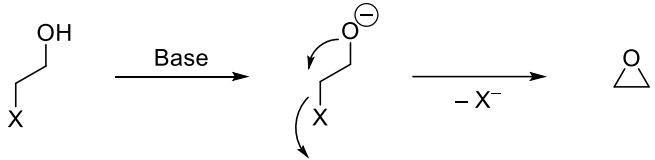
Karlsruher Institut für Technologie

Organische Chemie I – Teil 14

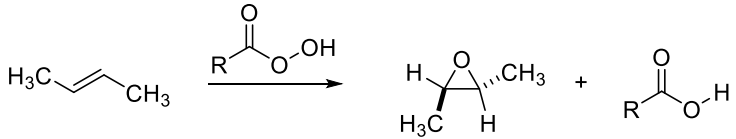
Stefan Bräse
Institut für Organische Chemie & Institut für Biologische und Chemische Systeme

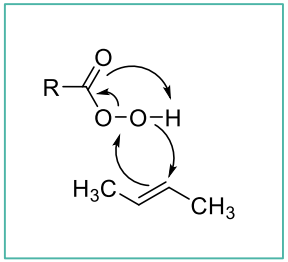
Epoxide

- Cyclische Ether
- Leicht zugänglich
  - Intramolekulare S_N2-Reaktion

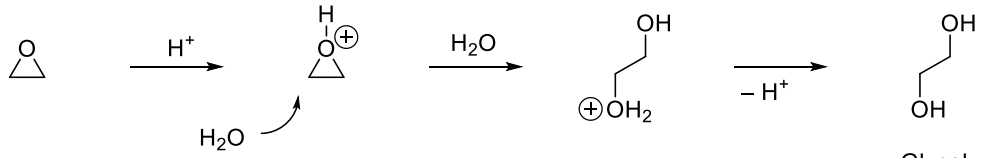


  - aus Alkenen mit Persäuren



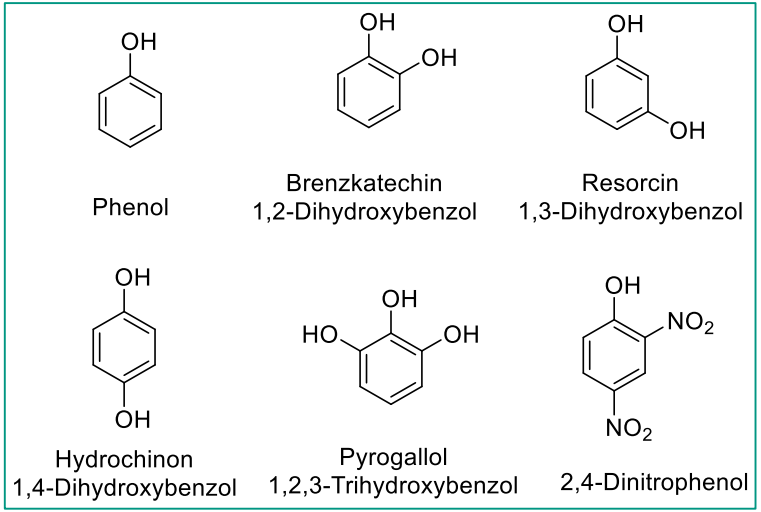


- Nucleophile Öffnung mittels schwacher Lewissäuren
  - Grund: Ringspannung

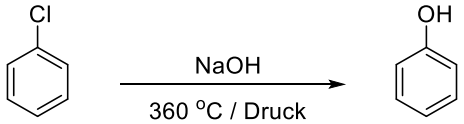


Phenole I

- Aromatische Alkohole
  - Grundkörper: Phenol

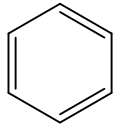


- Synthese über Chlorbenzol mit NaOH bei hohem Druck und hoher Temperatur (nucleophile Aromatensubstitution)

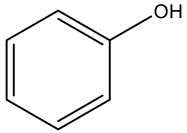


Phenole II

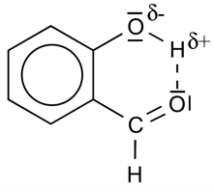
- Eigenschaften
  - Kristallin
  - Charakteristische Gerüche
  - Wasserstoffbrücken
    - Erhöhte Smp und Sdp im Vergleich zu Aromaten
    - Phenol: gute Löslichkeit in Wasser
    - Intramolekulare Wasserstoffbrücken möglich → ortho-Substitution



