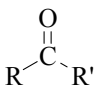
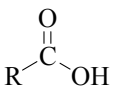
Kapitel 9 Carbonylverbindungen (Carbonsäuren, Aldehyde)

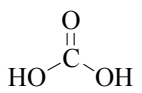
Aldehyde



Ketone



Carbonsäuren

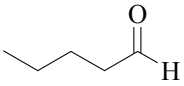


Kohlensäuren

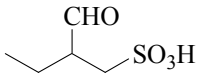
Nomenklatur

Aldehyde: NAME = KW-Stamm + „al“
-CHO als Substituent: Formyl-

Beispiel:



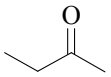
Pentanal



2-Formyl-butansulfonsäure

Ketone: NAME = KW-Stamm 1 + „yl“ + KW-Stamm 2 + „yl“ + „keton“
NAME = KW-Stamm + Pos + „on“
=O als Substituent: Oxo

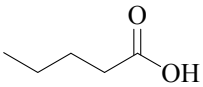
Beispiel:



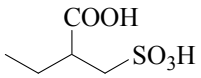
Ethylmethylketon
2-Butanon
2-Oxobutan

Carbonsäuren: NAME = KW-Stamm + „säure“
-COOH als Substituent: Hydroxycarbonyl

Beispiel:

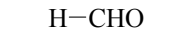


(Pentanansäure)
Valeriansäure

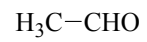


2-Hydroxycarbonyl
-butansulfonsäure

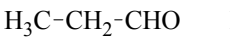
Wichtige Aldehyde



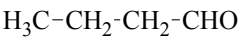
Formaldehyd



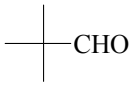
Acetaldehyd



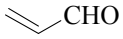
Propionaldehyd



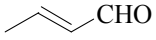
Butyraldehyd



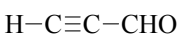
Pivalaldehyd



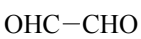
Acrolein



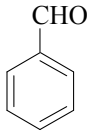
Crotonaldehyd



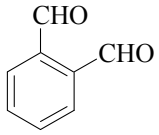
Propiolaldehyd



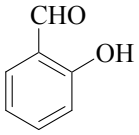
Glyoxal



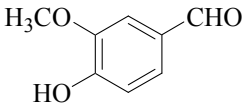
Benzaldehyd



Phthalaldehyd



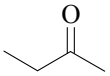
Salicylaldehyd



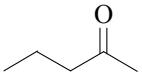
Vanilin

Wichtige Ketone

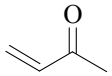
Aceton
(Dimethylketon)



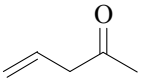
Butanon
(Ethylmethylketon)



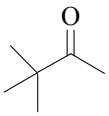
2-Pentanon
(Methylpropylketon)



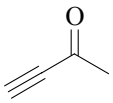
3-Buten-2-on
(Methylvinylketon)



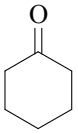
4-Penten-2-on
(Allylmethylketon)



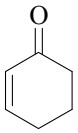
tert-Butylmethylketon
(3,3-Dimethylbutan-2-on)



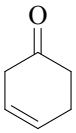
Ethinylmethylketon
(3-Pentin-2-on)



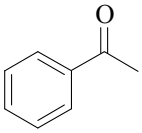
Cyclohexanon



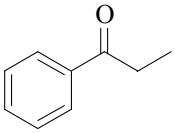
2-Cyclohexenon



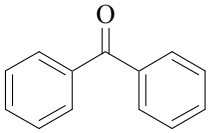
3-Cyclohexenon



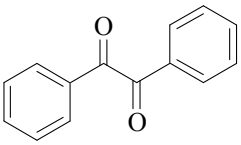
Acetophenon



Propiophenon



Benzophenon



Benzil

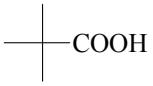
Wichtige Carbonsäuren (Namen der Salze)

H−COOH
Ameisensäure
(Methansäure)
Formiate

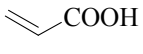
$H_3C-COOH$
Essigsäure
(Ethansäure)
Acetate

H_3C-CH_2-COOH
Propionsäure
(Propansäure)
Propionate

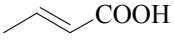
$H_3C-CH_2-CH_2-COOH$
Buttersäure
(Butansäure)
Butyrate



