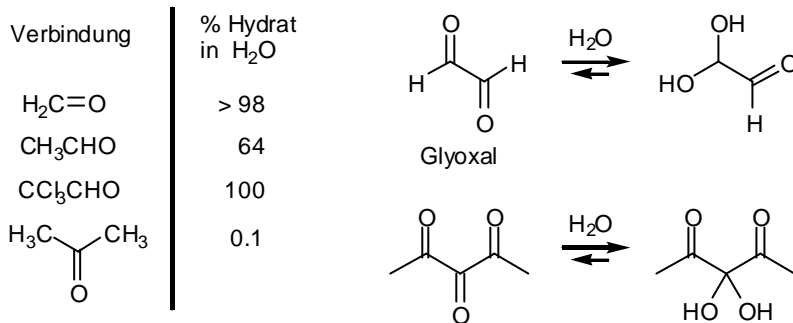
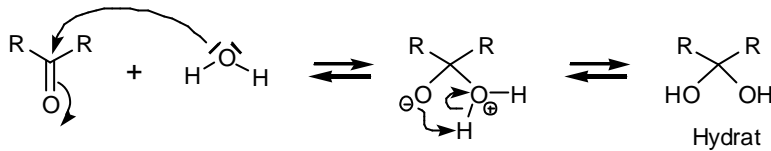
gekennzeichnete Esterkondensation



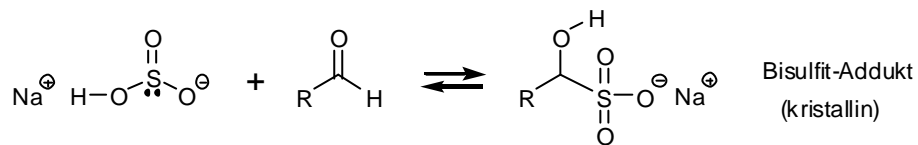
## 2) Reaktionen der Carbonylverbindungen

### 2.1. Addition nucleophiler Verbindungen

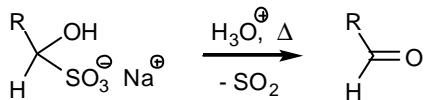
#### 2.1.1. Addition von Wasser



#### 2.1.2. Addition von NaHSO<sub>3</sub> (Hydrogensulfit)

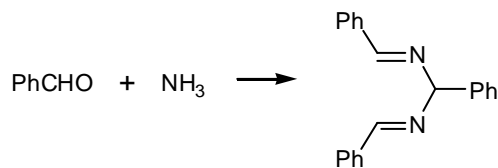
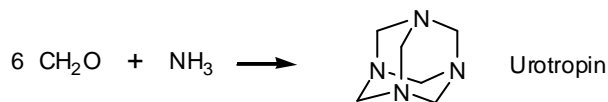
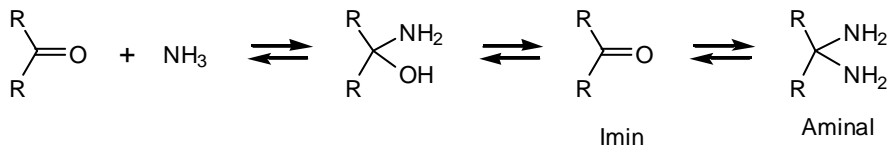


Spaltung des Adduktes durch H<sub>3</sub>O<sup>+</sup>



#### 2.1.3. Addition von Aminen

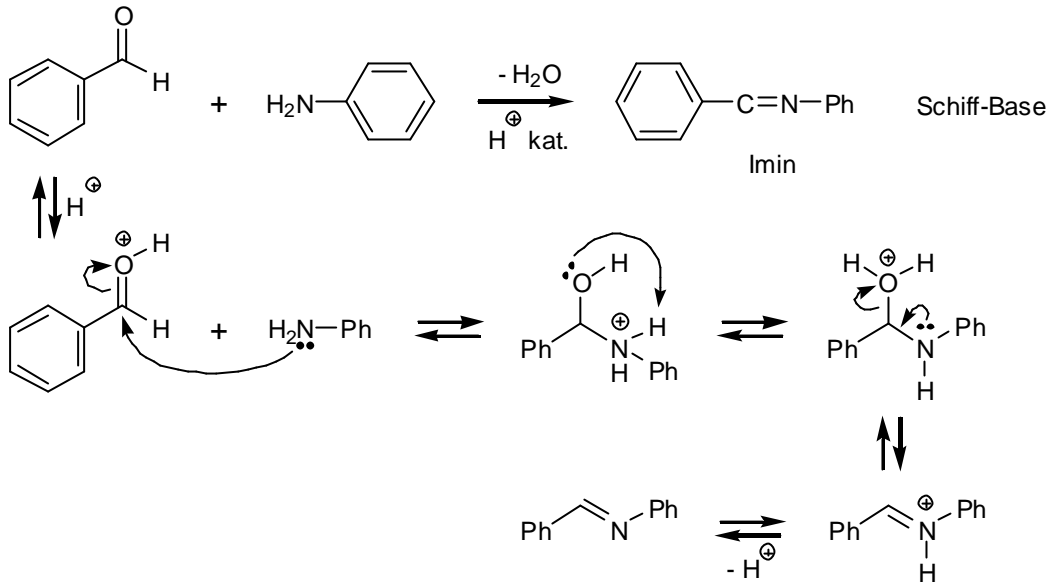
Ammoniak:



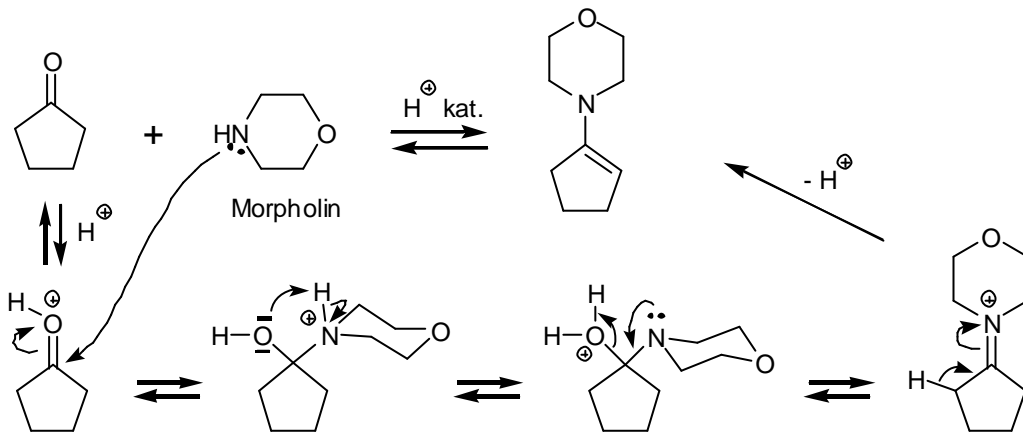
# 6. Gruppe: Carbonylverbindungen

5

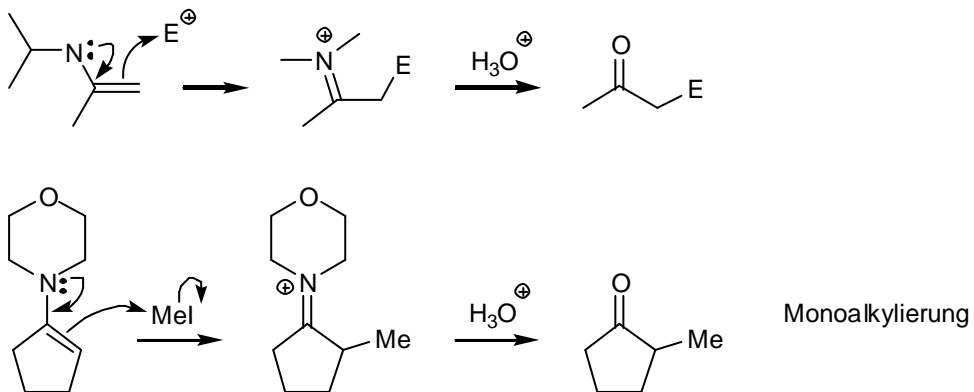
### Primäre Amine



### Sekundäre Amine

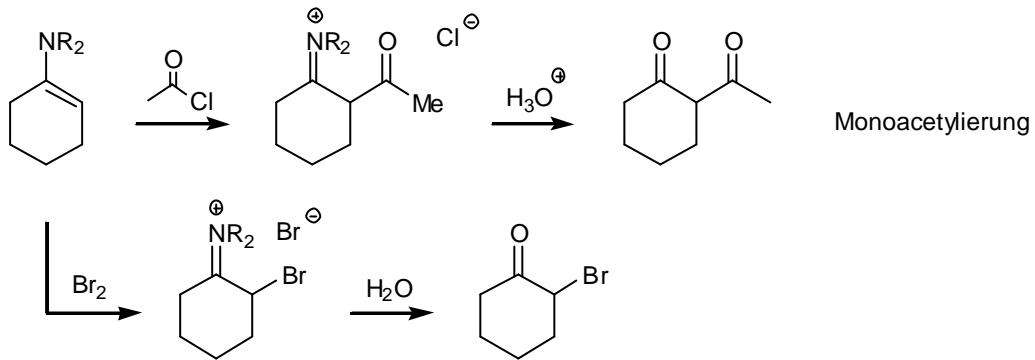


### Reaktivität von Enaminen

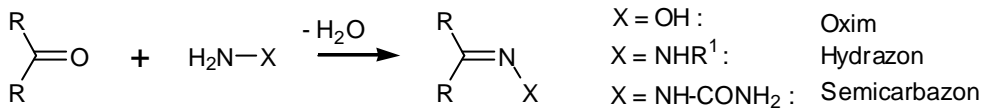


## 6. Gruppe: Carbonylverbindungen

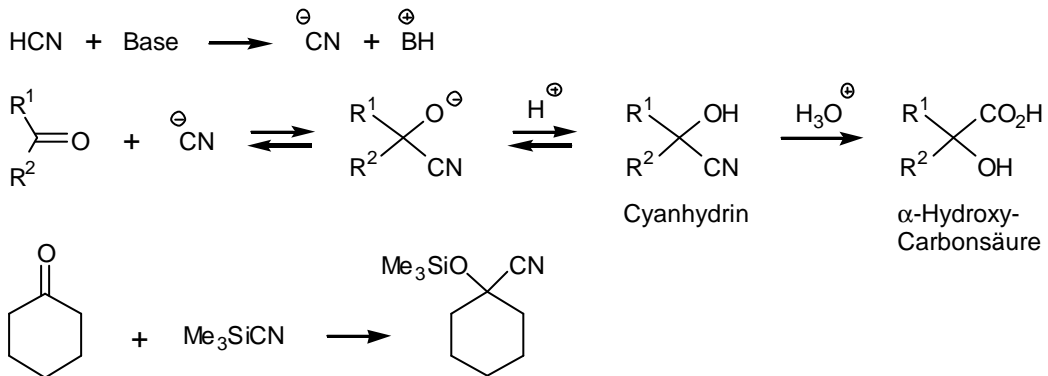
⑥



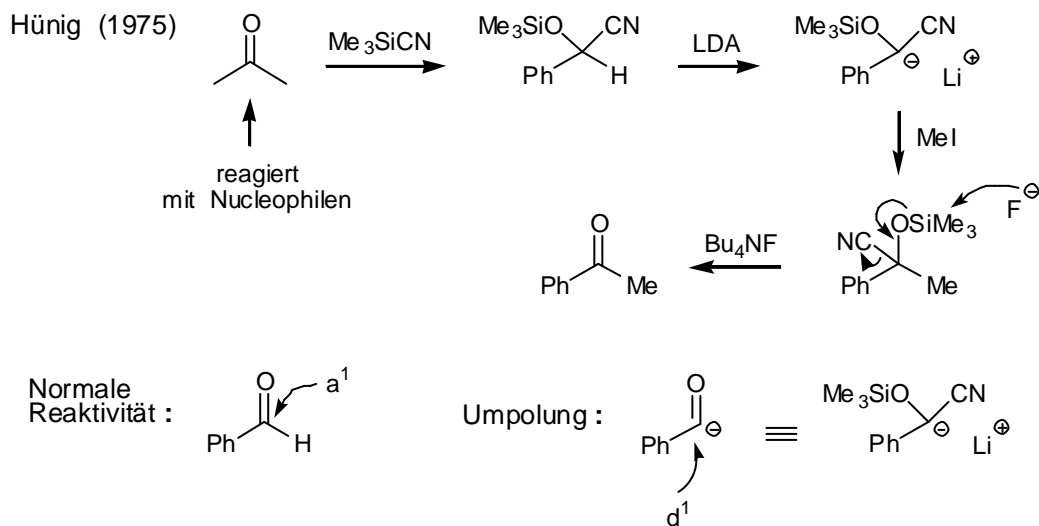
Hydroxylamin- und Hydrazin-Addition



### 2.1.4. Addition von HCN



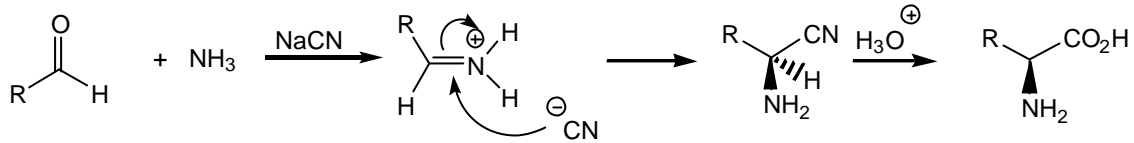
Umpolung der Reaktivität



## 6. Gruppe: Carbonylverbindungen

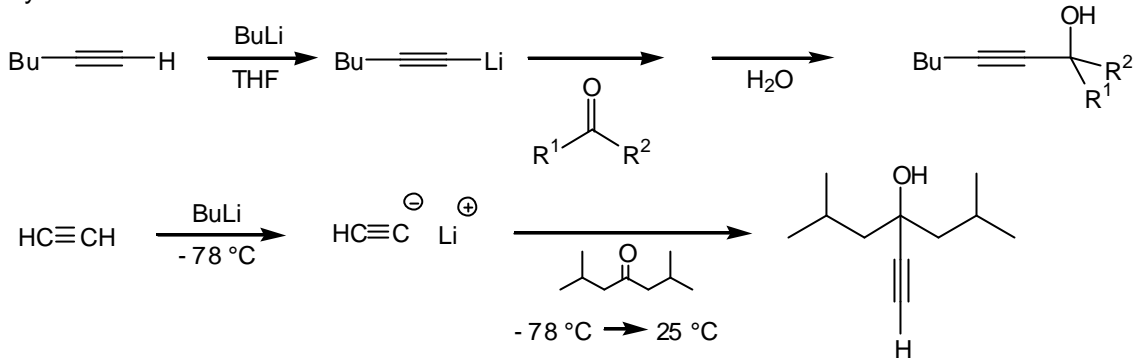
⑦

Strecker-Synthese von  $\alpha$ -Aminosäuren

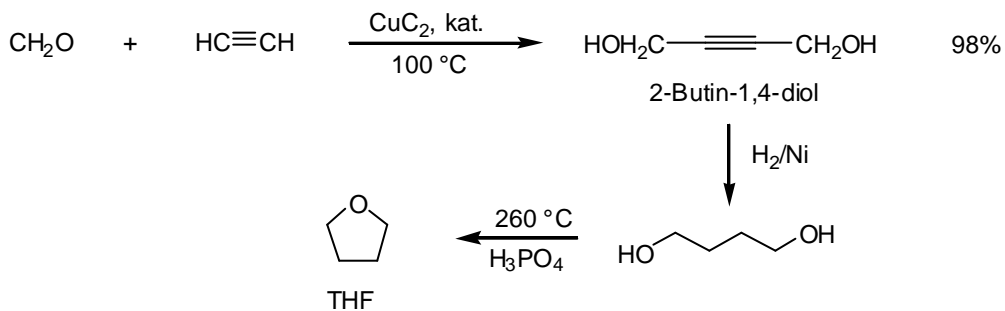


### 2.1.5. Addition von metallorganischen Reagenzien

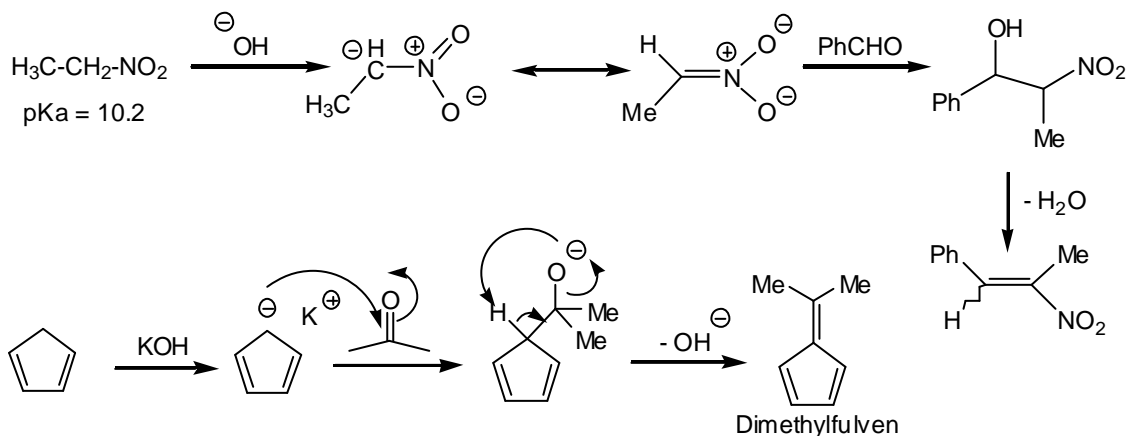
Alkyne



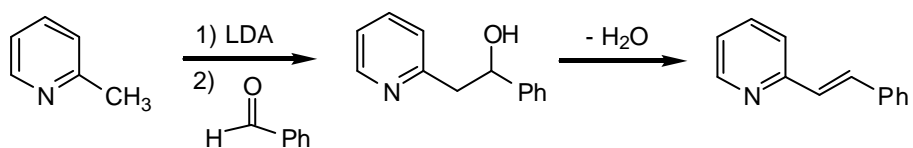
Reppe - Synthese (BASF)



