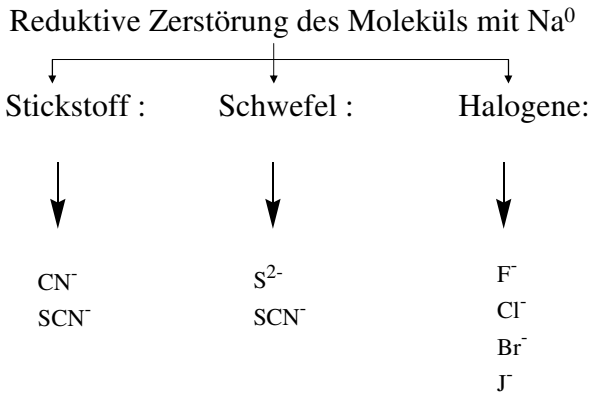
Farbreaktionen

- 1. elementaranalytische Nachweise
- 2. Nachweise funktioneller Gruppen
- 3. Nachweise bestimmter Arznei-stoffklassen

1.1 Lassaigne-Aufschluß



1.1 Lassaigne-Aufschluß

CN^-	S^{2-}	F^-, Cl^-, Br^-, J^-
SCN^-	SCN^-	

CN^-

$$Fe^{2+} + 6\ CN^- \longrightarrow [Fe(CN)_6]^{4-}$$

$$4\ Fe^{3+} + 3\ [Fe(CN)_6]^{4-} \xrightarrow{HCl} Fe_4[Fe(CN)_6]_3 \downarrow$$

Berliner Blau

SCN^-

$$Fe^{3+} + 3\ SCN^- \xrightarrow{HCl} Fe(SCN)_3$$

tiefrot

Beachte :

$$Fe(SCN)_3 + 6\ F^- \longrightarrow [FeF_6]^{3-} + 3\ SCN^-$$

1.1 Lassaigne-Aufschluß

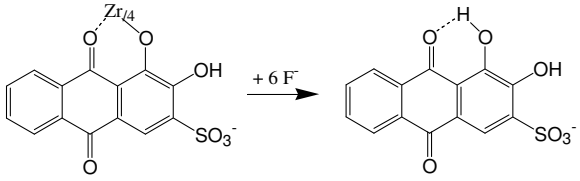
CN^-	S^{2-}	F^-, Cl^-, Br^-, J^-
SCN^-	SCN^-	

S^{2-}

$$Na_2S + Na_2[Fe(CN)_5NO] \xrightarrow{OH^-} Na_4[Fe(CN)_5NOS]$$ violett

$$Na_2S + Pb(CH_3COO)_2 \xrightarrow{HOAc} PbS \downarrow + CH_3COONa$$ schwarz

F^-



Zirkonium - Alizarin- S- Farblack

Alizarin S

$+ [ZrF_6]^{2-}$

1.1 Lassaigne-Aufschluß

CN^-	S^{2-}	F^-, Cl^-, Br^-, J^-
SCN^-	SCN^-	

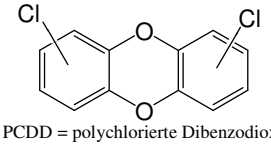
Cl^-, Br^-, J^- :

- Nachweis als schwerlösliche Silbersalze, (Fluorid bildet ein lösliches Silbersalz!)
- mit HNO_3 angesäuerte Lösung aufkochen, um H_2S, HCN und HSCN zu vertreiben, die auch schwerlösliche Silbersalze bilden !
- Silbernitratfällung auch immer mit der Ursubstanz durchführen (Hydrochlorid-Arzneistoffe!)

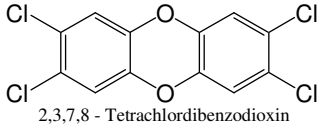
1.2 Beilstein- Probe

Halogene

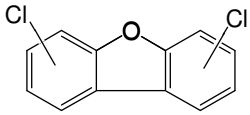
Cu-Draht, Cu-Cent + Halogen anorganisch oder organisch gebunden → (nichtleuchtende Bunsenbrennerflamme) grüne Flamme der verdampfenden Kupferhalogenide



PCDD = polychlorierte Dibenzodioxine



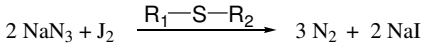
2,3,7,8 - Tetrachlordibenzodioxin



PCDF = polychlorierte Dibenzofurane

1.3 Schwefelnachweise

Jod - Azid- Reaktion



Nachweis von Schwefel als Sulfat

Oxidation mit H_2O_2 / Fe^{3+} zu Sulfat;
Fällung des Sulfat als schwerlösliches $BaSO_4$

2. Nachweise funktioneller Gruppen

- 2.1 Nachweise stickstoffhaltiger Verbindungen
- 2.2 Nachweise sauerstoffhaltiger Verbindungen
- 2.3 Nachweise weiterer Struktur-elemente

2.1 Dragendorff- Reagenz

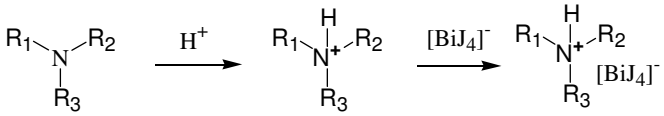
basischer Stickstoff

$BiONO_3$ / Eisessig / H_2O + KI / H_2O

↓

Kaliumtetraiodobismutat

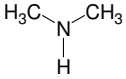
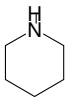
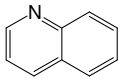
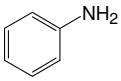
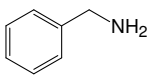
$K[BiJ_4]$



2.1 Dragendorff- Reagenz

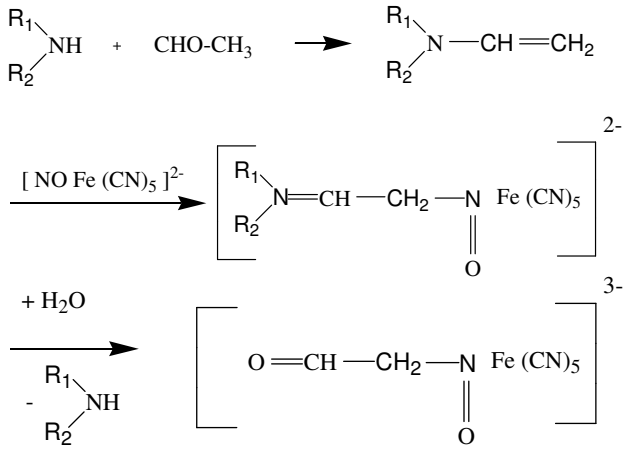
basischer Stickstoff

pks-Werte

Ammoniak	NH_3	9,2
Dimethylamin		10,6
Piperidin		11,2
Pyridin		5,2
Chinolin		4,8
Anilin		4,6
Benzylamin		9,4

