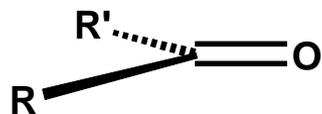
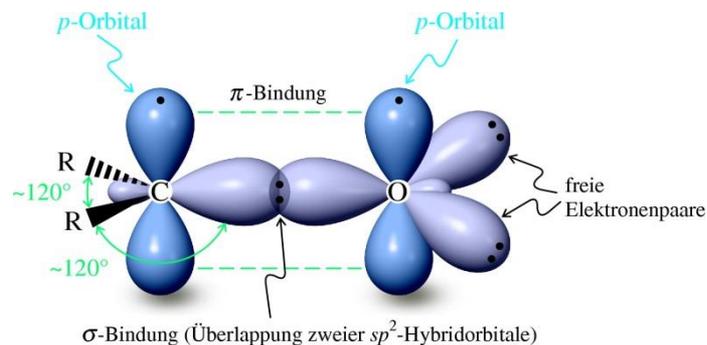
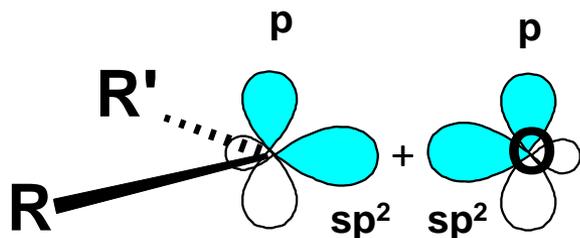
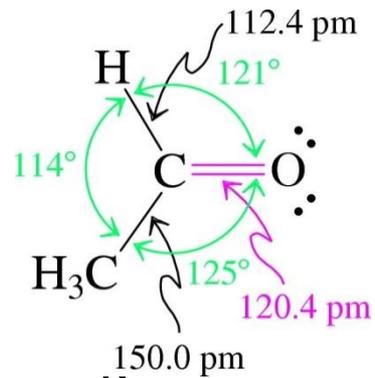


11 Aldehyde und Ketone

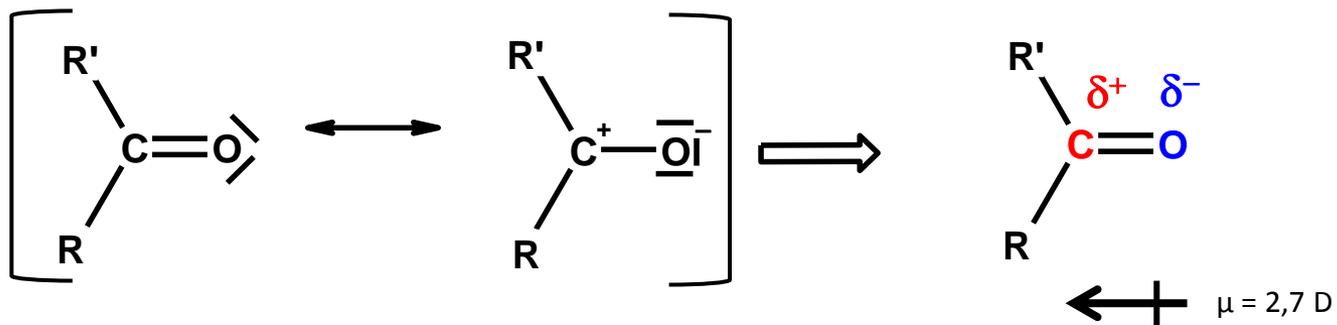
Bindungsverhältnisse an der Carbonylgruppe



$$DH^\circ = 730-750 \text{ kJ/mol}$$

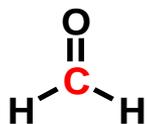


© 2012 Wiley-VCH Verlag GmbH & Co. KGaA
Vollhardt - Organische Chemie
ISBN: 9783527327546 Abb. 18-001

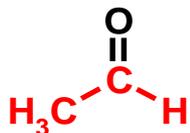


11 Aldehyde und Ketone

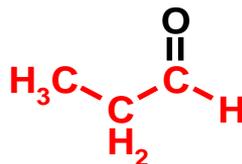
Nomenklatur der Aldehyde



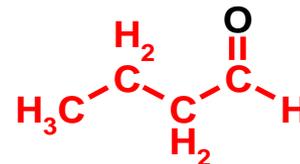
Methan al
(Formaldehyd)



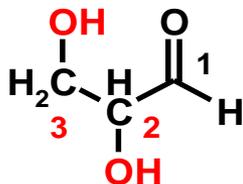
Ethan al
(Acetaldehyd)



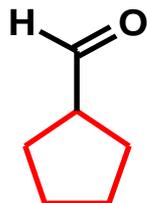
Propanal
(Propionaldehyd)



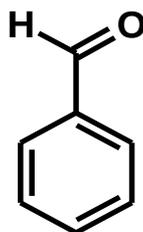
Butan al
(Butyraldehyd)



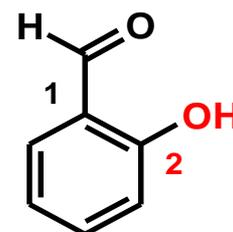
2,3-Dihydroxy propanal
(Glycerinaldehyd)



Cyclopentancarbaldehyd



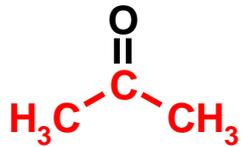
(**Benzol**carbaldehyd)
Benzaldehyd



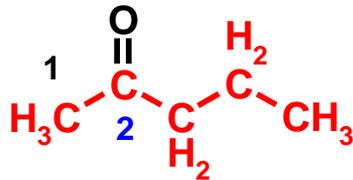
2-Hydroxy benzaldehyd
(Salicylaldehyd)

11 Aldehyde und Ketone

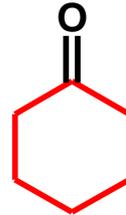
Nomenklatur der Ketone



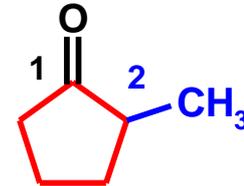
Propanon
(Aceton)



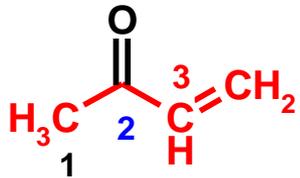
2-Pentanon
(Methylpropylketon)



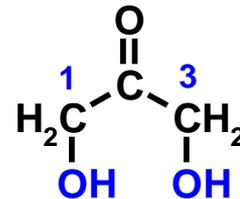
Cyclohexanon



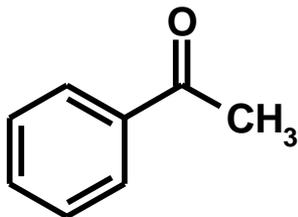
2-Methylcyclopentanon



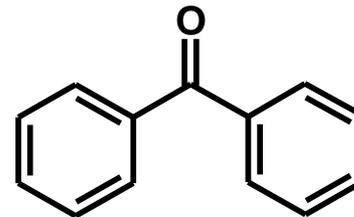
3-Buten-2-on
(Methylvinylketon)



1,3-Dihydroxypropanon
(1,3-Dihydroxyacetone)

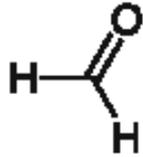


Acetophenon
(Methylphenylketon)

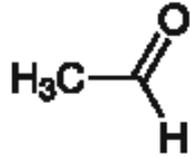


Benzophenon
(Diphenylketon)

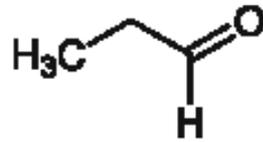
Aldehyde (oberste und mittlere Reihe) Ketone
(unterste Reihe)



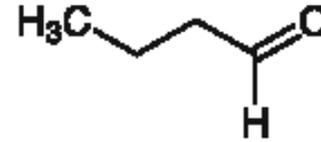
Formaldehyd



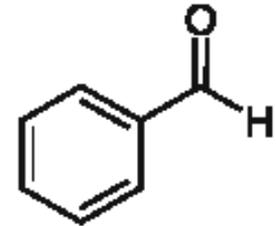
Ethanal
(Acetaldehyd)



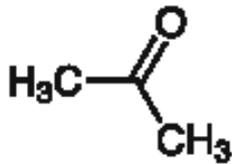
Propanal
(Propionaldehyd)



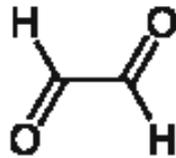
Butanal
(Butyraldehyd)



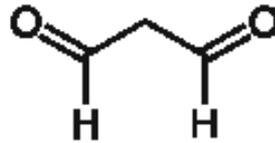
Benzaldehyd



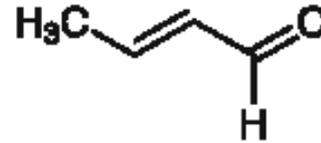
Propanon
(Aceton)



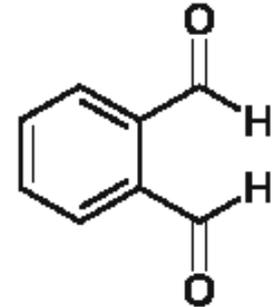
Ethandial
(Glyoxal)



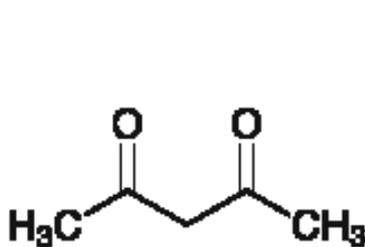
Propandial
(Malonaldehyd)



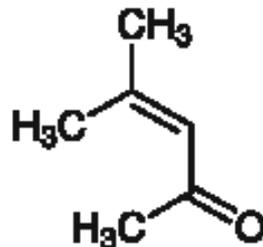
2-Butenal
(Crotonaldehyd)



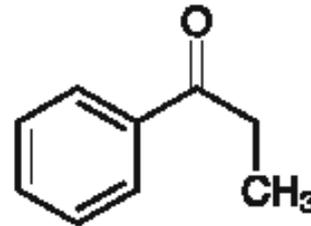
Phthalaldehyd



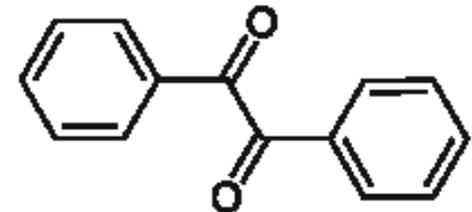
2,4-Pentandion
(Acetylaceton)