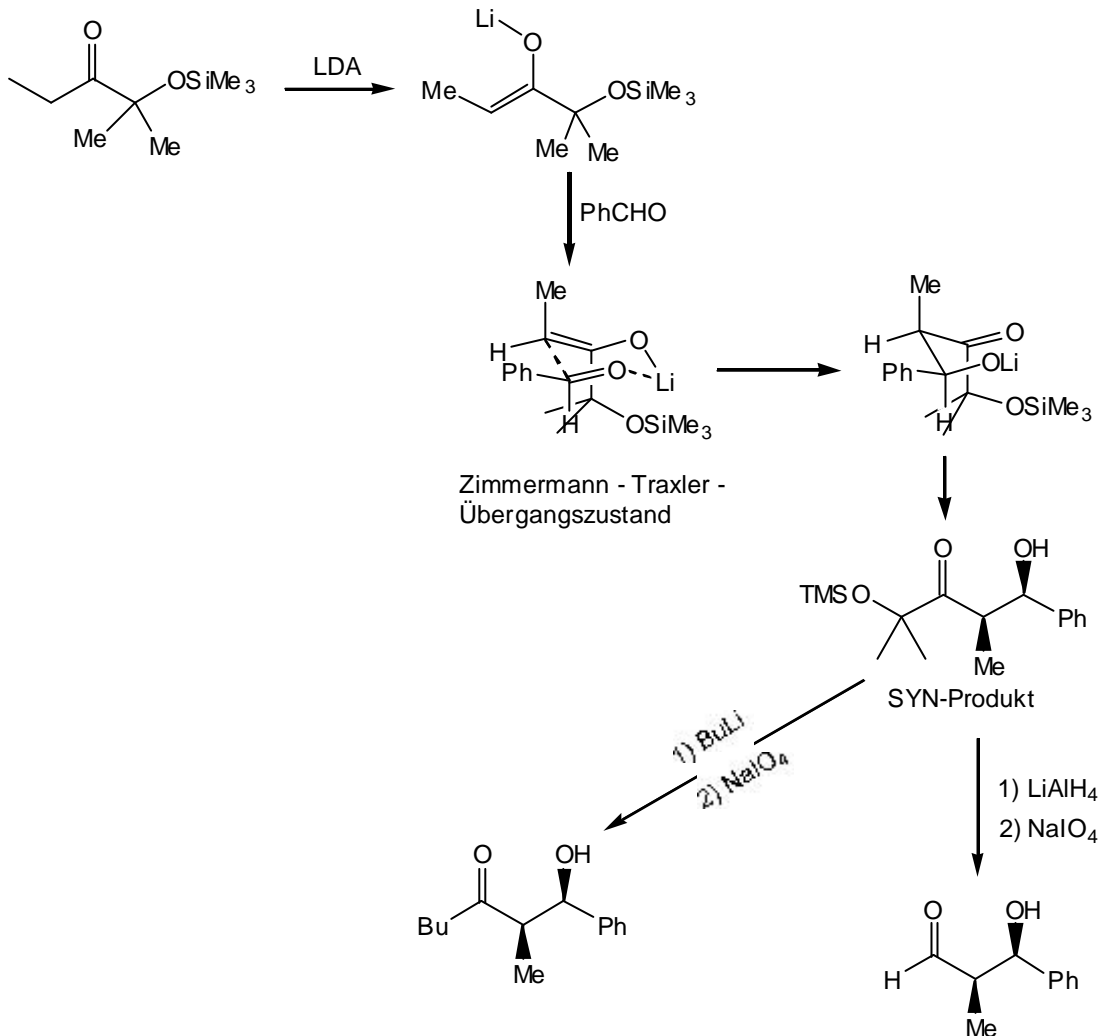
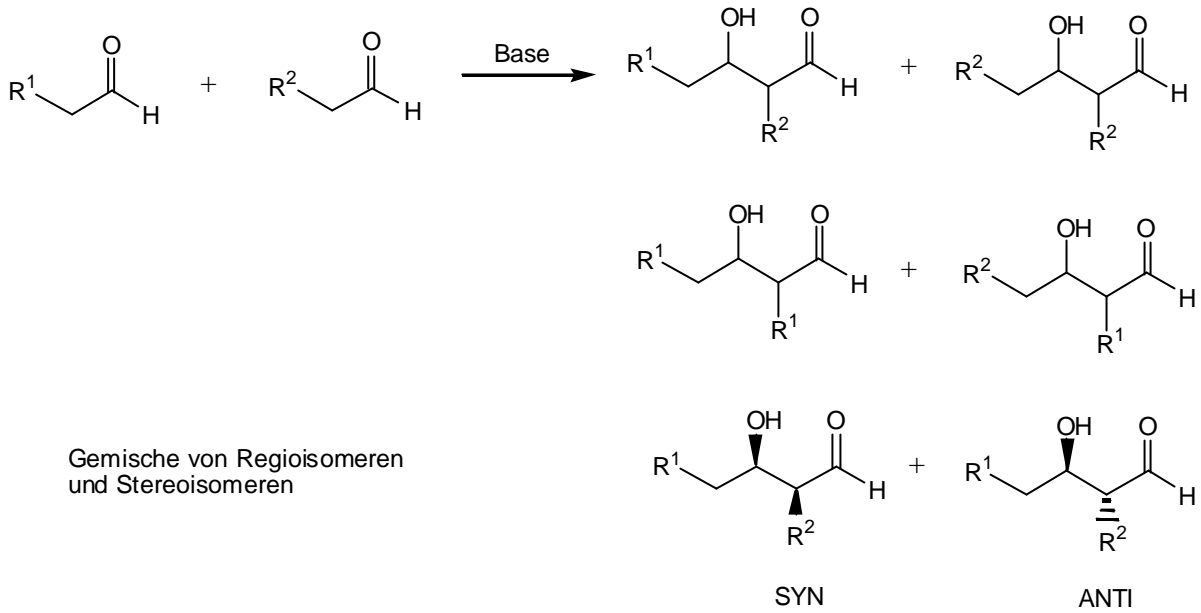
Addition von Nitroalkenen (Henry-Reaktion)



Picolin



2.2. Die Aldol - Reaktion

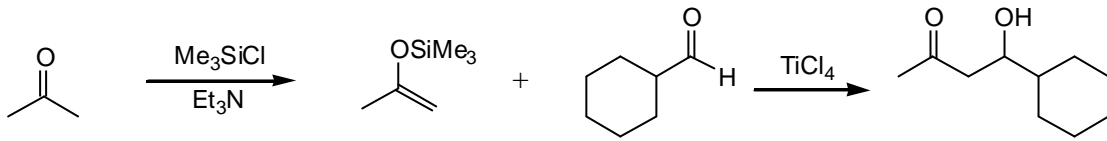




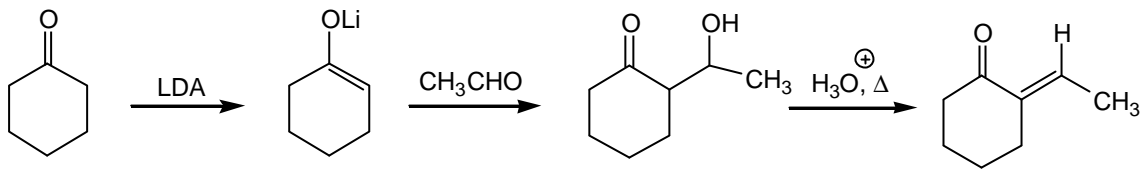
## 6. Gruppe: Carbonylverbindungen

9

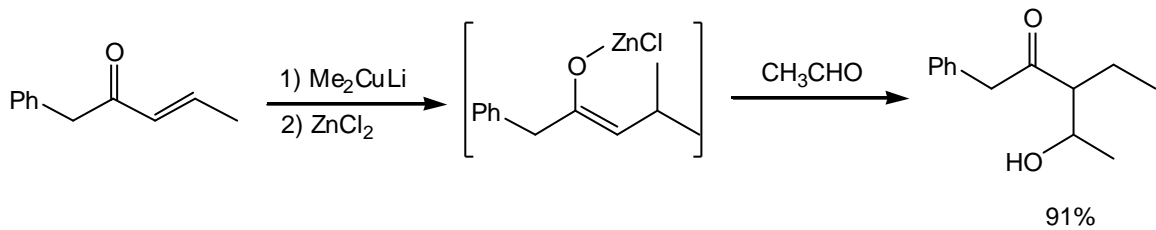
Mukaiyama - Methode



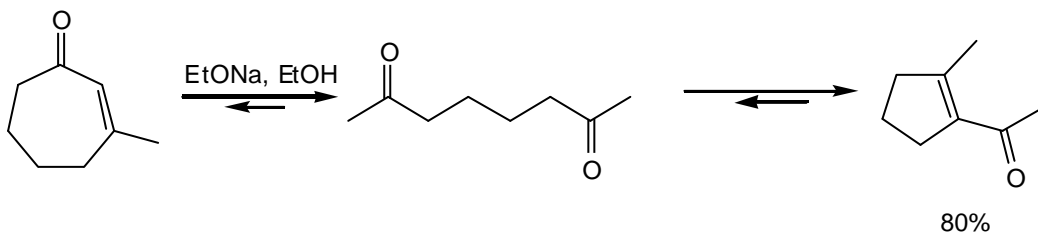
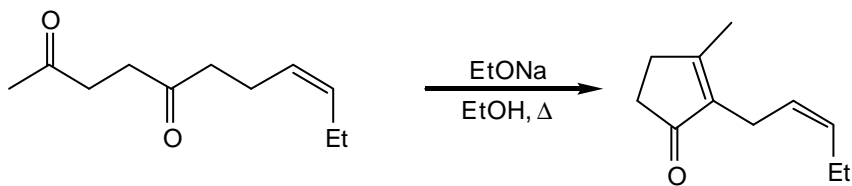
Aldol - Kondensation



Selektivität der Aldol - Reaktion



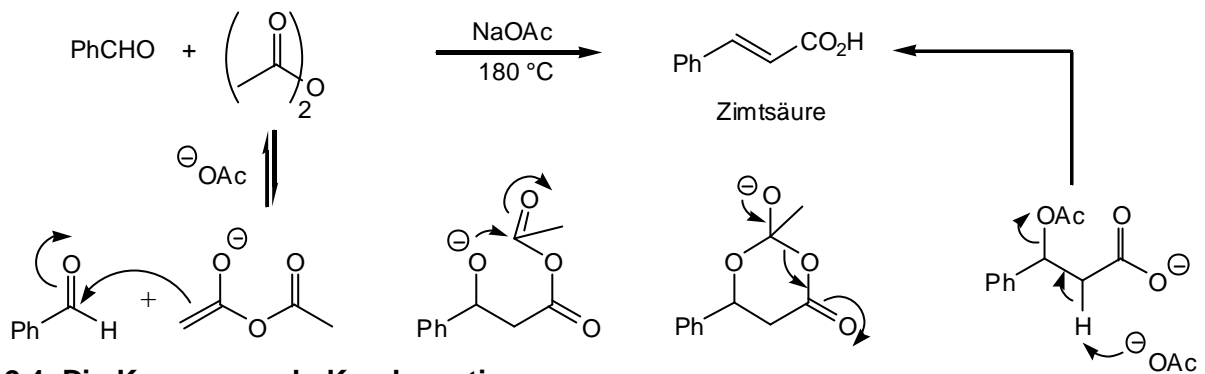
Cyclopentanone werden bevorzugt gebildet