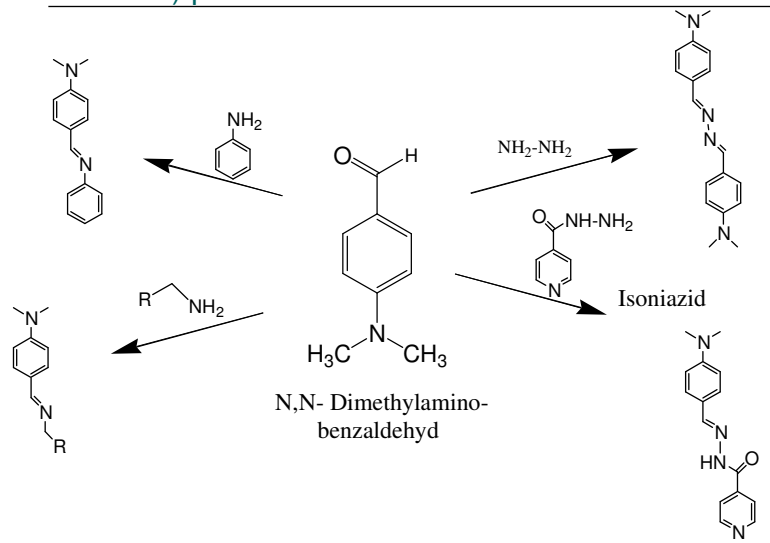
2.1 Analoge Simon-Awe-Reaktion

Sekundäre Amine



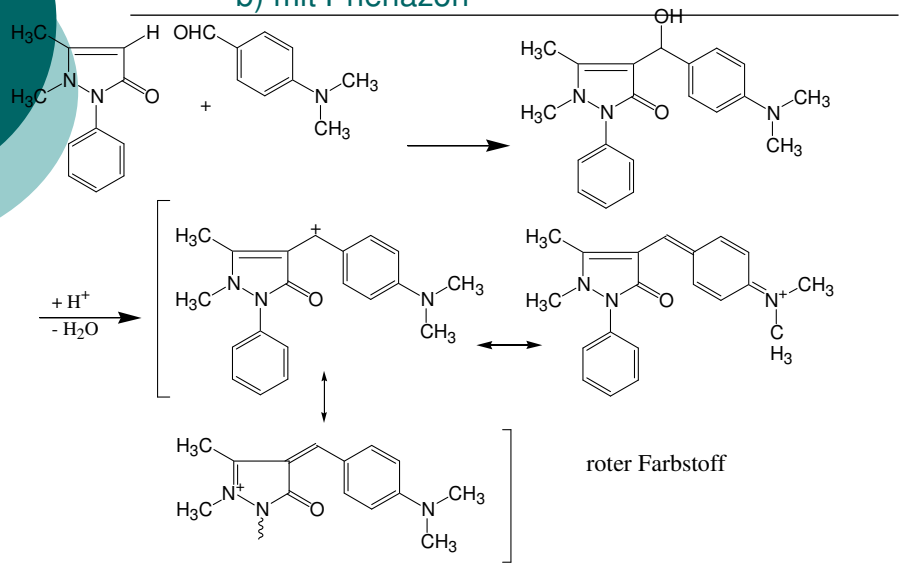
2.1 Ehrlich´s Reagenz

a) primäre Amine



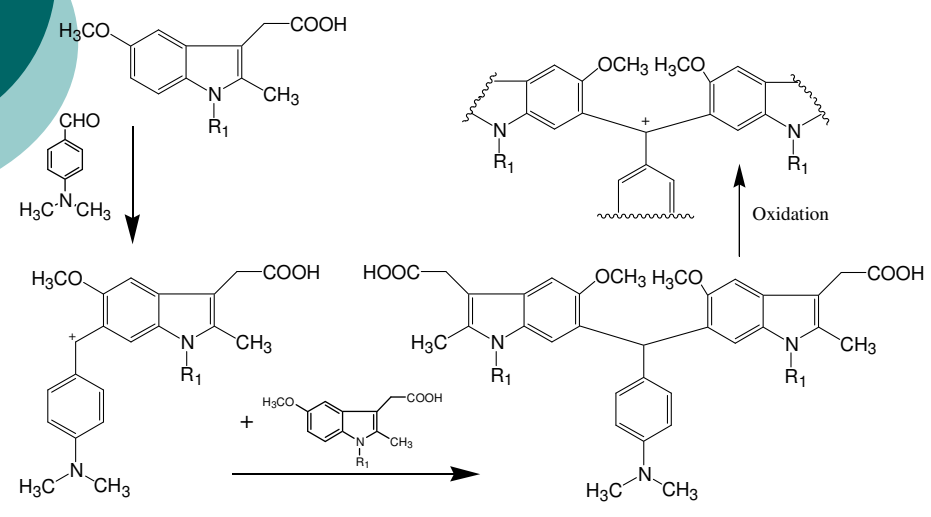
2.1 Ehrlich´s Reagenz

b) mit Phenazon



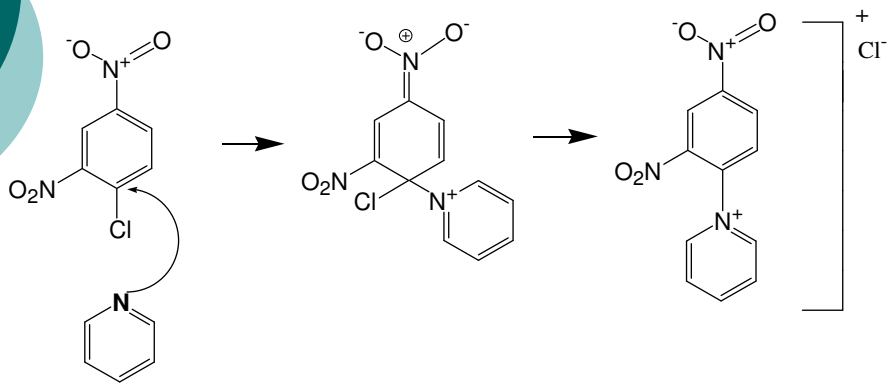
2.1 Ehrlich´s Reagenz

c) mit Indometacin



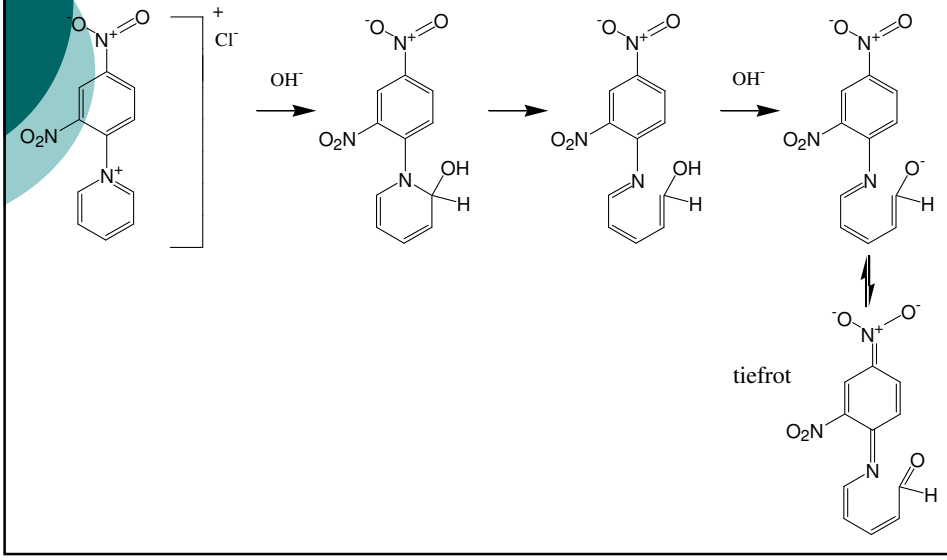
2.1 Zincke-König-Spaltung

Pyridinderivate



2.1 Zincke-König-Spaltung

Pyridinderivate



2.1 Diazotierung

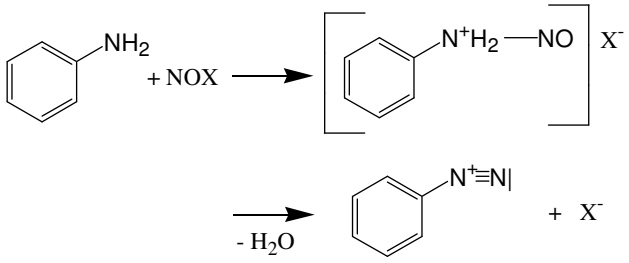
primäre aromatische Amine

