

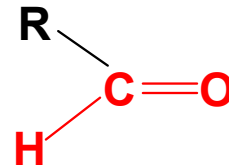
# 1.9. Aldehyde und Ketone (Carbonylverbindungen)

Nomenklatur: Nachsilbe **-al**  
**-on**

*Funktionelle Gruppe*

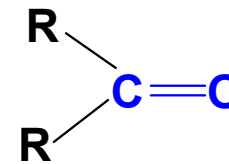
Carbonylgruppe

Oxo-Gruppe



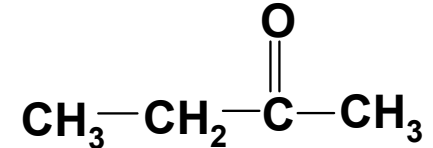
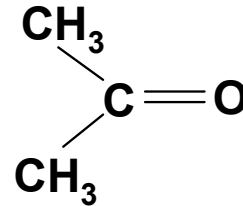
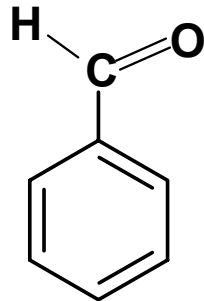
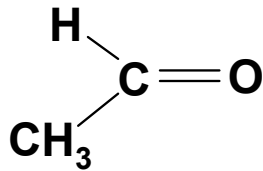
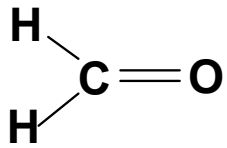
Aldehyd

Alkohol **dehydrogenatus**



Keton

Oxidationsstufe + II



Methanal  
Formaldehyd

Ethanal  
Acetaldehyd

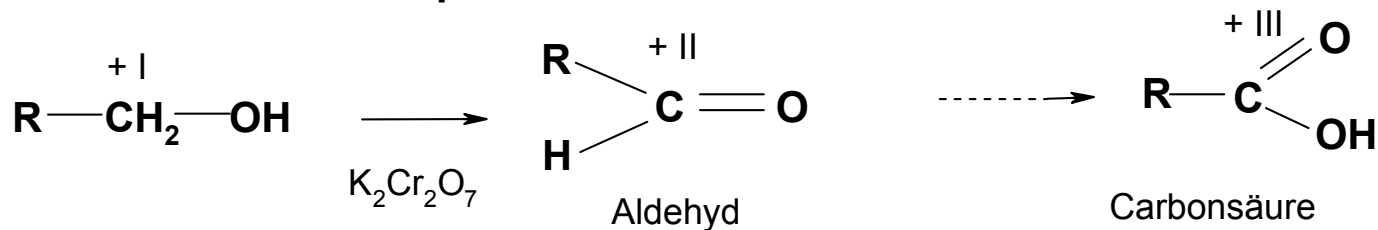
Benzaldehyd

Propanon  
Aceton

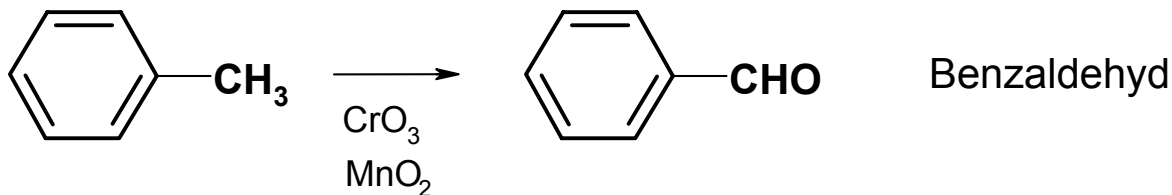
2-Butanon  
Ethyl-methyl-keton

# Herstellung von Aldehyden

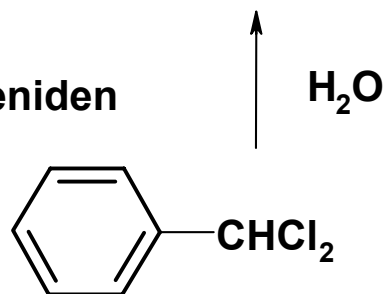
## 1. Selektive Oxidation primärer Alkohole



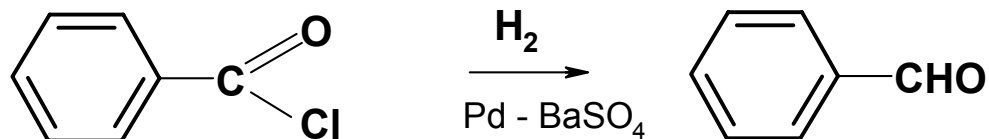
## 2. Oxidation aromatischer Methylgruppen