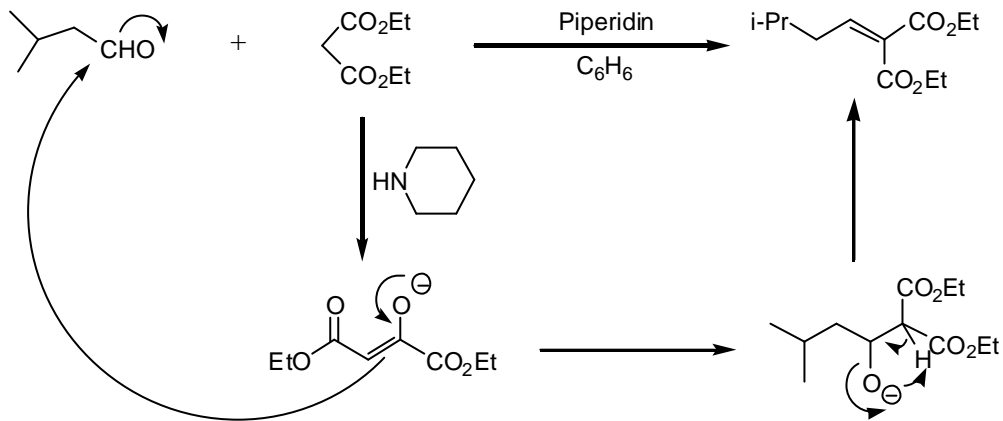
## 6. Gruppe: Carbonylverbindungen

10

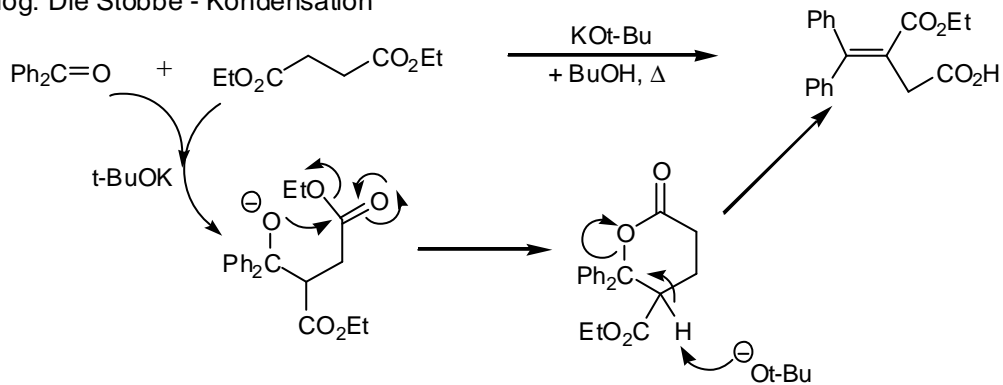
### 2.3. Die Perkin - Reaktion



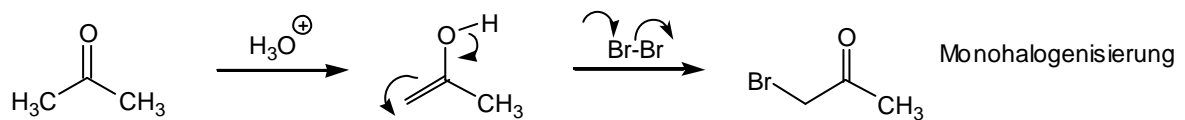
### 2.4. Die Knoevenagel - Kondensation



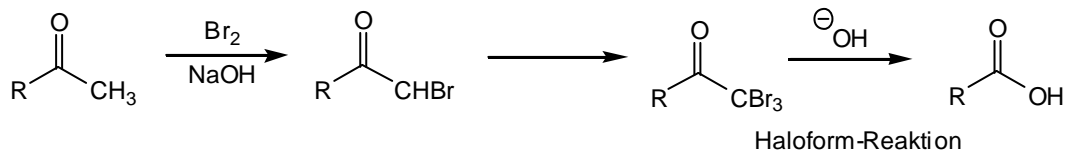
Analog: Die Stobbe - Kondensation



### 2.5. $\alpha$ -Halogenierung von Aldehyden und Ketonen



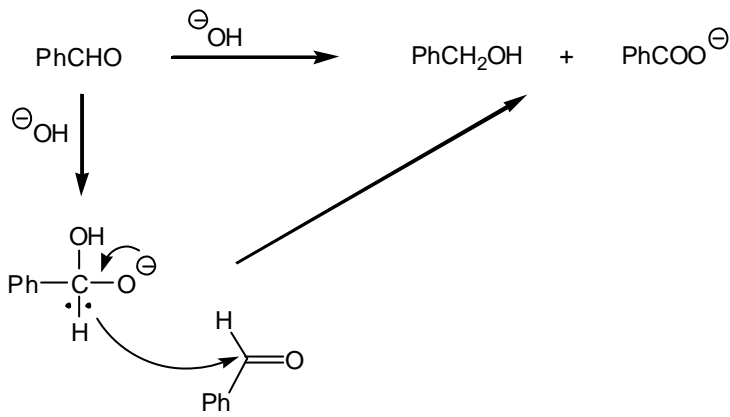
Geschw. =  $k[\text{Aceton}][\text{H}_3\text{O}^+]$ . In basischen Medien wird eine Polybromierung beobachtet.



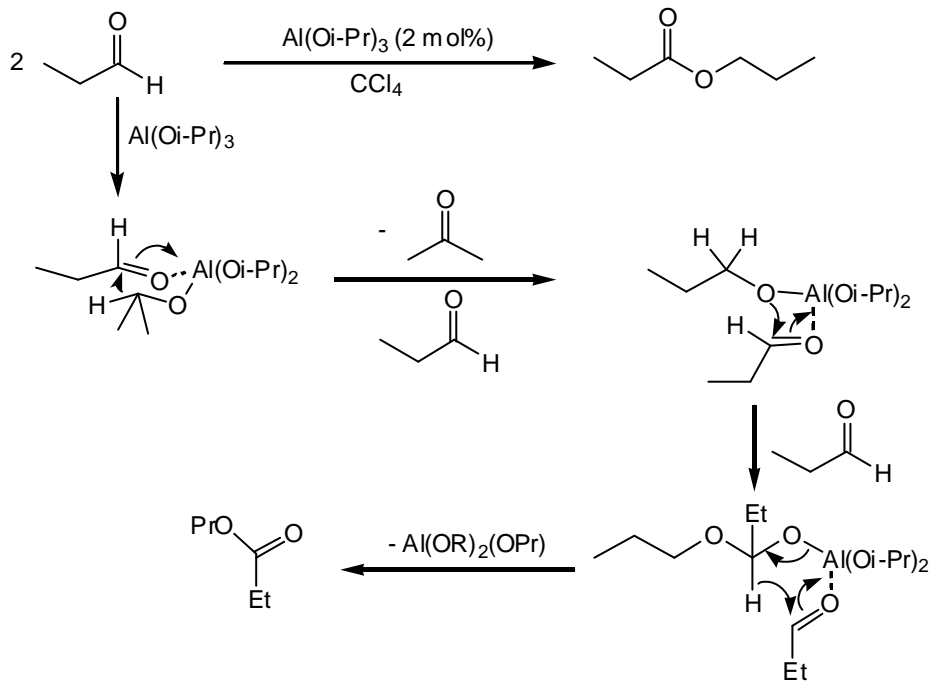
## 6. Gruppe: Carbonylverbindungen

11

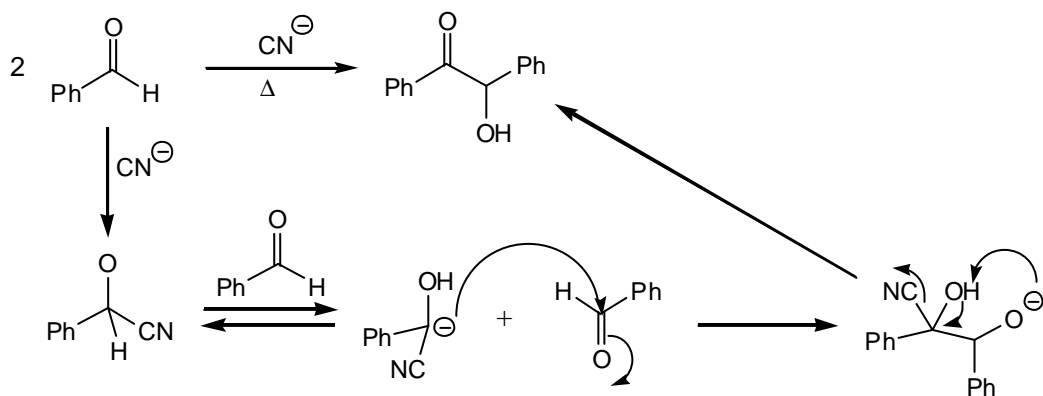
### 2.6. Cannizzaro - Reaktion



### Tischenko - Claisen - Reaktion



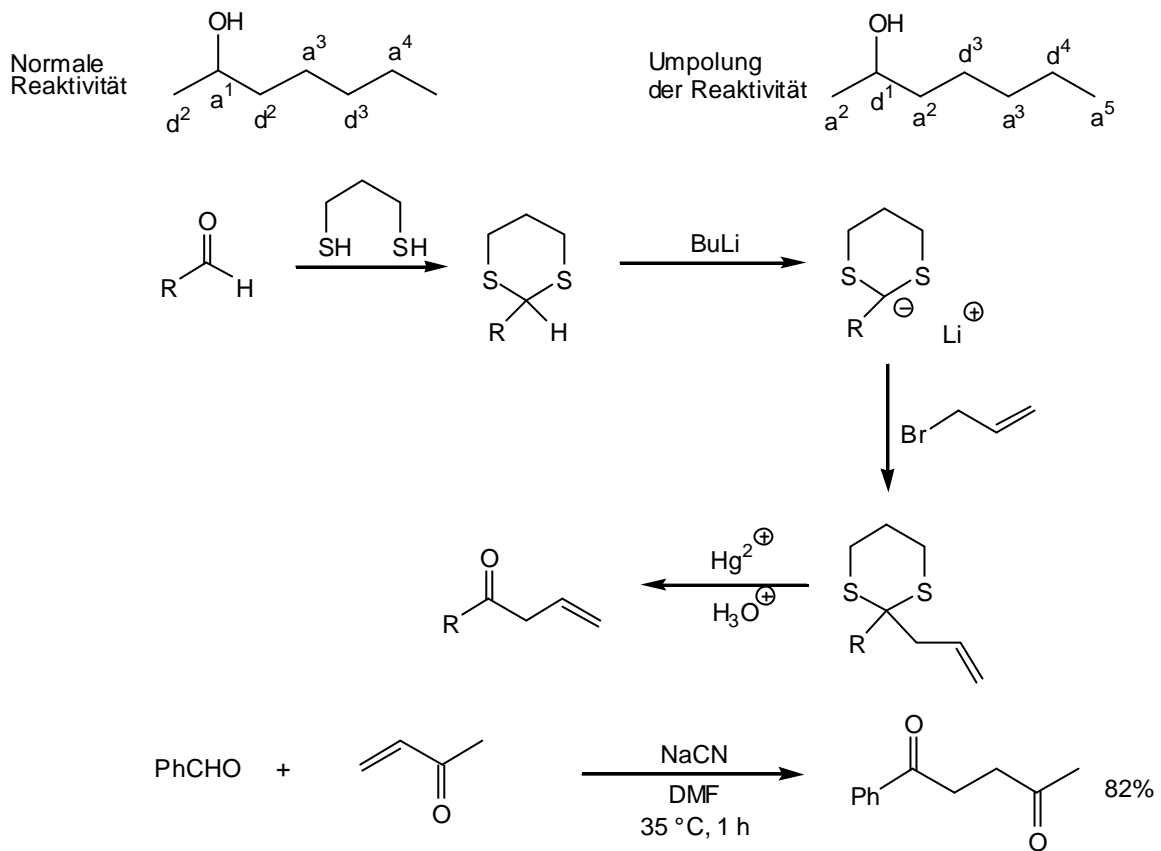
### Die Benzoin - Kondensation



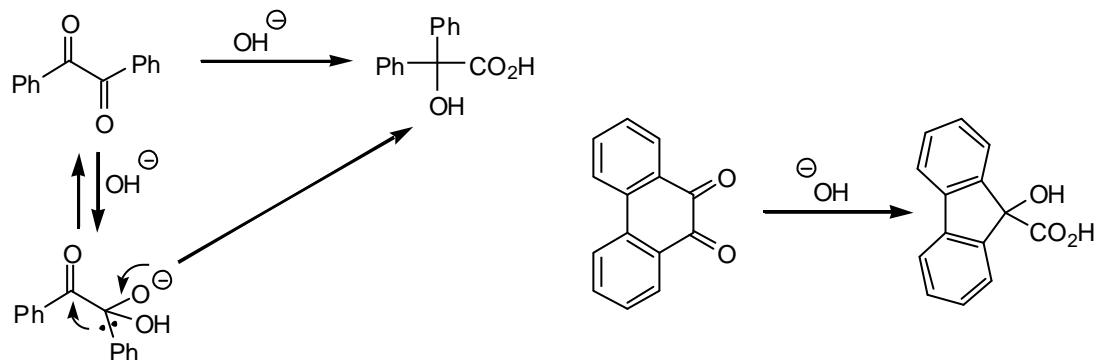
Umpolung der Reaktivität

## 6. Gruppe: Carbonylverbindungen

(12)

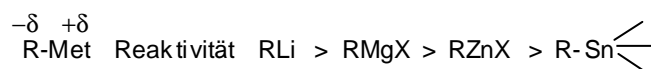


### 2.7. Die Benzilsäure - Umlagerung



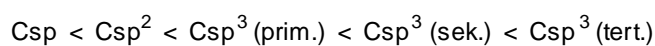
### 2.8. Reaktionen mit metallorganischen Verbindungen

#### 2.8.1. Einführung



Je elektropositiver das Metall, desto reaktiver ist die entsprechende metallorganische Spezies.