A. Diazotierung

$NO_2^- + H_3O^+ \rightarrow HNO_2 + H_2O$

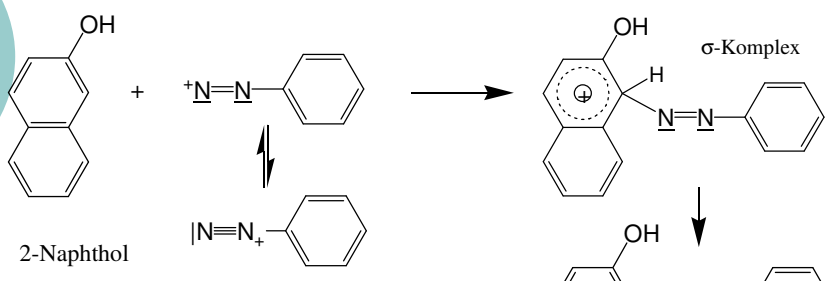
$HNO_2 + H_3O^+ + X^- \rightarrow NOX + 2\ H_2O$

X = Br, Cl



2.1 Diazotierung

primäre aromatische Amine

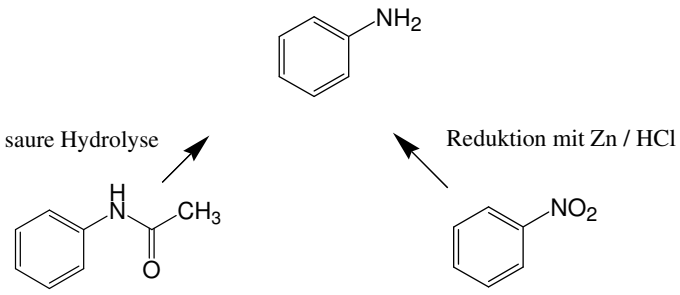


2-Naphthol

Alternativ: Bratton-Marshall Reagenz im schwach sauren Milieu

2.1 Diazotierung

indirekt



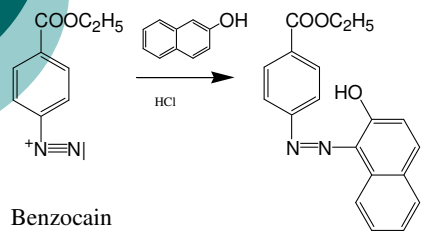
Amide

Nitroverbindungen

2.1 Diazotierung

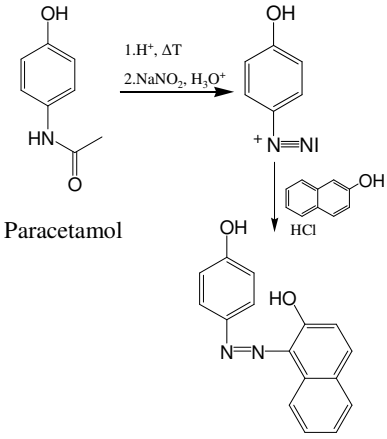
direkt/indirekt

direkt:



Benzocain

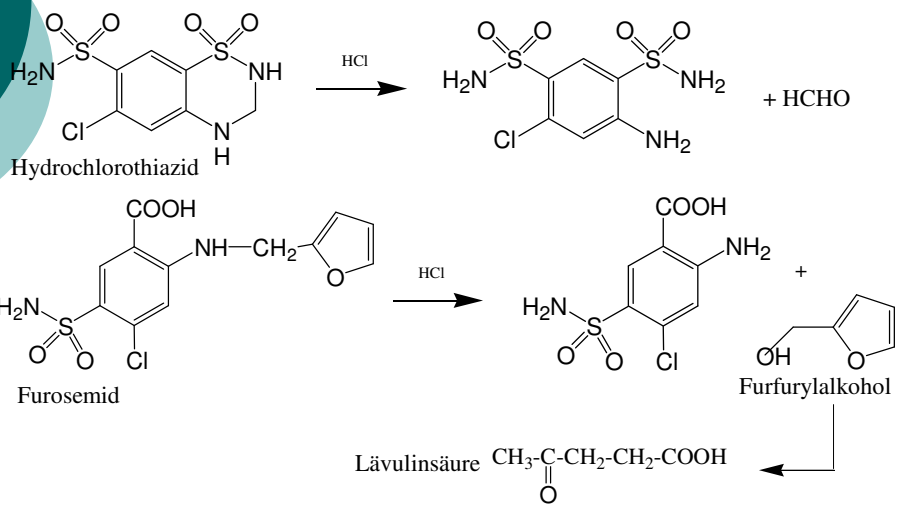
indirekt:



Paracetamol

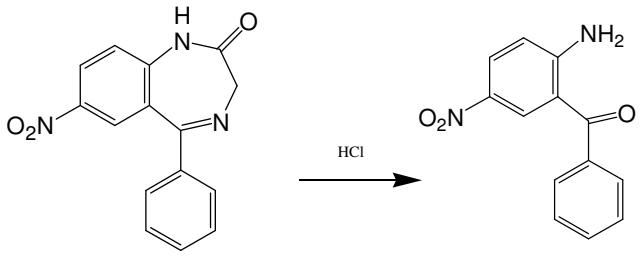
2.1 Diazotierung

direkt/indirekt



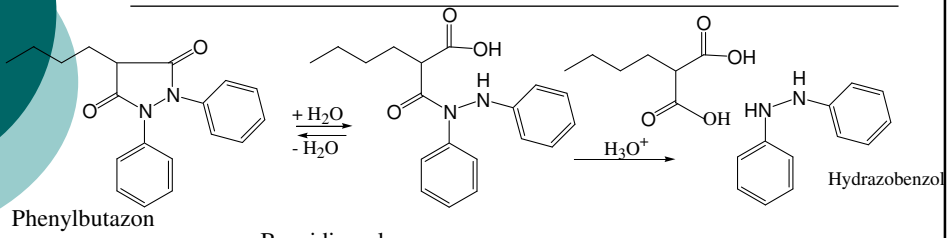
2.1 Diazotierung

direkt/indirekt



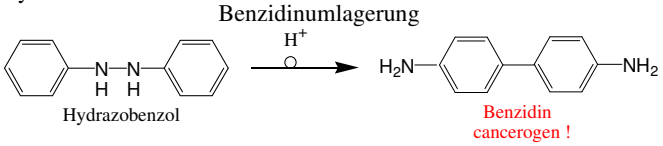
2.1 Diazotierung

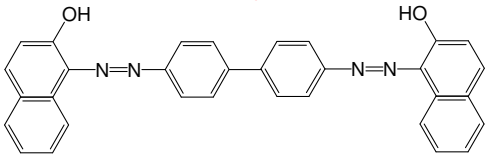
direkt/indirekt



Phenylbutazon

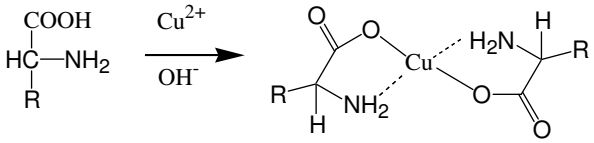
Benzidinumlagerung

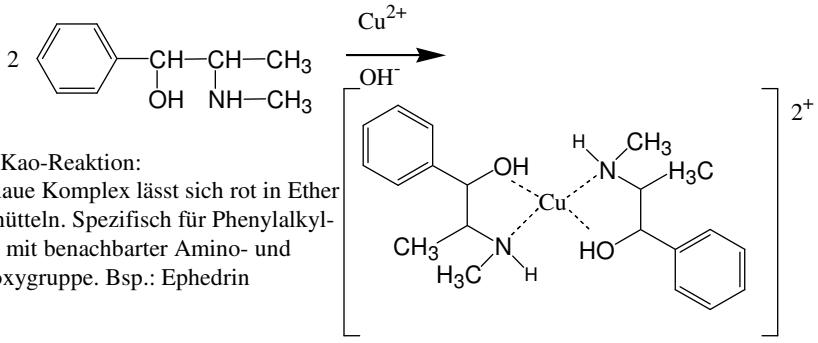




2.1/2.2 Farbkomplex mit $CuSO_4$

α-Aminosäuren, Ethanolamine

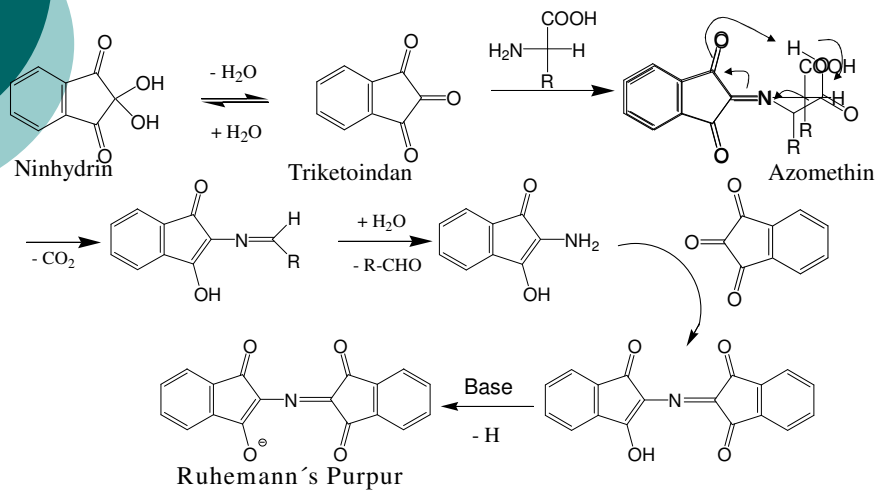




Chen-Kao-Reaktion:
Der blaue Komplex lässt sich rot in Ether ausschütteln. Spezifisch für Phenylalkyl-amine mit benachbarter Amino- und Hydroxygruppe. Bsp.: Ephedrin

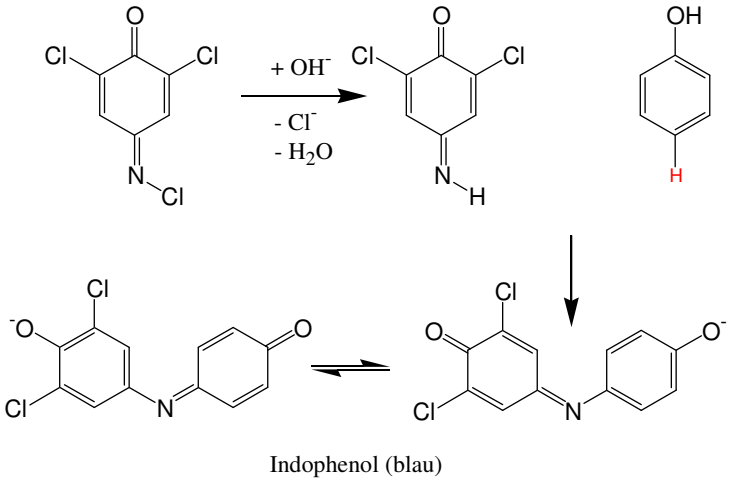
2.1/2.2 Ninhydrin - Reaktion

α-Aminosäuren



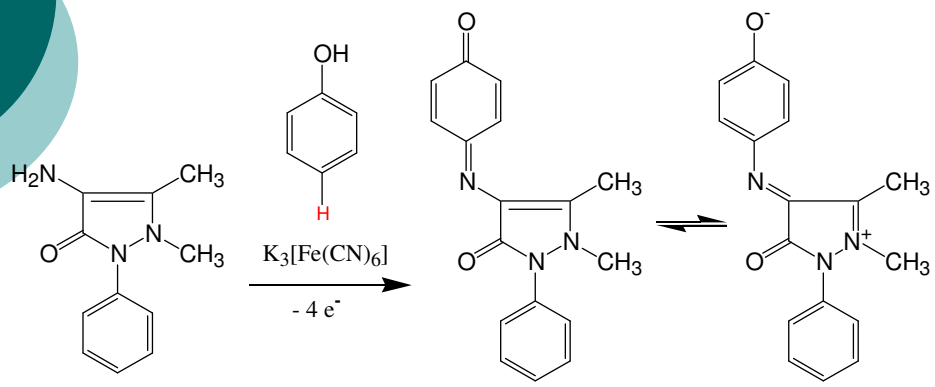
2.2 Gibb´s Reagenz

Phenole



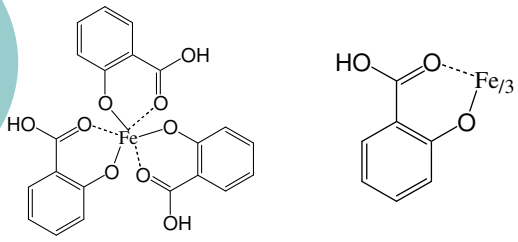
2.2 Emerson-Reaktion

Phenole

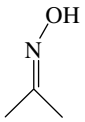


2.2 Eisen (III)-chlorid

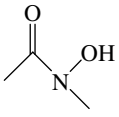
Phenole, Enole...

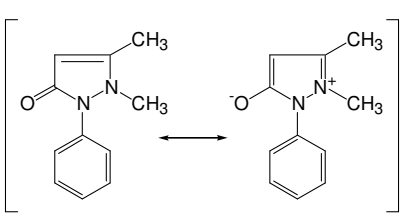


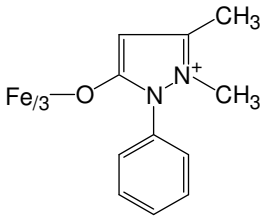
Oxime



Hydroxamsäuren

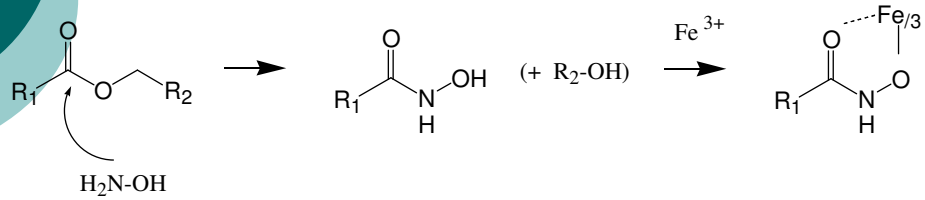






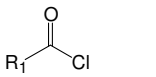
2.2 Hydroxamsäurereaktion

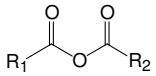
Carbonsäuren & Derivate



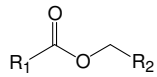
2.2 Hydroxamsäurereaktion

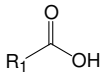
Carbonsäuren & Derivate

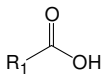


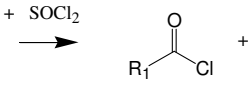


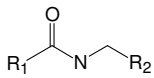
geben Hydrazamsäurereaktion









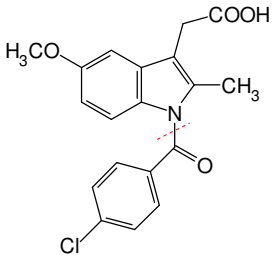


Reaktion nur in Ausnahmefällen !