Pivalalinsäure
Pivalinate



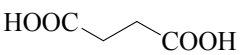
Acrylsäure
Acrylate



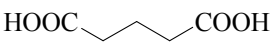
Crotonsäure
Crotonate

H−C≡C−COOH
Propiolsäure
Propiolate

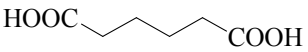
HOOC−COOH
Oxalsäure
Oxalate



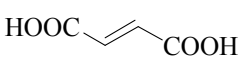
Bernsteinsäure
Succinate



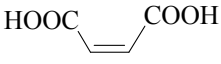
Glutarsäure
Glutarate



Adipinsäure
Adipate

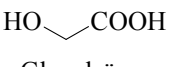


Fumarsäure
Fumarate

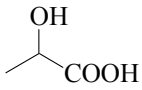


Maleinsäure
Maleinate

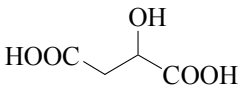
Acetylendicarbonsäure



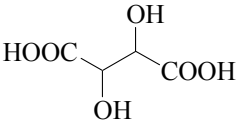
Glycolsäure
Glycolate



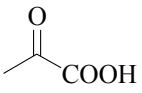
Milchsäure
Lactate



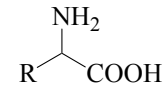
Äpfelsäure
Malate



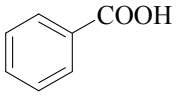
Weinsäure
Tartrate



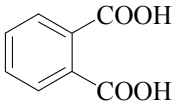
Brenztraubensäure
Pyruvate



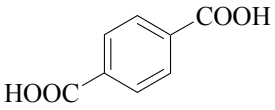
Aminosäuren



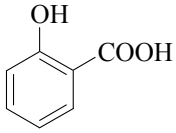
Benzoesäure
Benzoate



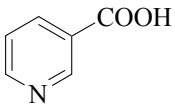
Phthalsäure
Phthalate



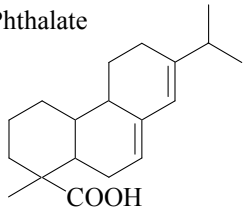
Terephthalsäure
Terephthalate



Salicylsäure
Salicylate

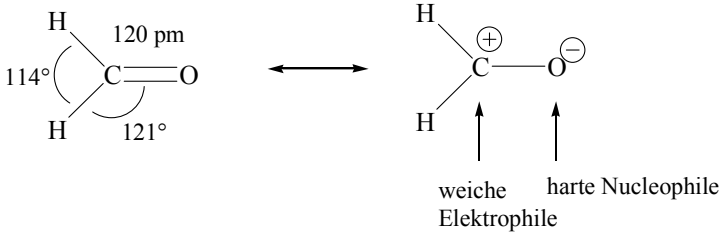


Nicotinsäure



Abietinsäure
(Harzsäure)

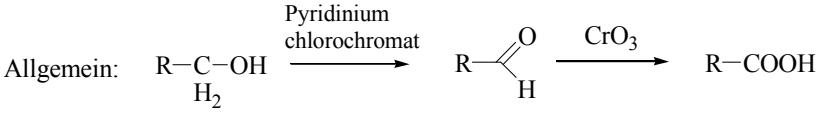
Struktur

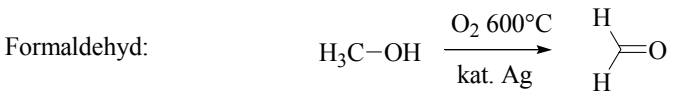


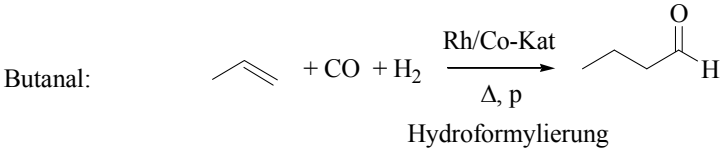
Allg. Eigenschaften

Höhere Siedepunkte als KW:	H-CHO	-21°C
	Me-CHO	+21°C
	Aceton	+56°C
	H-COOH	100°C

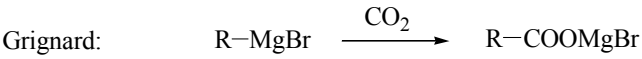
Darstellung

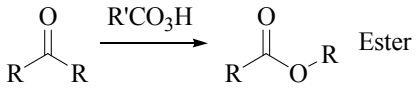




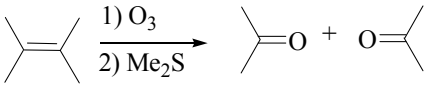


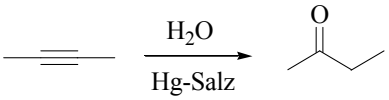
Hydroformylierung

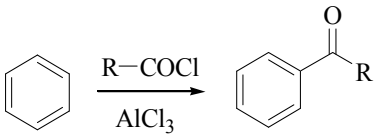
Grignard: 