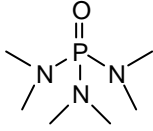
Die Reaktivität steigt auch nach erhöhtem p - Charakter:



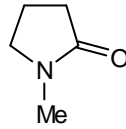
## 6. Gruppe: Carbonylverbindungen

13

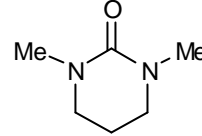
Metallorganische Verbindungen sind meistens reaktiver in THF als in Ether und reaktiver in Ether als in Hexan. Die Verwendung eines polaren Lösungsmittels wie HMPT oder NMP beschleunigt viele metallorganische Reaktionen. (DMPU ist auch gut geeignet)



HMPT

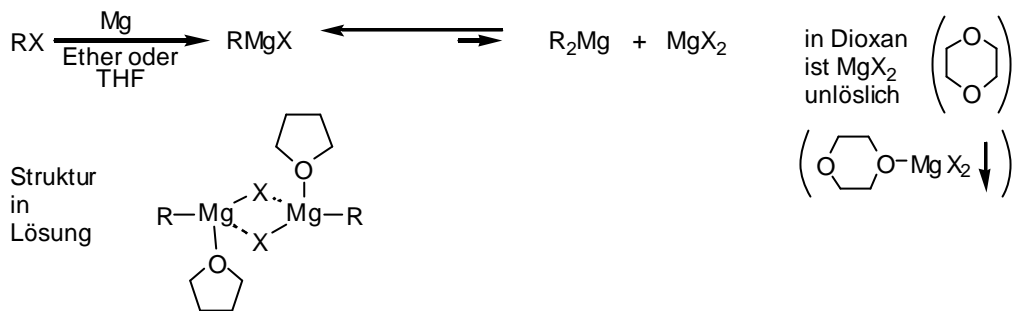


NMP

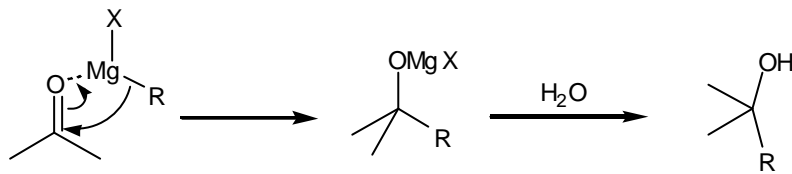


DMPU

### 2.8.2 Reaktionen von Grignard - Verbindungen:



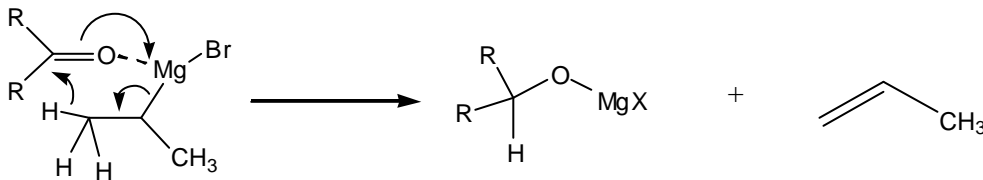
Reaktion mit Carbonylverbindungen:



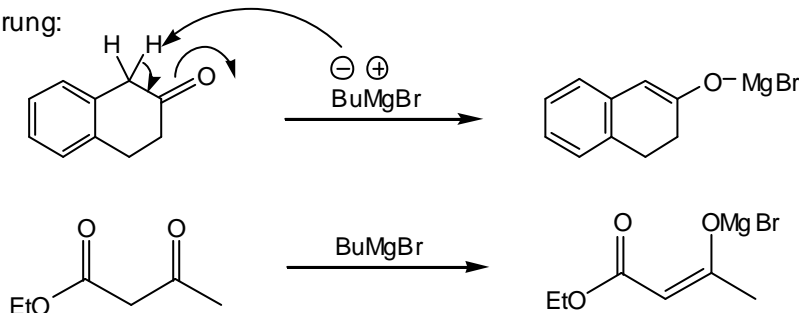
Aldehyde	→	sek. Alkohole
Ketone	→	tert. Alkohole
$\text{CH}_2\text{O}$	→	prim. Alkohole

Nebenreaktionen:

Reduktion:



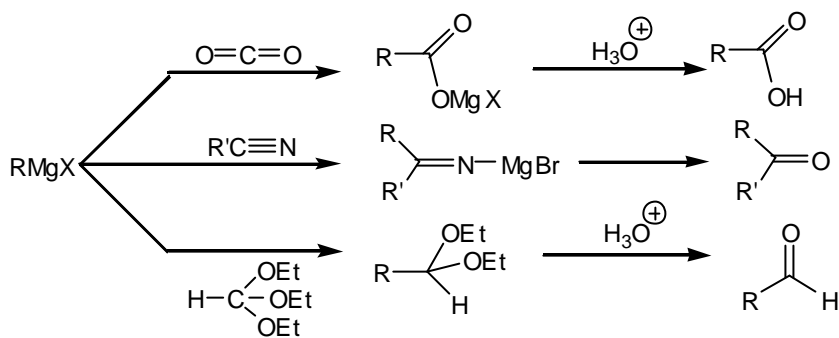
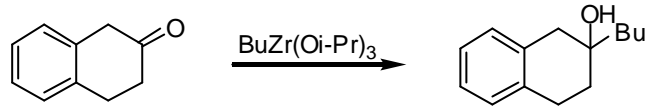
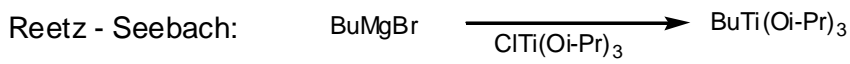
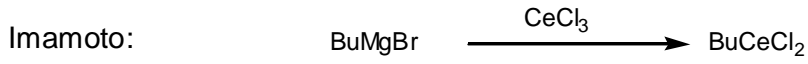
Enolisierung:



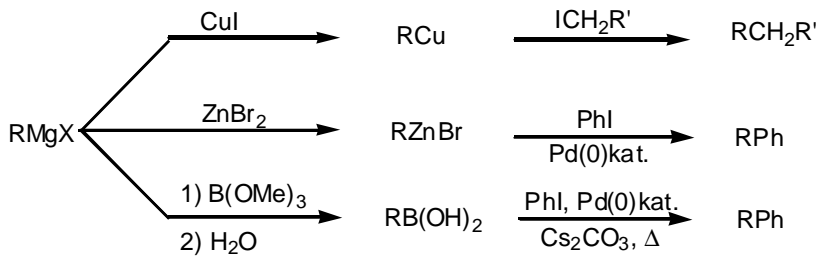
# 6. Gruppe: Carbonylverbindungen

14

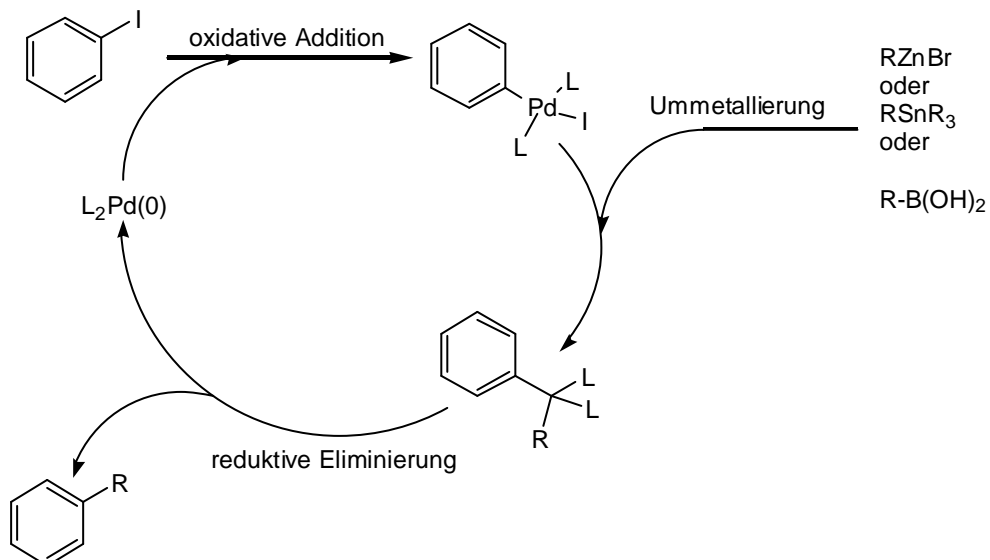
Lösung des Problems: Ummetallierung



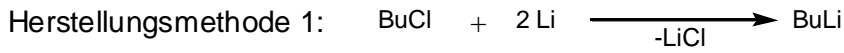
Substitutionsreaktionen:



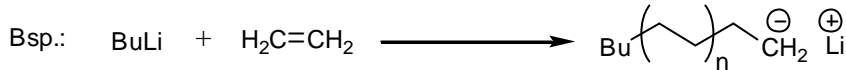
Substitution an  $\text{C}_{\text{sp}^2}$ -Zentren:



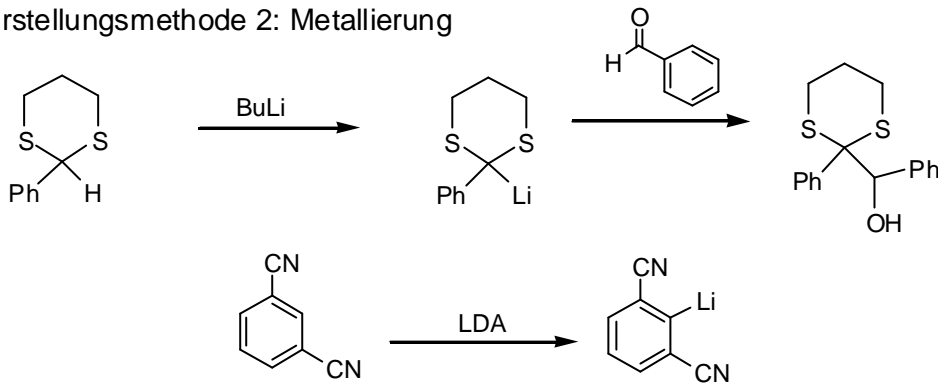
2.8.3 Reaktionen und Synthesen von Lithium - Verbindungen:



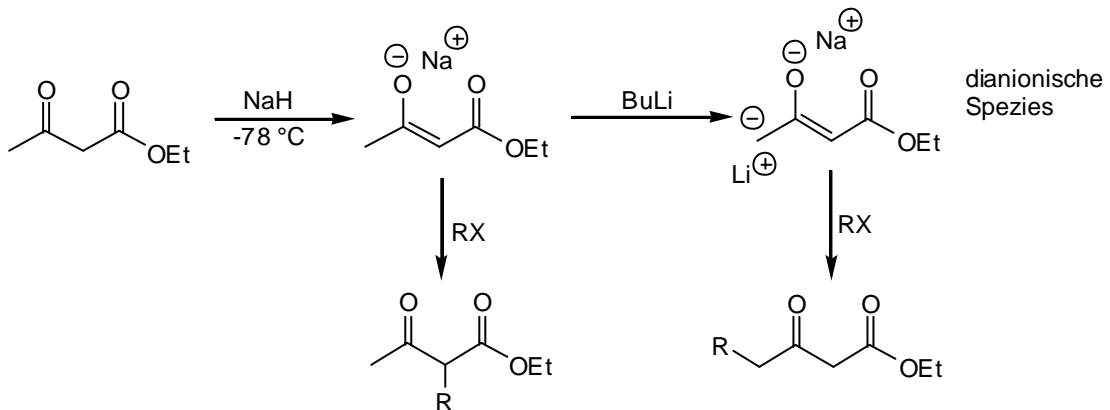
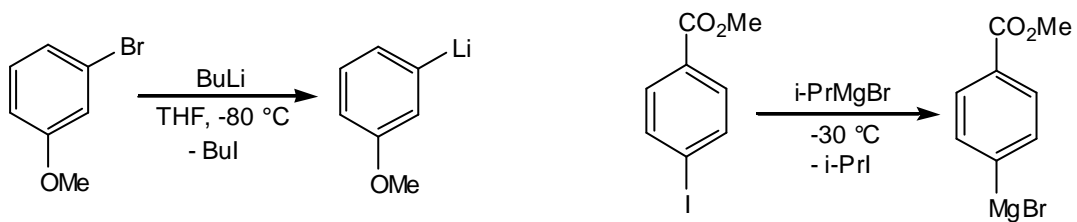
BuLi ist reaktiver als BuMgBr



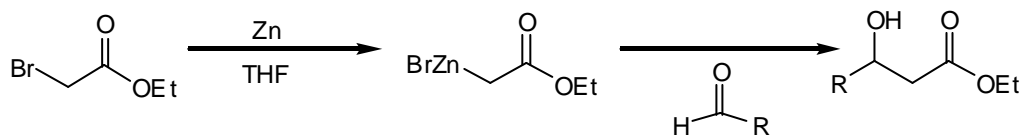
Herstellungsmethode 2: Metallierung



Herstellungsmethode 3: Halogen - Lithium - Austausch

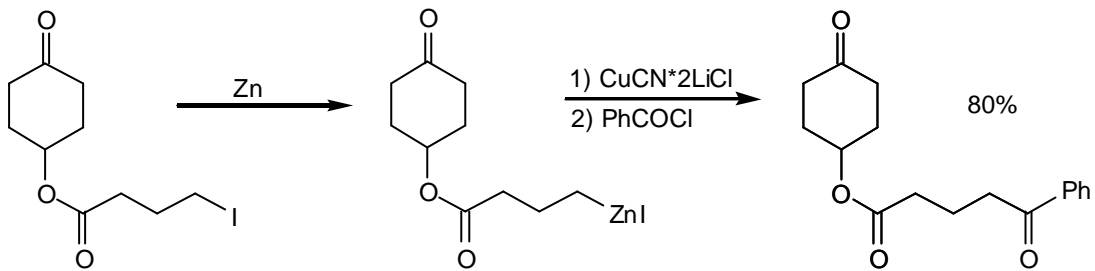


2.8.4 Zinkorganometallische Verbindungen:

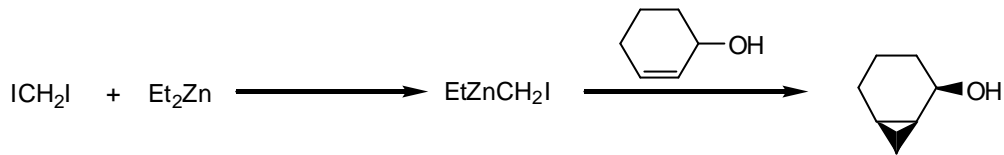


## 6. Gruppe: Carbonylverbindungen

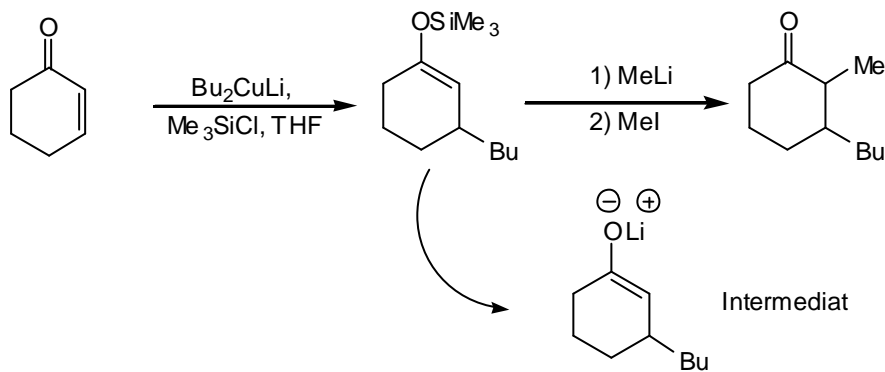
16



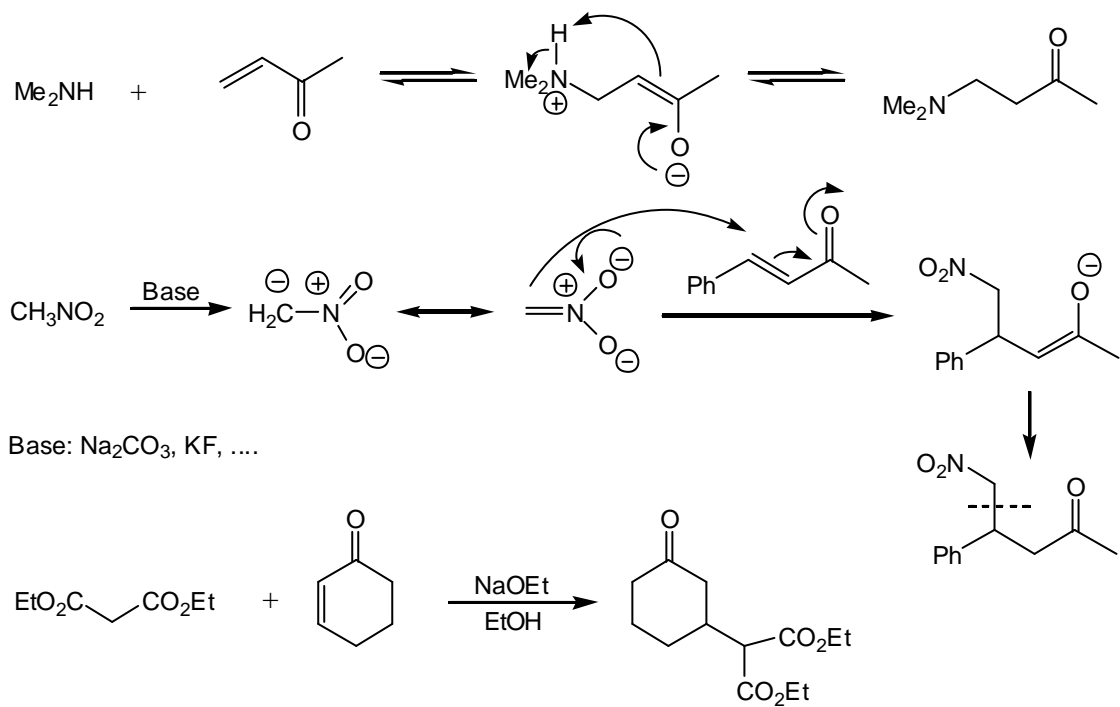
Simmons - Smith - Reaktion: Cyclopropansynthese