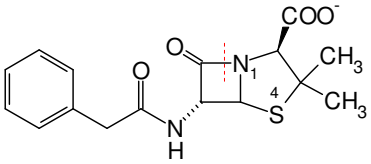
2.2 Hydroxamsäurereaktion

Carbonsäuren & Derivate

Beispiele für Amide / Lactame , die reaktiv genug sind :



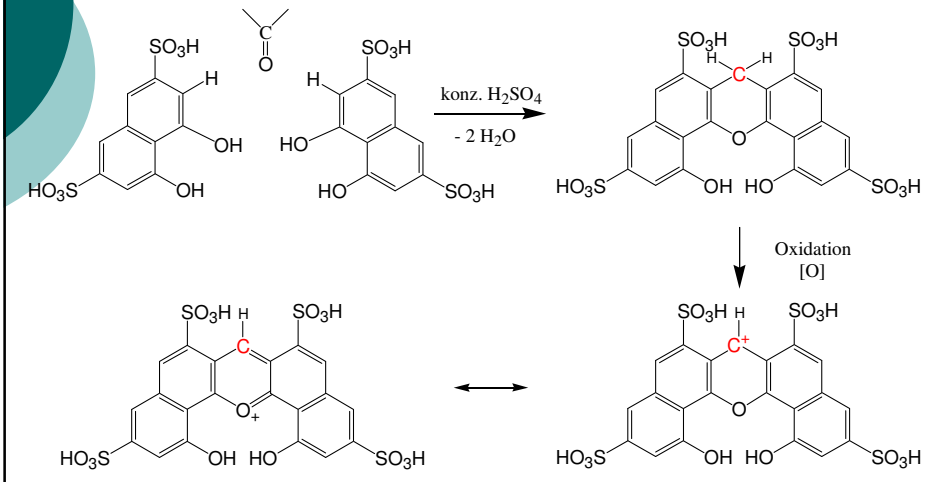
Indometacin



Benzylpenicillin

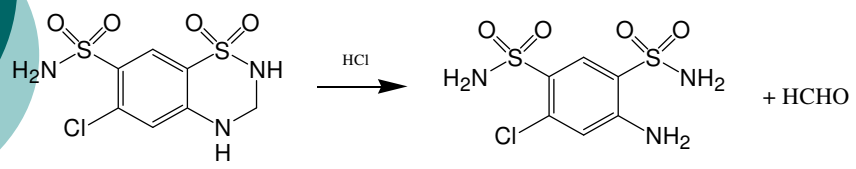
2.2 Chromotropsäure-Reaktion

freigesetzter Formaldehyd

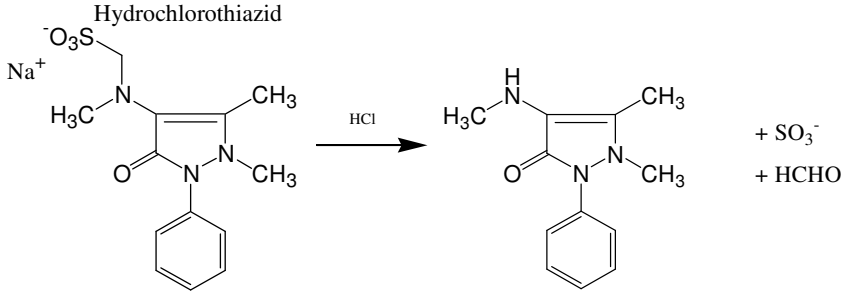


2.2 Chromotropsäure-Reaktion

freigesetzter Formaldehyd



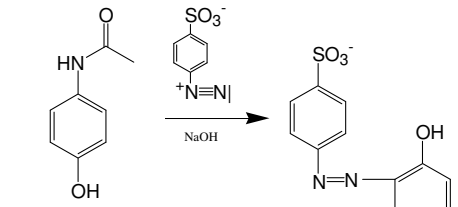
Hydrochlorothiazid



Metamizol-Na

2.3 Kupplung mit diazotierter Sulfanilsäure kupplungsfähige Aromaten

z.B. Phenole oder Imidazole

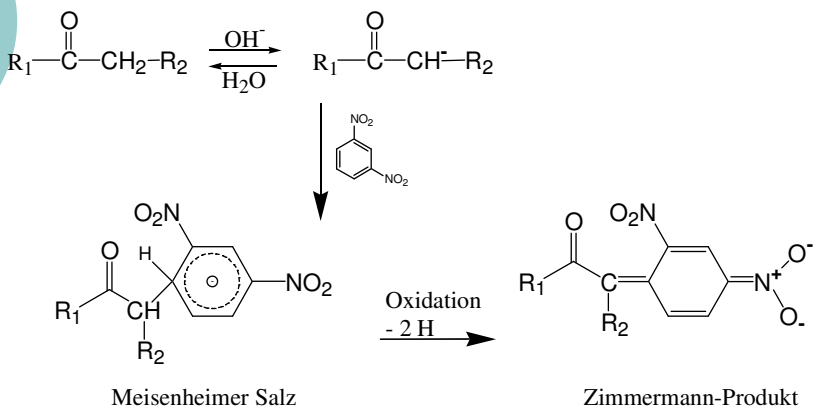


Paracetamol

rot-orange

2.3 Zimmermann - Reaktion

aktive Methylengruppen



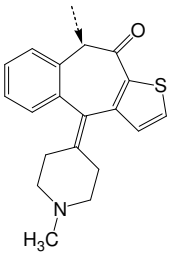
Meisenheimer Salz

Zimmermann-Produkt

2.3 Zimmermann - Reaktion

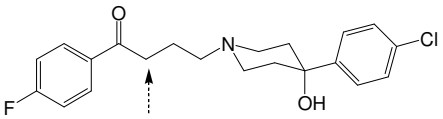
aktive Methylengruppen

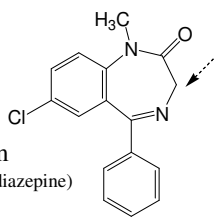
Ketotifen:



Haloperidol:

auch Zimmermann-Verbindung





Diazepam

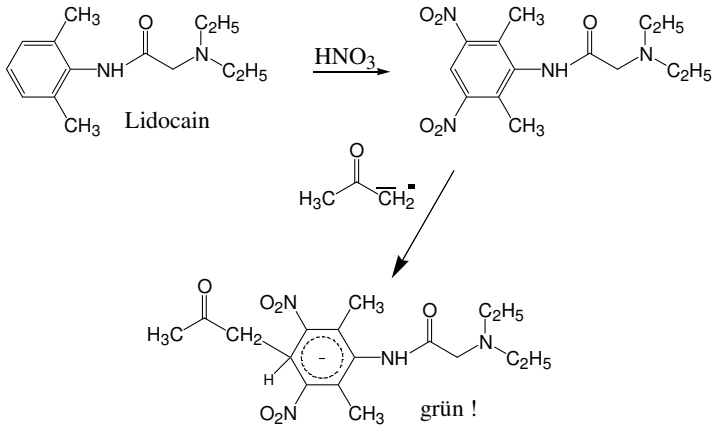
(u.a. Benzodiazepine)

nur bis zum

Meisenheimer-Salz

2.3 Vitali - Morin

a) nitrierbare Aromaten

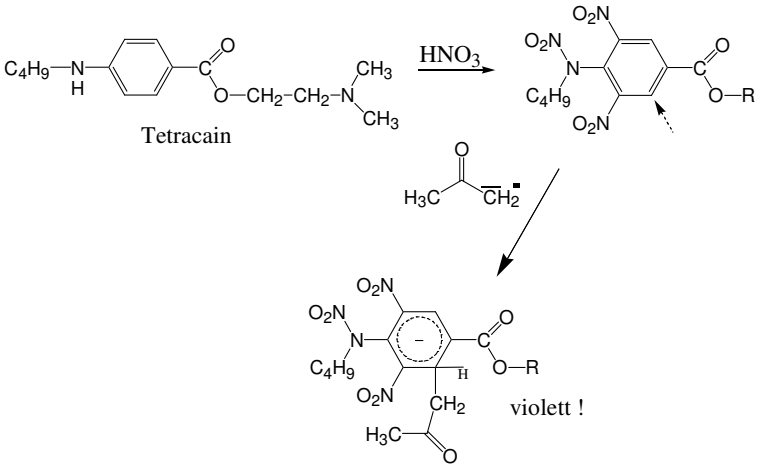


Lidocain

grün !

2.3 Vitali - Morin

a) nitrierbare Aromaten

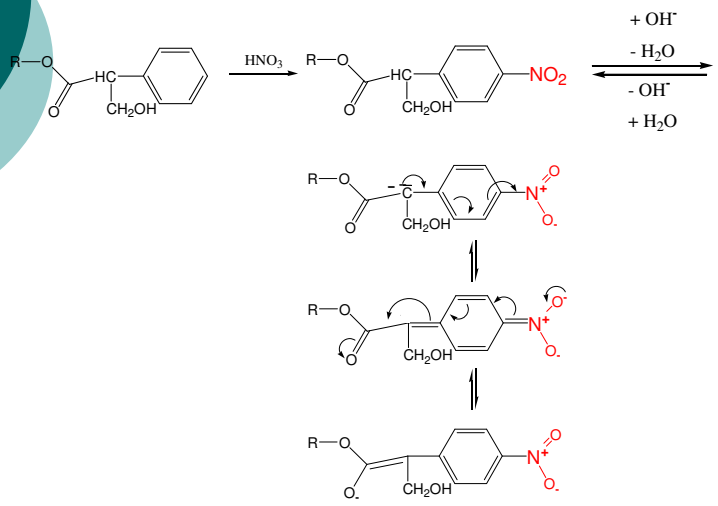


Tetracain

violett !

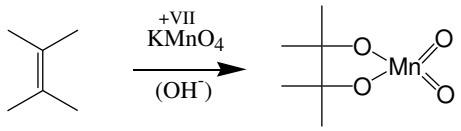
2.3 Vitali – Variante (ohne Aceton)

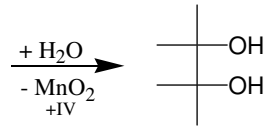
b) Tropasäureester



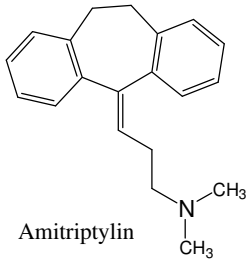
2.3 Bayersche-Probe

olefinische Doppelbindungen





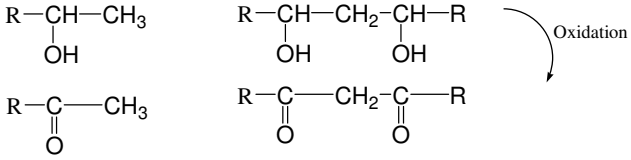
Entfärbung von $KMnO_4$
auch durch Ascorbinsäure



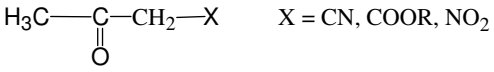
Amitriptylin

2.3 Iodoform – Probe

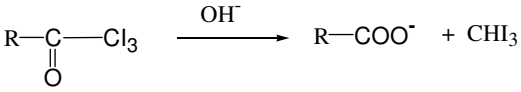
Nachweis von…



Keine Reaktion ergeben :



Mechanismus:
1. Halogenierung
2. Hydrolyse : Es entsteht Jodoform und die um ein C-Atom verkürzte Säure

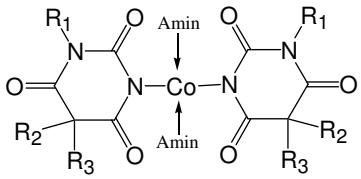


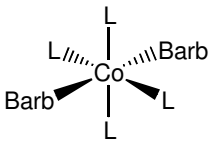
3. Nachweise bestimmter Arznei-stoffklassen

- 1. Barbiturate
- 2. Xanthine
- 3. Morphin-Derivate
- 4. Steriode
- 5. Endiole (Ascorbinsäure)
- 6. Papaverin

3.1 Zwikker-Reaktion

Barbiturate





mit Amin (Piperidin) :

tetraedrischer Komplex
höhere Empfindlichkeit da
10 fach höhere Absorption
bei 560-570 nm

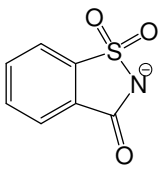
ohne Aminzusatz :

oktaedrischer Komplex
Barb = Barbiturat-Anion
L = Solvens, z.B. MeOH

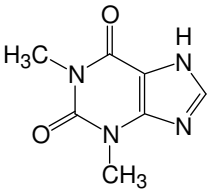
3.1 Zwikker-Reaktion

Barbiturate

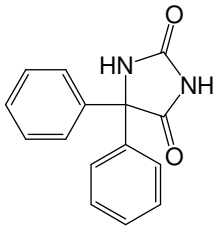
Beispiele für ebenfalls positiv reagierende Stoffe:



Saccharin-Na



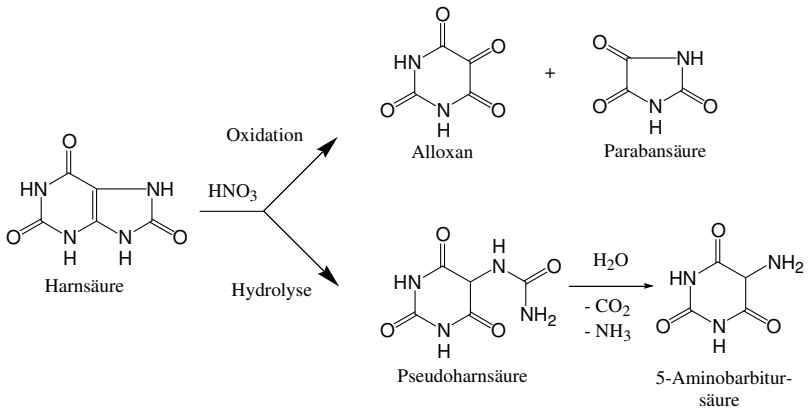
Theophyllin



Phenytoin

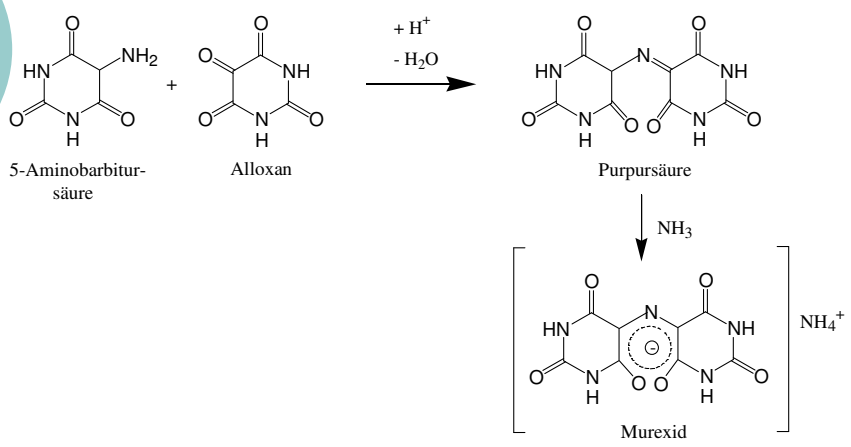
3.2 Murexid - Reaktion

Xanthine



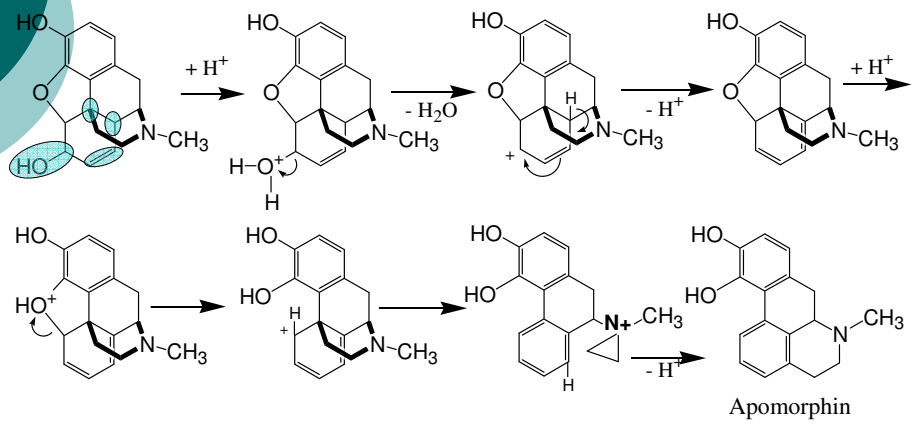
3.2 Murexid - Reaktion

Xanthine



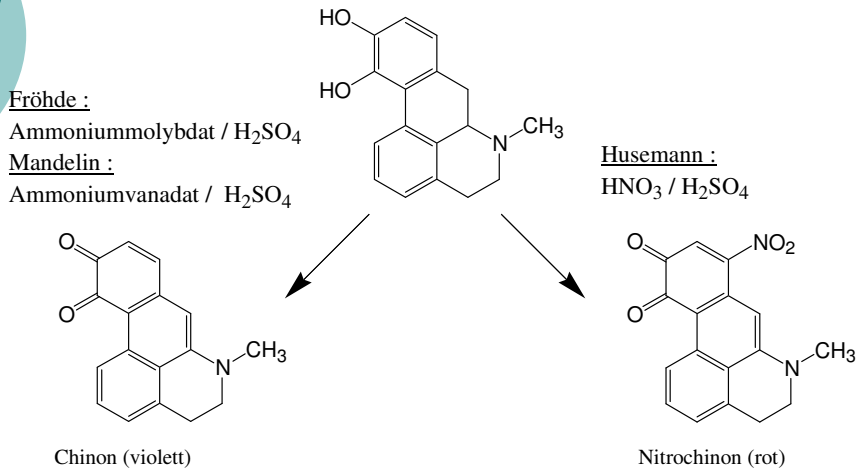
3.3 Apomorphin – Umlagerung

Morphin Derivate mit …



3.3 Apomorphin – Umlagerung

Morphin Derivate

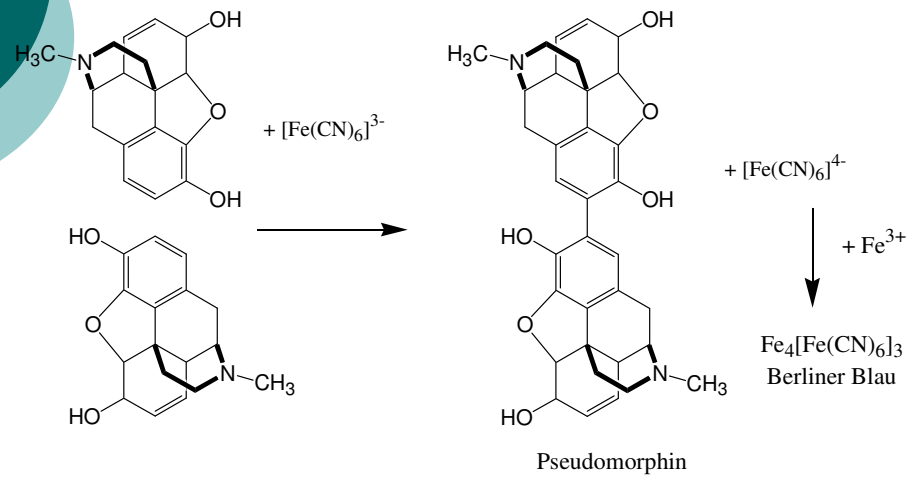


Fröhde :
Ammoniummolybdat / H_2SO_4
Mandelin :
Ammoniumvanadat / H_2SO_4

Husemann :
HNO_3 / H_2SO_4

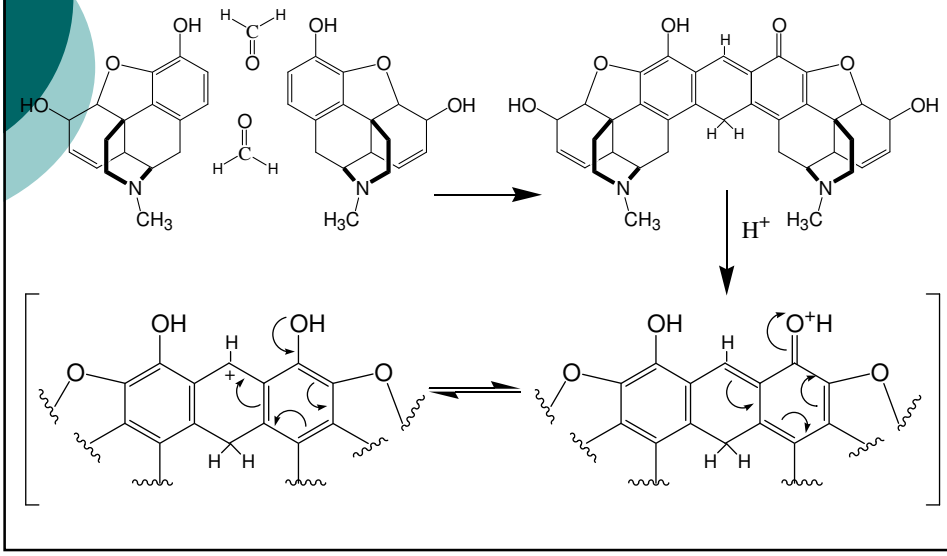
3.3 Morphin- Nachweis nach Kiefer

Morphin-Derivate



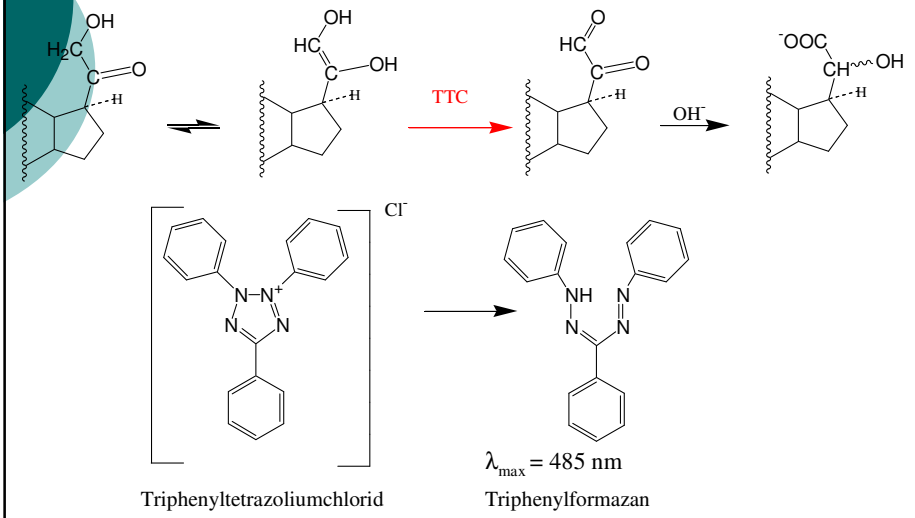
3.3 Morphin- Nachweis nach Marquis

Morphin Derivate



3.4 TTC - Reaktion

α- Ketol- Steroide

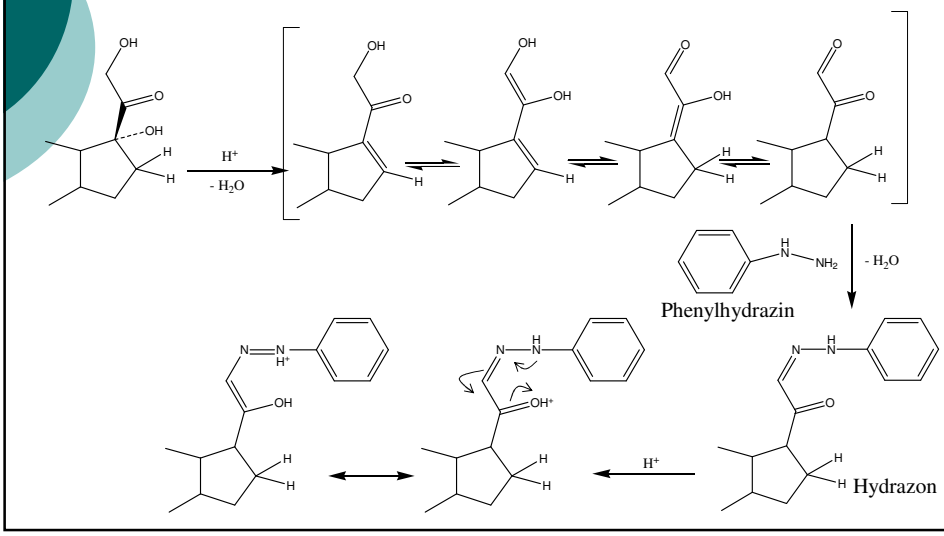


Triphenyltetrazoliumchlorid

Triphenylformazan

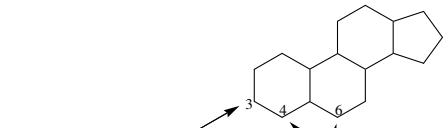
3.4 Porter-Silver Reaktion

AS mit Dihydroxyacetonstruktur



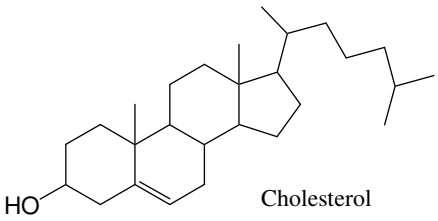
3.4 Liebermann - Burchard

Steroide



Hydroxy-Funktion
oder "latente Hydroxyfunktion"
wie z.B. in Glykosiden

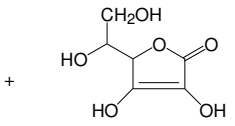
Doppelbindung an C_4
oder C_6



Cholesterol

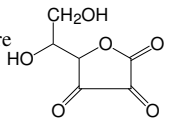
3.5 Tillmann´s Reagenz

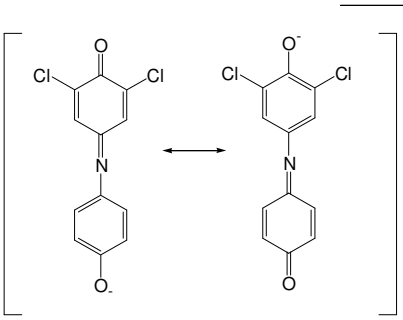
Ascorbinsäure

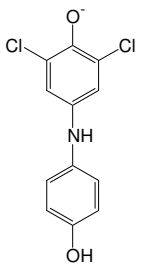


+

Oxidation zu Dehydroascorbinsäure

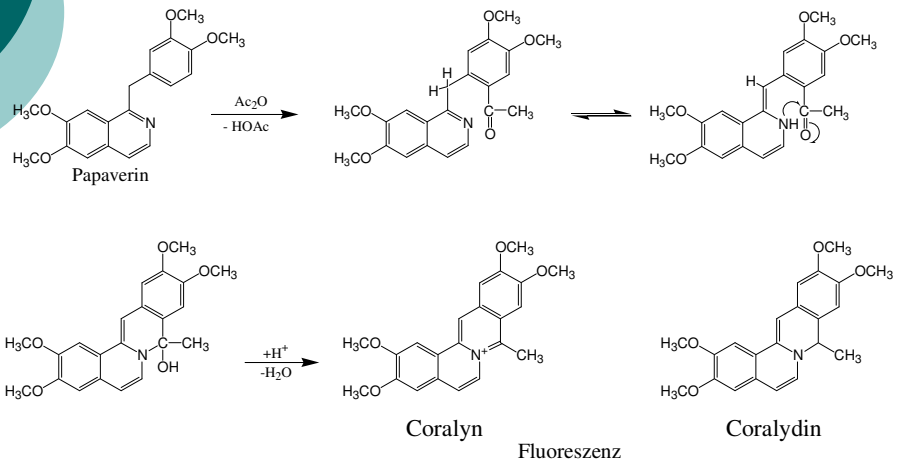






3.6 Coralyn - Reaktion

Papaverin



Papaverin

Coralyn

Coralydin

Fluoreszenz