## 3. Hydrolyse von Dihalogeniden

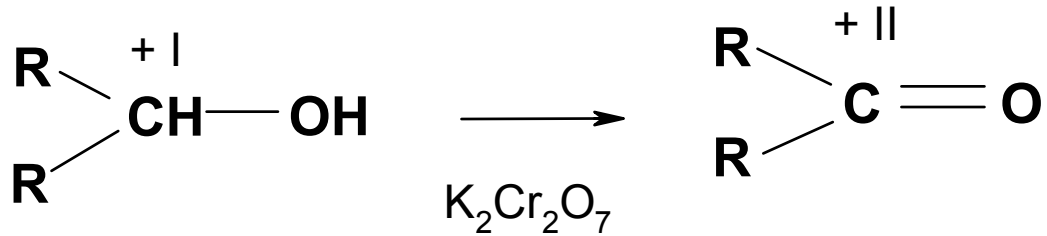


## 4. Reduktion von Säurechloriden

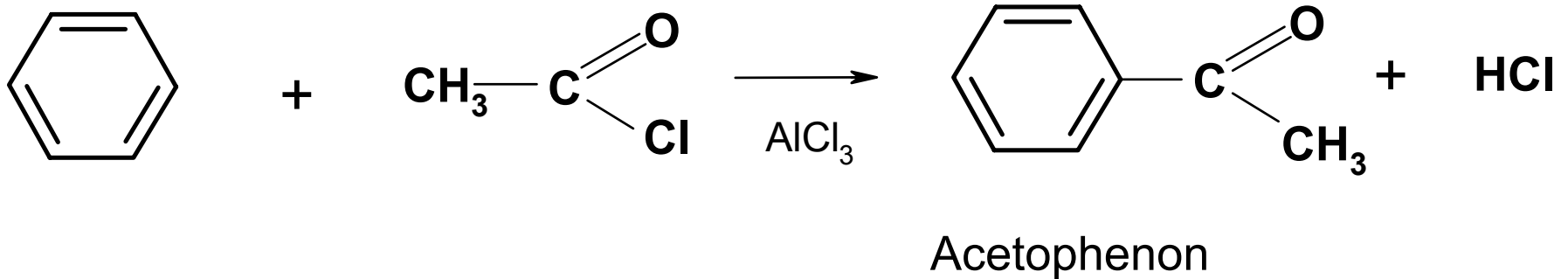


# Herstellung von Ketonen

## 1. Oxidation sekundärer Alkohole

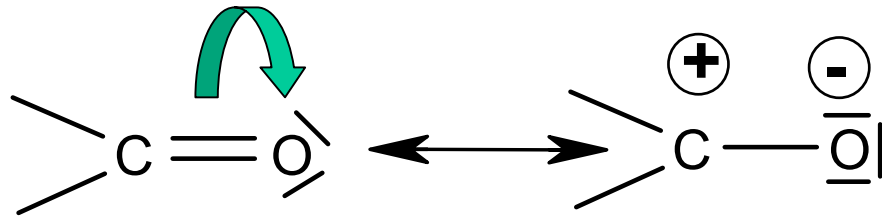


## 2. Friedel-Crafts Acylierung



# Reaktionen

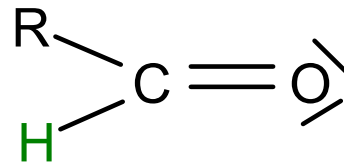
Eigenschaften der  
C=O Doppelbindung



Dipolmoment

Mesomerie

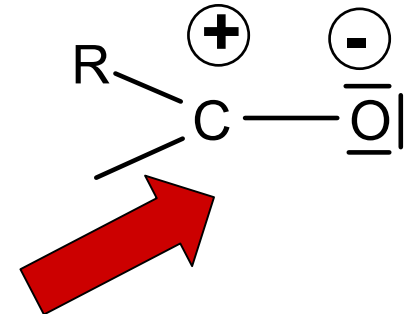
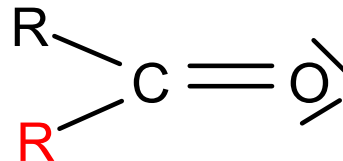
Reaktivität



Aldehyde

?

**Ketone**

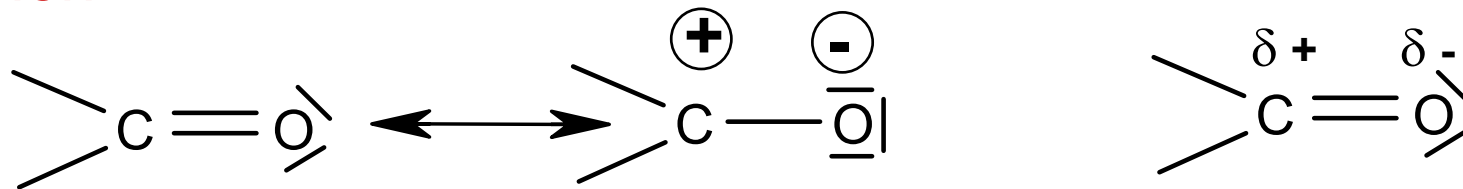


1. Durch den + I Effekt der zweiten Alkylgruppe wird die positive „Ladung“ am C-Atom der C=O Bindung reduziert
2. Die zweite Alkylgruppe blockiert räumlich die Reaktion am C-Atom



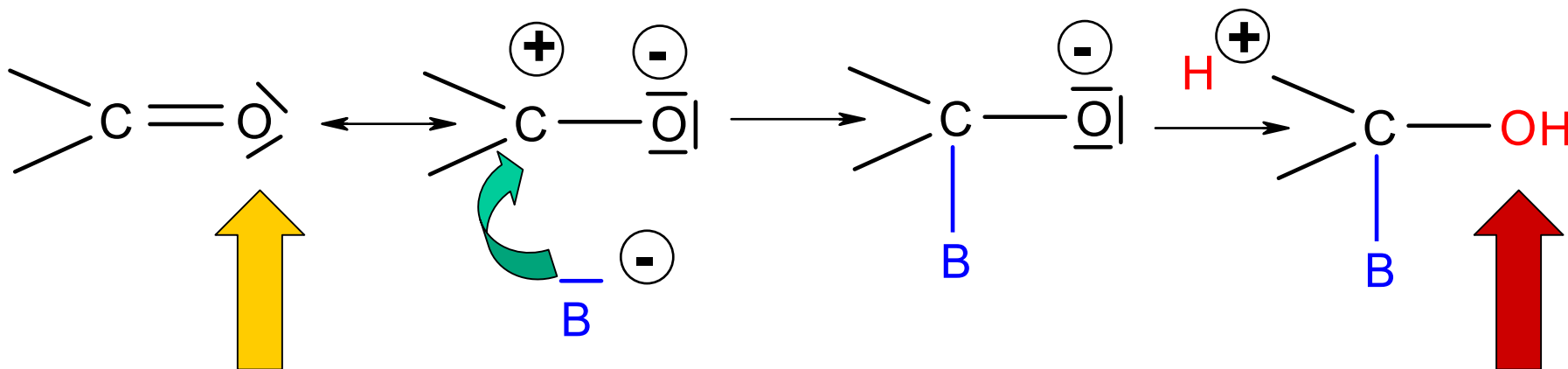
Aldehyde sind daher reaktiver als Ketone

# Reaktionen



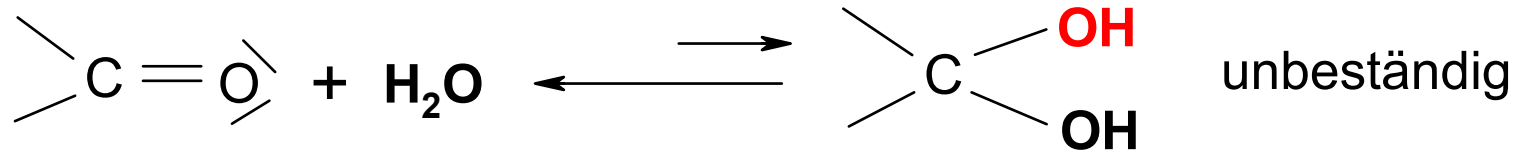
Allgemeine Reaktion:

1. Addition von Nukleophilen an die C=O Doppelbindung
- (2. Eliminierung von Wasser)

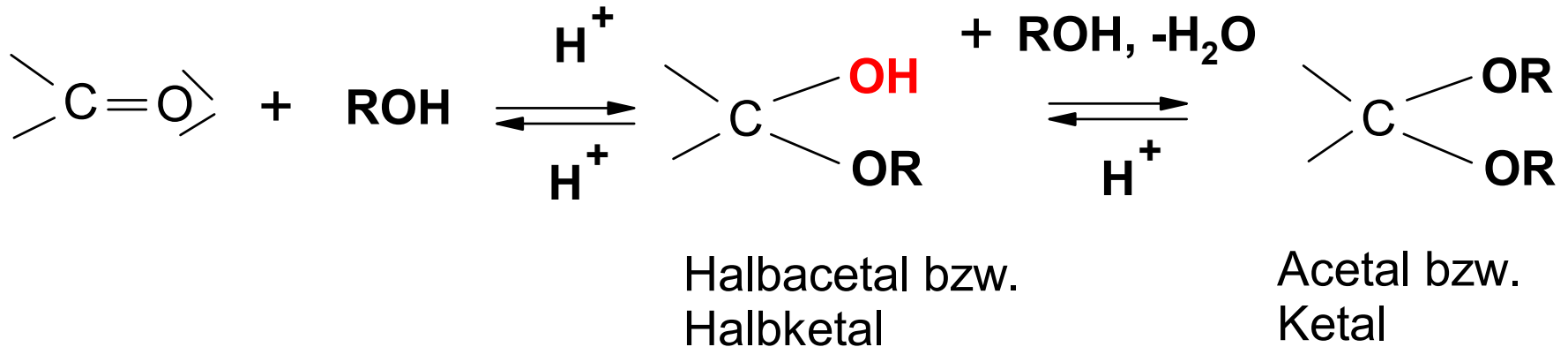


# Reaktionen

## 1. Hydratbildung

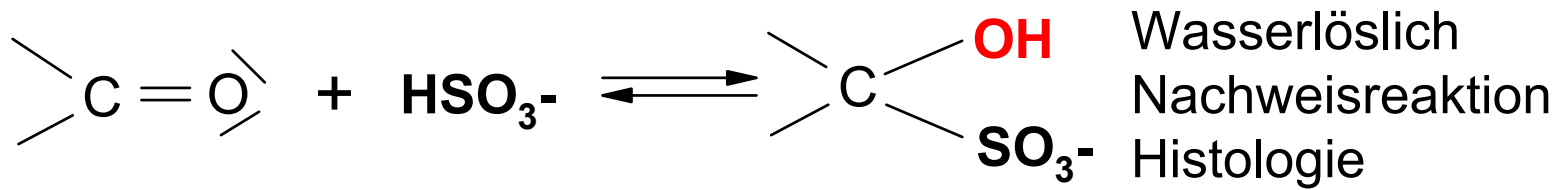


## 2. Addition von Alkoholen: Halbacetale und Acetale /Ketale



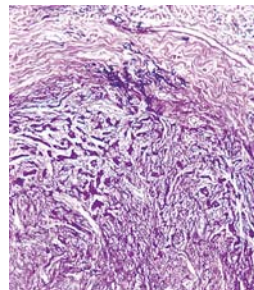
Basenstabil

## 3. Bisulfitaddition

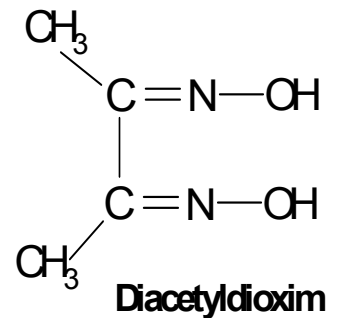
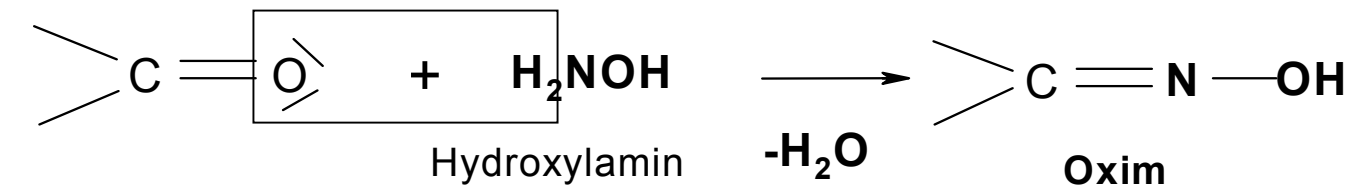
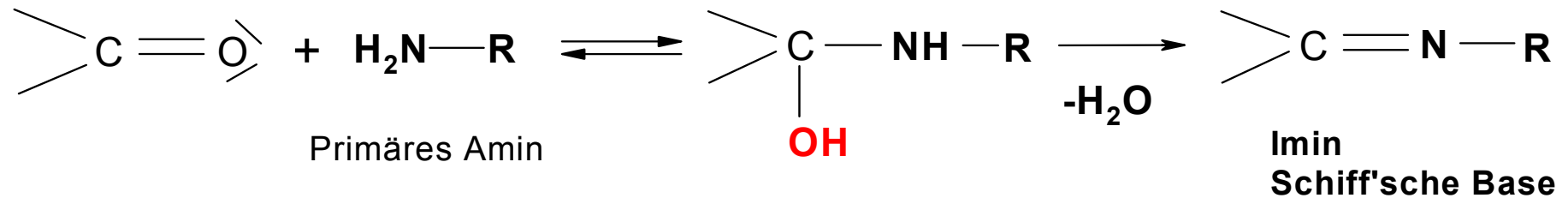


Fuchsin

Fuchsin-SO<sub>3</sub>H

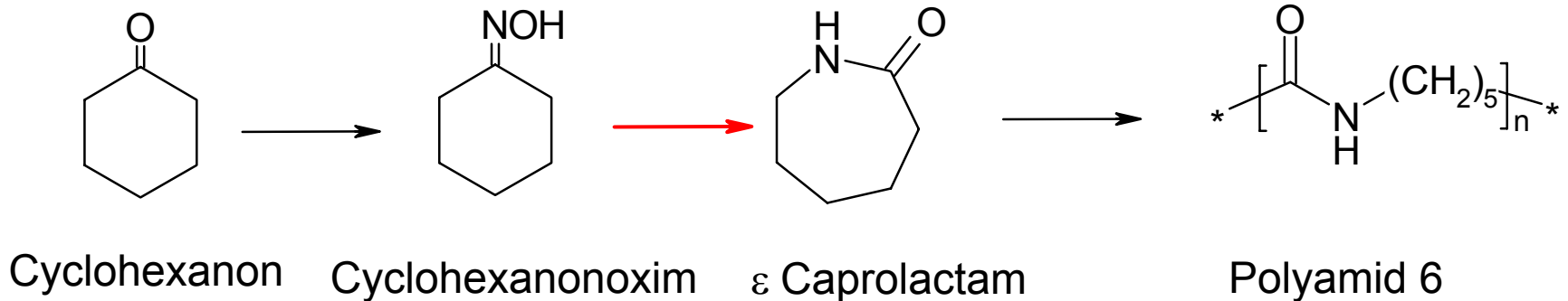


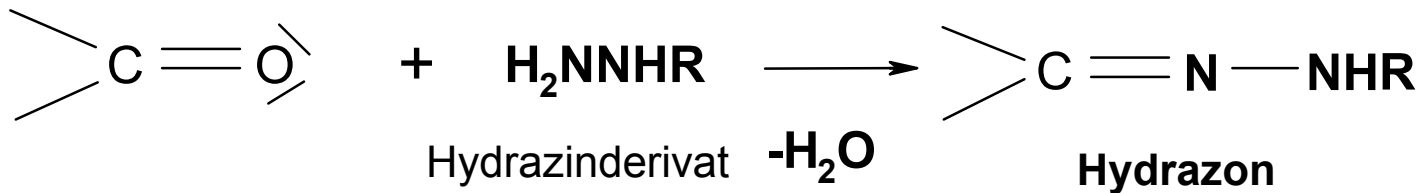
## 4. Addition von Aminogruppen



Synthese von Polyamiden – Beckmannumlagerung  
(Ketoxim - Carbonsäureamid)