4-Methyl-
3-penten-2-on



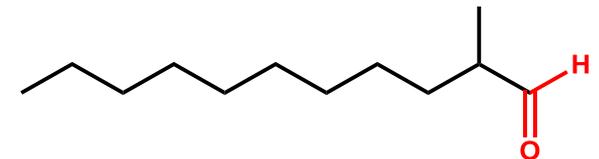
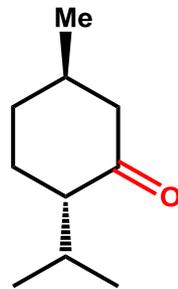
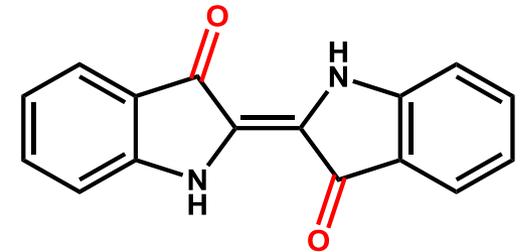
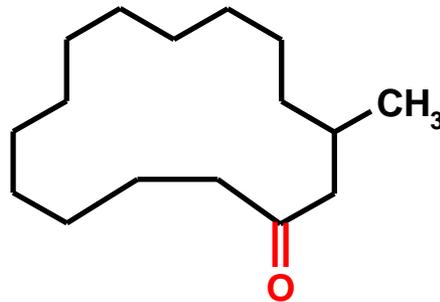
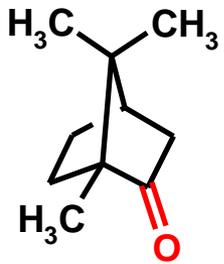
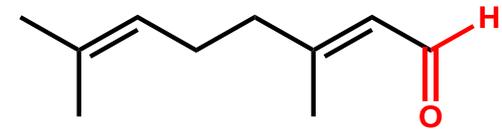
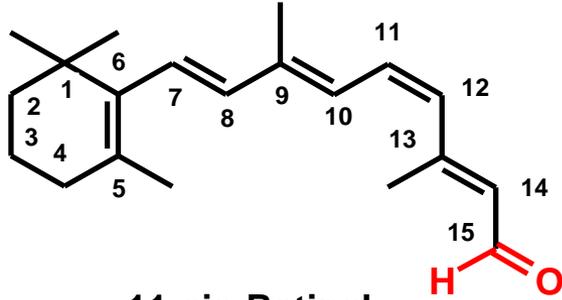
Propiophenon



Diphenylethanone (Benzil)

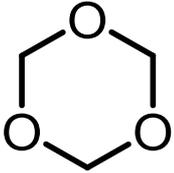
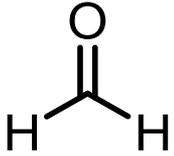
11 Aldehyde und Ketone

Natürlich vorkommende Aldehyde und Ketone (Beispiele)



11 Aldehyde und Ketone

Einschub: Anwendungen von Formaldehyd



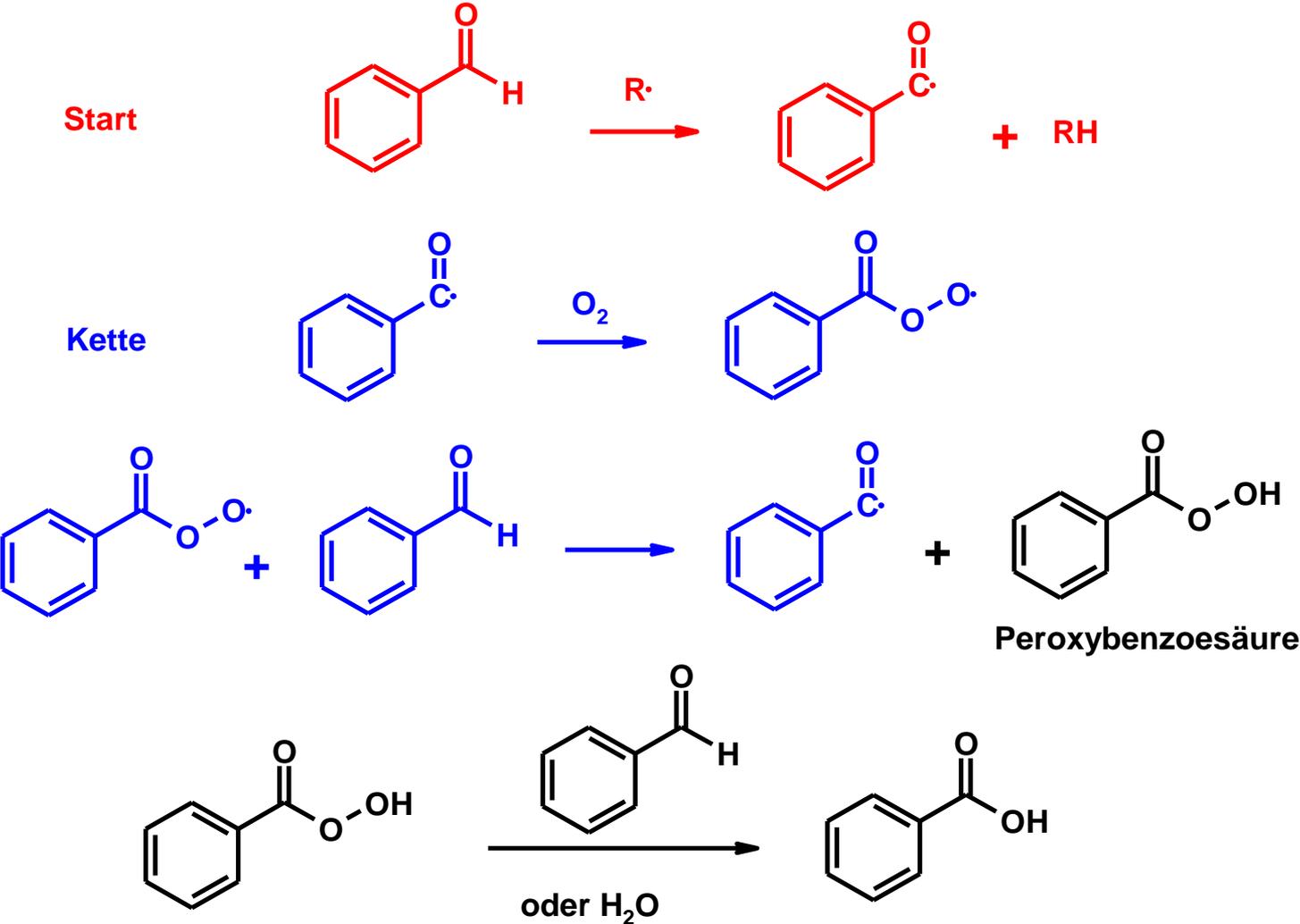
- Weltjahresproduktion 21 **Megatonnen** (2007)
- Ausgangsstoff für weitere Synthesen (nützliche **Oxidationsstufe**)
- Ausgangsstoff für **Polymerisation** (direkt: „POM“; mit Phenol: „Bakelit“)
- Um unerwünschte Polymerisation auszuschließen, verwendet man in der Synthese häufig **Trioxan** (Trimeres Acetal des Formaldehyds)

- 4-8%ige Formalinlösung wird häufig zur **Konservierung von Präparaten und Leichen** verwendet
- Mechanismus: **Quervernetzung** durch Bildung von X-CH₂-X Brücken (insbesondere mit Peptiden)
- Kann durch **Hydrolyse** rückgängig gemacht werden



11 Aldehyde und Ketone

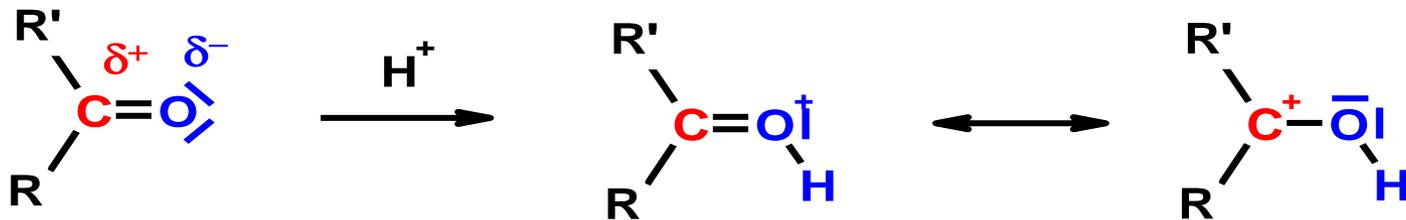
Oxidation von Aldehyden: Autoxidation von Benzaldehyd