Bayer-Villiger-Ox.: 

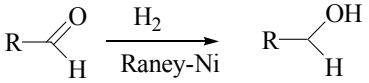
Ester

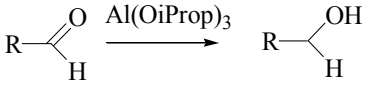
Ozonolyse: 

Hydratisierung: 

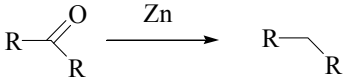
Friedel-Crafts-Acyl.: 

Reaktionen

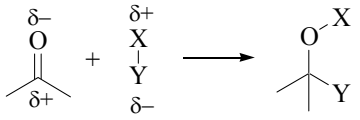
Hydrierung: 



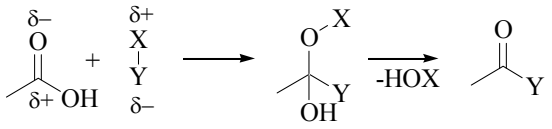
Meerwein-Pondorf-Verley-Reduktion



Clemensen-Reduktion

Ionische Additionen: 

Reagenz		Typ/Name	Produkt
X-Y:	B-H ($NaBH_4$)	Reduktion	Alkohole
	H-OH	Hydratisierung	Hydrate
	BrMg-R	Grignard-Rkt.	Alkohole
	H-OR	Addition/Konden.	Acetale
	H-CN	Addition	Canhydrine
	H-NHR	Kondensation	Imine
	H-NHOH	Kondensation	Oxime
	H-N_2H_3	Kondensation	Hydrazone

Ionische Additionen: 

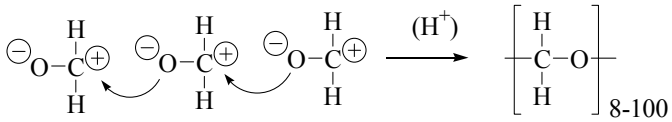
Reagenz		Typ/Name	Produkt
X-Y:	B-H ($LiAlH_4$)	Reduktion	Alkohole
	H-OR (H^+)	Veresterung	Ester
	H-NHR	Kondensation	Amide
	H-Cl ($SOCl_2$)	Add./Elimin.	Säurechloride
	H-OOCR	Kondensation	Anhydride

Nachweisreaktionen:

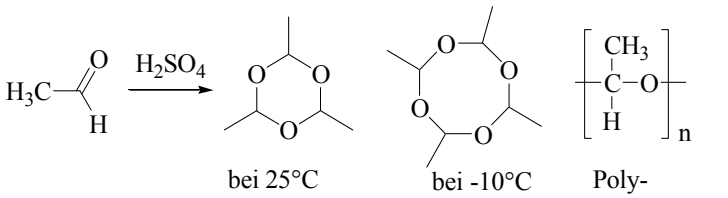
Fehling-Probe: $R\text{-}CHO + 2\ Cu^{2+} + 5\ OH^- \rightarrow Cu_2O\downarrow + RCOO^- + 3\ H_2O$

Tollens-Probe: $R\text{-}CHO + 2\ [Ag(NH_3)_2]^+ + 2\ OH^- \rightarrow RCOOH + 2\ Ag\downarrow + 4\ NH_3 + H_2O$

Oligomerisierung / Polymerisierung:



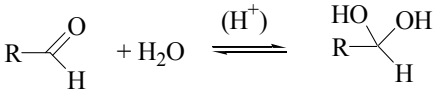
Formaldehyd — Paraformaldehyd



bei 25°C Paraldehyd — bei -10°C Metaldehyd — Poly-methaldehyd

Carbonylaktivität / Hydratbildung

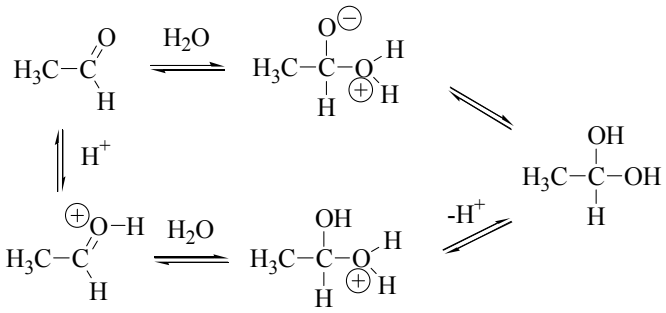
Je weniger gut das Carbeniumion in der zwitterionischen mesomeren Grenzstruktur stabilisiert ist, desto höher ist die Carbonylaktivität!



Aldehydhydrat

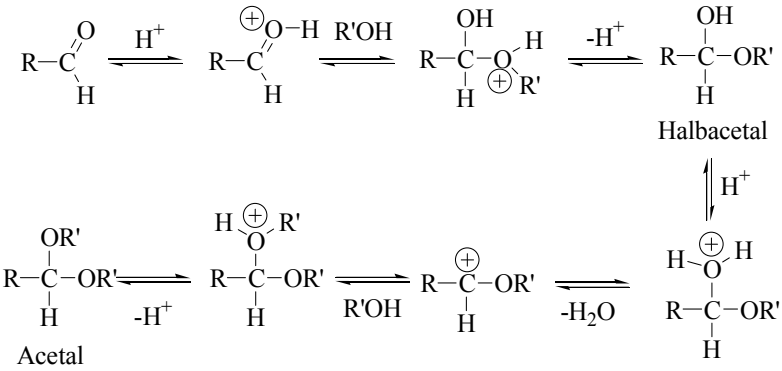
R=H	hohe Carbonylaktivität	98% Hydrat
$R=CH_3$	mittlere Carbonylaktivität	58% Hydrat
R=Ph	niedrige Carbonylaktivität	<1% Hydrat
$R=CCl_3$	sehr hohe Carbonylakt.	100% Chloralhydrat (stabil)

Erlenmeyer-Regel: keine 2 OH-Gruppen gleichzeitig an einem C



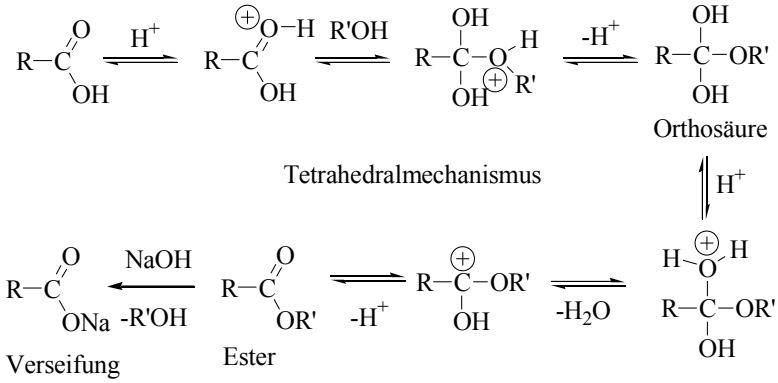
allg. Säurekatalyse / Tetrahedralmechanismus

Halbacetal-/Acetalbildung



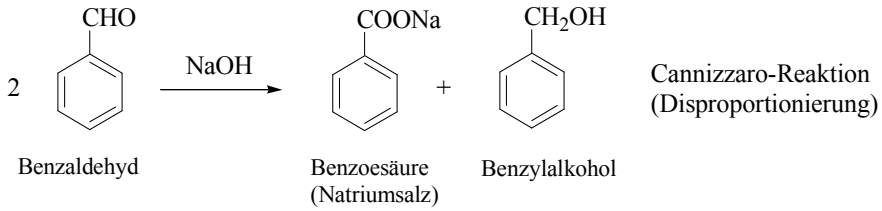
Merke! Acetale sind im Basischen stabil
Acetale spalten im Sauren (saure Hydrolyse)
Acetale sind Schutzgruppen für Carbonyle