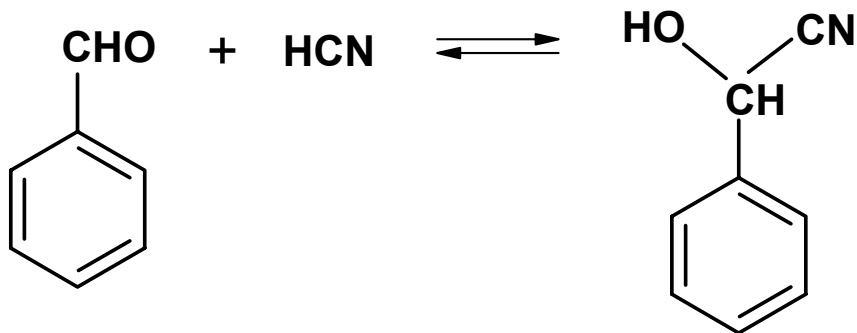
Ni<sup>2+</sup>-Nachweis





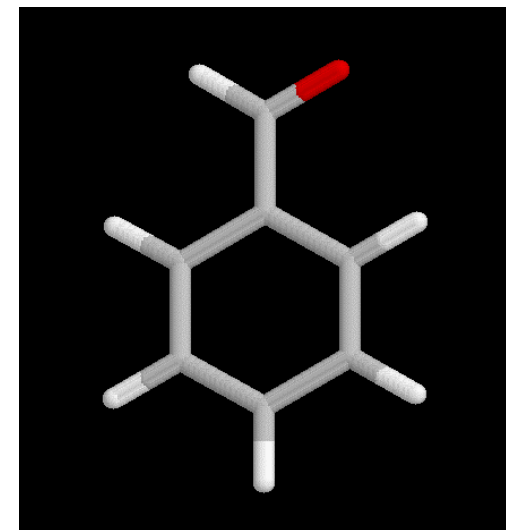
## 5. Reaktionen mit C-Nukleophilen

### 5.1. Cyanhydrinreaktion



Mandelsäurenitril  
Cyanhydrin des Benzaldehyds

Beispiel  
Cyanogene Glykoside - Amygdalin

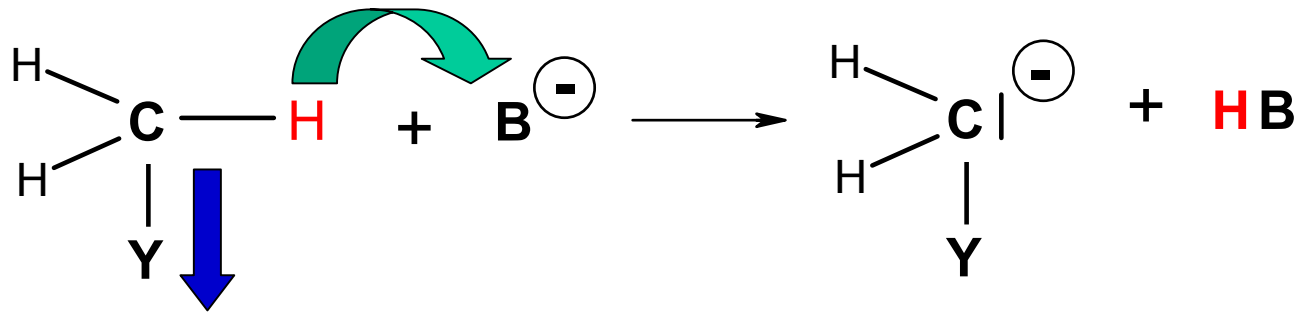




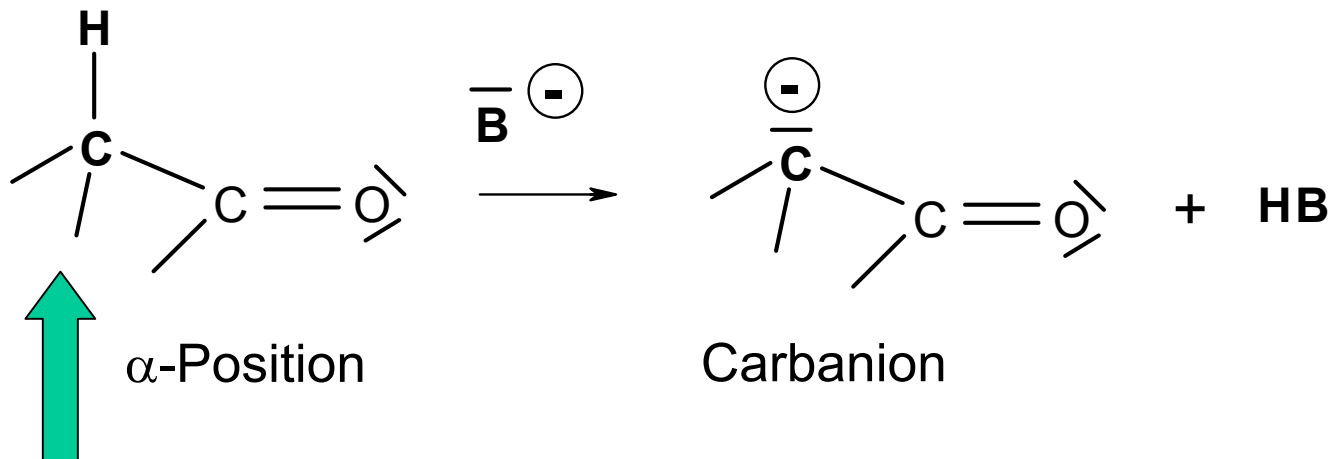
## 5.2. Aldoladdition (-kondensation)

Addition von Carbanionen

C-H **acide** Verbindungen

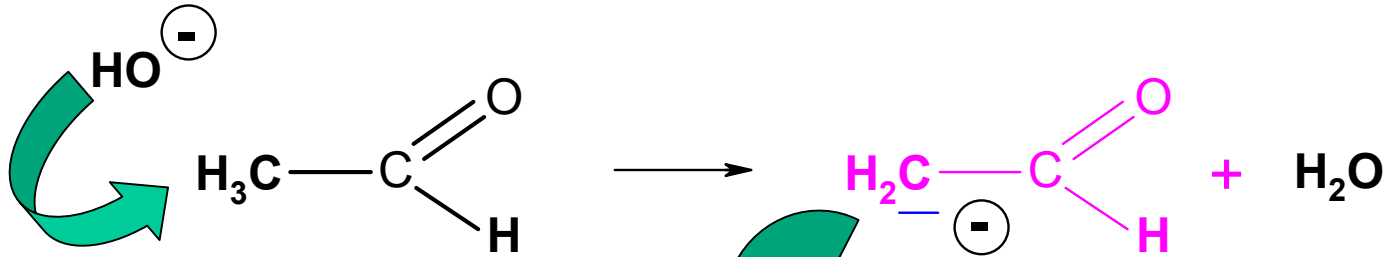


Y = elektronenabziehende Gruppen: -CN, -COOH, -COOR, -C=O, -SO<sub>2</sub>, -NO<sub>2</sub>