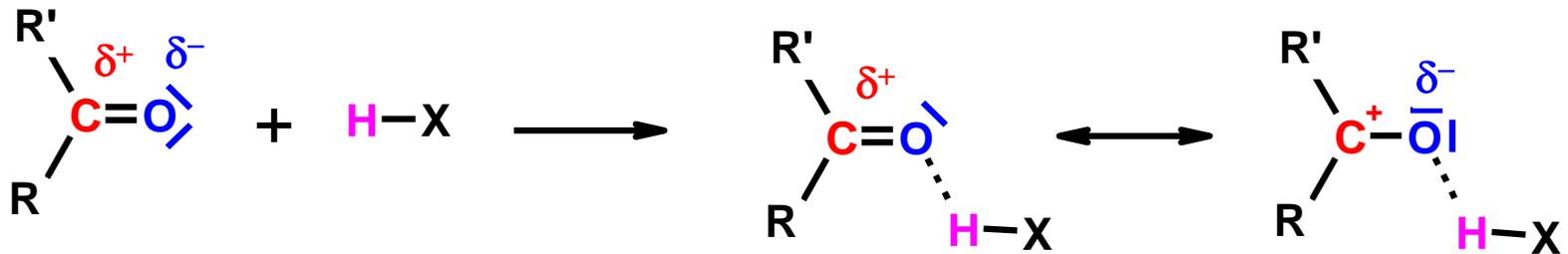
11 Aldehyde und Ketone

Reaktivität von Carbonylverbindungen

schwach basische Eigenschaften

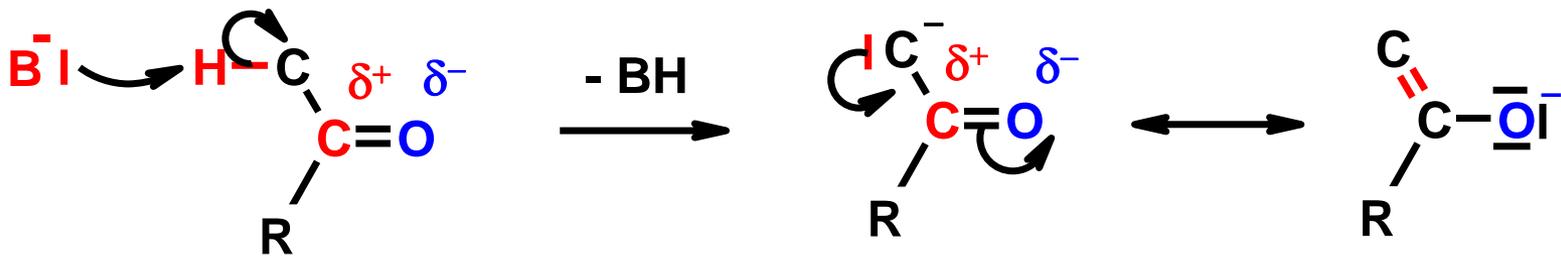
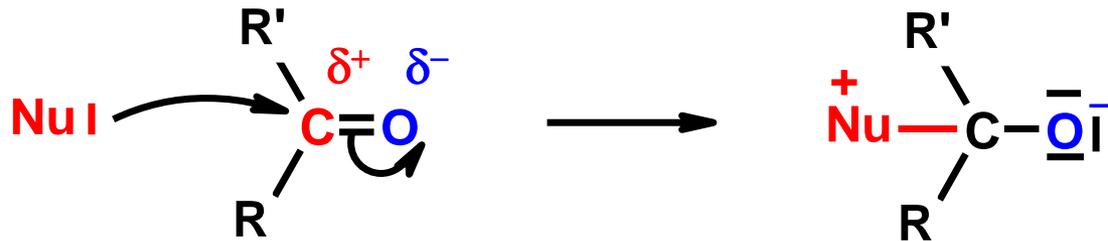


Akzeptoren für Wasserstoffbrücken



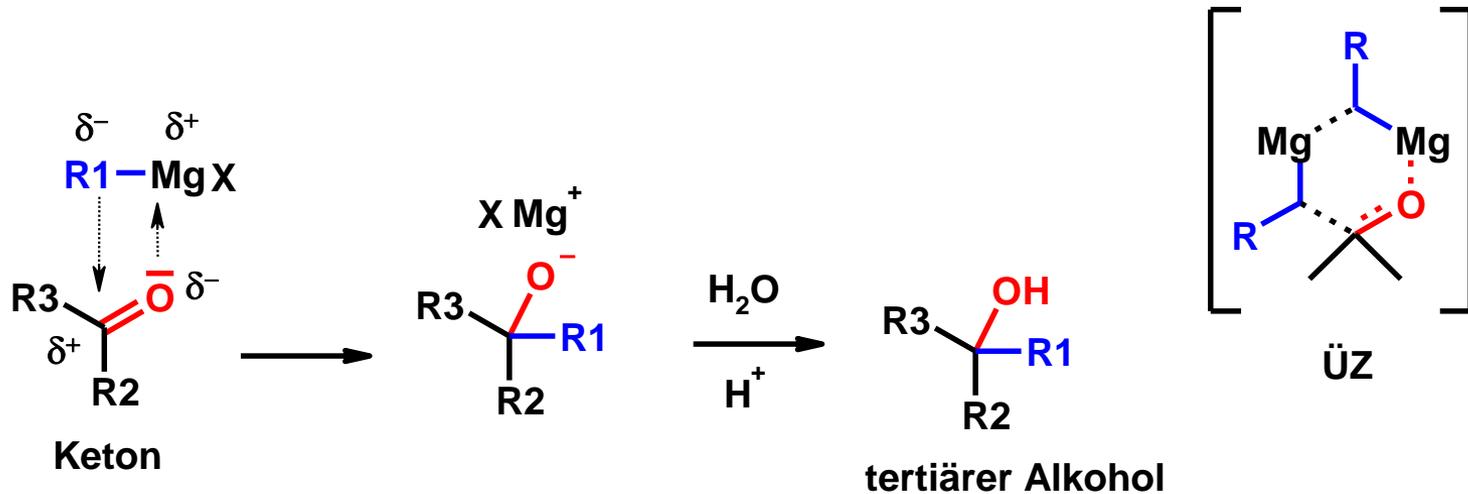
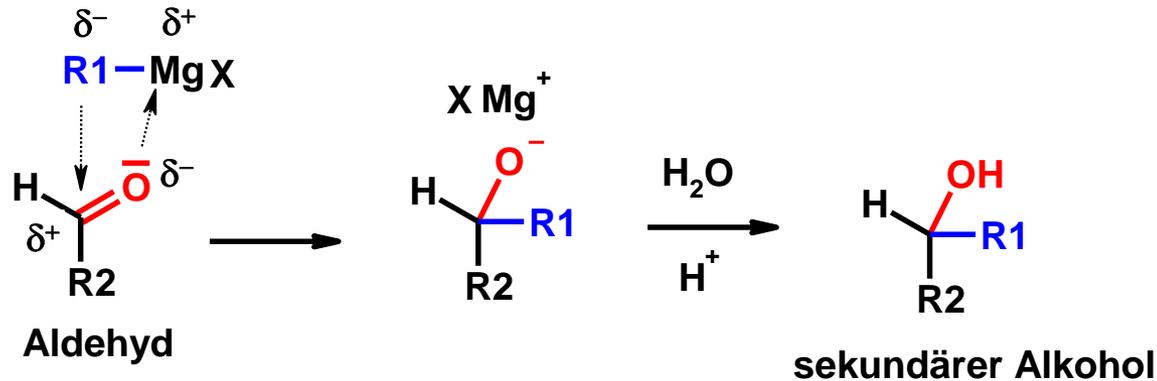
11 Aldehyde und Ketone