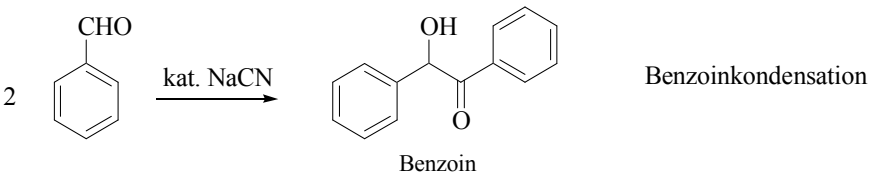
Esterbildung / Verseifung



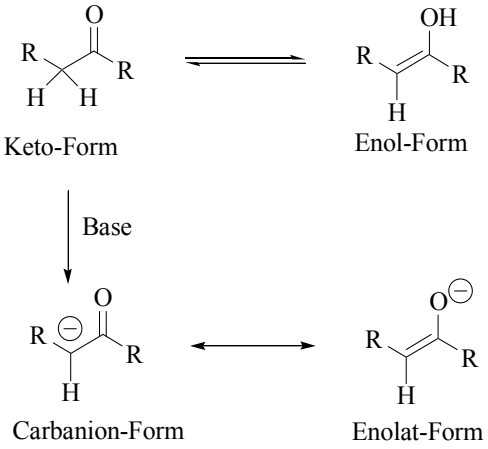
Merke! Ester bilden sich unter Säurekatalyse
Ester hydrolysieren im Sauren
Ester spalten im Alkalischen (Verseifung)

Spezielle Reaktionen

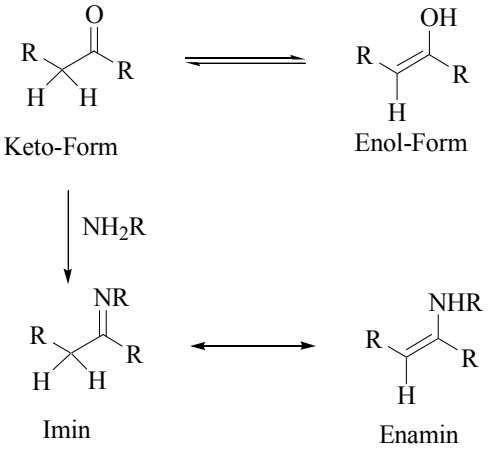




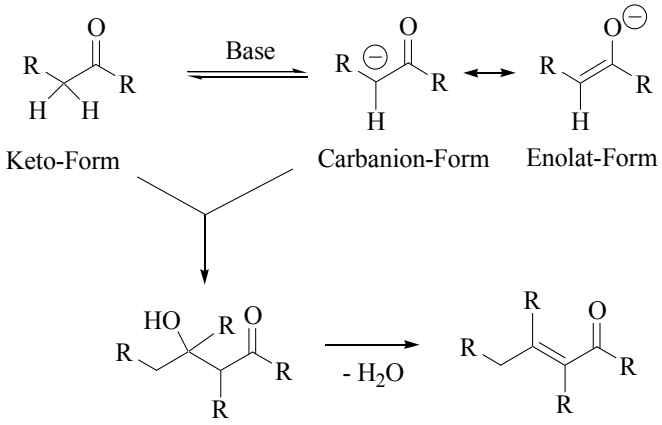
Keto-Enol-Tautomerie: α-CH-Gruppe in Carbonylen ist sauer (pK_S = 11-25)



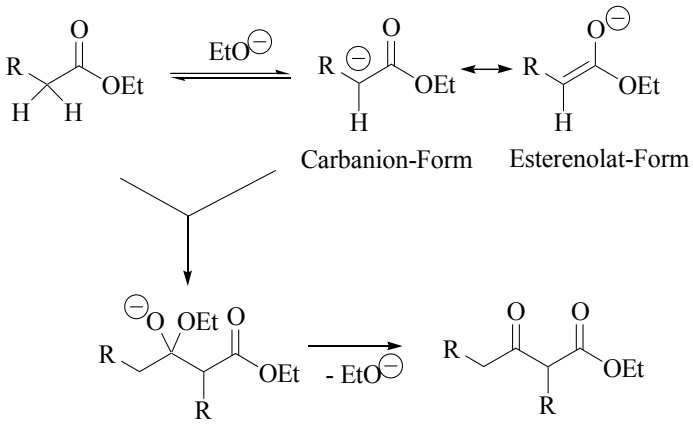
Enaminbildung:



Aldol-Reaktion, -Kondensation



Claisen-Kondensation



Mannich-Reaktion (Aminomethylierung)