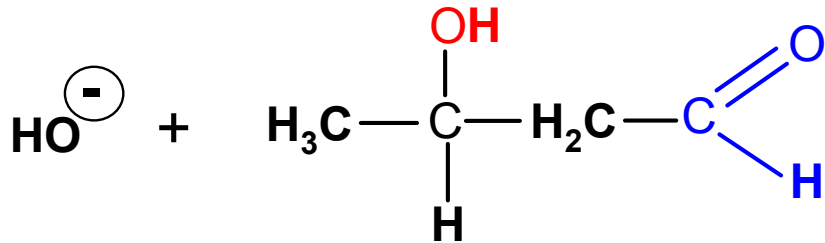
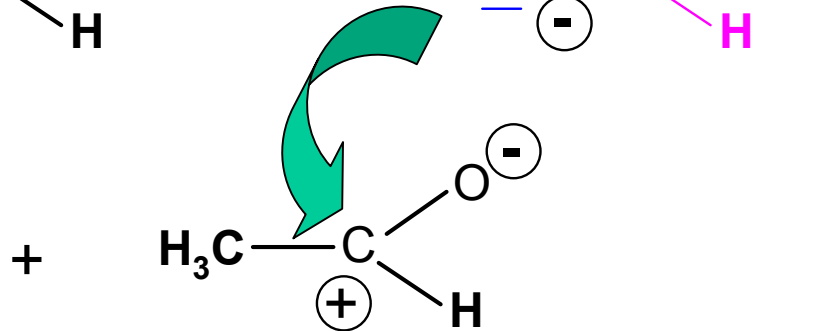


## 5.2. Aldoladdition von Acetaldehyd (Bildung von Acetaldol)

1. Schritt  
Bildung des Carbanions  
in  $\alpha$ -Stellung

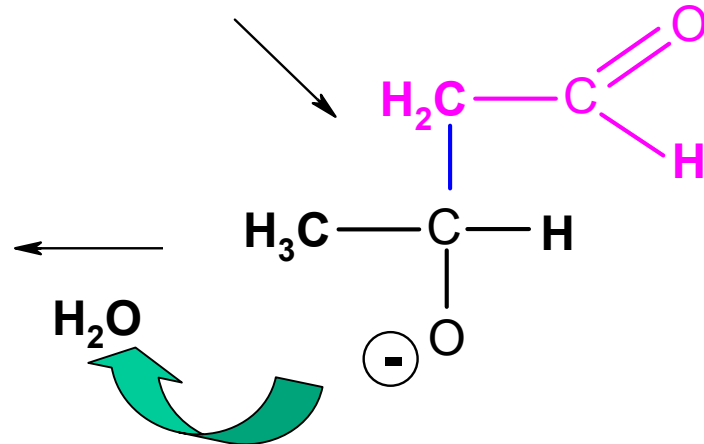


2. Schritt  
Anlagerung eines zweiten  
Moleküls Acetaldehyd



Acetaldol  
 $\beta$ -Hydroxybutyraldehyd

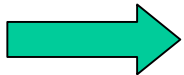
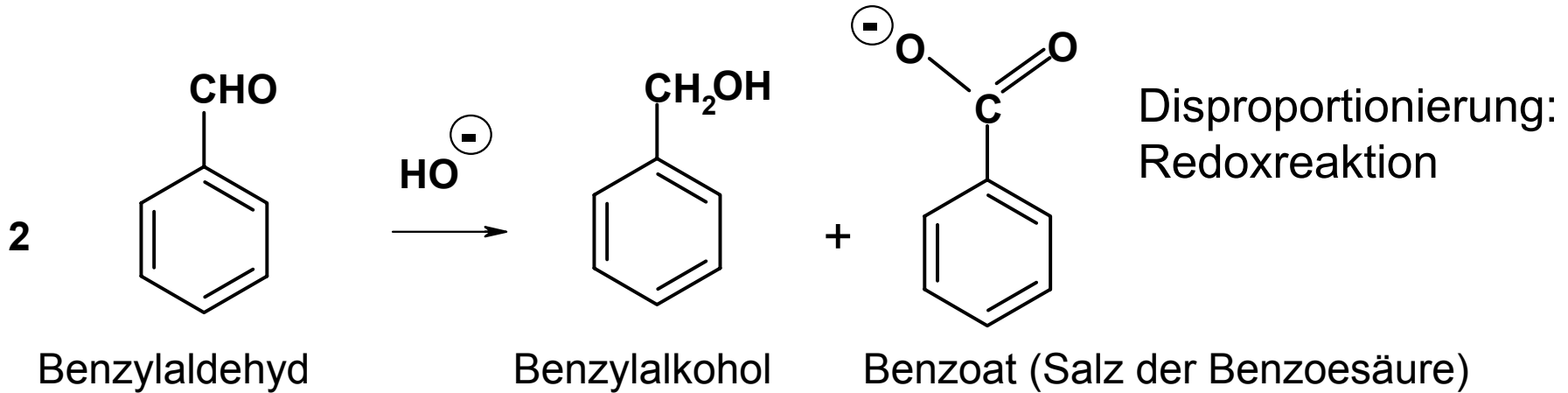
3. Schritt  
Protonierung der Alkoholatgruppe