Reaktivität von Carbonylverbindungen

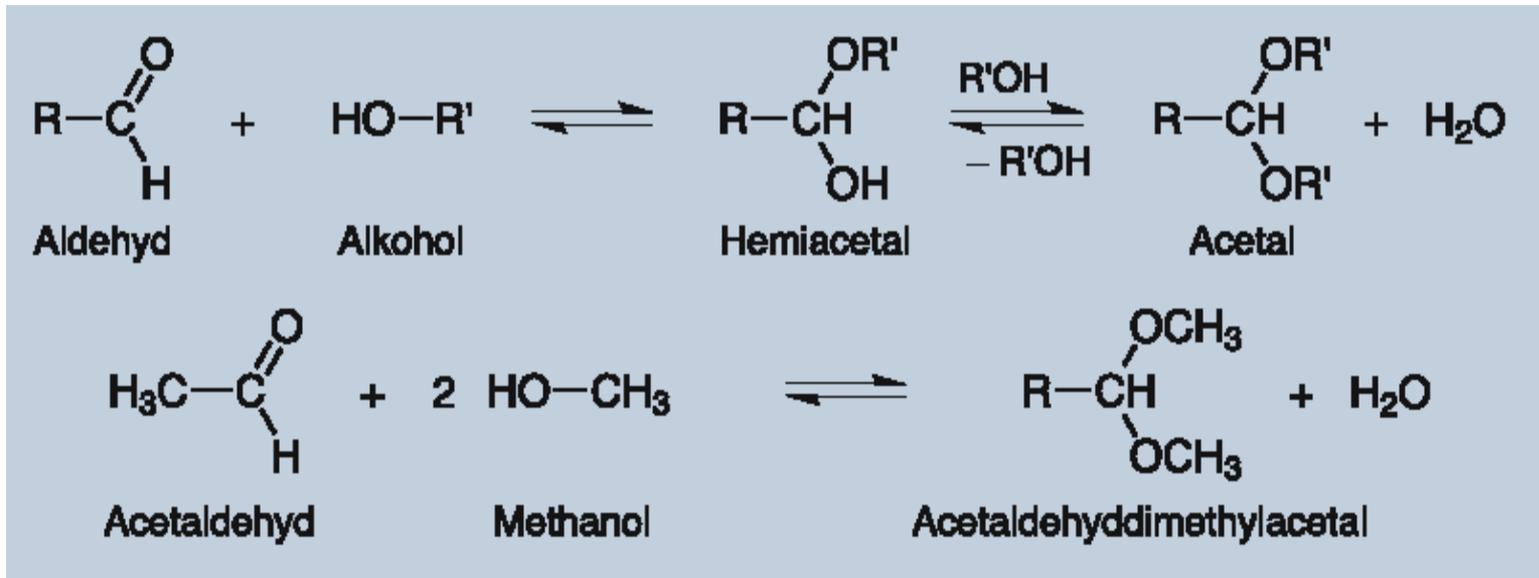


11 Aldehyde und Ketone

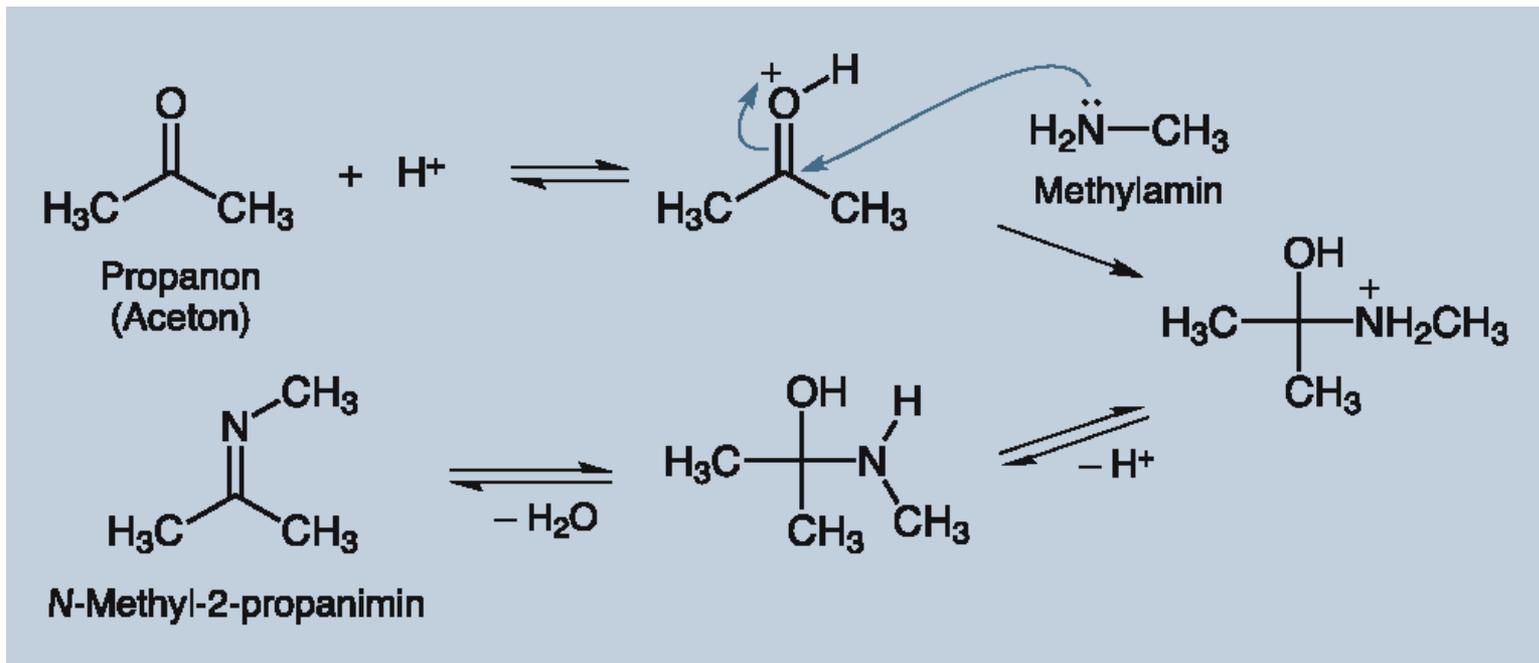
Addition von Grignard-Verbindungen (C-Nucleophile) an Aldehyde und Ketone



Addition an Carbonylgruppe:

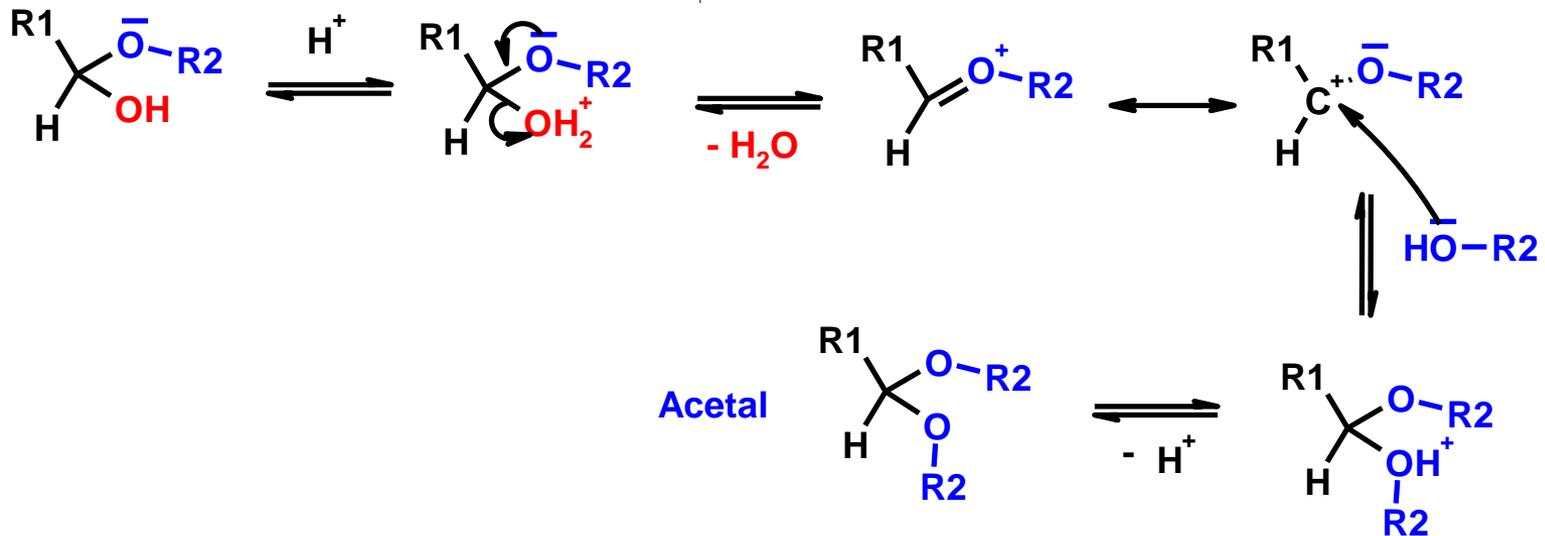
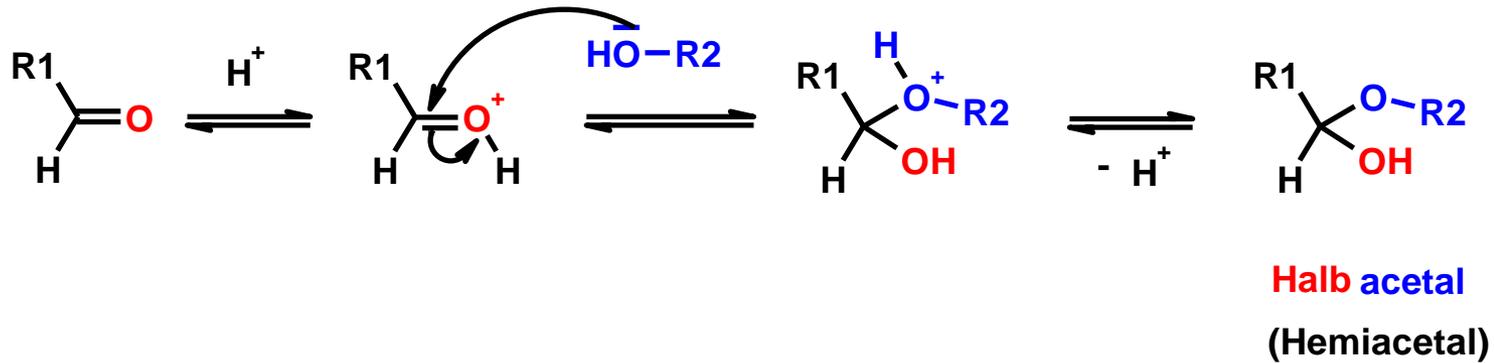


Addition/Eliminierung an Carbonylgruppe:



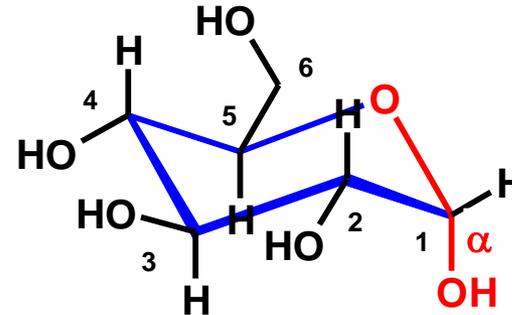
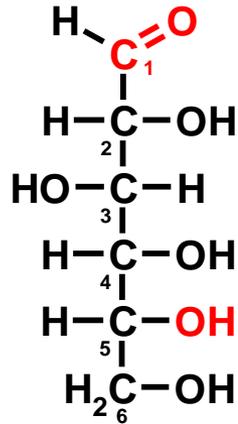
11 Aldehyde und Ketone

Addition von Alkoholen: Bildung von Halbacetalen und Acetalen

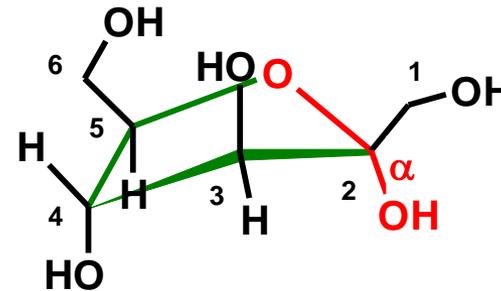
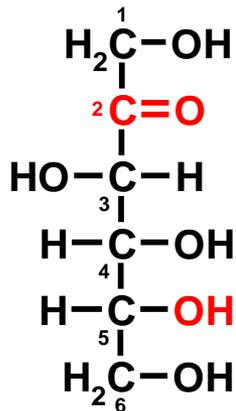