Smp: 6 °C
Sdp: 80 °C



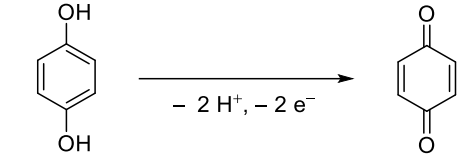
Smp: 41 °C
Sdp: 182 °C



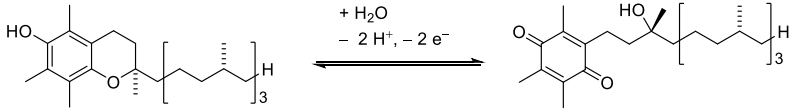
Chelat des Hydroxybenzaldehyds

Phenole III

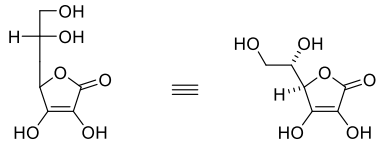
- 1,4-Dihydroxybenzol (Hydrochinon) zum Chinon oxidiert
- Natur:
  - Beseitigung von Radikalen
  - Substrat: Vitamin E/ Tocopherol



Hydrochinon Chinon



Vitamin E, Tocopherol

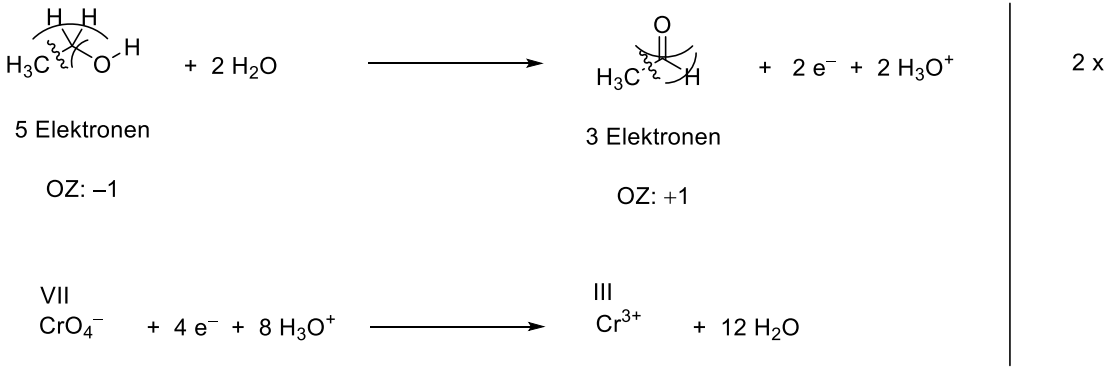


Vitamin C, Ascorbinsäure

- Redox-Reaktion: reversibel
- Tocopherol kann mit Ascorbinsäure regeneriert werden

Allgemeines I

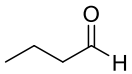
- Carbonyl-Verbindungen
- Entstehen durch Oxidation von Alkoholen



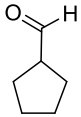
Allgemeines II

- Aldehyde entstehen aus primären Alkoholen
  - RHC=O
- Ketone entstehen aus sekundären Alkoholen
  - RR‘C=O
- Nomenklatur:
  - Alkylstamm
  - Aldehyde: Endung –al oder –carbaldehyd
  - Ketone: Endung –on
  - Gebräuchliche Trivialnamen:

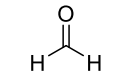
Butanon



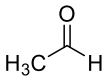
Butanal



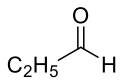
Cyclopentancarbaldehyd



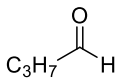
Formaldehyd



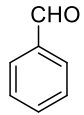
Acetaldehyd



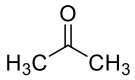
Propionaldehyd
Propanal



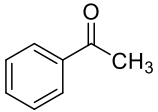
Butyraldehyd
Butanal



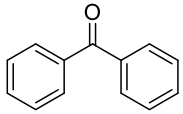
Benzaldehyd



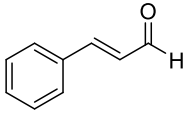
Aceton



Acetophenon



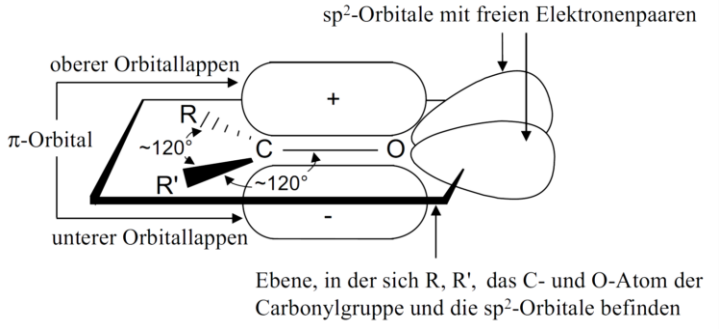
Benzophenon

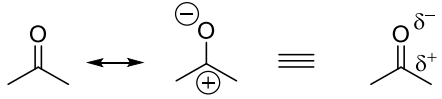


Zimtaldehyd

Allgemeines III

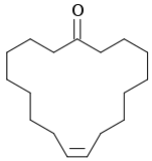
- Hybridisierung



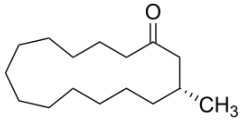


Mesomere Grenzformeln

- Mittelgroße cyclische Ketone sind typische Parfümgrundstoffe



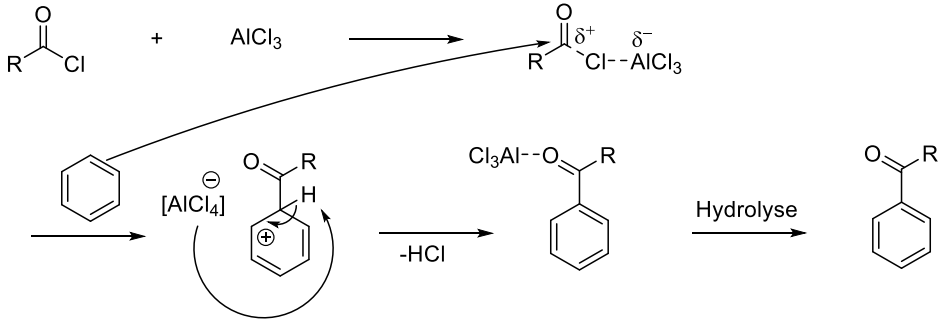
Zibeton



Muscon

Synthese I

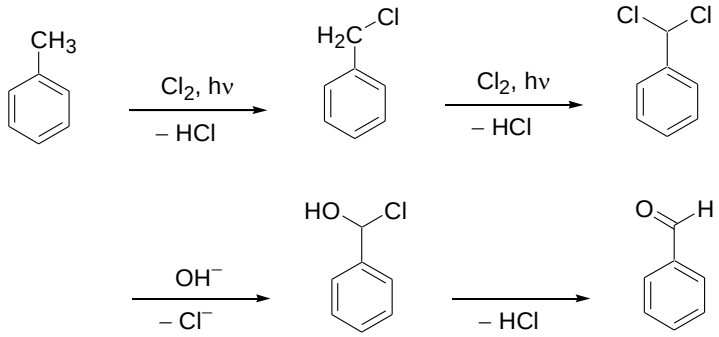
- Oxidation von Alkoholen
- Selektive Reduktion von Carbonsäure-Derivaten
  - Schwer zu kontrollieren
- Ozonolyse
- Elektrophile Addition von Wasser an Alkine
  - Enole → Tautomere: Ketone
- Elektrophile Acylierung (Formylierung) von Aromaten → Aromatische Ketone (und Aldehyde)



Friedel-Crafts Acylierung

Synthese II

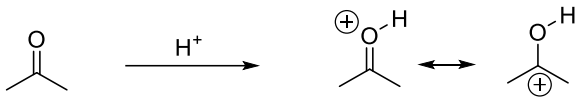
- Benzaldehyd-Synthese:
  - Radikalische Chlorierung von Toluol:



Wichtige Regeln:
KKK: Kälte, Katalysator → Kern
SSS: Sonne, Siedehitze → Seitenkette

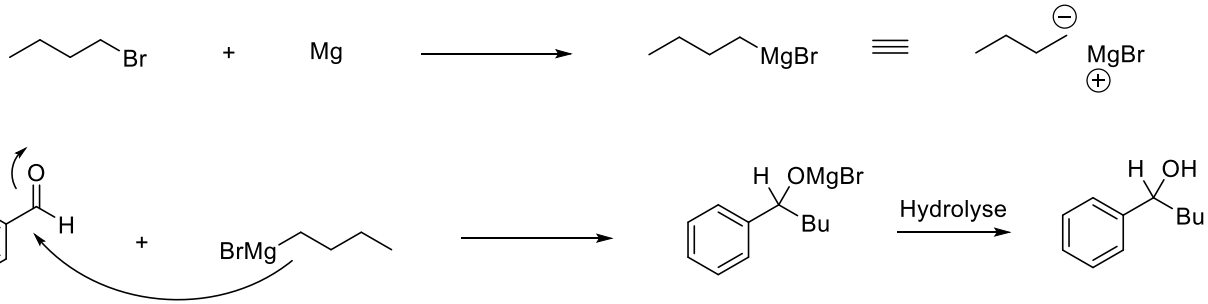
Reaktionen I

- (Lewis-)Säureempfindlich:



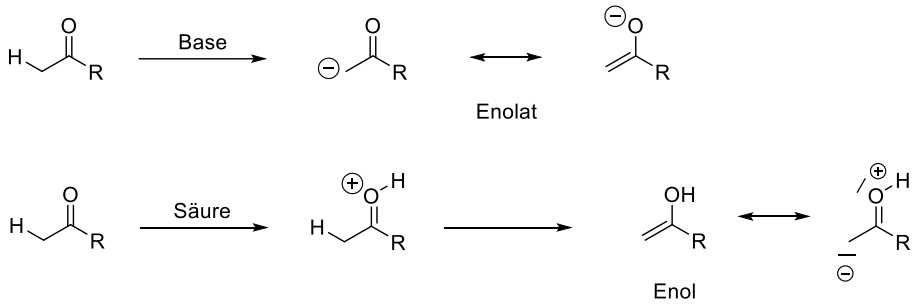
Erhöhung des elektrophilen Charakters

- Nukleophiler Angriff:
  - z.B. Metallorganische Verbindungen, Grignard Reaktion



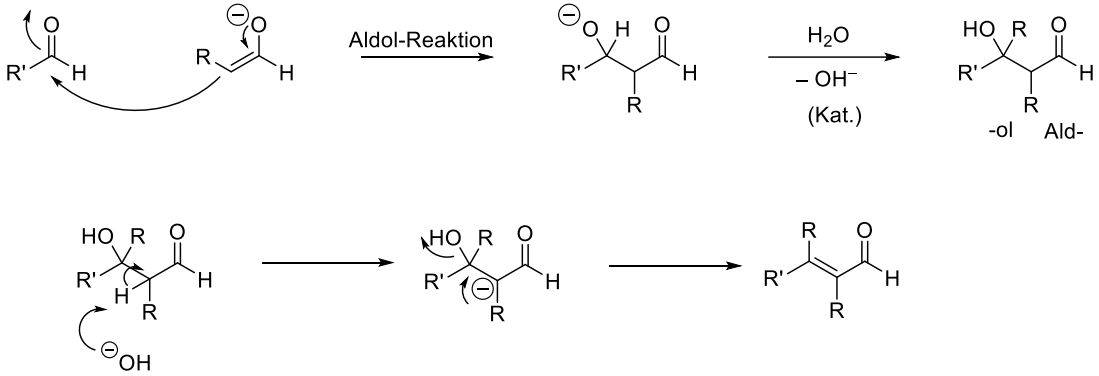
Reaktionen II

- Carbonyl-Verbindungen in α-Position acide
  - Deprotonierung Säure- oder Basen-induziert → Enole / Enolate, als Nucleophile



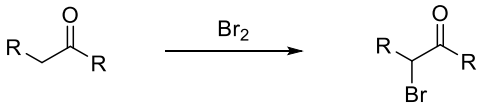
Reaktionen III

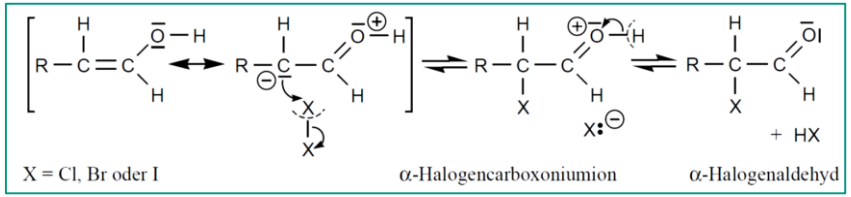
- Aldol-Reaktionen oder Aldol-Kondensation
  - Konjugierte Carbonyl-Verbindungen (α,β-ungesättigte Carbonyle / Michaelsysteme) besonders stabil
  - Kondensationen: Reaktion zweier oder mehrerer Komponenten unter Freisetzung kleiner Moleküle, z.B. Wasser



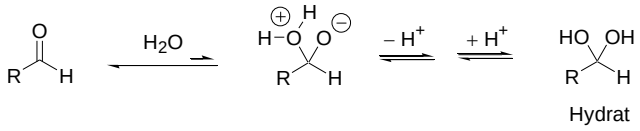
Reaktionen IV

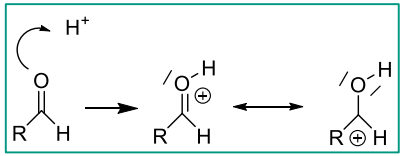
- α-Halogenierung

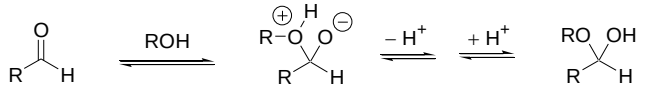


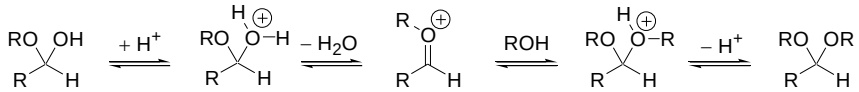


- Ausbildung von Hydraten und (Halb-)Acetalen

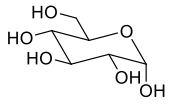


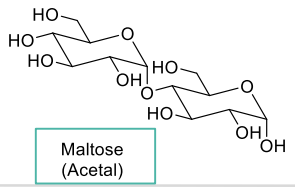






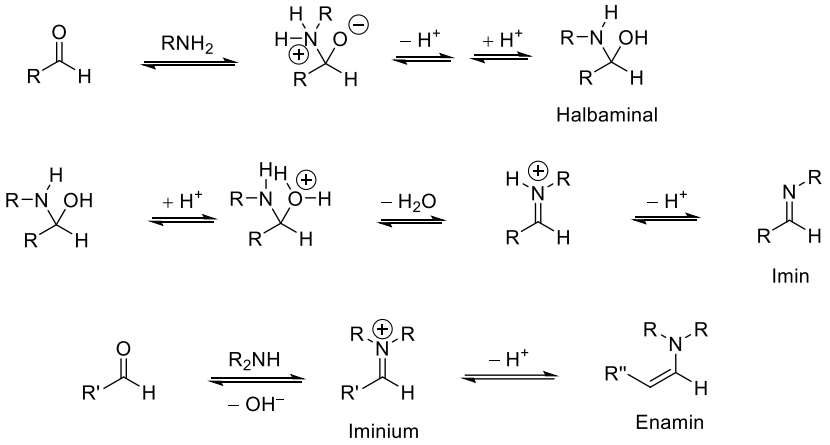
z.B. zur Synthese von:



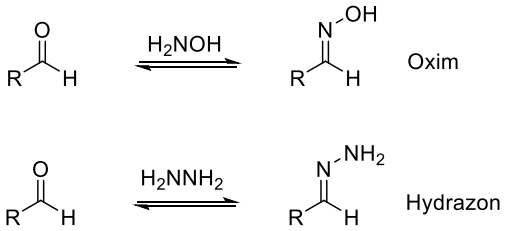


Reaktionen V

- Mit Aminen → Halbaminale → Imine

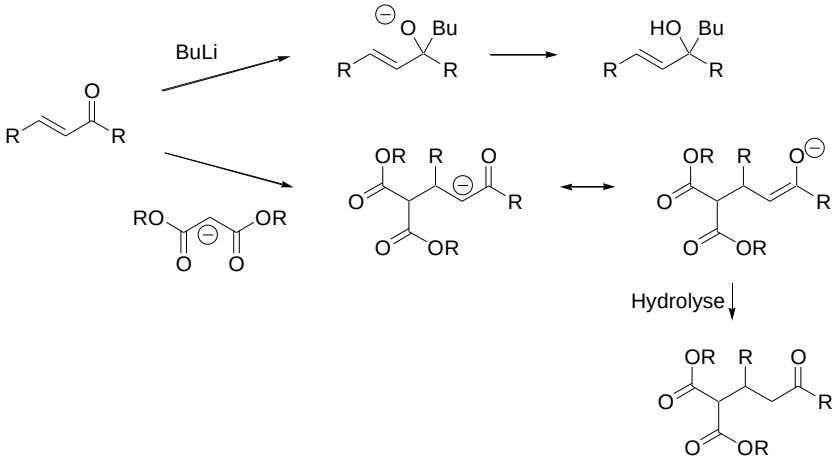


Reaktionen VI



- Synthese von Hydrazonen und Oximen

- An α,β-ungesättigten Carbonyl-Verbindungen konjugierter nucleophiler Angriff



Fragen?