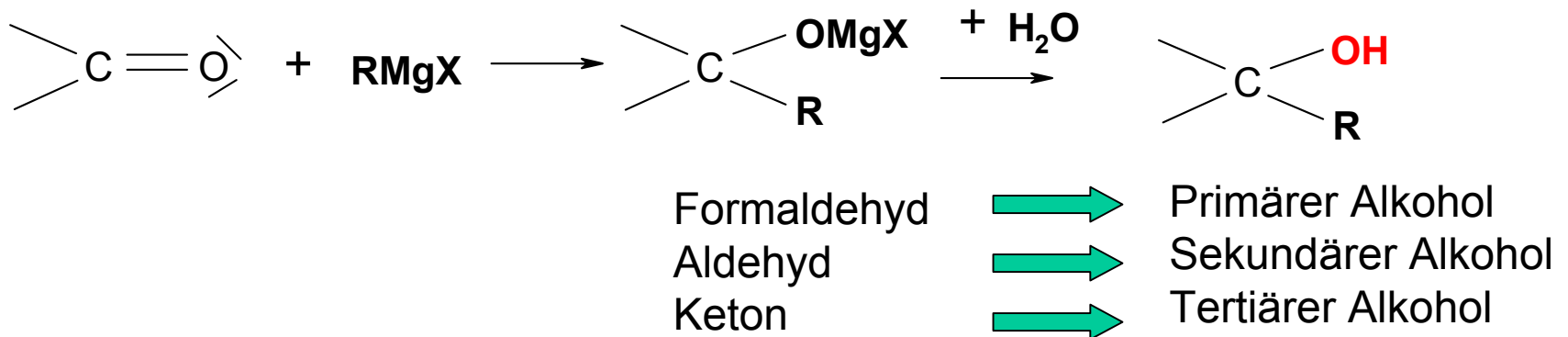
## Reaktionen

### 5.3. Cannizzaro-Reaktion

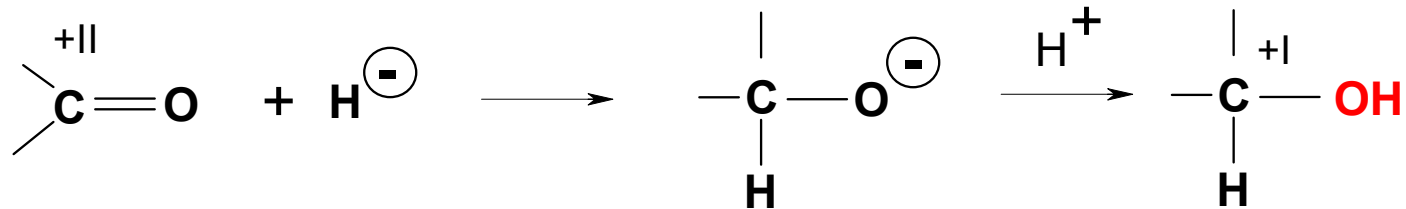


Aldehyde sind alkalilabil ! (Aldolreaktion, wenn  $\alpha$ -CH vorhanden, sowie Cannizzaro-Reaktion (Aromat. Aldehyde))

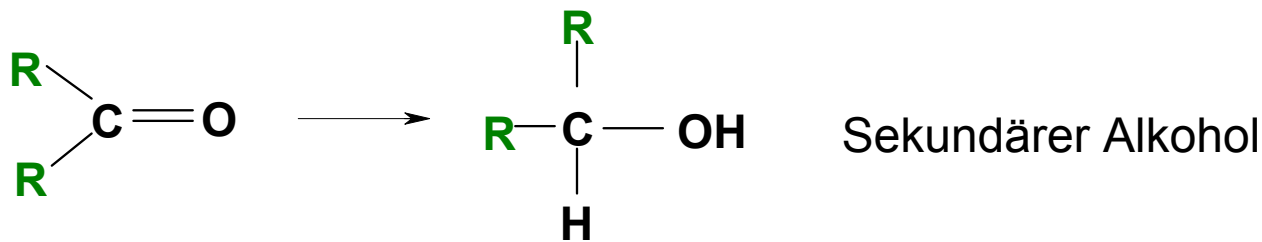
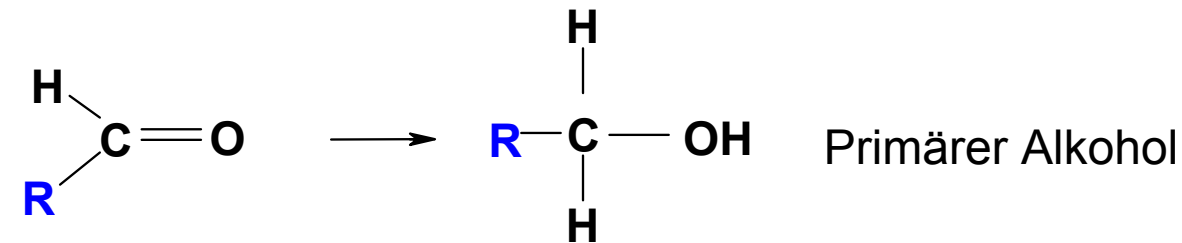
### 5.4. Addition von Grignardverbindungen



## 6. Reduktion von C=O Doppelbindungen

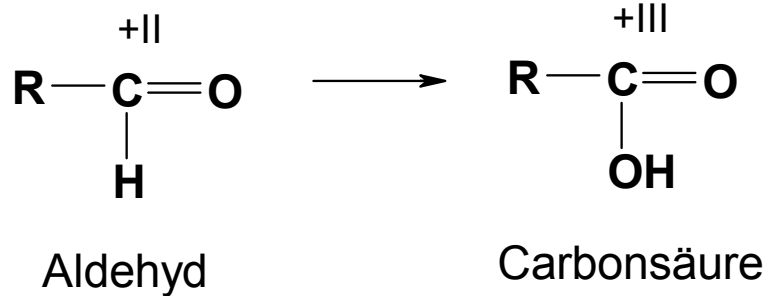


Addition von Hydrid-ionen ( $\text{LiAlH}_4$ ,  $\text{NaBH}_4$ ) oder katalytische Hydrierung mit  $\text{H}_2$



## 7. Oxidation (Dehydrierung)

Ox. Mittel:  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{O}_2/\text{Pt}$

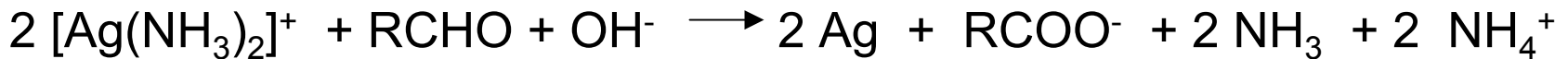


Autoxidation

Nachweis der reduzierenden Eigenschaften der Aldehydgruppe:

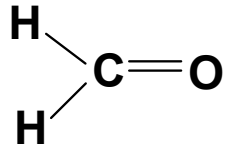
Reduktion von

$\text{Ag}^+$  (Tollens-Reagens) zu elementarem Ag (Silberspiegelprobe):

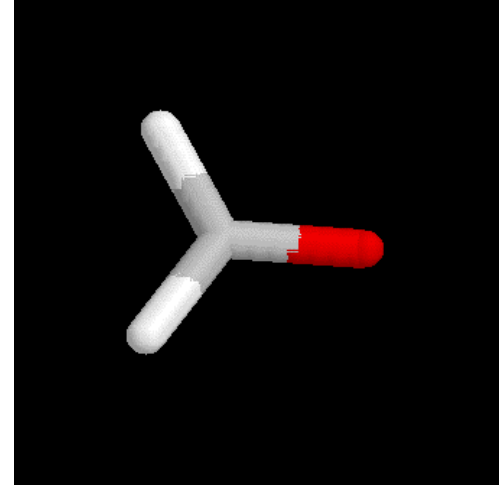


$\text{Cu}^{2+}$  (Fehling-Reagens) zu  $\text{Cu}_2\text{O}$

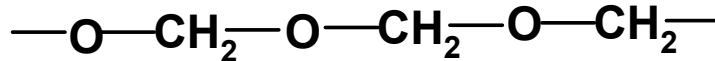
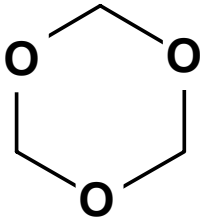
Formaldehyd  
(Methanal)



Reaktivster Aldehyd



Farbloses, stechend riechendes giftiges Gas, mutagen  
polymerisiert leicht zu cyclischen  
und höhermolekularen Produkten:

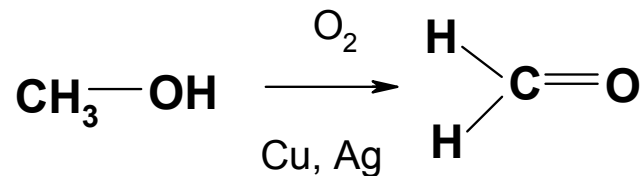


Trioxan

Polyoxymethylen (POM), Paraformaldehyd, 8-100 Monomere

Wässrige Lösung: Formalin (ca. 40%)

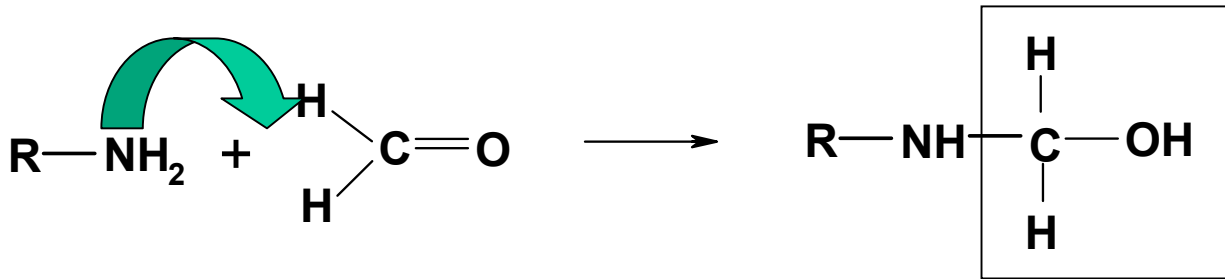
## Herstellung



# Reaktionen mit Aminogruppen

# Reaktionen

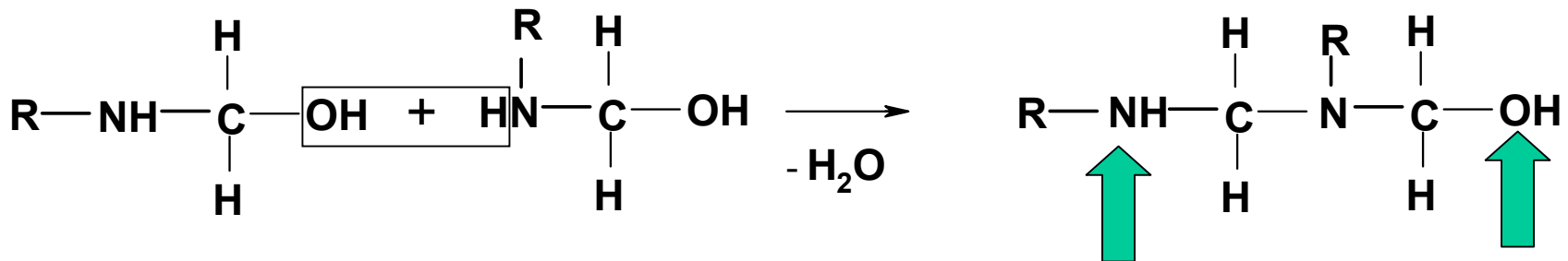
Härtung und Konservierung von Eiweiss (Präparate)



Addition an die C=O Doppelbindung  $\longrightarrow$  Hydroxymethylierung

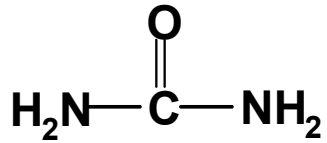
Weiterreaktion unter Wasserabspaltung (Polykondensation):