11 Aldehyde und Ketone

Halbacetalbildung bei Zuckern



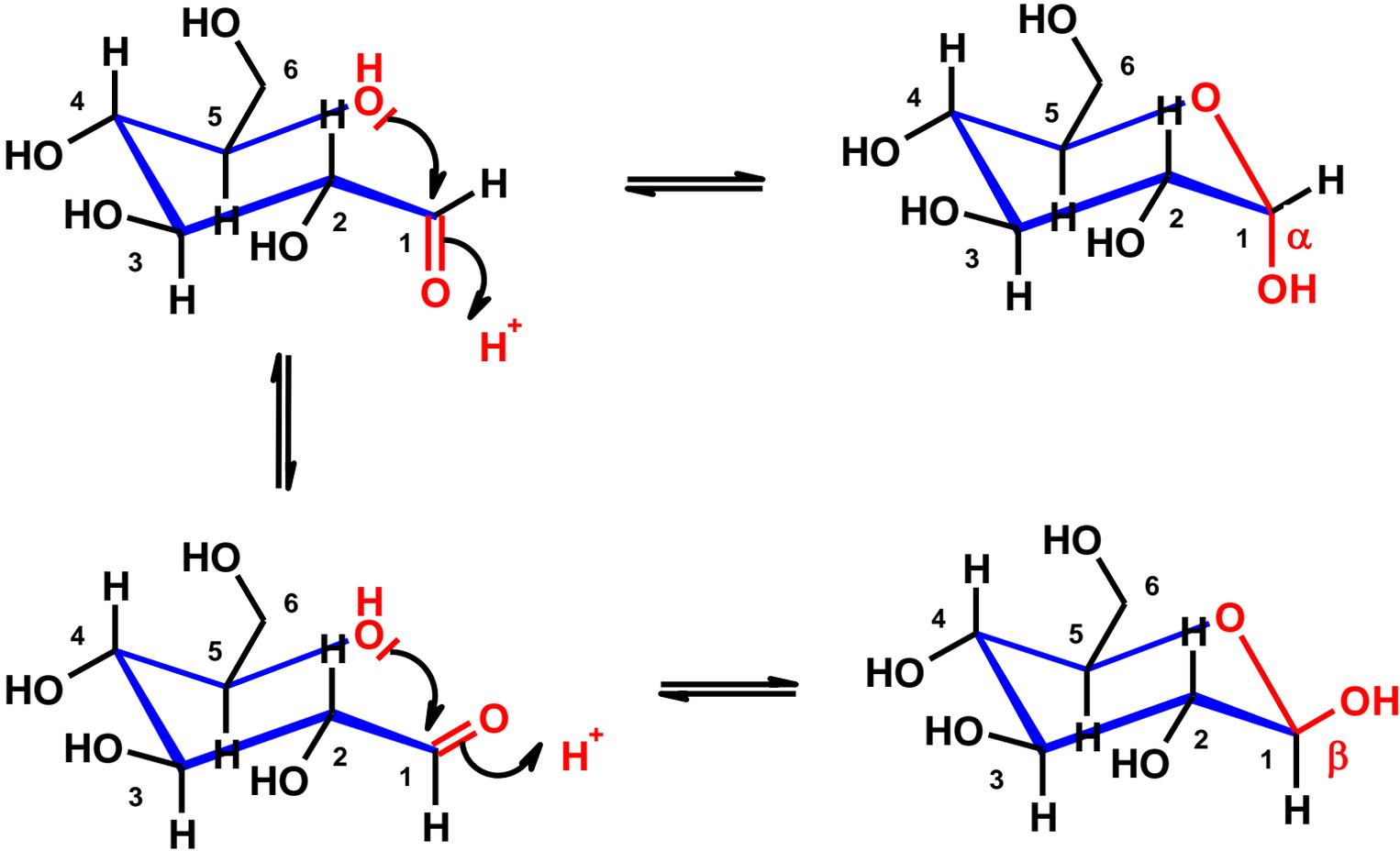
α -D-Glucose
(Pyranose)



α -D-Fructose
(Furanose)

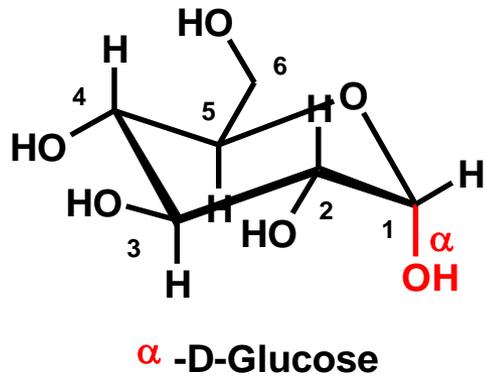
11 Aldehyde und Ketone

Anomere Formen der D-Glucose



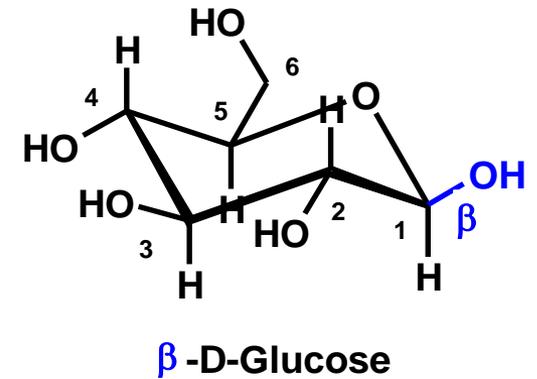
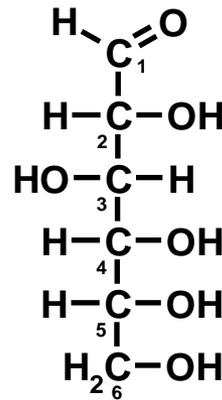
11 Aldehyde und Ketone

Mutarotation der Glucose



$$[\alpha] = +112 \text{ [}^\circ \text{ / (dm} \cdot \text{g/ml)} \text{]}$$

37%

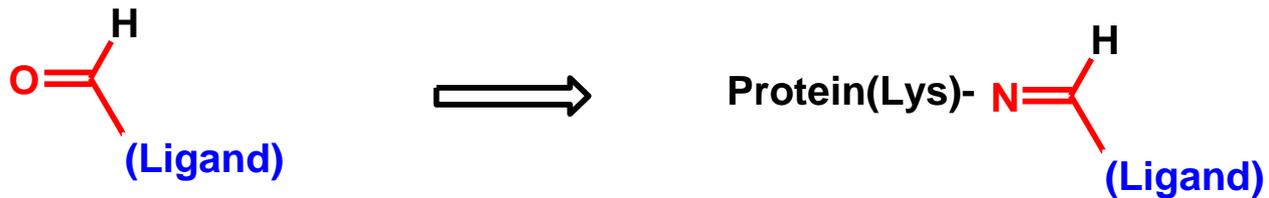
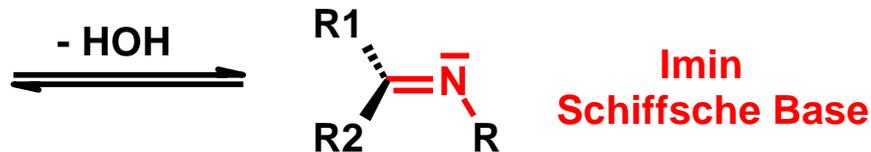
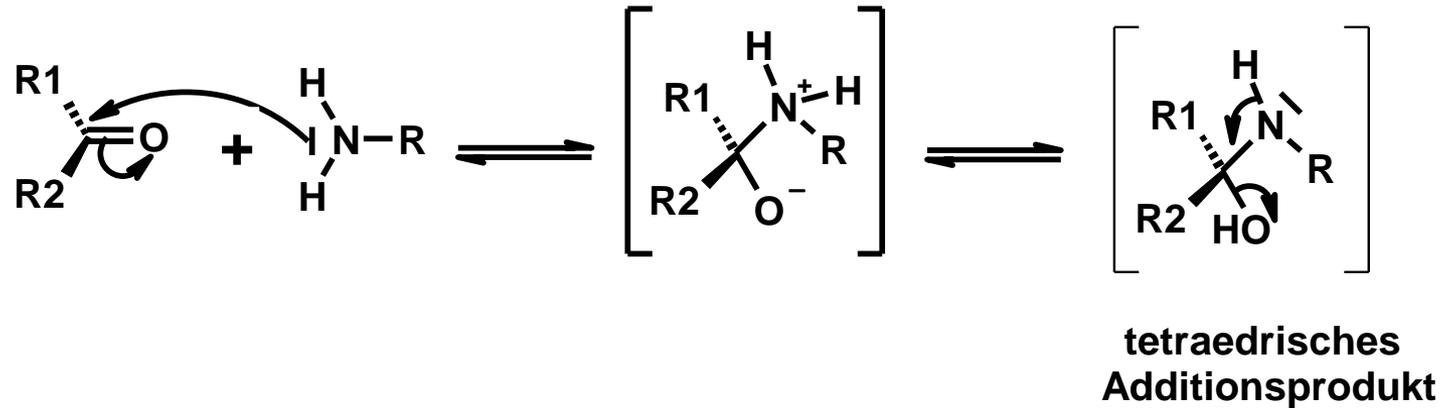


$$[\alpha] = +19 \text{ [}^\circ \text{ / (dm} \cdot \text{g/ml)} \text{]}$$

63%

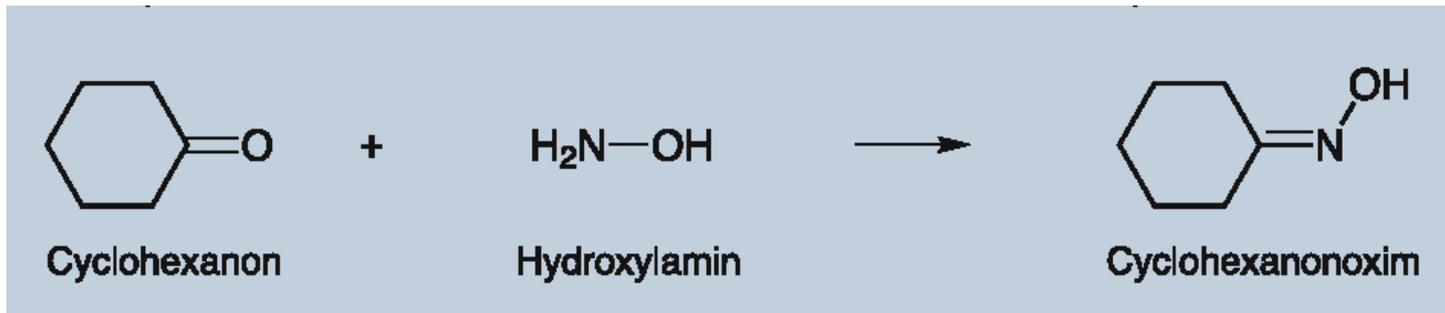
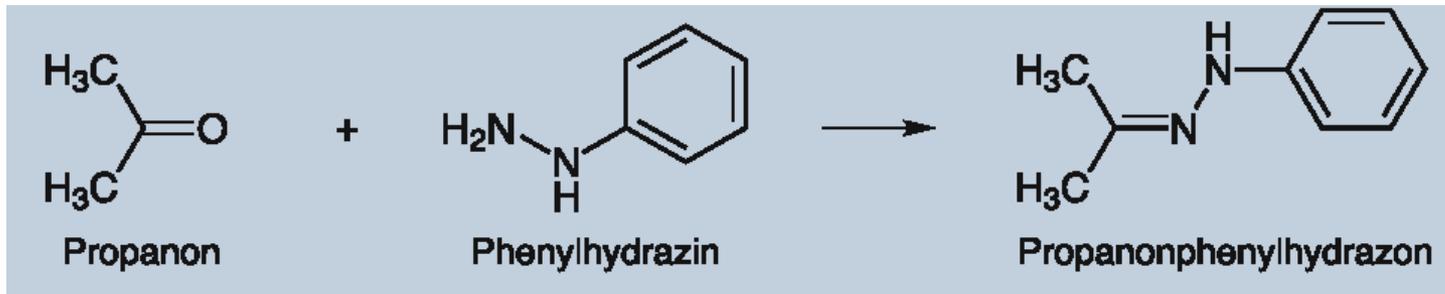
11 Aldehyde und Ketone

