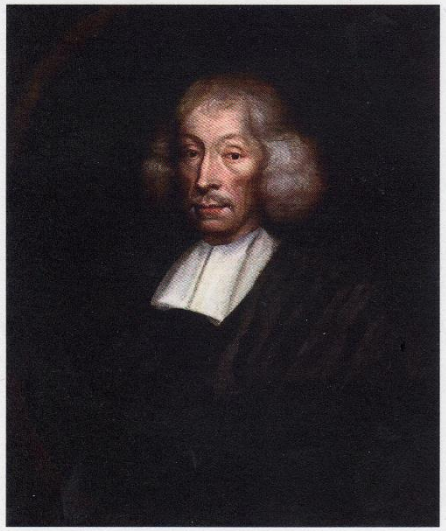


John Ray (1627-1705)
1671 Entdeckung der Ameisensäure

Johann Wiegelb (1732-1800)
1769 Entdeckung der Oxalsäure

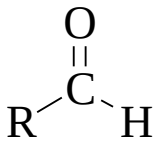
Jöns Jakob Berzelius (1779-1849)
1814 Aufklärung der Essigsäure

Alexander Butlerow (1828-1886)
1855 Entdeckung des Formaldehyds

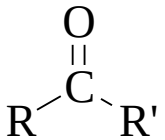
Carl Wilhelm Scheele (1742-1786)
1781 Entdeckung des Acetaldehyds

Andreas Labavius (1555-1616)
1606 Darstellung von Aceton

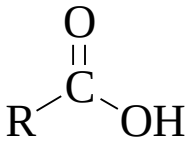
Carbonylverbindungen (Carbonsäuren, Aldehyde, Ketone)



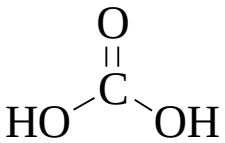
Aldehyde



Ketone



Carbonsäuren

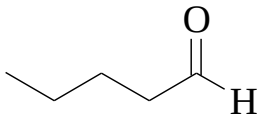


Kohlensäuren

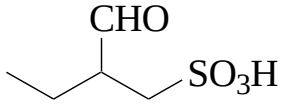
Nomenklatur

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

Beispiel:



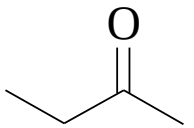
Pentanal



2-Formyl-butansulfonsäure

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

Beispiel:

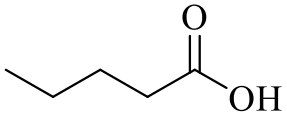


Ethylmethylketon
2-Butanon
2-Oxobutan

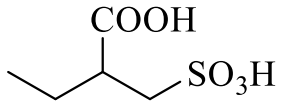
Nomenklatur

Säuren: NAME = KW-Stamm + „säure“
NAME = KW-Stamm -1 + „carbonsäure“
-COOH als Substituent: carboxy-

Beispiel:

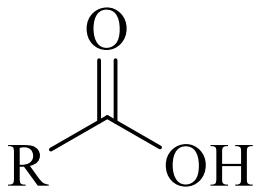


Pentansäure
Butancarbonsäure
Valeriansäure

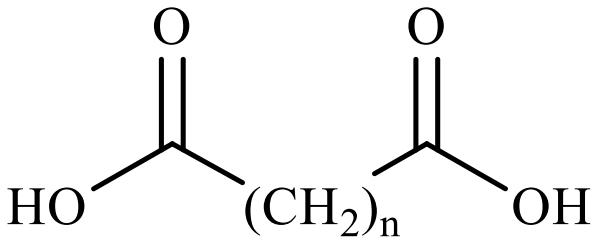


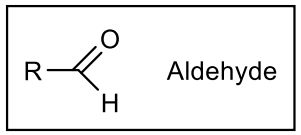
2-Carboxy-butansulfonsäure

Trivialname	sys. Name	C-Atome	Summenformel	mp °C	bp °C	pK_a
Ameisensäure	Methansäure	1	CH_2O_2	8,3	101	3,75
Essigsäure	Ethansäure	2	$C_2H_4O_2$	16,64	117,9	4,756
Propionsäure	Propansäure	3	$C_3H_6O_2$	−20,5	141,15	4,87
Buttersäure	Butansäure	4	$C_4H_8O_2$	−5,1	163,75	4,83
Valeriansäure	Pentansäure	5	$C_5H_{10}O_2$	−33,6	186,1	4,83
Capronsäure	Hexansäure	6	$C_6H_{12}O_2$	−4	205,2	4,85
Önanthsäure	Heptansäure	7	$C_7H_{14}O_2$	−7,2–7,5	222,2	4,89
Caprylsäure	Octansäure	8	$C_8H_{16}O_2$	16,5	239	4,89
Pelargonsäure	Nonansäure	9	$C_9H_{18}O_2$	12,4	254,5	4,96
Caprinsäure	Decansäure	10	$C_{10}H_{20}O_2$	31,4	268,7	

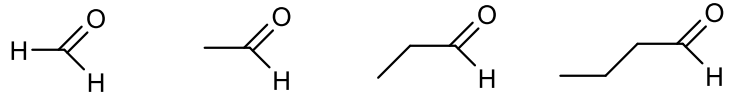


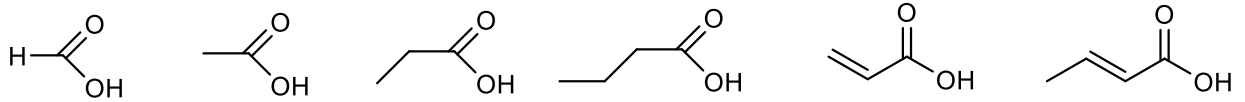
gesättigte Dicarbonsäuren					
Ketten-länge	Trivialname	Chemische Bezeichnung	Bruttoformel	Vorkommen	mp °C
2	Oxalsäure	Ethandisäure	HOOC–COOH	Rhabarber, Knöterichgewächse	189,5
3	Malonsäure	Propandisäure	HOOC–CH_2–COOH	Zuckerrübensaft	135,6
4	Bernsteinsäure	Butandisäure	HOOC–C_2H_4–COOH		185–187
5	Glutarsäure	Pentandisäure	HOOC–C_3H_6–COOH	Saft unreifer Zuckerrüben	97–98
6	Adipinsäure	Hexandisäure	HOOC–C_4H_8–COOH	Zuckerrübe, Rote Beete	153
7	Pimelinsäure	Heptandisäure	HOOC–C_5H_{10}–COOH		105
8	Korksäure, Suberinsäure	Octandisäure	HOOC–C_6H_{12}–COOH		142
9	Azelainsäure	Nonandisäure	HOOC–C_7H_{14}–COOH		106,5
10	Sebacinsäure	Decandisäure	HOOC–C_8H_{16}–COOH	Wunderbaum (Rizinusöl)	134,5
11		Undecandisäure	HOOC–C_9H_{18}–COOH		
12		Dodecandisäure	HOOC–$C_{10}H_{20}$–COOH		126,5–127
13	Brassylsäure	Tridecandisäure	HOOC–$C_{11}H_{22}$–COOH		112–113
14		Tetradecandisäure	HOOC–$C_{12}H_{24}$–COOH		125,8
16	Thapsiasäure	Hexadecandisäure	HOOC–$C_{14}H_{28}$–COOH		124–124,2