**Aminoplaste**

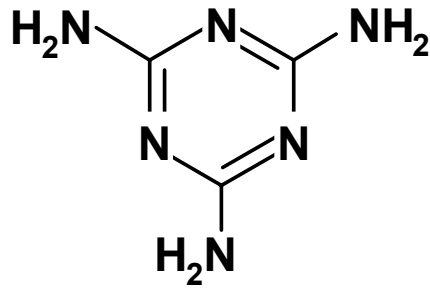




Aminoplaste



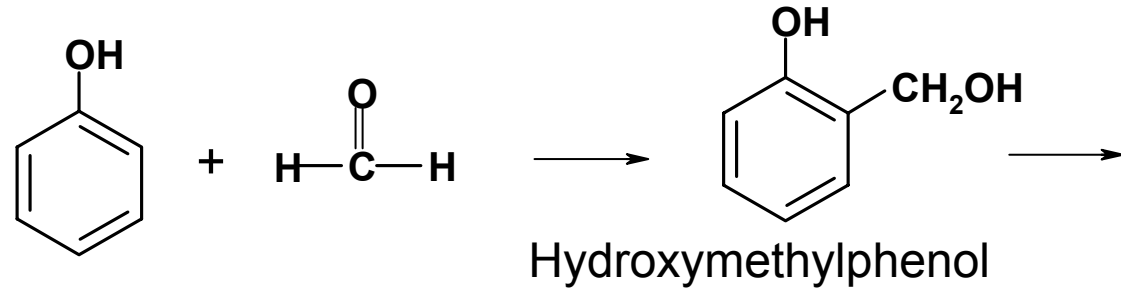
Harnstoff



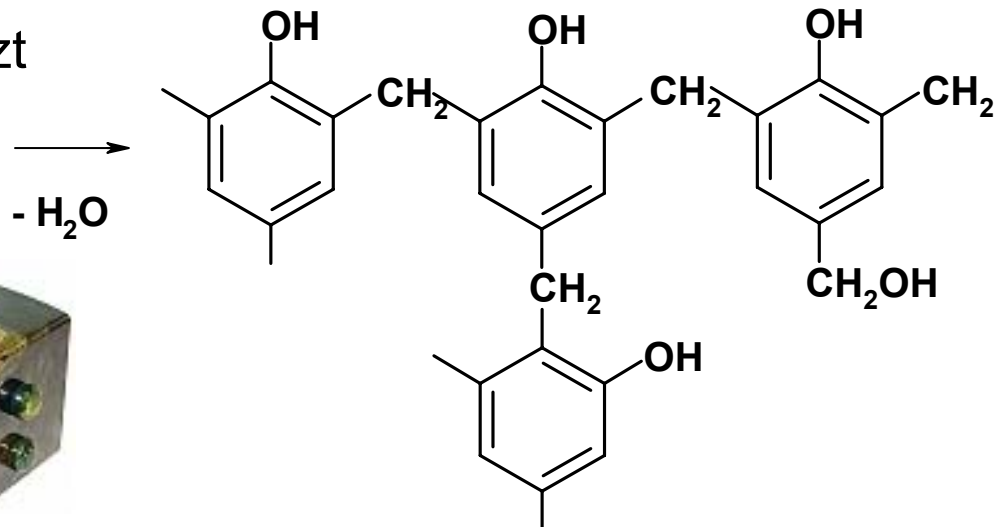
Melamin

Reaktionen

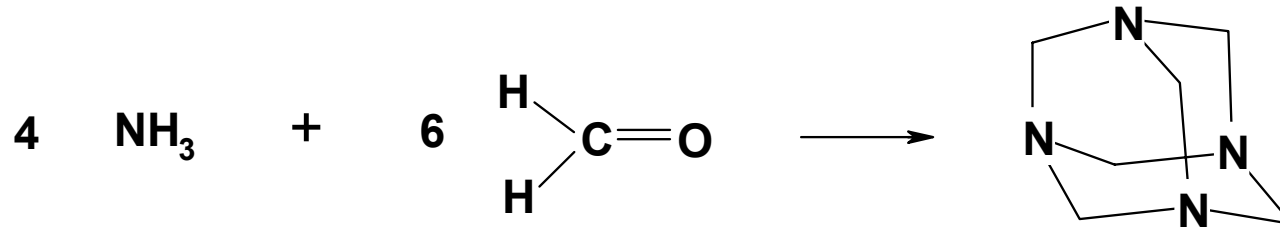
**Phenoplaste** –  
Phenol-Formaldehydharze  
Hart, spröde  
„Duroplaste“  
dreidimensional stark vernetzt



Aushärtung

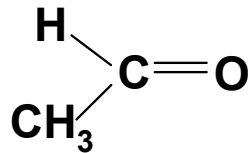


## Reaktion mit Ammoniak Urotropinreaktion

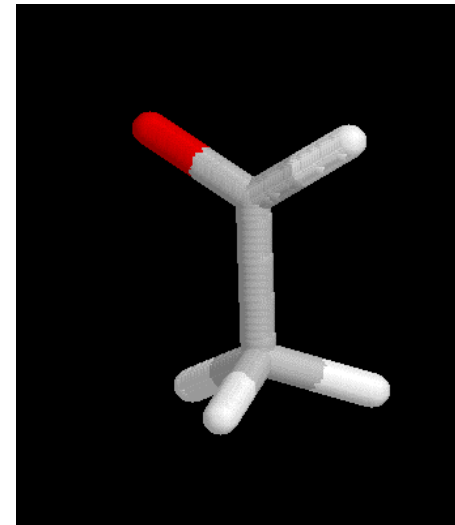


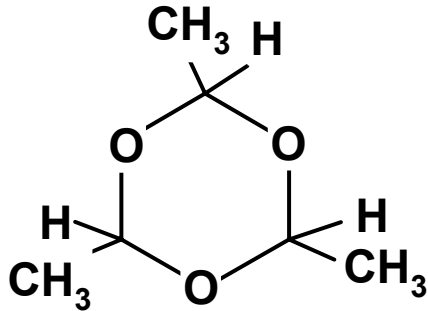
Hexamethylenetetramin  
(Urotropin)

**Acetaldehyd**  
(Ethanal)

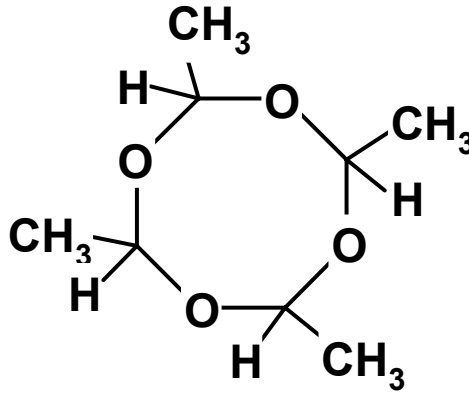


Farblose Flüssigkeit  
Kp.: 21°



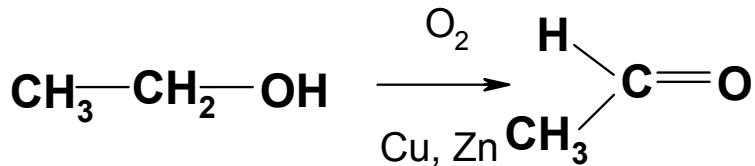
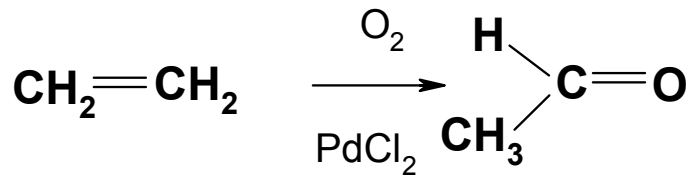


Paraldehyd



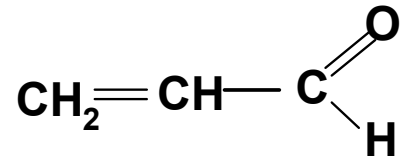
Metaldehyd

## Herstellung



Zwischenprodukt der alkoholischen Gärung

**Acrolein**

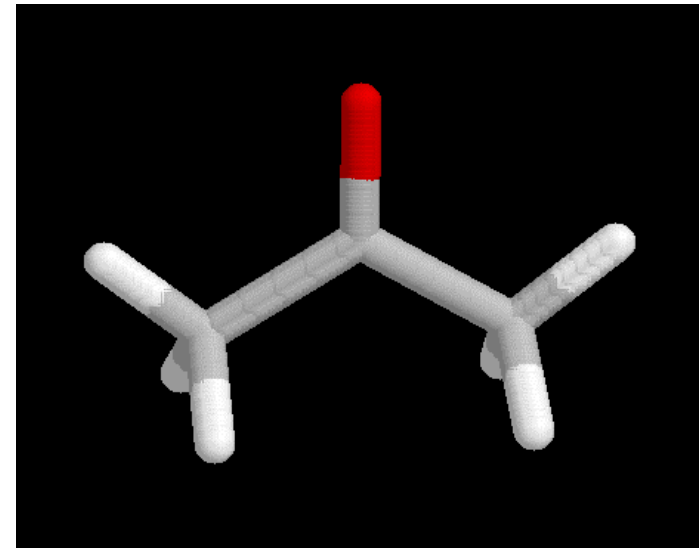
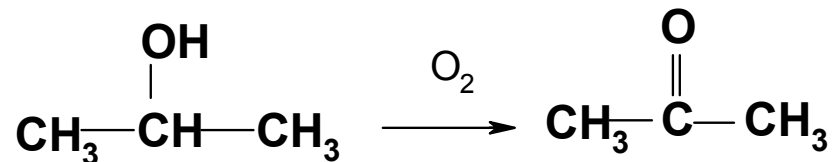


Tränenreizende Flüssigkeit

**Aceton**

**Propanon**

Herstellung



1. Oxidation von 2-Propanol
2. Nebenprodukt der Phenolsynthese (Cumolverfahren)

Stoffwechselprodukt bei Diabetes mellitus: „Acetonkörper“