Addition von Aminen: Bildung von Iminen

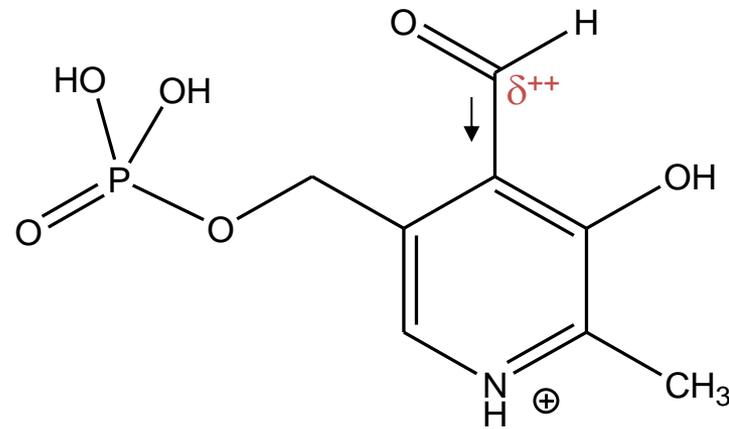


z.B. Retinal, Pyridoxalphosphat

Addition/Eliminierung Carbonylgruppe:

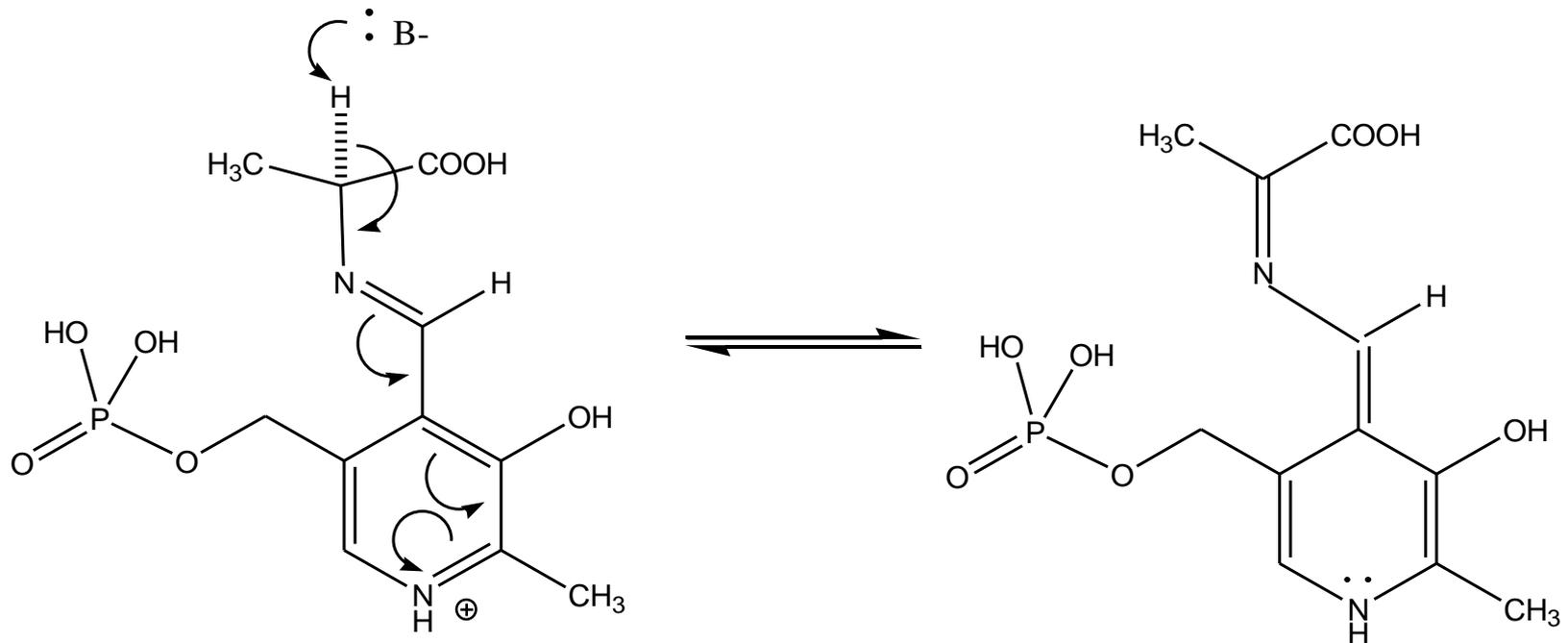


Pyridoxalphosphat: hoch-reaktiver „Superaldehyd“

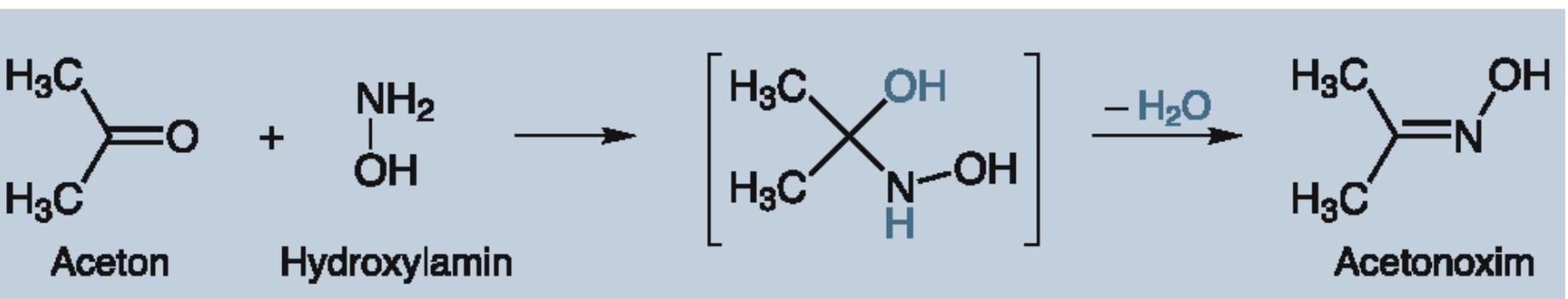
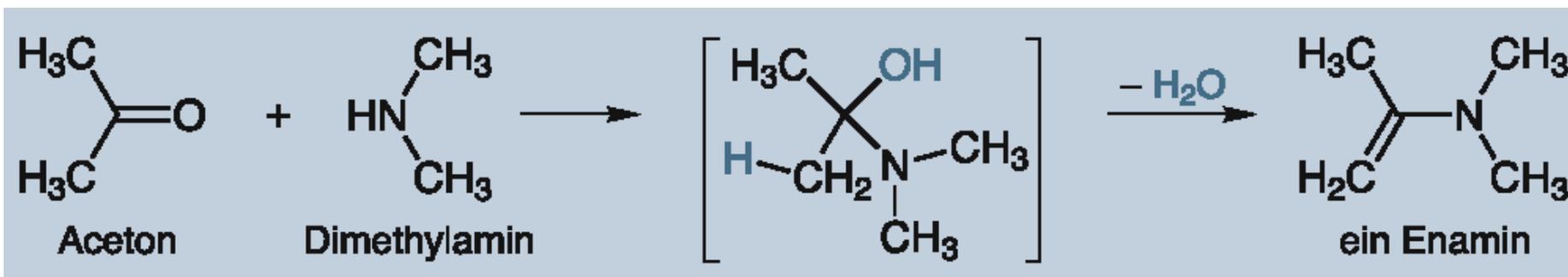
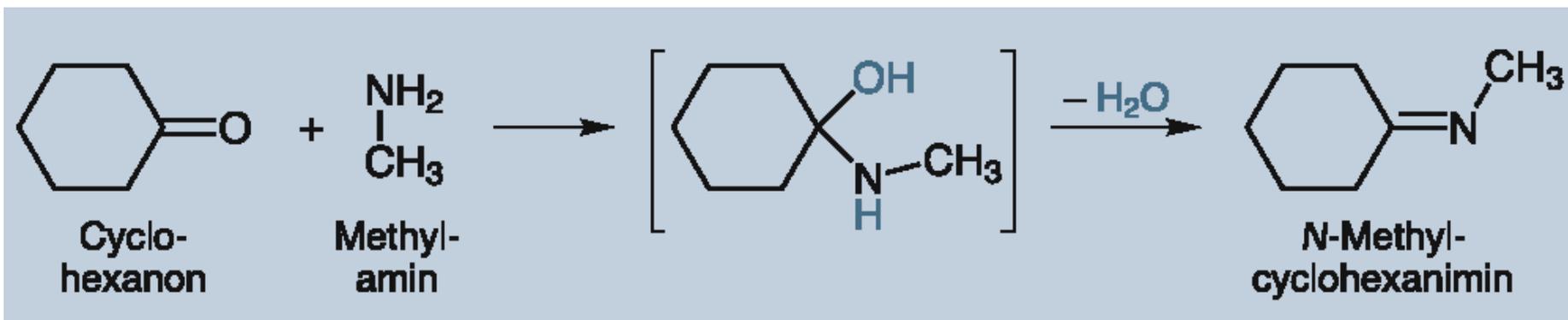


Elektronenzug durch Pyridiniumsystem als „Elektronenpapierkorb“

Reagiert mit Aminosäuren zu Aldimin, das zum Ketimin umprotoniert wird. Hydrolyse Ketimin führt zur Brenztraubensäure (eine α -Ketosäure): Transaminase-Reaktion

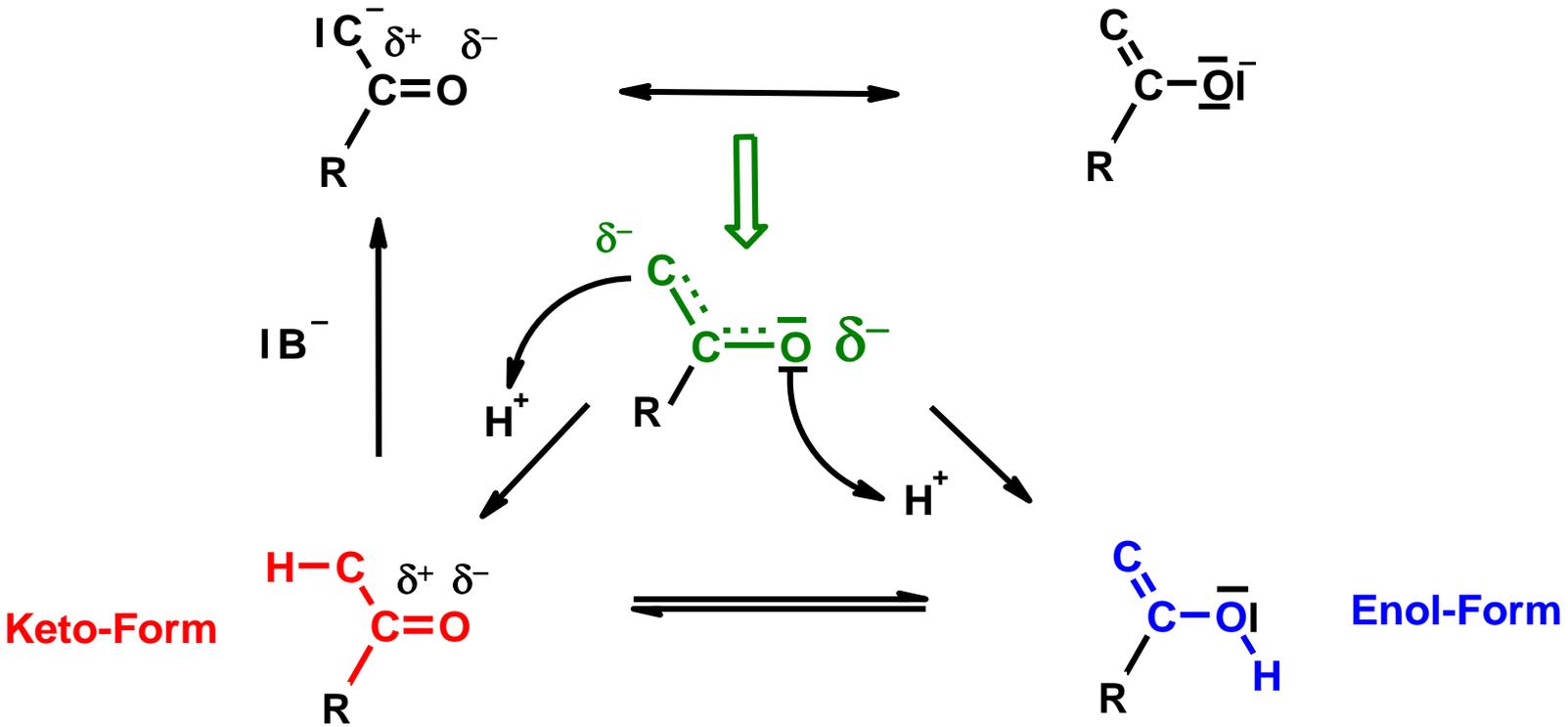


Imine, Enamine, Oxime:



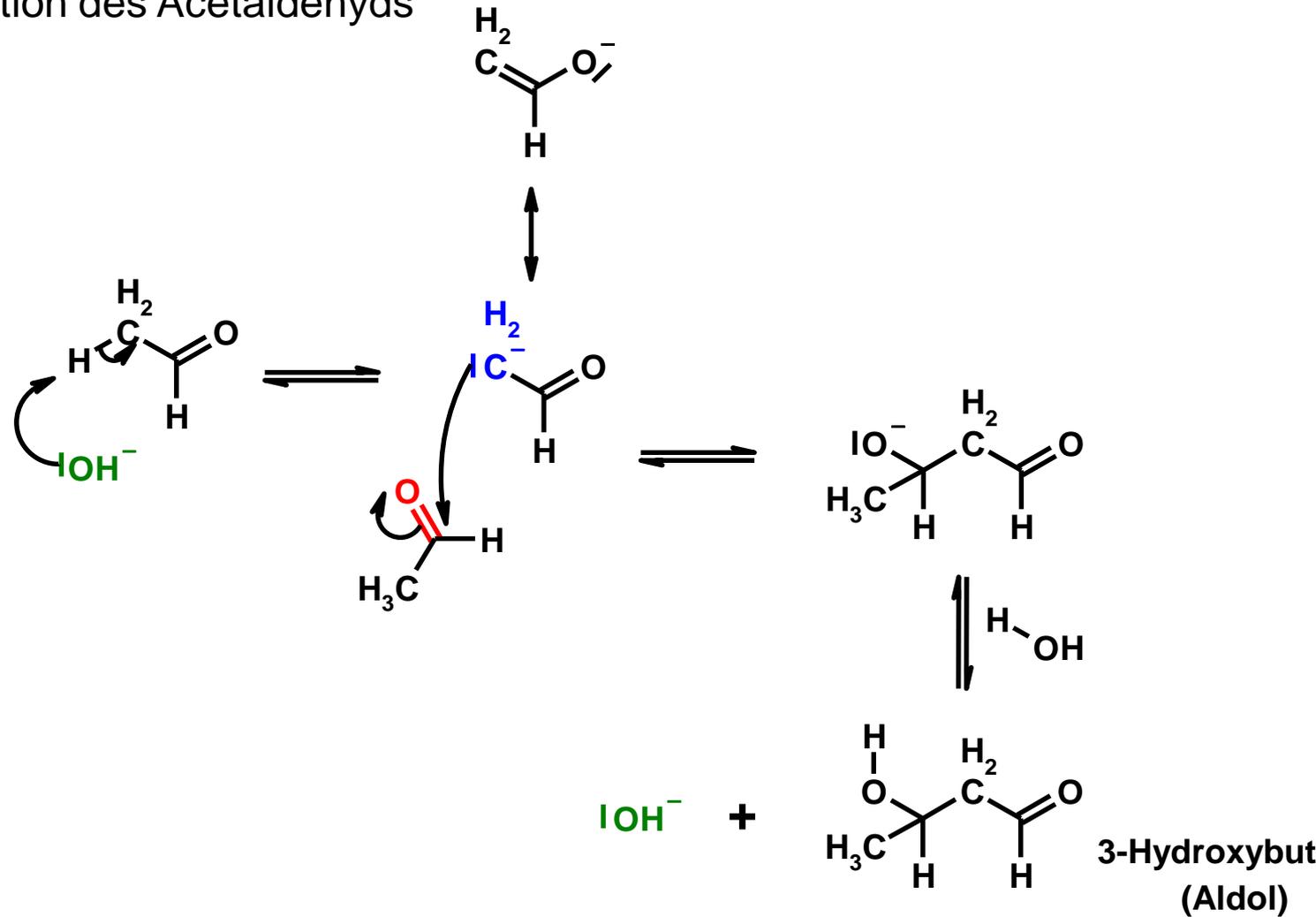
11 Aldehyde und Ketone

Keto-Enol-Tautomerie

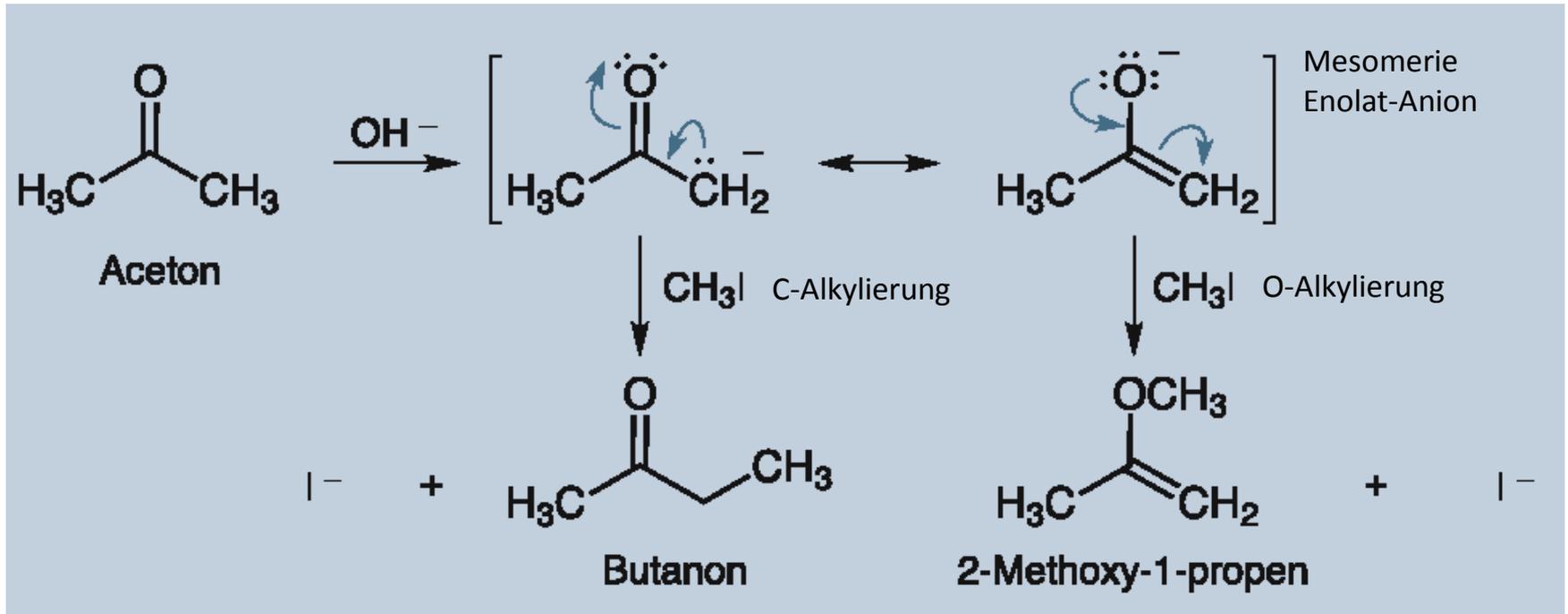


11 Aldehyde und Ketone

Enolate: Aldolreaktion des Acetaldehyds



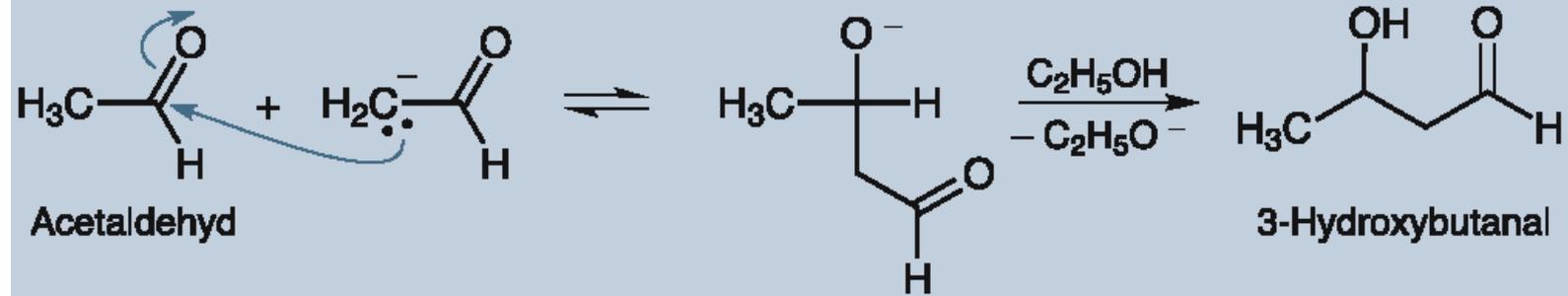
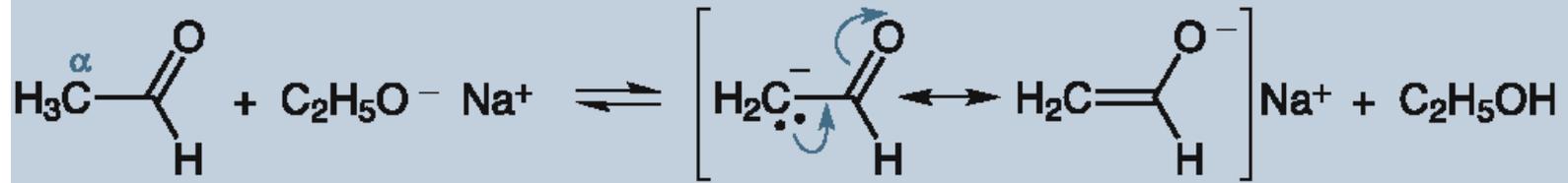
CH-Acidität:



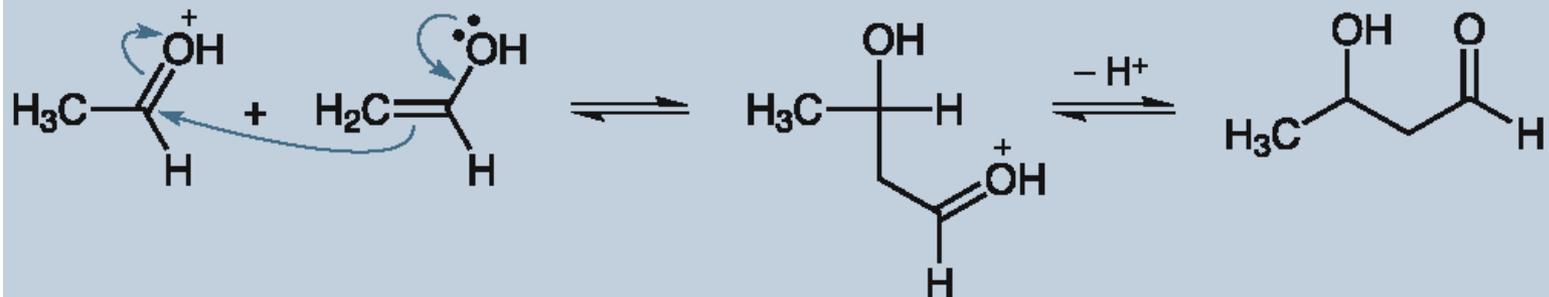
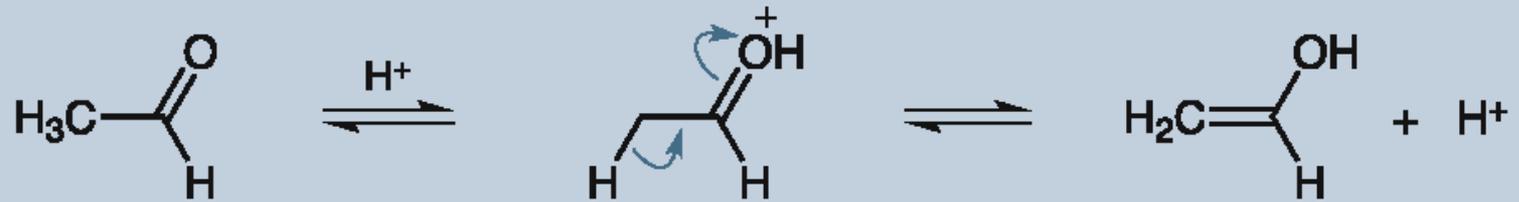
Elektronenzug auf C-H Bindung durch benachbarte CO-Gruppe

Mesomeriestabilisierung Carbanion-Enolat

Aldolreaktion, basenkatalysiert

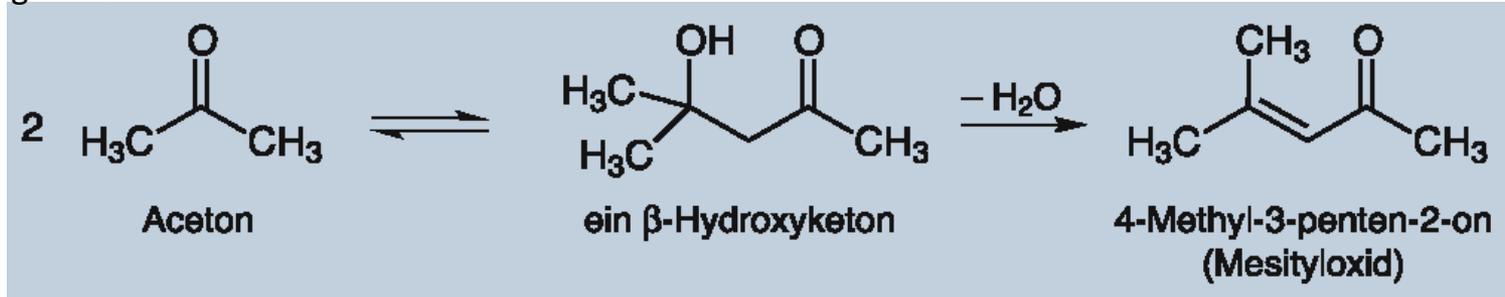


Aldolreaktion, säurekatalysiert

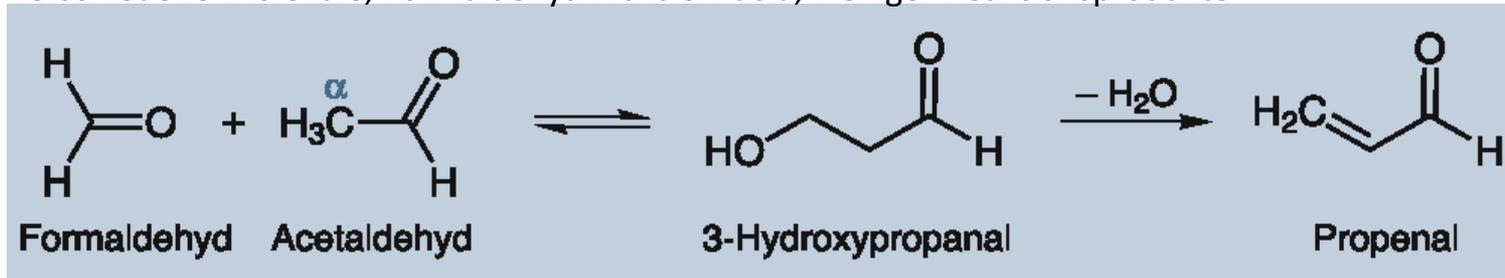


Aldolkondensation:

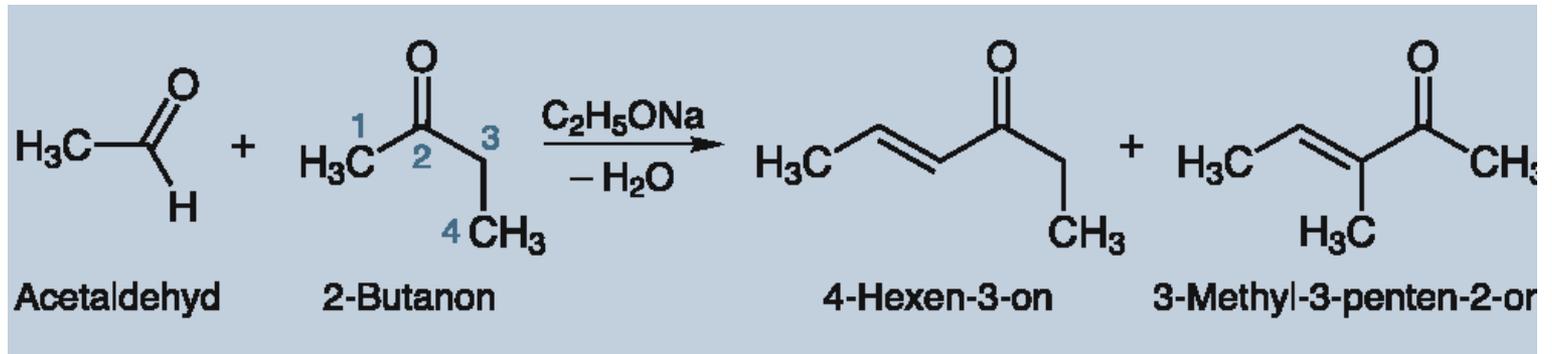
gleiche Moleküle



verschiedene Moleküle, Formaldehyd nicht CH-acid, weniger Reaktionsprodukte



1 und 3 CH-acid, 2 Konstitutionsisomere



als Carbonylkomponente reaktiv