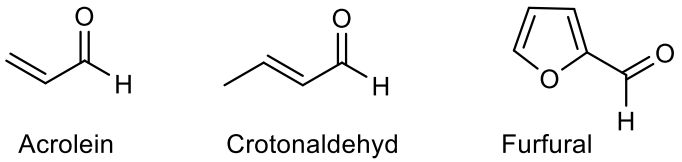


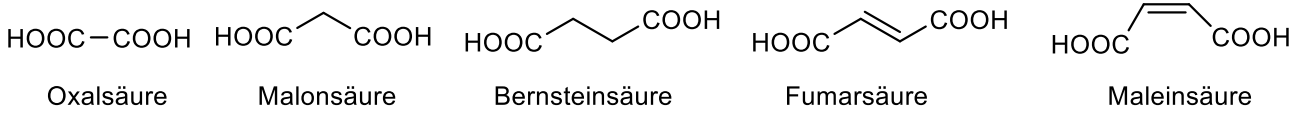

R
O
H
Aldehyde

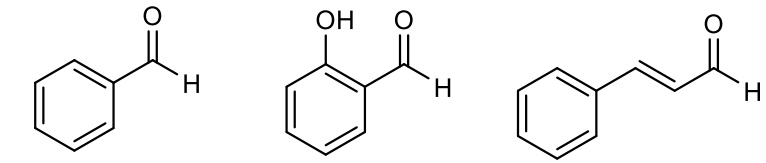

R
O
OH
Carbonsäuren
R
O
OR'
Ester
R
O
NH2
Amide
R–C≡N
Nitrile

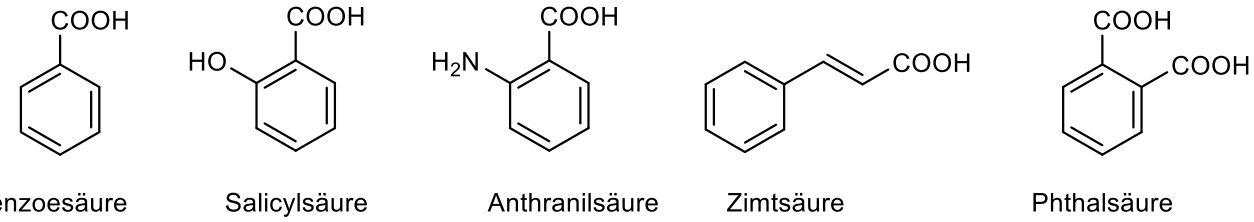

Formaldehyd
Acetaldehyd
Propionaldehyd
Butyraldehyd

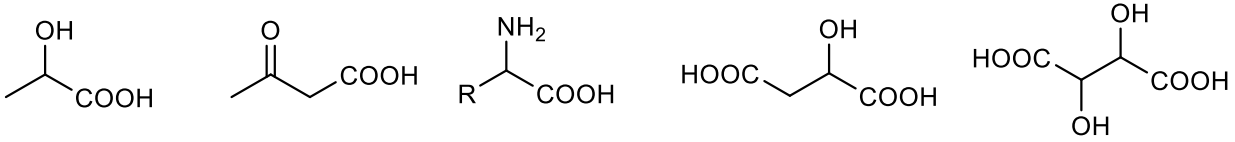

Ameisensäure
Essigsäure
Propionsäure
Buttersäure
Acrylsäure
Crotonsäure

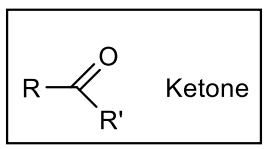

Acrolein
Crotonaldehyd
Furfural

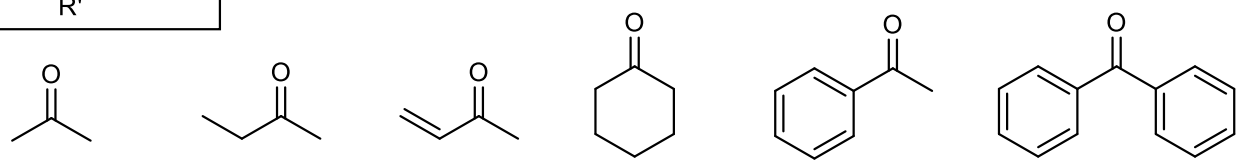

HOOC–COOH
Oxalsäure
HOOC
COOH
Malonsäure
HOOC
COOH
Bernsteinsäure
HOOC
COOH
Fumarsäure
HOOC
COOH
Maleinsäure


Benzaldehyd
Salicylaldehyd
Zimtaldehyd

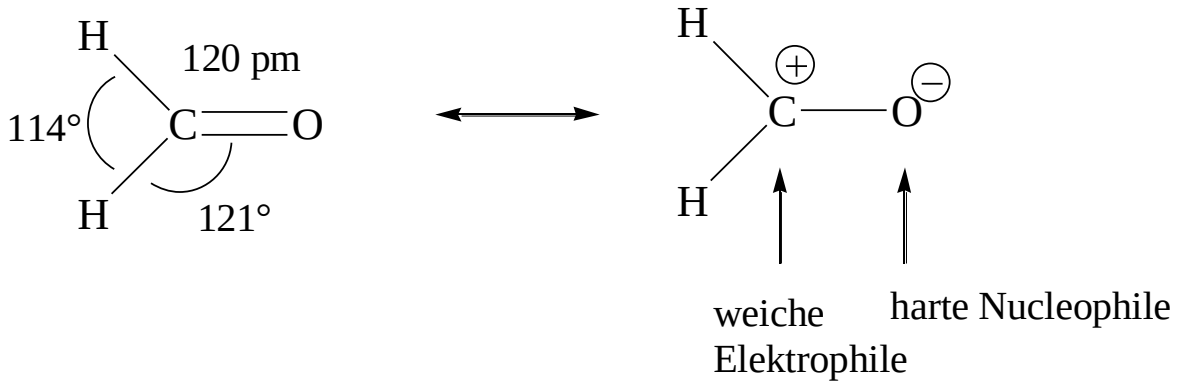

Benzoesäure
Salicylsäure
Anthranilsäure
Zimtsäure
Phthalsäure


Milchsäure
Acetessigsäure
Aminosäure
Äpfelsäure
Weinsäure


R
O
R'
Ketone

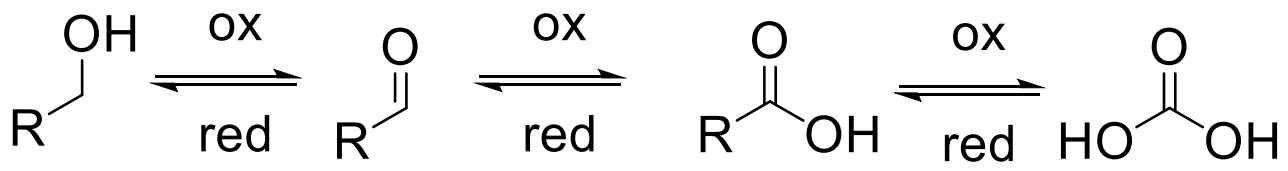

Aceton
Ethylmethylketon
Methylvinylketon
Cyclohexanon
Acetophenon
Benzophenon

Struktur



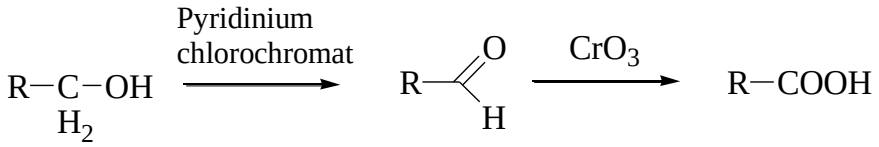
Allg. Eigenschaften

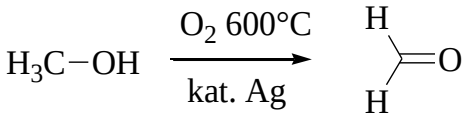
Höhere Siedepunkte als KW:	H-CHO	-21°C
	Me-CHO	+21°C
	Aceton	+56°C
	H-COOH	100°C

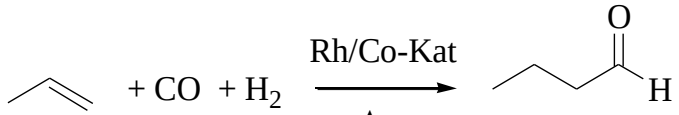


Oxidations-stufe	I	II	III	IV

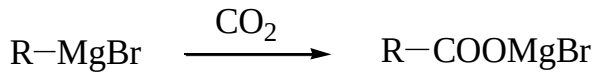
Darstellung

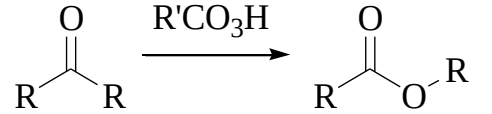
Allgemein: 

Formaldehyd: 

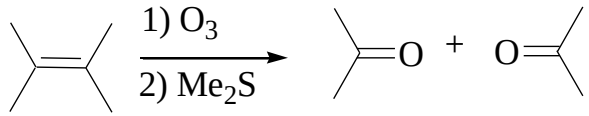
Butanal: 

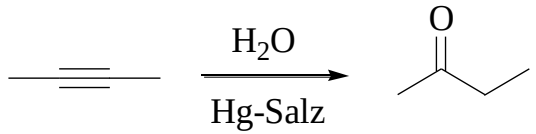
Hydroformylierung

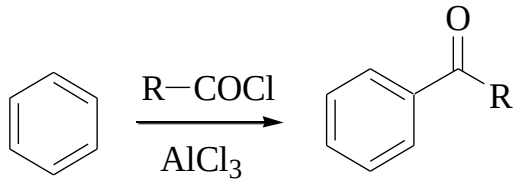
Grignard: 

Bayer-Villiger-Ox.: 

Ester

Ozonolyse: 

Hydratisierung: 

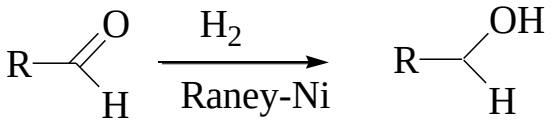
Friedel-Crafts-Acyl.: 

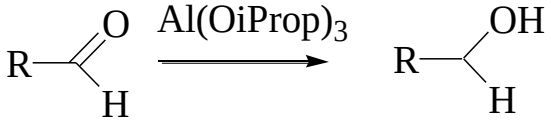
Industrielle Produktion:

Ethanol	127 Mio t/Jahr
Formaldehyd	21 Mio t/Jahr
Aceton	13 Mio t/Jahr
Essigsäure	6 Mio t/Jahr

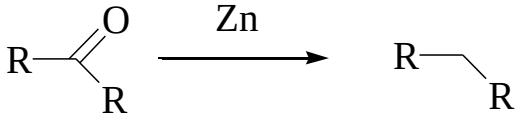
Reaktionen

Hydrierung:



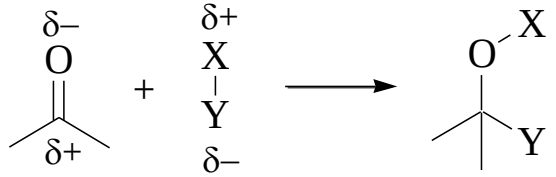


Meerwein-Pondorf-Verley-Reduktion



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
	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

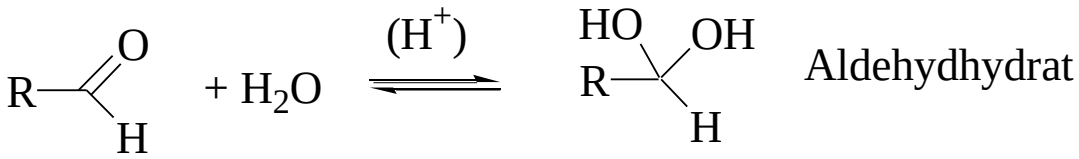
Nachweisreaktionen:

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

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

Carbonylaktivität / Hydratbildung

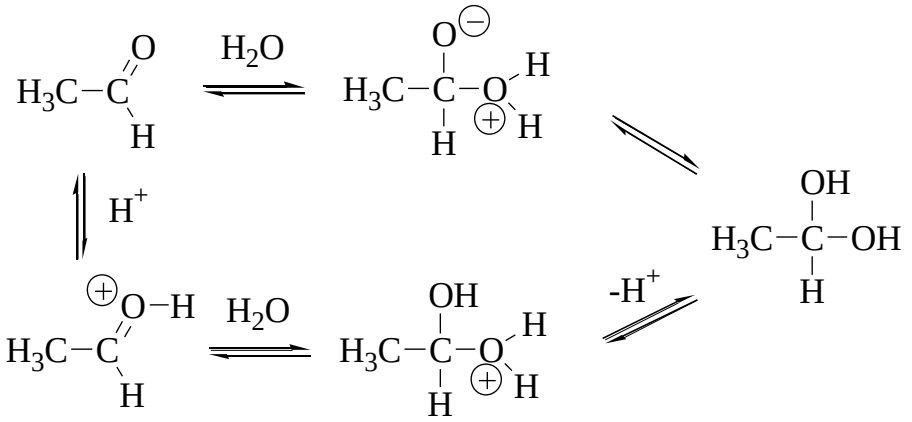
Je weniger gut das Carbeniumion in der zwitterionischen mesomeren Grenzstruktur stabilisiert ist, desto höher ist die Carbonylaktivität!



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)

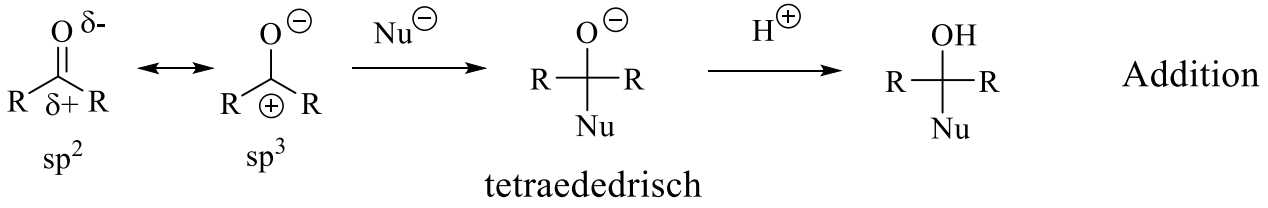
Erlenmeyer-Regel: keine 2 OH-Gruppen gleichzeitig an einem C



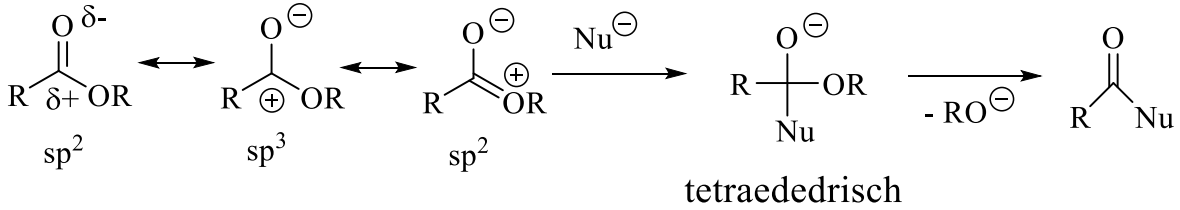
allg. Säurekatalyse / Tetrahedralmechanismus

Nucleophile Addition an Carbonyle

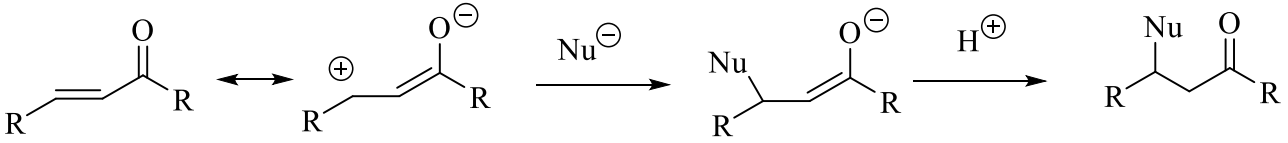
Tetrahedral-Mechanismus



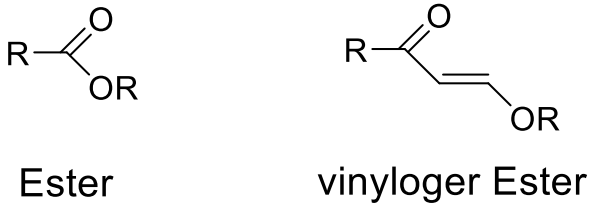
Addition



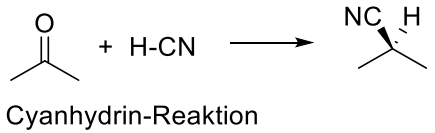
Substitution
(Addition-Eliminierung)

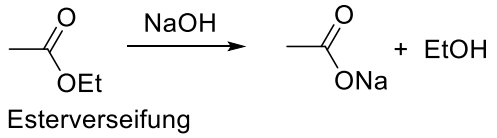


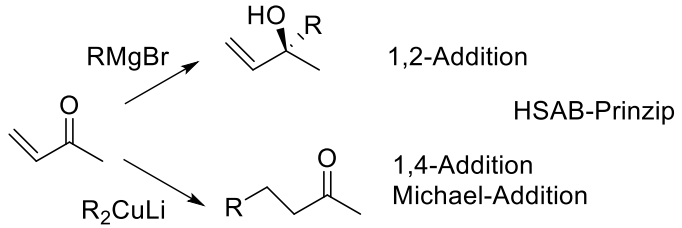
Vinylogie-Prinzip



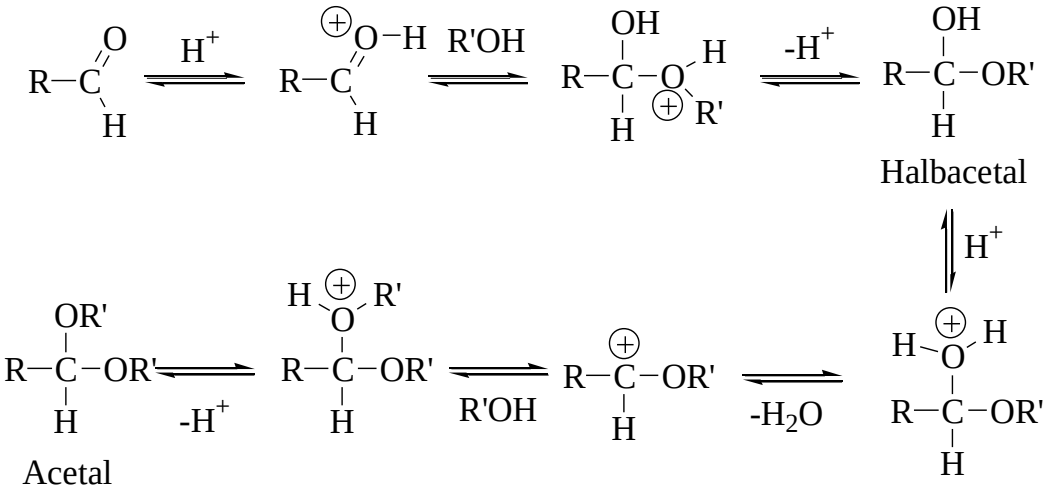
Beispiele





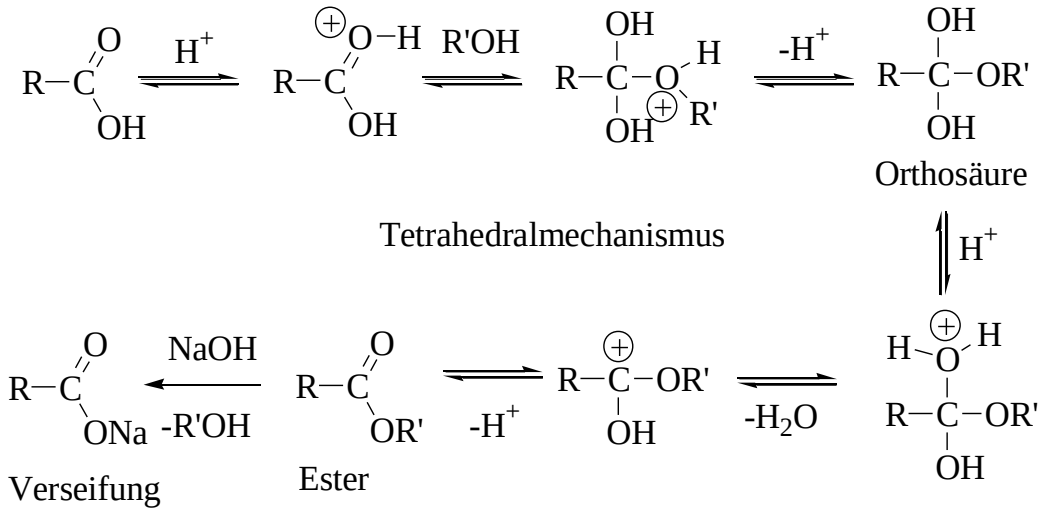


Halbacetal-/Acetalbildung



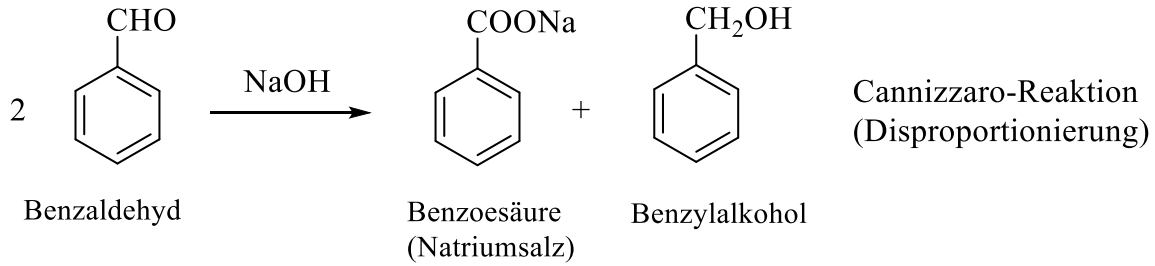
Merke! Acetale sind im Basischen stabil
Acetale spalten im Sauren (saure Hydrolyse)
Acetale sind Schutzgruppen für Carbonyle

Esterbildung / Verseifung

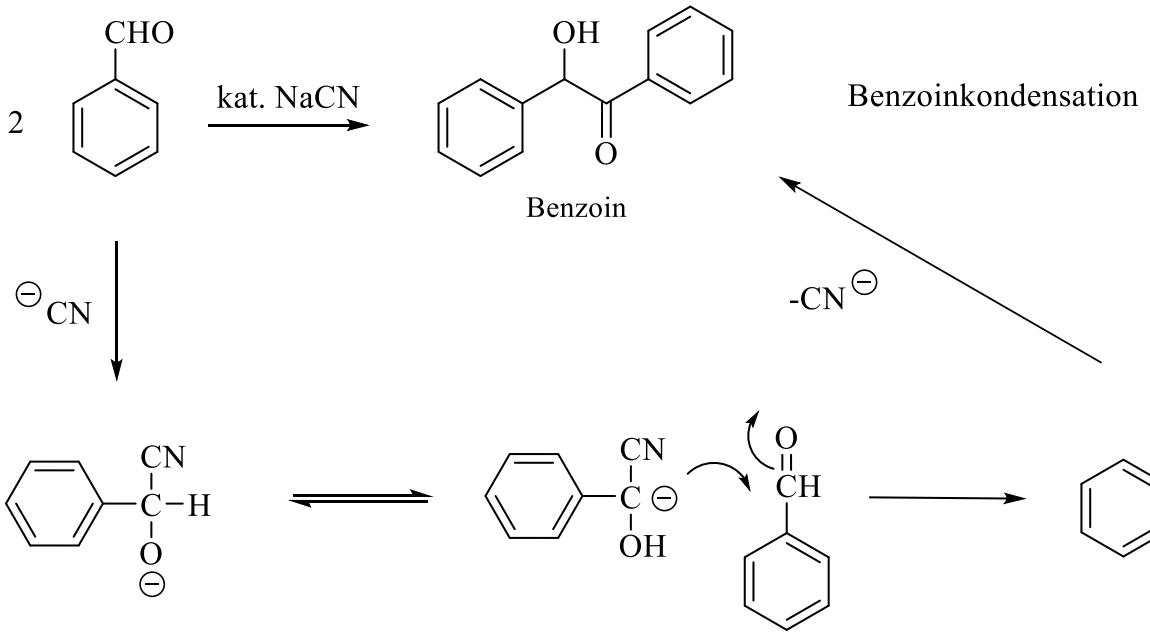


Merke! Ester bilden sich unter Säurekatalyse
Ester hydrolysieren im Sauren
Ester spalten im Alkalischen (Verseifung)

Spezielle Reaktionen

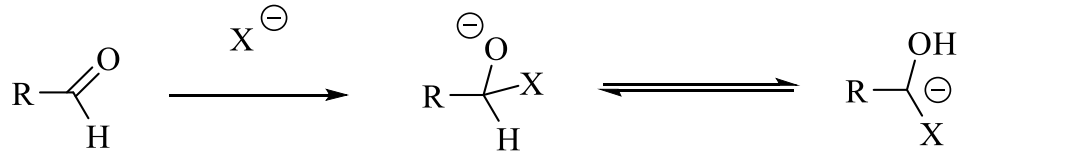


Cannizzaro-Reaktion
(Disproportionierung)

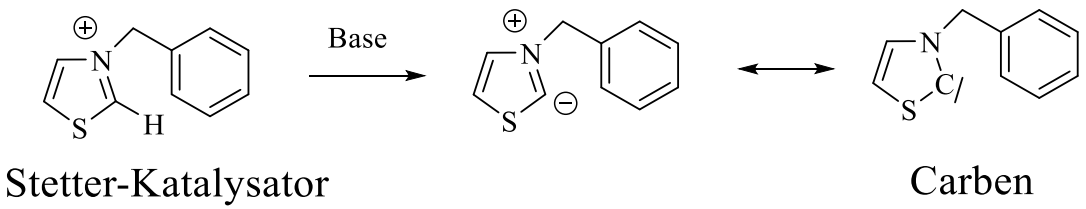


Benzoinkondensation

Umpolung



C-Nucleophil



Stetter-Katalysator

Carben

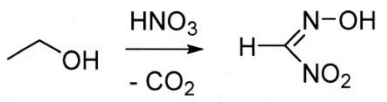
Mesomerie / Tautomerie

Justus von Liebig
1803-1873

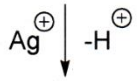
AgCNO
Silberfulminat

Friedrich Wöhler
1800-1882

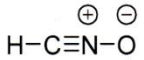
AgOCN
Silbercyanat



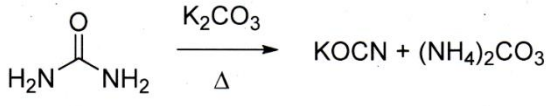
Methannitrolsäure



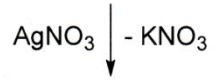
AgCNO
Silberfulminat



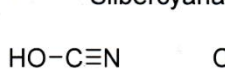
Knallsäure



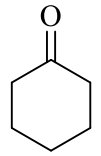
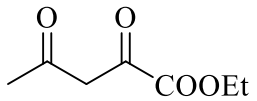
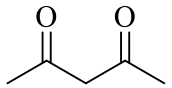
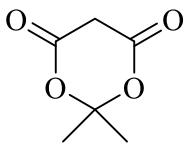
Kaliumcyanat



AgOCN
Silbercyanat



Cyansäure

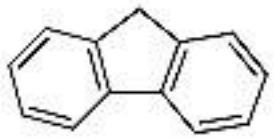
	pKa	% Enol
	20	0,00025
	17	0,02
	11	8
	9	80
	5	99,9

Azidität pK_a

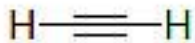
$H_2O + HX \rightarrow H_3O^+ + X^-$ $\qquad K_a = \dfrac{[H_3O^+][X^-]}{[HX]}$ $\qquad pK_a = -\lg K_a$

Kohlenwasserstoffe

Cyclopentadien
16



Fluoren
23



Acetylen
25

Ph_3CH

Triphenylmethan
32

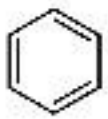
Ph_2CH_2

Diphenylmethan
33.5

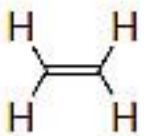
$PhCH_3$

Toluol
41

Propen
43



Benzol
43



Ethen
44

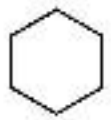
Cyclopropan
46

CH_4

Methan
49

$H_3C{-}CH_3$

Ethan
50



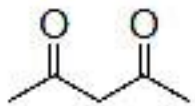
Cyclohexan
51

H_2

Wasserstoff
35

Azidität pK_a

Aktivierte *CH*-acide Verbindungen



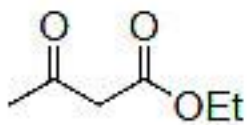
Acetylaceton
9.0

H–CN

Blausäure
9.2

$H_3C–NO_2$

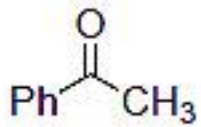
Nitromethan
10.2



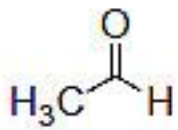
Acetessigester
11.0

Malonitril
11.2

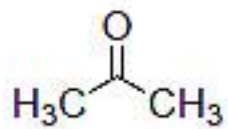
Diethylmalonat
12.7



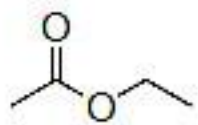
Acetophenon
15.8



Acetaldehyd
17



Aceton
20



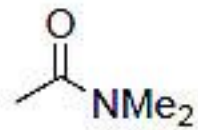
Essigsäureethylester
24.5

$H_3C–CN$

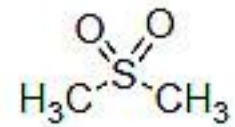
Acetonitril
25

$CHCl_3$

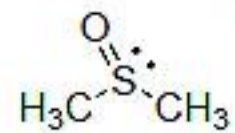
Chloroform
25



N,N-Dimethyl-acetamid
30



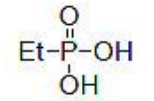
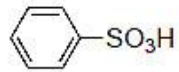
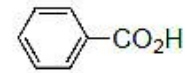
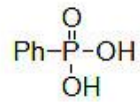
Dimethylsulfon
~ 31



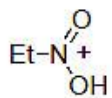
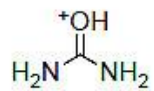
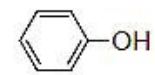
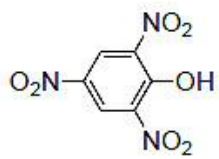
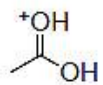
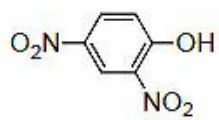
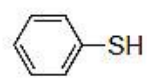
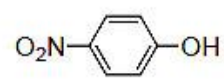
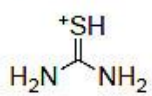
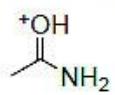
Dimethylsulfoxid
~ 35

Azidität pK_a

Organische Carbon-, Sulfon-, und Phosphonsäuren

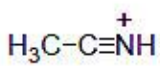
F_3C-SO_3H	Trifluormethansulfonsäure ~ -13	Cl_3C-CO_2H	Trichloressigsäure 0.7		Ethylphosphonsäure 2.4, 8
	Benzolsulfonsäure ~ -2.5	Cl_2HC-CO_2H	Dichloressigsäure 1.29	HCO_2H	Ameisensäure 3.7
H_3C-SO_3H	Methansulfonsäure ~ -2	ClH_2C-CO_2H	Chloressigsäure 2.86		Benzoesäure 4.2
F_3C-CO_2H	Trifluoressigsäure 0.2		Phenylphosphonsäure 2.2, 7.2	H_3C-CO_2H	Essigsäure 4.76

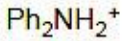
OH- und *SH*-acide Verbindungen

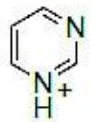
	Nitroethan·H^+ ~ -11		Uronium 0.1		Phenol 10.0
	Aceton·H^+ -7.2		Pikrinsäure 0.25	$MeSH$	Methanthiol 10.0
	Essigsäure·H^+ ~ -6		2,4-Dinitrophenol 4.0	$EtSH$	Ethanthiol 10.6
$Et_2\overset{+}{O}H$	Diethyloxonium -3.6	H_2S	Schwefelwasserstoff 7.0	F_3C-CH_2OH	Trifluorethanol 12.4
$Et\overset{+}{O}H_2$	Ethyloxonium -2.4		Thiophenol 7	H_2O	Wasser 15.74
H_3O^+	Oxonium -1.74		*p*-Nitrophenol 7.2	$MeOH$	Methanol 15.5
	Thiuronium -1	$PhB(OH)_2$	Phenylboronsäure 8.8	$EtOH$	Ethanol 16
	Acetamid·H^+ 0			^tBuOH	*tert*-Butanol 18

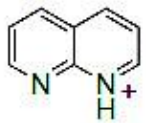
Azidität pK_a

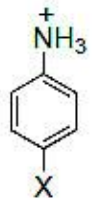
NH-acide Verbindungen


Acetonitril·H^+
~ -10


Diphenylammonium
0.8


Pyrimidinium
1.3

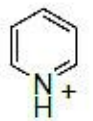

Naphthyridinium
3.4

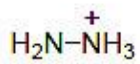

Anilinium, mit X =

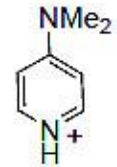
H:	4.60
NO_2:	1.00
CN:	1.74
CF_3:	2.75
Cl:	3.98
CH_3:	5.10
OCH_3:	5.34

HN_3
Stickstoffwasserstoff-säure
4.7

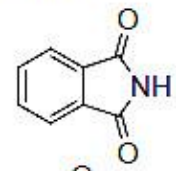
$PhNMe_2H^+$
N,N-Dimethylanilinium
5.1

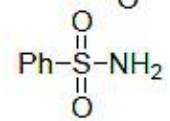

Pyridinium
5.2


Hydrazinium
8.1


4-(Dimethylamino)-pyridinium
9.2

NH_4^+
Ammonium-
9.2

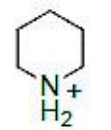

Phthalimid
9.6


Benzolsulfonamid
10

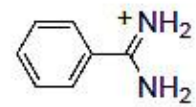
$EtNH_3^+$
Ethylammonium
10.6

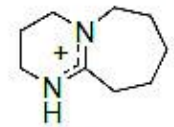
Et_3NH^+
Triethylammonium
10.7

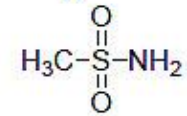
$Et_2NH_2^+$
Diethylammonium
10.9

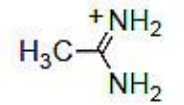

Piperidinium
11.1

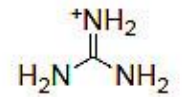
$^iPr_2EtNH^+$
Hünig-Base
11.4

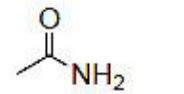

Benzamidinium
11.4


DBU·H^+
12

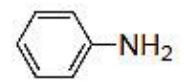

Methan-sulfonamid
~12


Ethanamidinium
12.4


Guanidinium
13.4


Acetamid
15

$(Me_3Si)_2NH$
Hexamethyldi-silazan (HMDS)
26

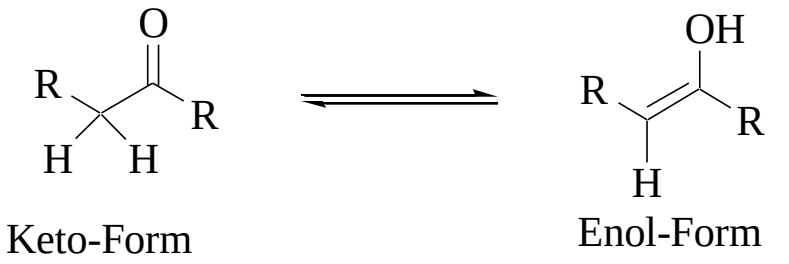

Anilin
27

NH_3
Ammoniak
36

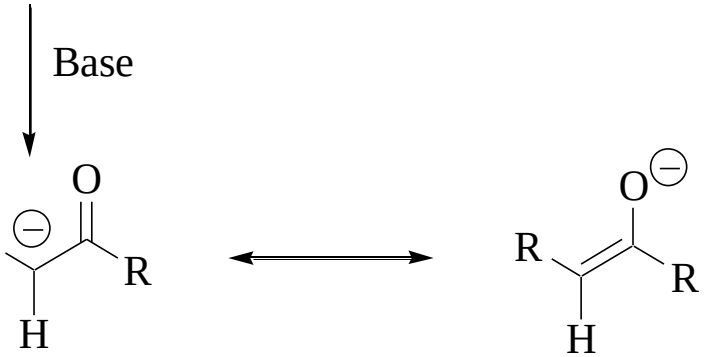
$^iPr_2NH$
Diisopropylamin
38

Keto-Enol-Tautomerie:

α-CH-Gruppe in Carbonylen ist sauer (pK_S = 11-25)

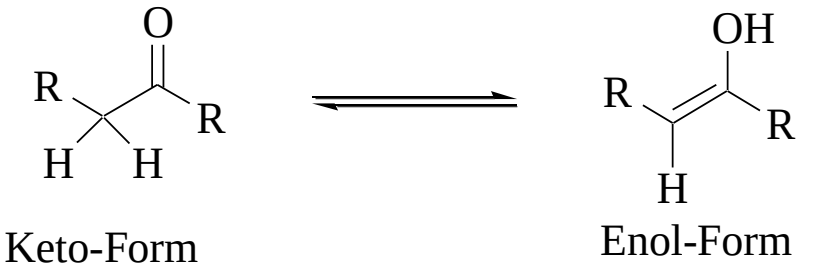


Keto-Form Enol-Form

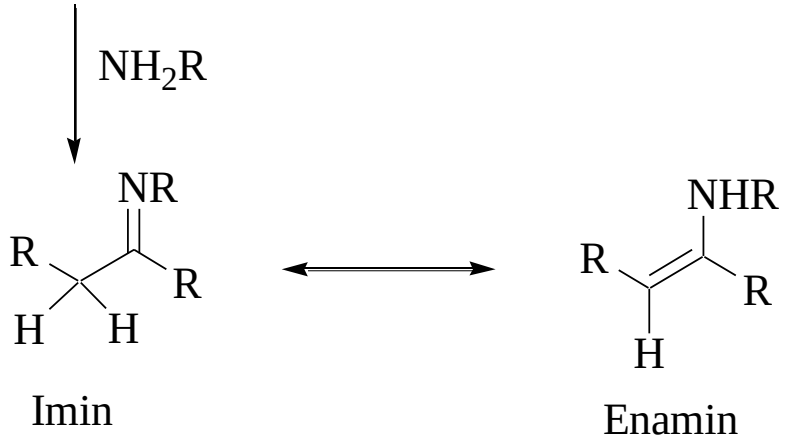


Carbanion-Form Enolat-Form

Enaminbildung:

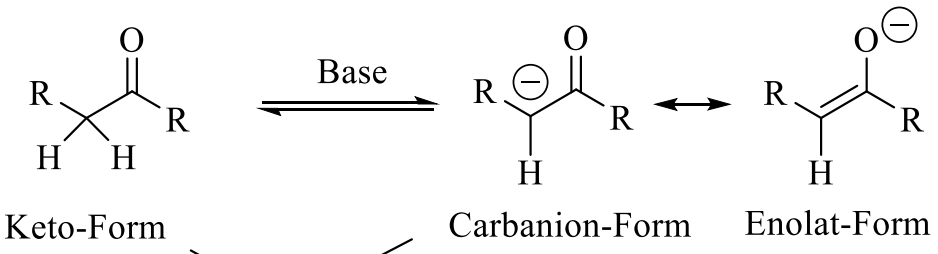


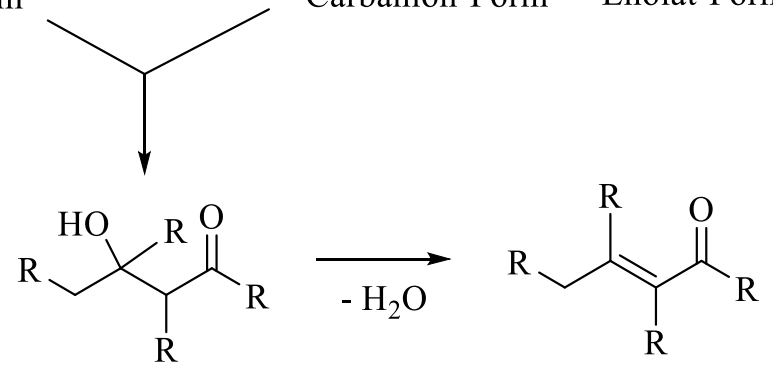
Keto-Form Enol-Form



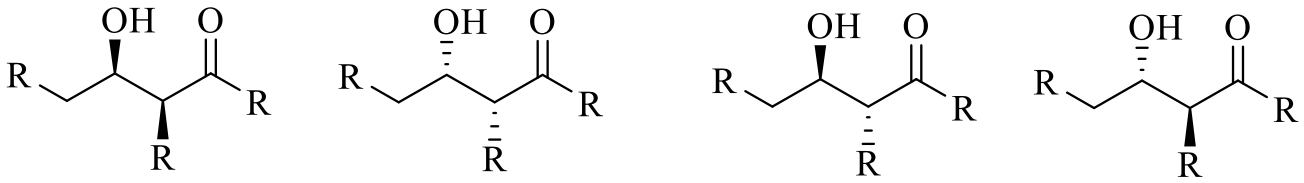
Imin Enamin

Aldol-Reaktion, -Kondensation

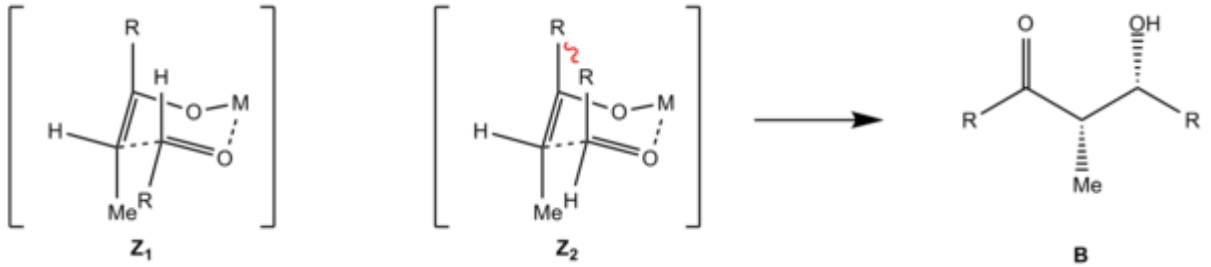




Aldolreaktion Aldolkondensation

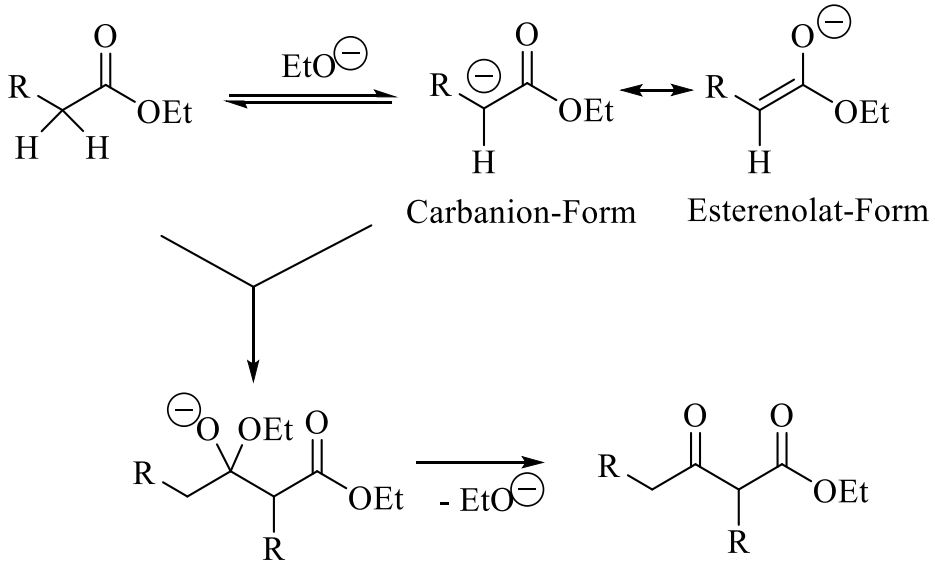


syn-Enantiomers Hauptprodukt syn/anti-Diastereomers anti-Enantiomers

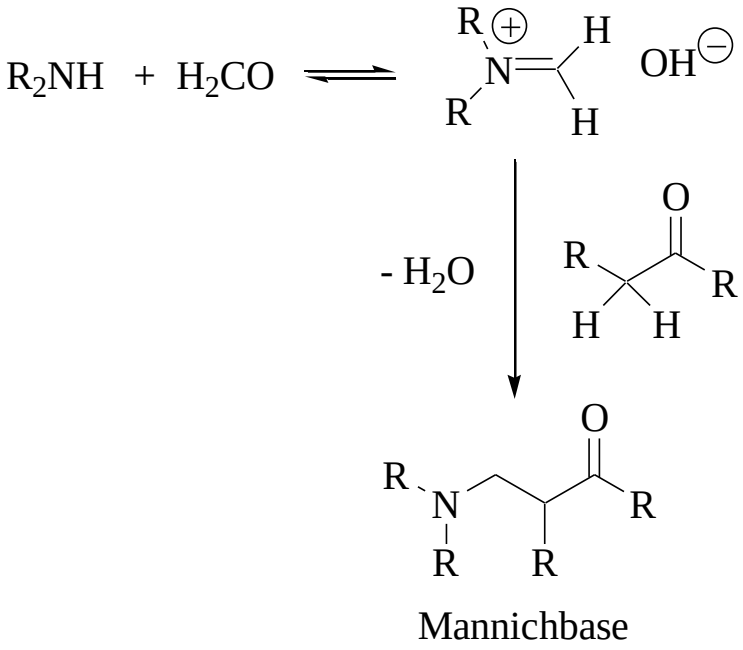


Zimmermann-Traxler-Modell

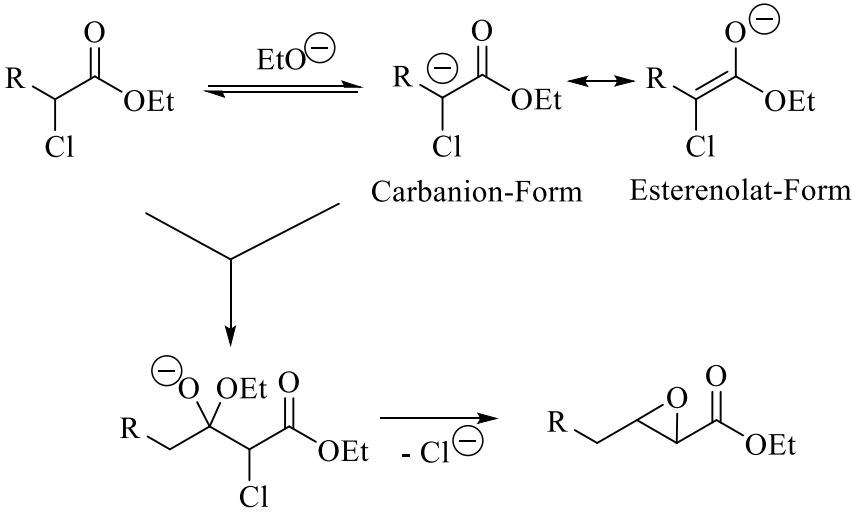
Claisen-Kondensation



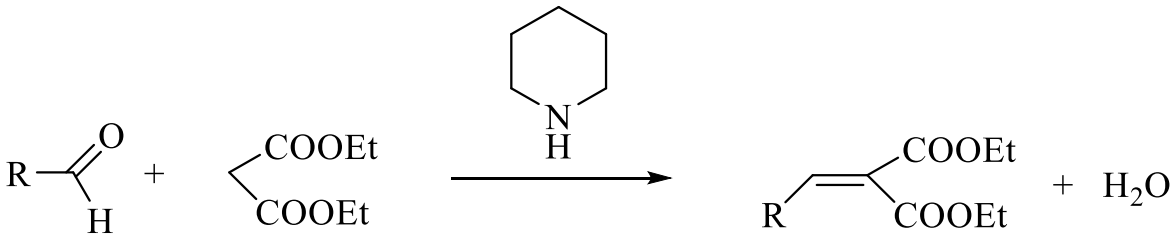
Mannich-Reaktion (Aminomethylierung)



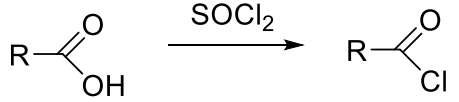
Darzens-Glycidester-Synthese

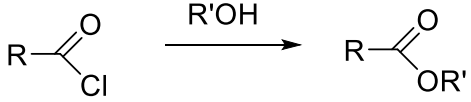


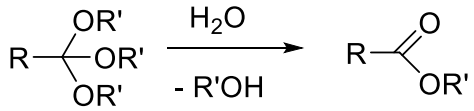
Knoevenagel-Kondensation

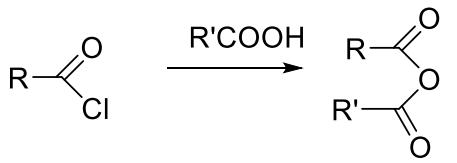


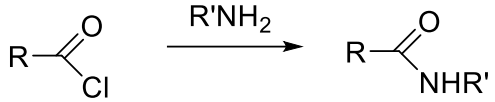
Carbonylverbindungen

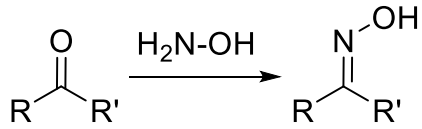
Carbonsäurechloride 

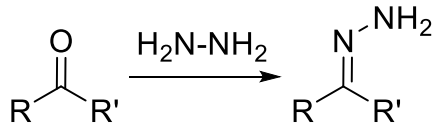
Carbonsäureester 

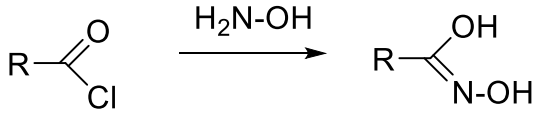
Carbonsäureorthoester 

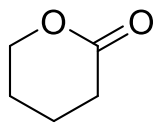
Carbonsäureanhydride 

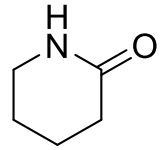
Carbonsäureamide 

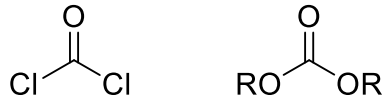
Oxime 

Hydrazone 

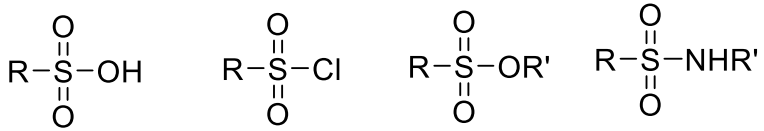
Hydroxamsäuren 

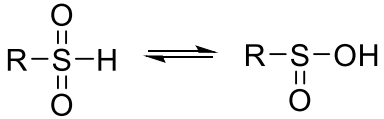
Lactone 

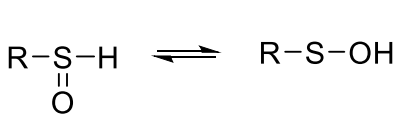
Lactame 

Phosgen / Carbonate 

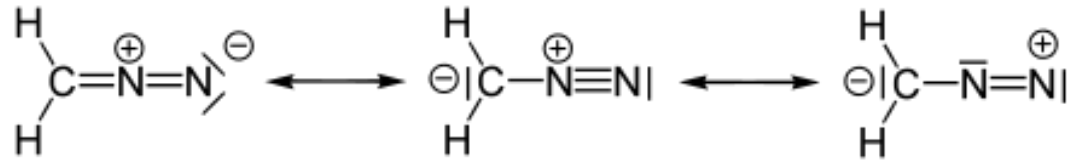
Carbaminsäure / Urethane 

Sulfonsäuren / chloride / ester / amide 

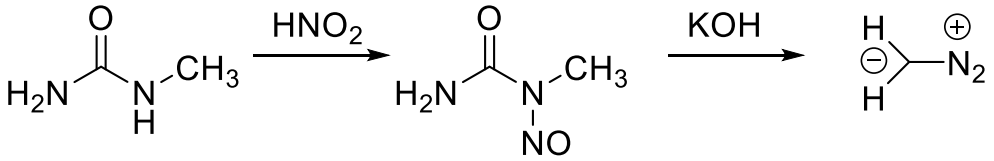
Sulfensäuren 

Sulfinsäuren 

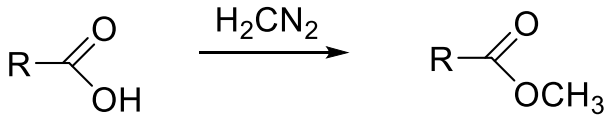
Diazomethan



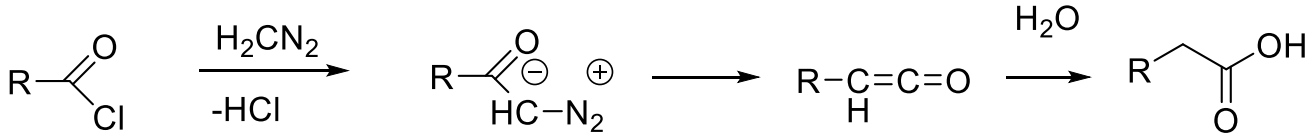
Darstellung

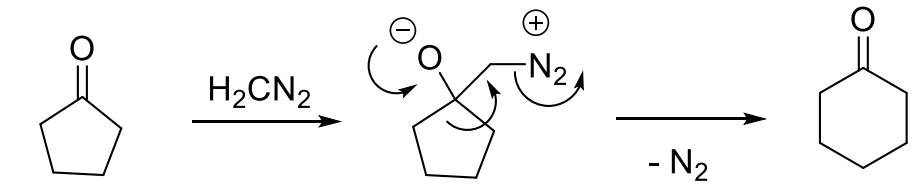


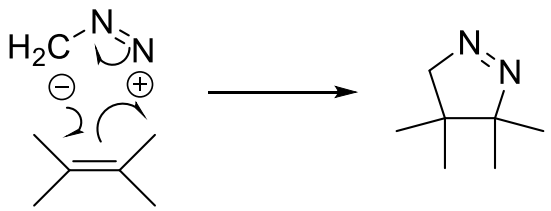
Reaktionen



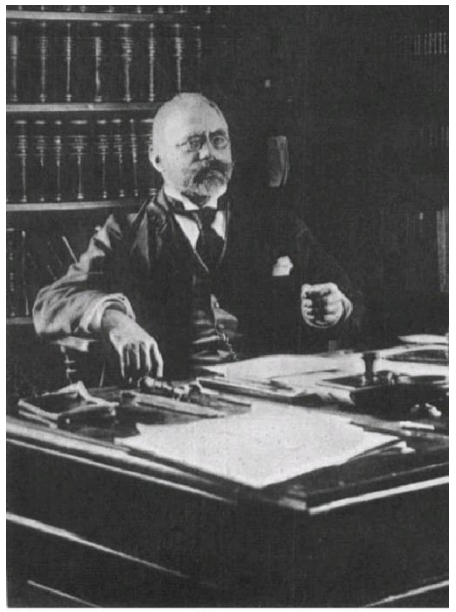
Arndt-Eistert-Synthese







Cycloaddition



Hans Freiherr von Pechmann (1850-1902)
Diazomethan 1894