### 2. 8. 5. Kupferorganometallische Verbindungen:

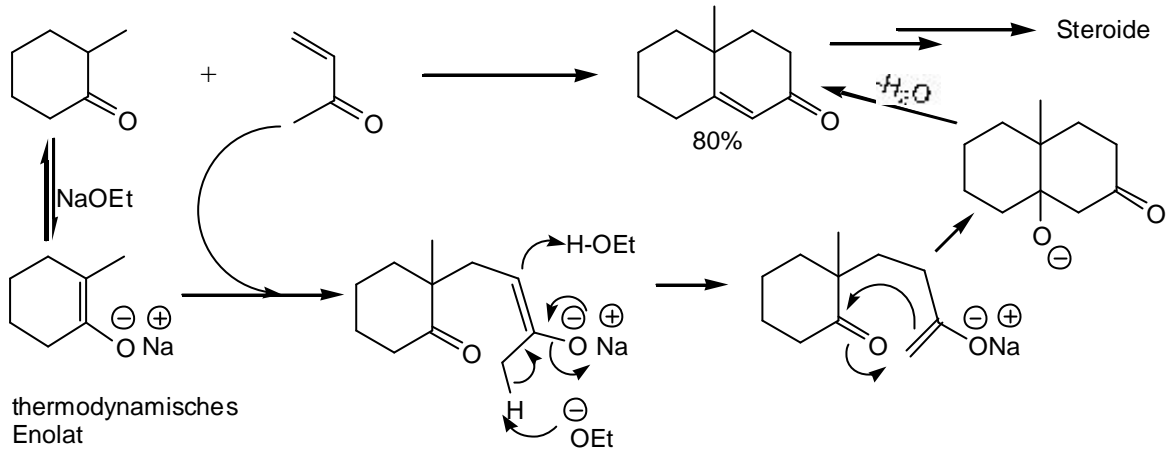


### 2. 9 Die Michael - Addition:

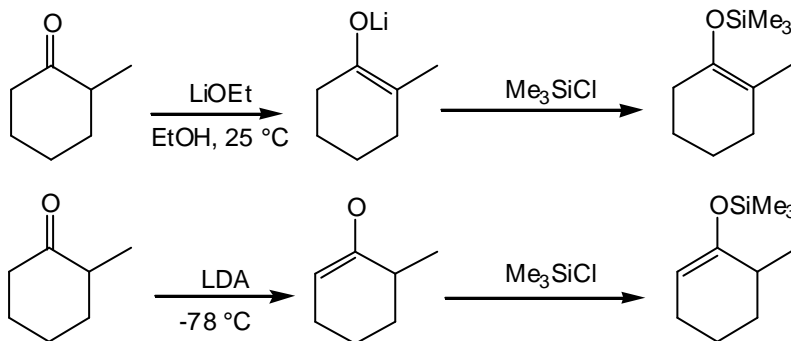




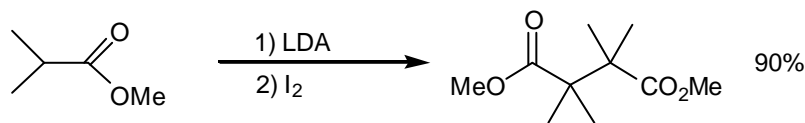
Robinson - Annellierung



Das kinetische Enolat kann unter Nicht - equilibrierungsbedingungen hergestellt werden z.B.: mit LDA

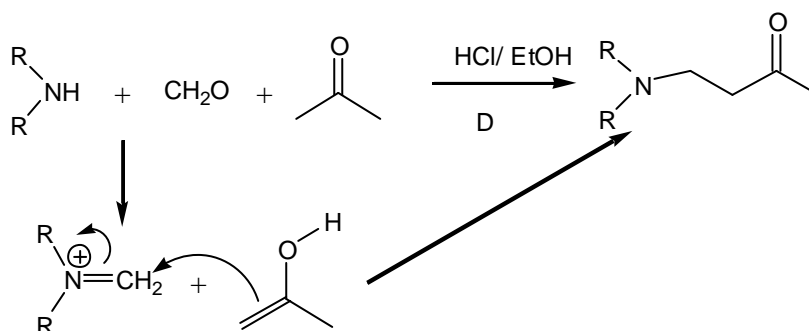


Dimerisierung von Enolaten



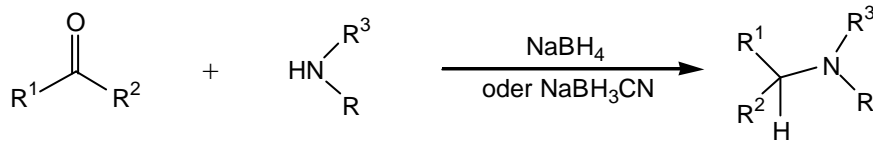
2. 10 Die Mannich - Reaktion:

wichtige Reaktion in der Alkaloiden Synthese

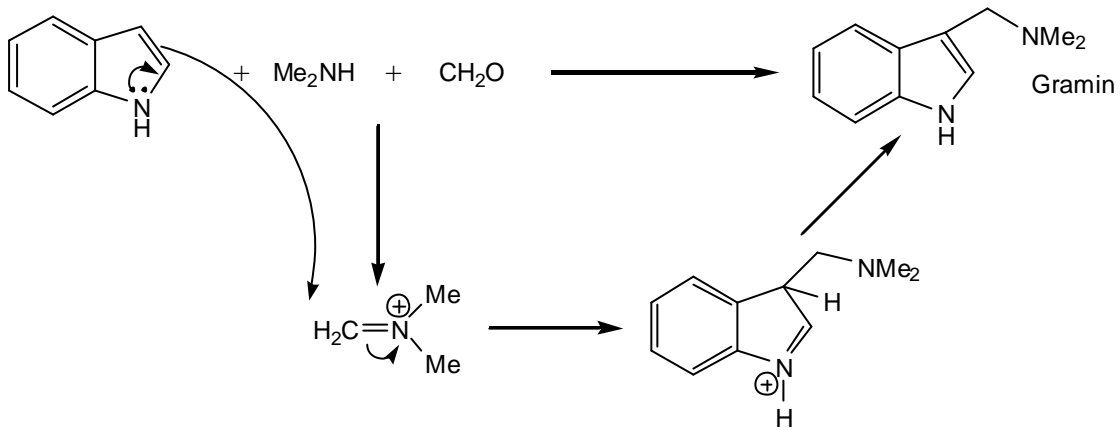


## 6. Gruppe: Carbonylverbindungen

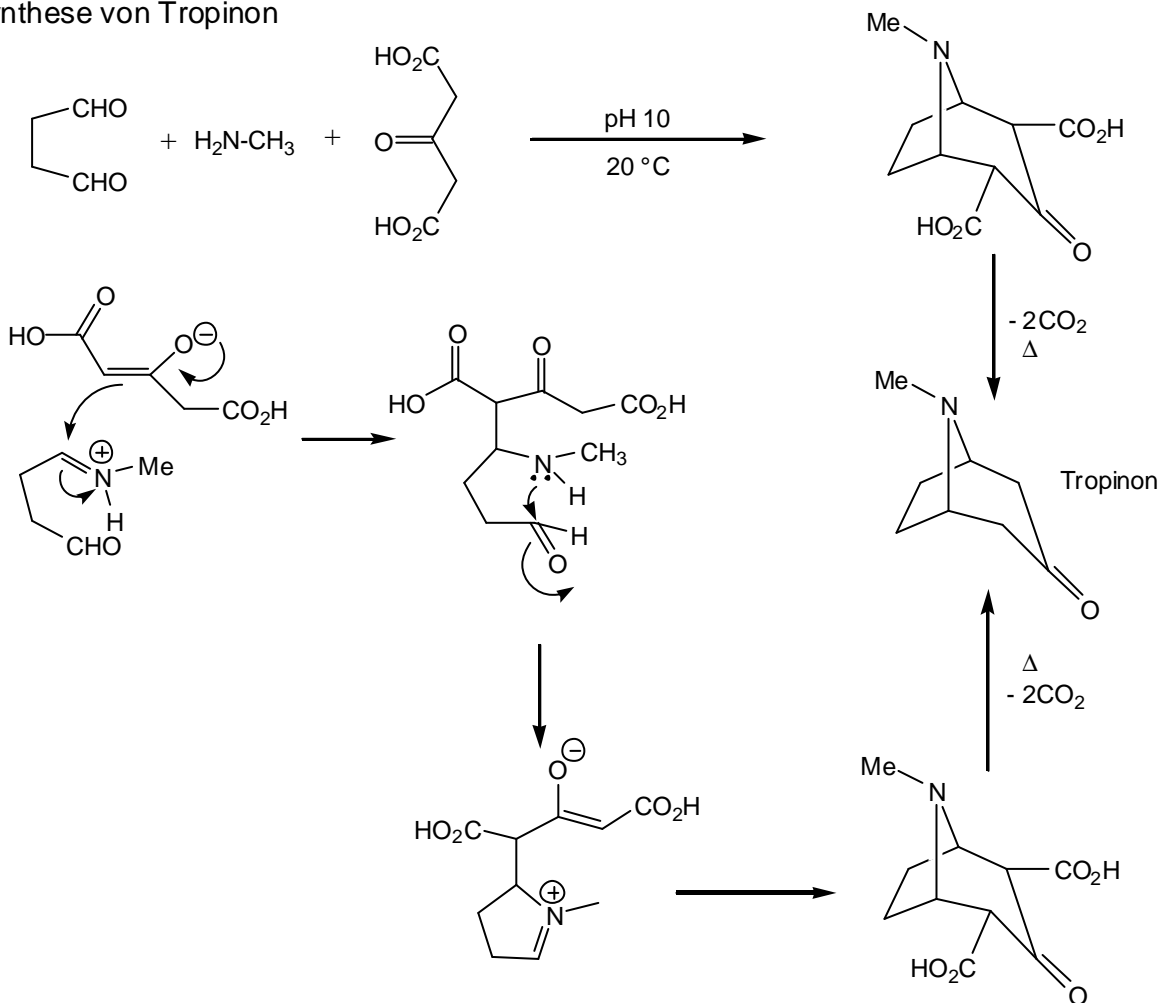
Vgl. mit der reduktiven Aminierung von Carbonyl - Verbindungen



Synthese von Gramin

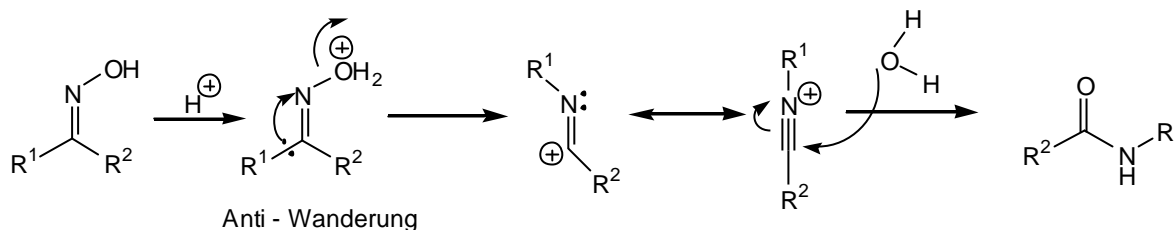


Synthese von Tropinon

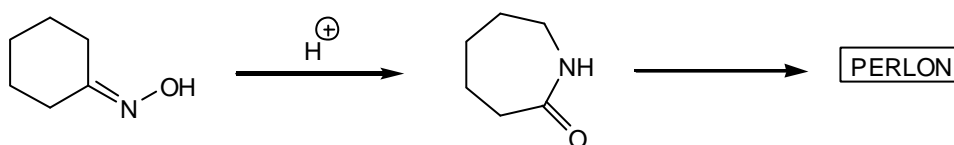


## 3. Umlagerungsreaktionen

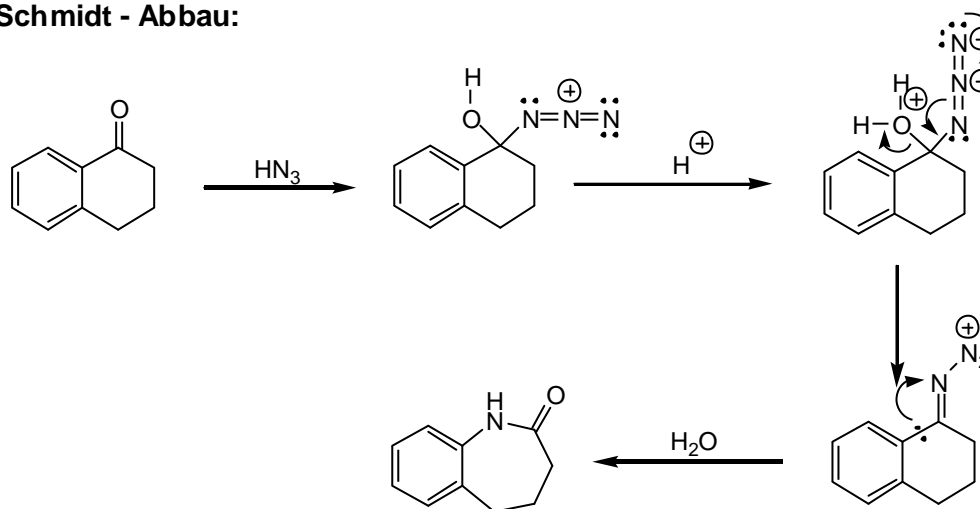
## 3.1 Die Beckmann - Umlagerung



von Cyclohexanon zu Perlon:

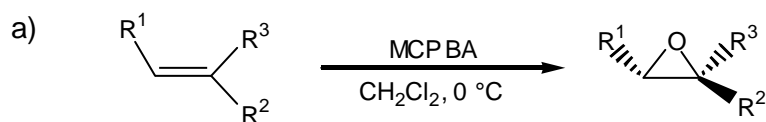


## 3.2 Schmidt - Abbau:

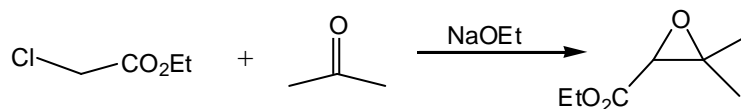


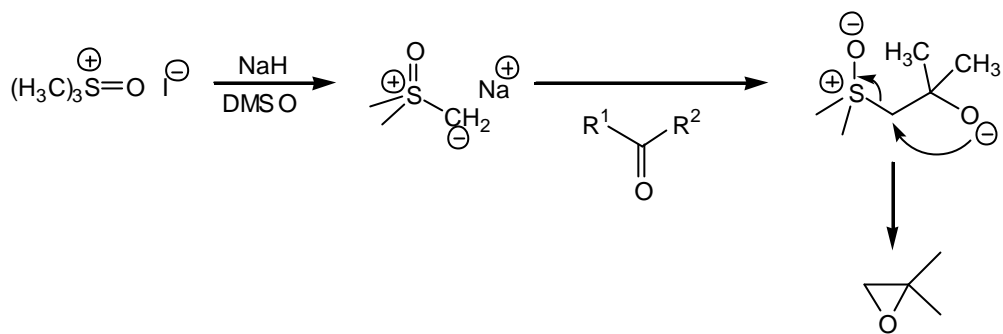
## 4. Synthese ausgewählter Heterocyklen:

## 4. 1 Oxirane:

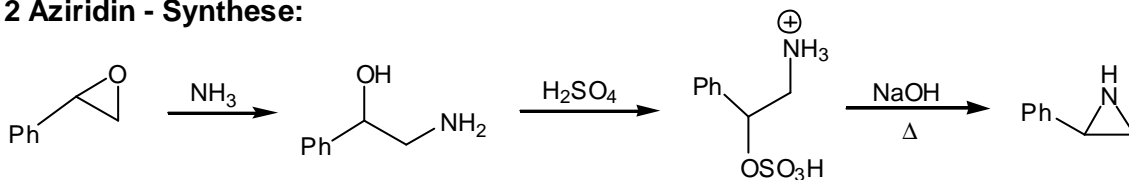


b) Darzens - Glycidester - Synthese:

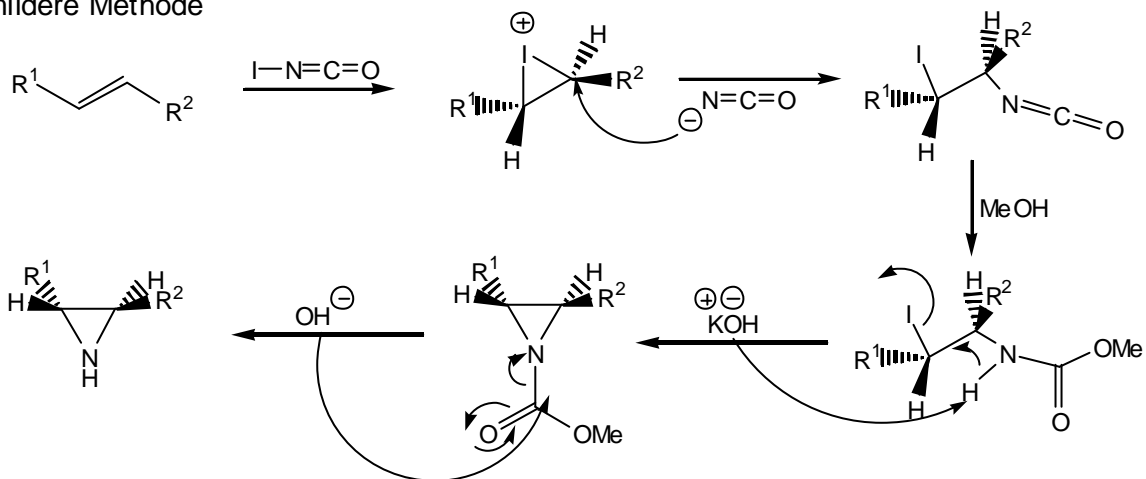




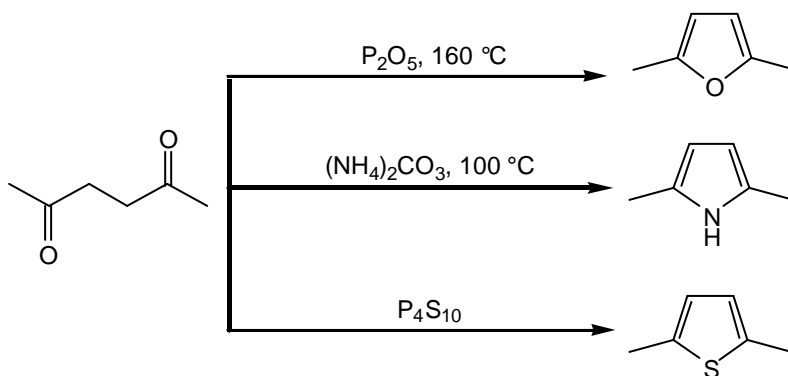
4. 2 Aziridin - Synthese:



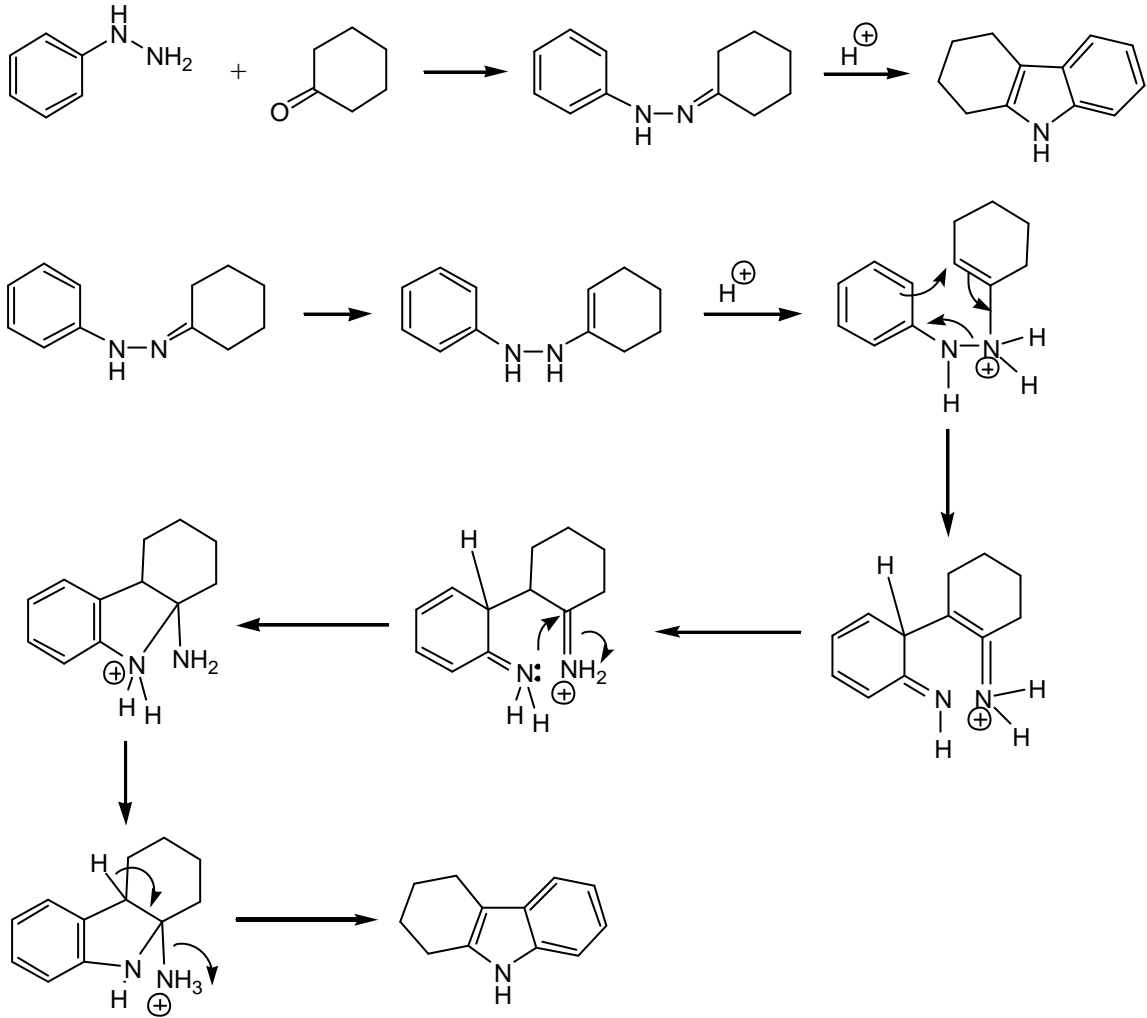
mildere Methode



4. 3 Furane, Pyrrole und Thiophene:



4. 4 Fischer - Indolsynthese:



4. 5 Hantzsch - Pyridinsynthese:

