

FARBREAKTIONEN

Praktikum:

Arzneimittelanalytik, Toxikologie, Drug monitoring und umweltrelevante Untersuchungen
– 8. Semester –

Farbreaktionen

2

- 1. elementaranalytische Nachweise
- 2. Nachweise funktioneller Gruppen
- 3. Nachweise bestimmter Arzneistoffklassen

1.1 Lassaigne-Aufschluß

3

Stickstoff :



CN^-
 SCN^-

Schwefel :



S^{2-}
 SCN^-

Halogene:



F^-
 Cl^-
 Br^-
 I^-

1.1 Lassaigne-Aufschluß

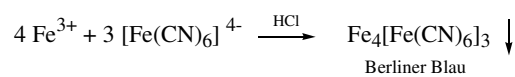
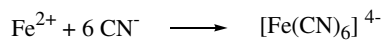
4

CN^-
 SCN^-

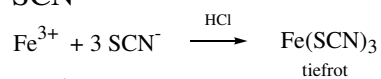
S^{2-}
 SCN^-

F^- , Cl^- , Br^- , I^-

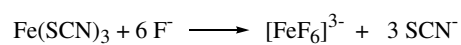
CN^-



SCN^-



Beachte :



1.1 Lassaigne-Aufschluß

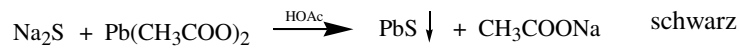
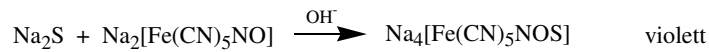
5

CN⁻
SCN⁻

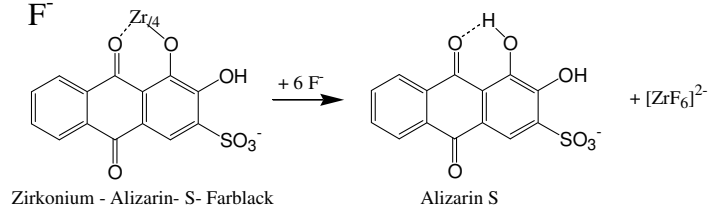
S²⁻
SCN⁻

F⁻, Cl⁻, Br⁻, I⁻

S²⁻



F⁻



1.1 Lassaigne-Aufschluß

6

CN⁻
SCN⁻

S²⁻
SCN⁻

F⁻, Cl⁻, Br⁻, I⁻

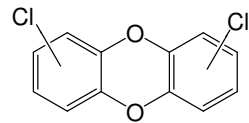
Halogenide :

- Nachweis als schwerlösliche Silbersalze,
Fluorid bildet ein lösliches Silbersalz !
- mit HNO₃ angesäuerte Lösung aufkochen, um
H₂S, HCN und HSCN zu vertreiben, die auch
schwerlösliche Silbersalze bilden !
- Silbernitratfällung auch immer mit der Ursubstanz
machen (Hydrochlorid-Arzneistoffe!)

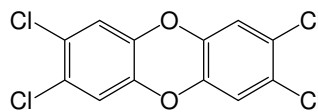
1.2 Beilstein- Probe

7

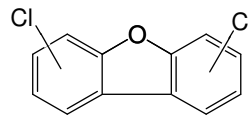
Cu-Draht, Cu-Cent + Halogen anorganisch oder organisch gebunden $\xrightarrow{\text{nichtleuchtende Bunsenbrennerflamme}}$ grüne Flamme der verdampfenden Kupferhalogenide



PCDD = polychlorierte Dibenzodioxine



2,3,7,8 - Tetrachlordibenzodioxin

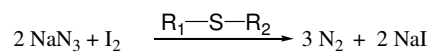


PCDF = polychlorierte Dibenzofurane

1.3 Schwefelnachweise

8

Jod - Azid- Reaktion



Nachweis von Schwefel als Sulfat

Oxidation mit H_2O_2 / Fe^{3+} zu Sulfat;

Fällung des Sulfat als schwerlösliches BaSO_4

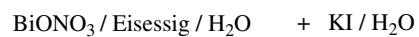
2. Nachweise funktioneller Gruppen

9

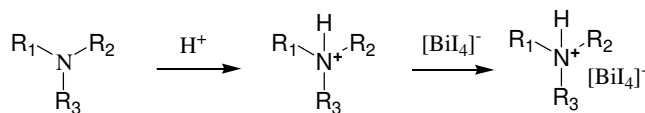
- 2.1 Nachweise stickstoffhaltiger Verbindungen
- 2.2 Nachweise sauerstoffhaltiger Verbindungen
- 2.3 Nachweise weiterer Strukturelemente

2.1 Dragendorff- Reagenz -basischer Stickstoff -

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Kaliumtetraiodobismutat
 $\text{K}[\text{BiI}_4]$



2.1 Dragendorff- Reagenz - basischer Stickstoff -

11

pKs-Werte

Ammoniak NH_3 9,2

Dimethylamin $\text{H}_3\text{C}-\text{N}(\text{CH}_3)_2$ 10,6

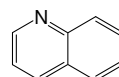
Piperidin  11,2

Pyridin



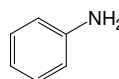
5,2

Chinolin



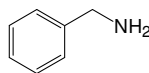
4,8

Anilin



4,6

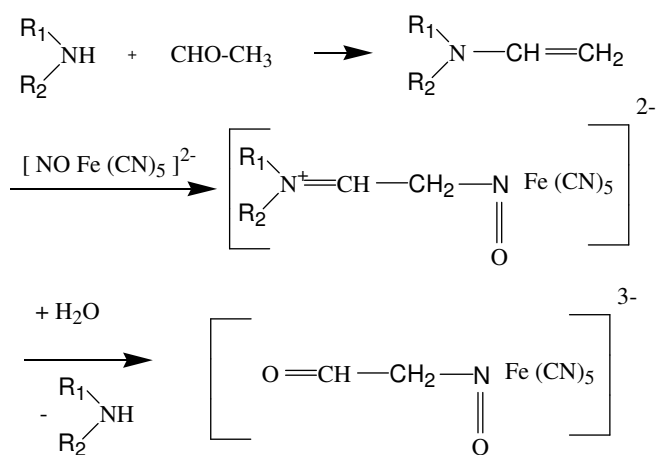
Benzylamin



9,4

2.1 Analoge Simon- Awe- Reaktion - Sekundäre Amine -

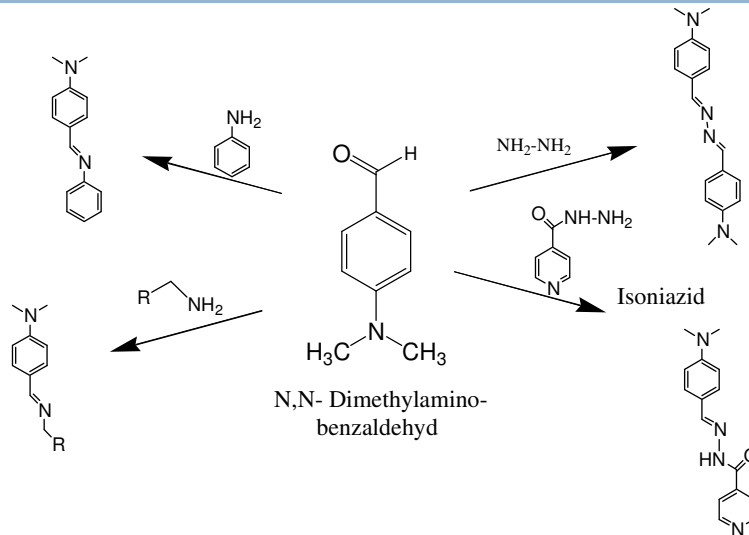
12



2.1 Ehrlichs Reagenz

a) primäre Amine

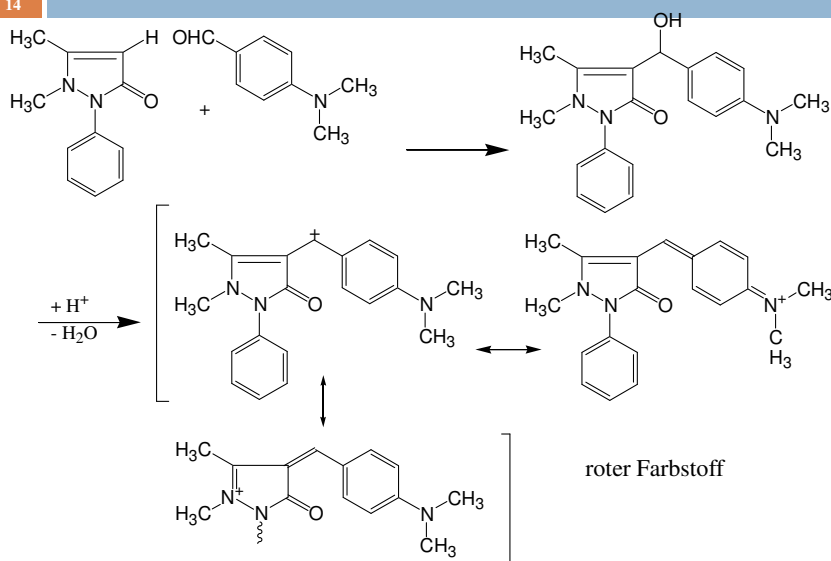
13



2.1 Ehrlichs Reagenz

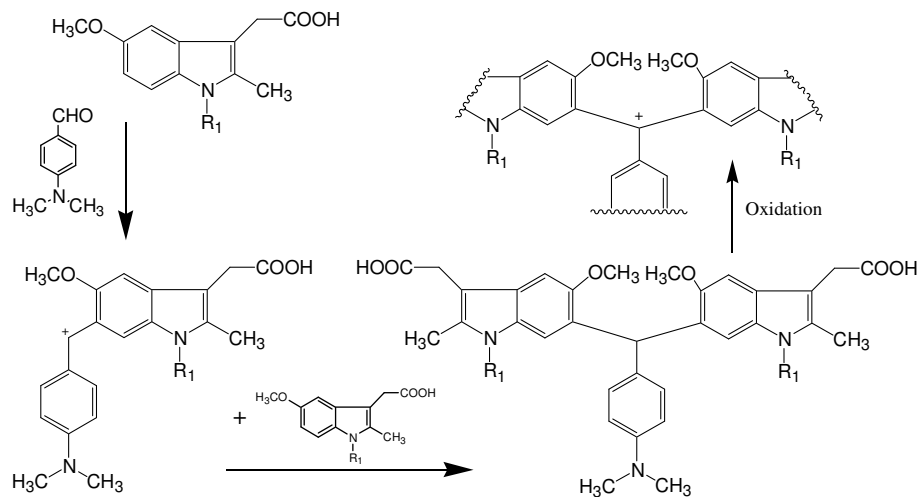
b) mit Phenazon

14



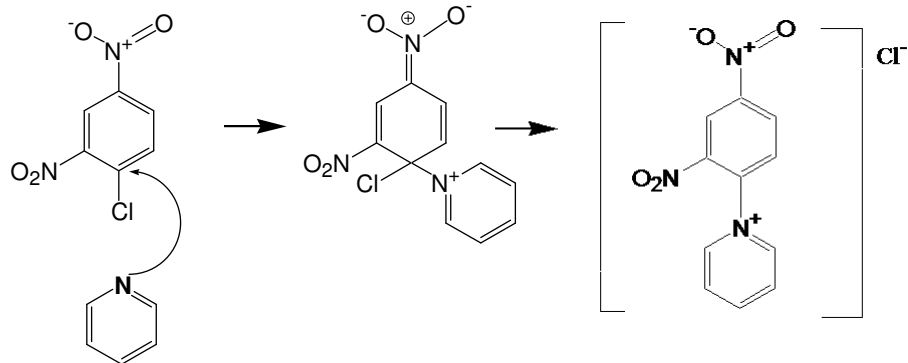
2.1 Ehrlichs Reagenz c) mit Indometacin

15



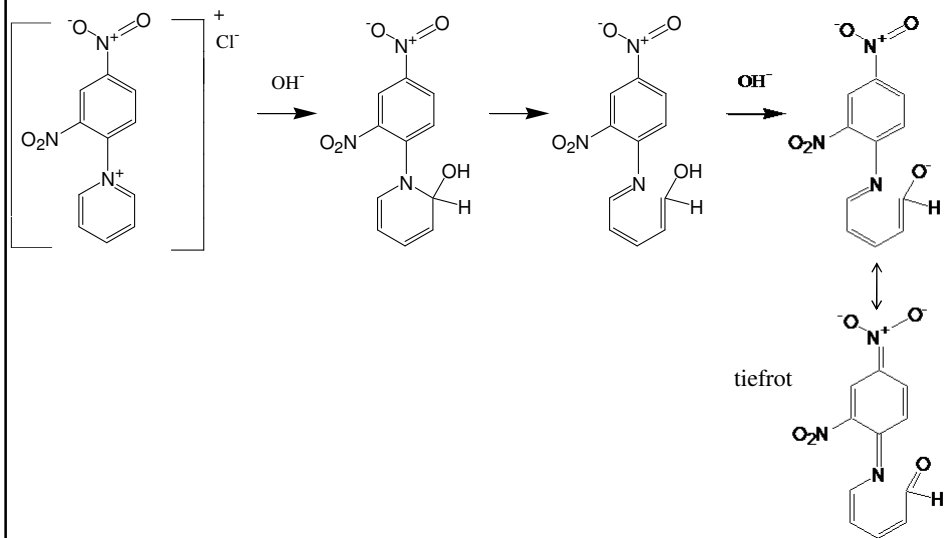
2.1 Zincke-König-Spaltung - Pyridinderivate -

16



2.1 Zincke-König-Spaltung - Pyridinderivate -

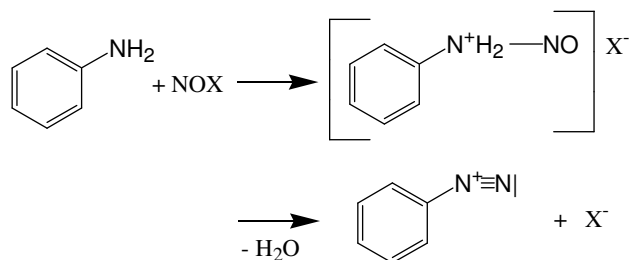
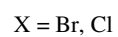
17



2.1 Diazotierung primäre aromatische Amine

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A. Diazotierung

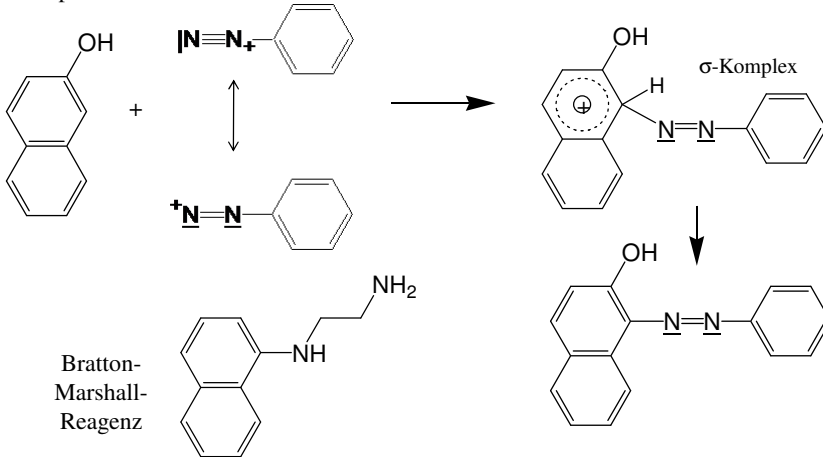


2.1 Diazotierung

primäre aromatische Amine

19

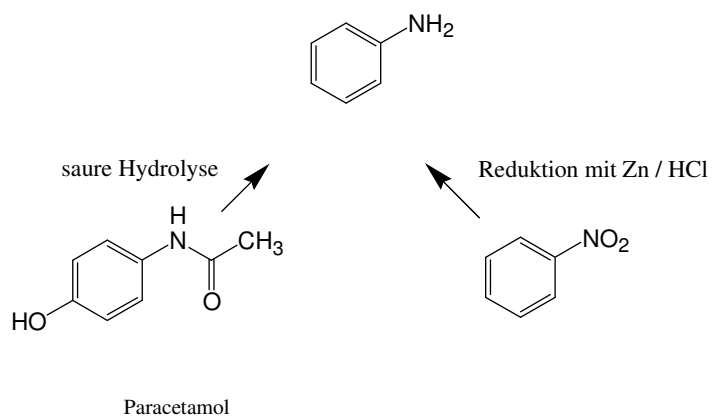
2-Naphthol



2.1 Diazotierung

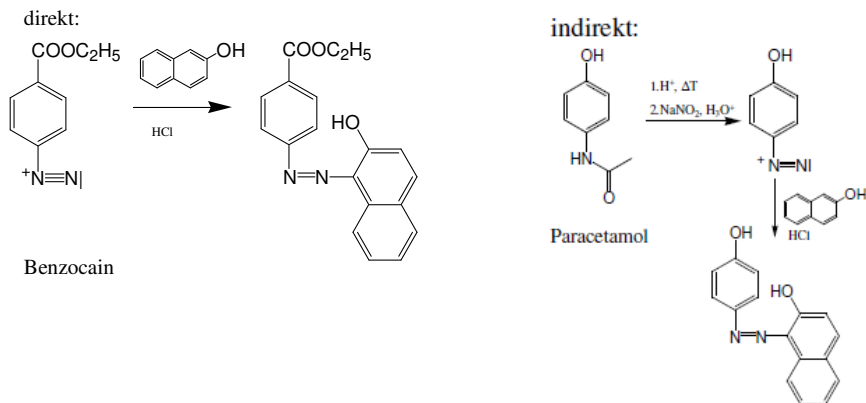
indirekt

20



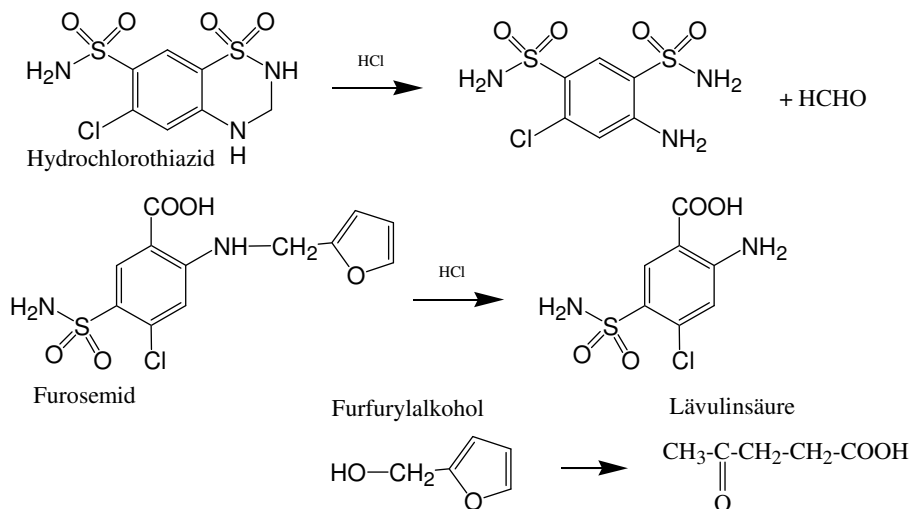
2.1 Diazotierung direkt/indirekt

21



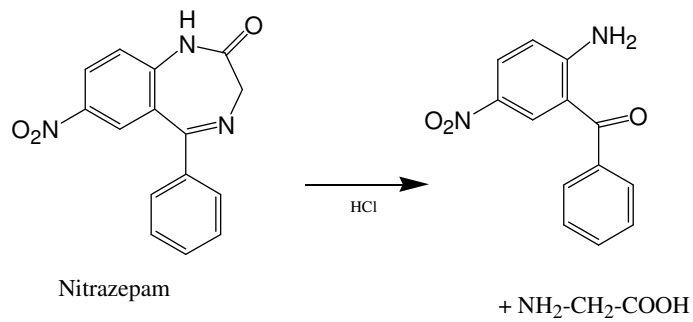
2.1 Diazotierung nach saurer Hydrolyse

22



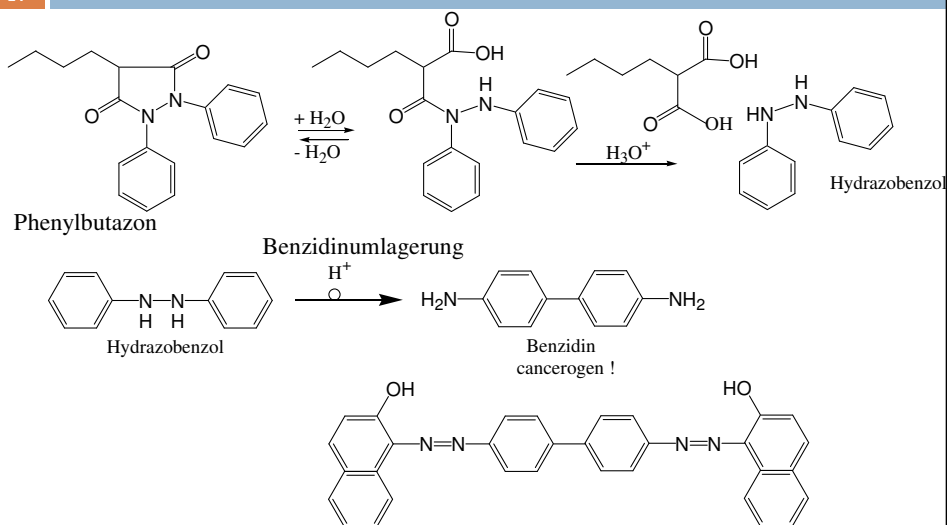
2.1 Diazotierung nach saurer Hydrolyse

23



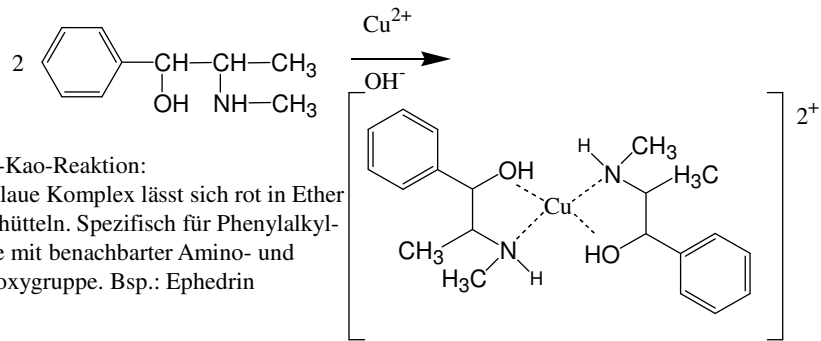
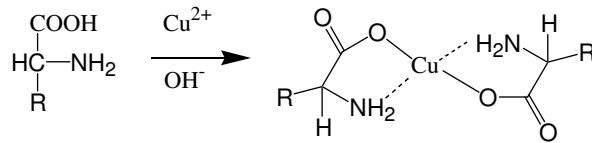
2.1 Diazotierung nach saurer Hydrolyse

24



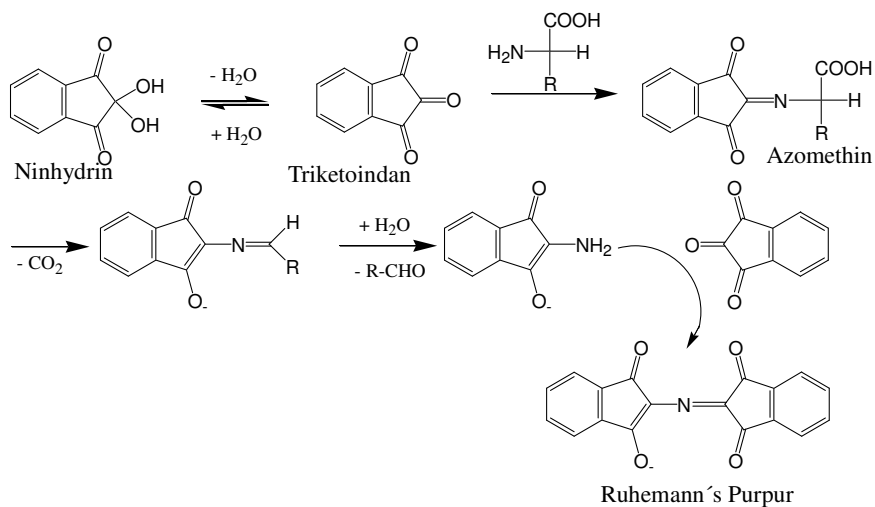
2.1/2.2 Farbkomplex mit CuSO_4 - Aminosäuren, Ethanolamine -

25



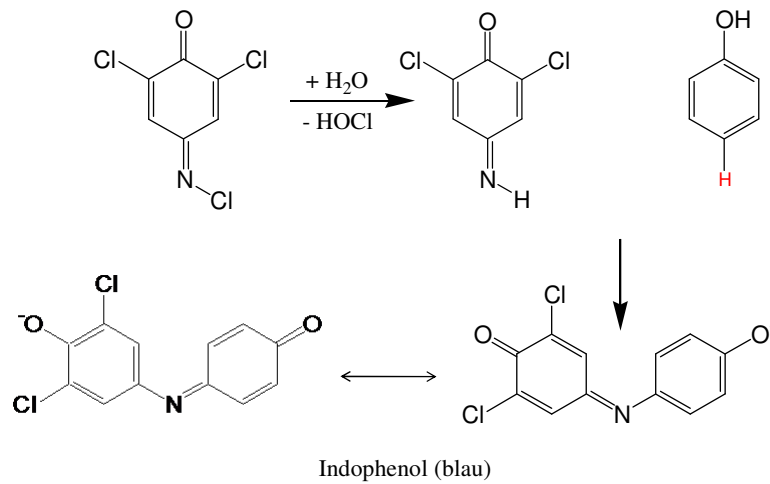
2.1/2.2 Ninhydrin - Reaktion -Aminosäuren-

26



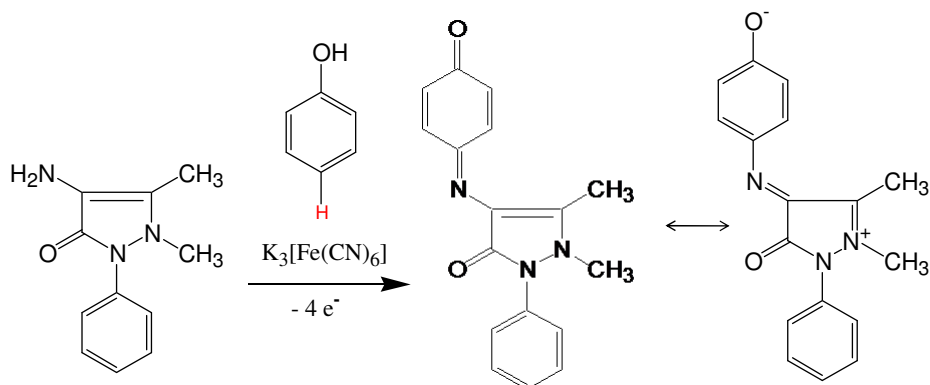
2.2 Gibbs Reagenz - Phenole -

27



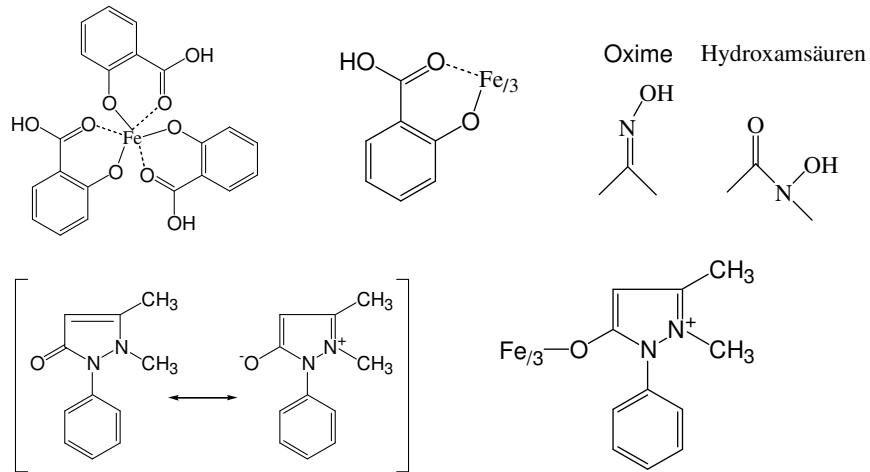
2.2 Emerson-Reaktion - Phenole -

28



2.2 Eisen (III)-chlorid - Phenole, Enole...-

29



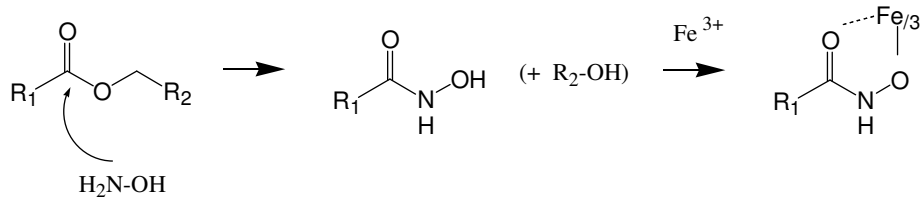
Vielen Dank für die Aufmerksamkeit!

30

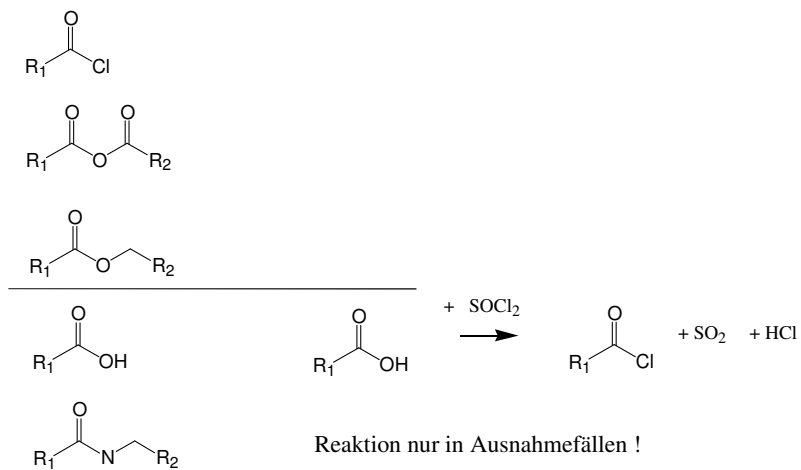
□ Farbreaktionen Teil 2: **Dienstag**

2.2 Hydroxamsäurereaktion - Carbonsäuren & Derivate -

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2.2 Hydroxamsäurereaktion - Carbonsäuren & Derivate -

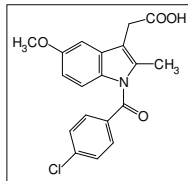


32

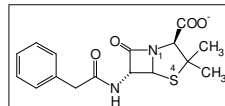
2.2 Hydroxamsäurereaktion - Carbonsäuren & Derivate -

33

Beispiele für Amide / Lactame , die reaktiv genug sind :



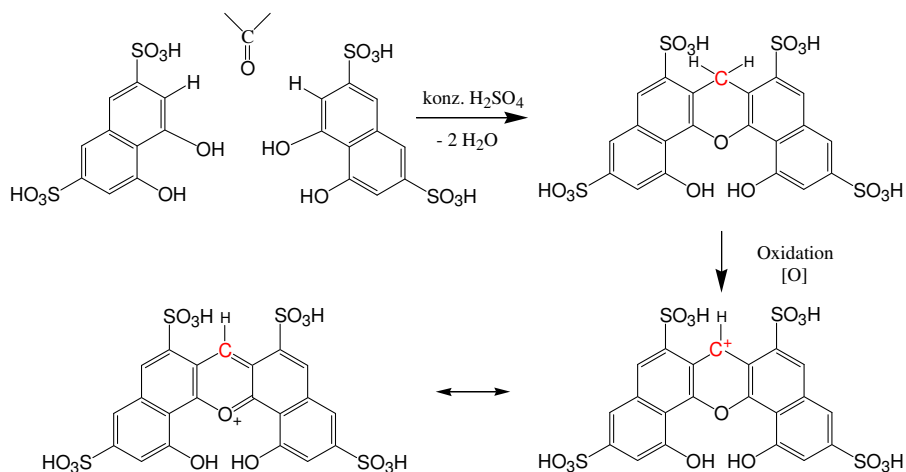
Indometacin



Benzylpenicillin

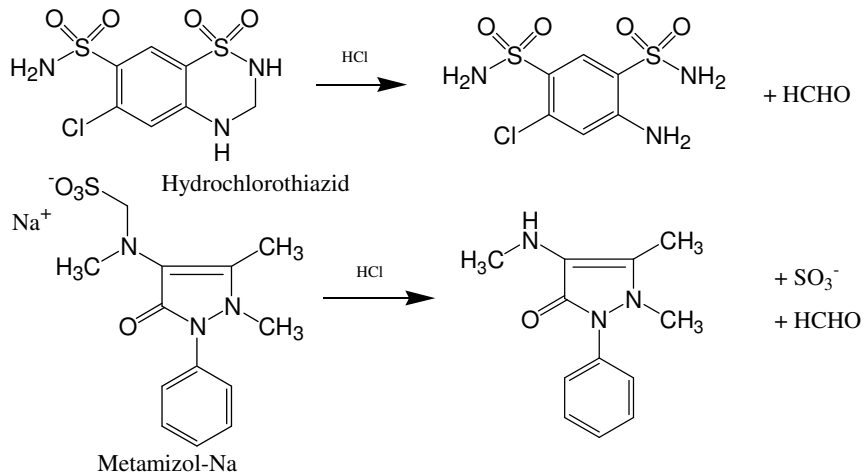
2.2 Chromotropsäure-Reaktion - freigesetzter Formaldehyd -

34



2.2 Chromotropsäure-Reaktion - freigesetzter Formaldehyd -

35

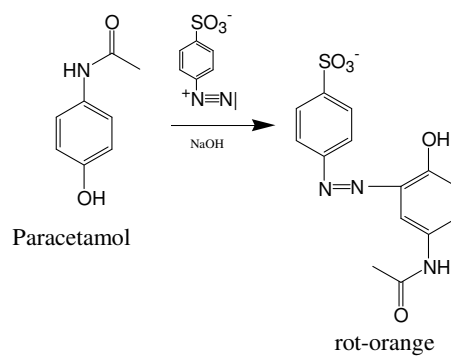


2.3 Kupplung mit diazotierter - Sulfanilsäure -

36

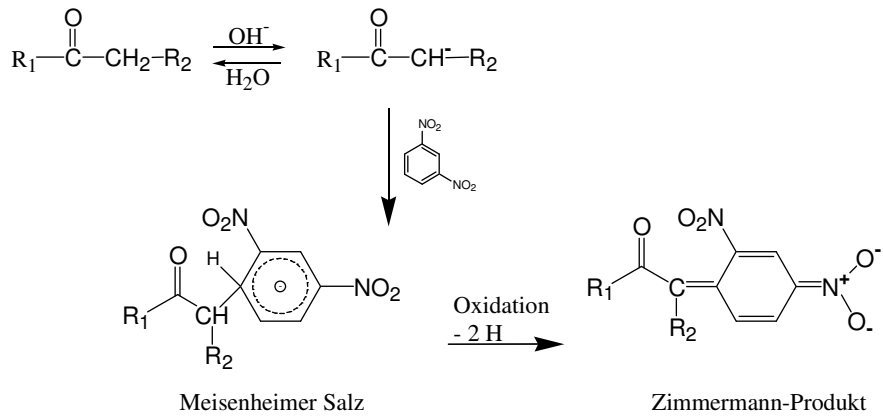
Kupplungsfähige Aromaten :

z.B. Phenole oder Imidazole



2.3 Zimmermann - Reaktion - aktive Methylengruppen -

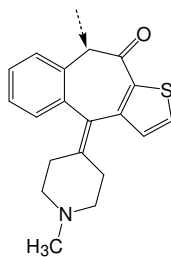
37



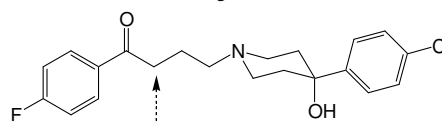
2.3 Zimmermann - Reaktion - aktive Methylengruppen -

38

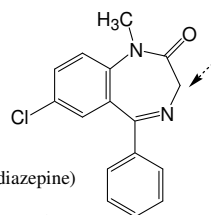
Ketotifen :



Haloperidol :
auch Zimmermann-Verbindung



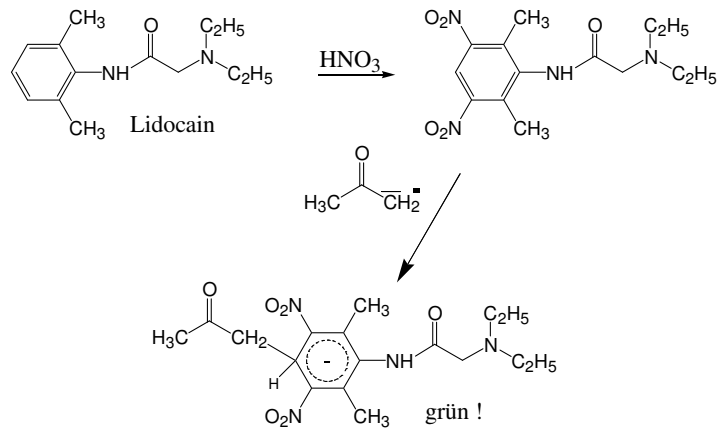
Diazepam
(u.a. Benzodiazepine)
nur bis zum
Meisenheimer-Salz



2.3 Vitali - Morin

- a) nitrierbare Aromaten -

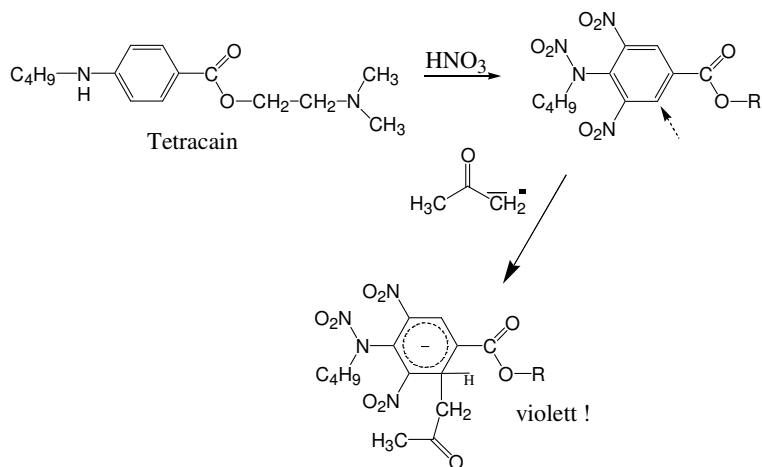
39



2.3 Vitali - Morin

- a) nitrierbare Aromaten -

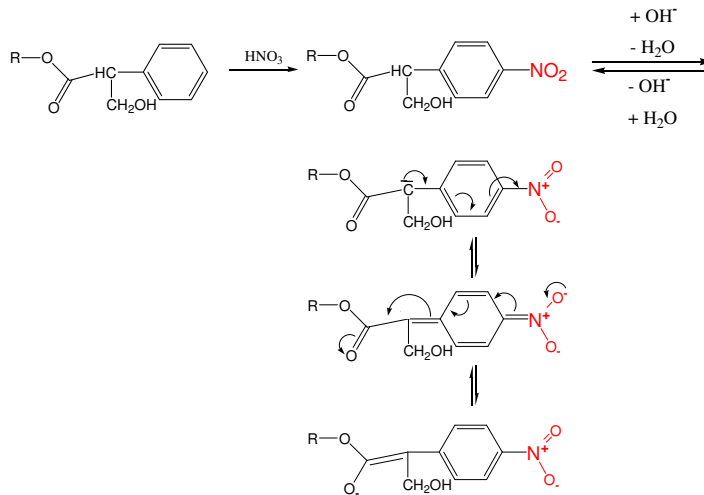
40



2.3 Vitali-Variante(ohne Aceton)

- b) Tropasäureester -

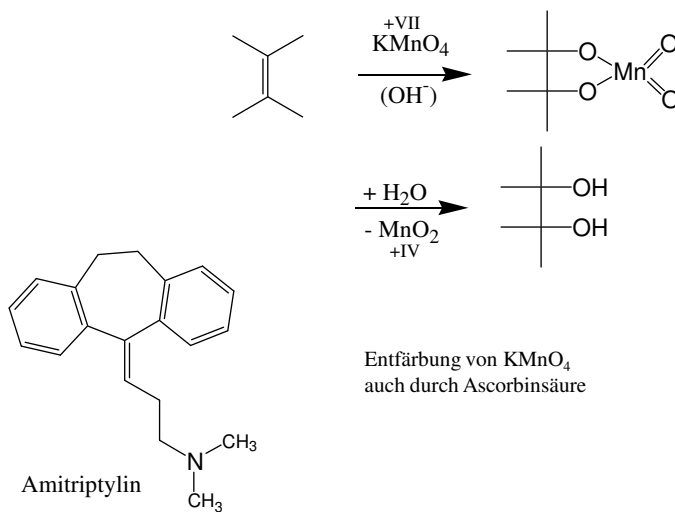
41



2.3 Bayersche-Probe

- olefinische Doppelbindungen -

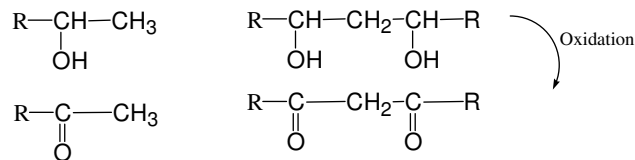
42



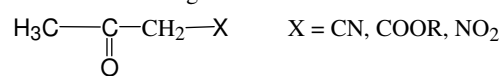
2.3 Iodoform - Probe

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Nachweis folgender Strukturelemente:

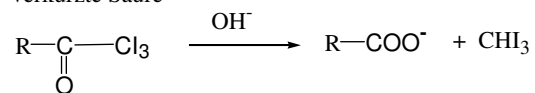


Keine Reaktion ergeben :



Mechanismus:

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



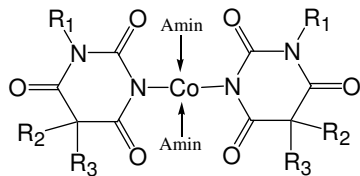
3. Nachweis bestimmter Arzneistoffklassen

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

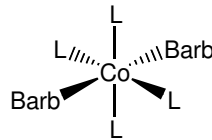
3.1 Zwikker-Reaktion - Barbiturate -

45



mit Amin (Piperidin) :

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



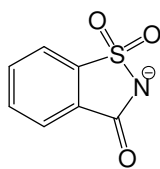
ohne Aminzusatz :

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

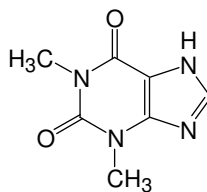
3.1 Zwikker-Reaktion - Barbiturate -

46

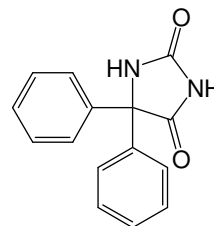
Beispiele für ebenfalls positiv reagierende Stoffe:



Saccharin-Na



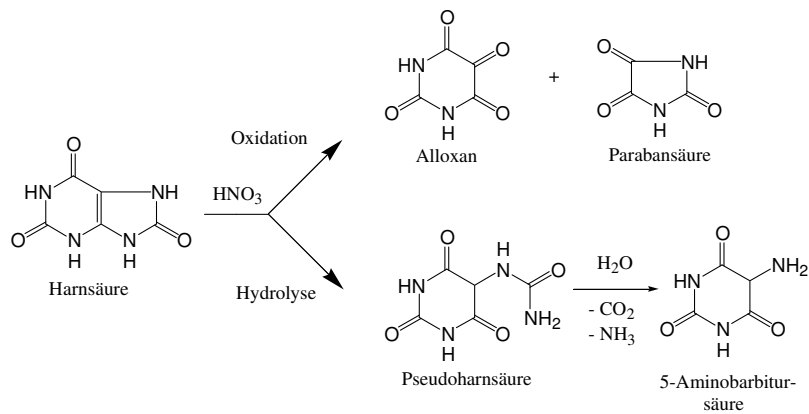
Theophyllin



Phenytoin

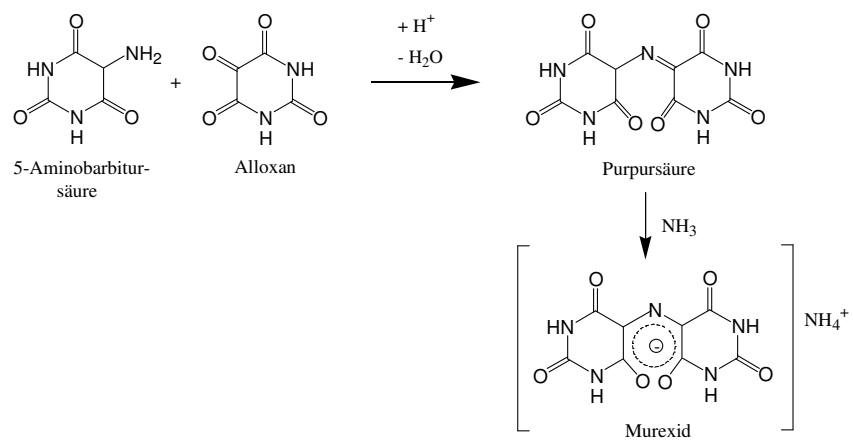
3.2 Murexid - Reaktion - Xanthine -

47



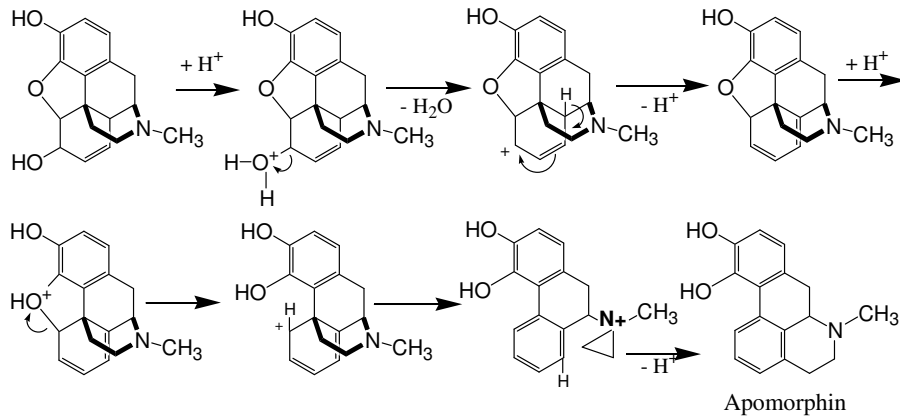
3.2 Murexid - Reaktion - Xanthine -

48



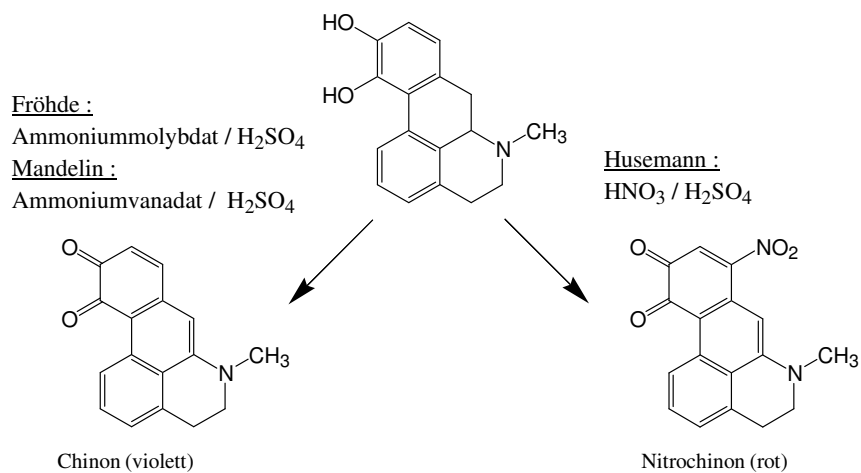
3.3 Apomorphin - Umlagerung

49



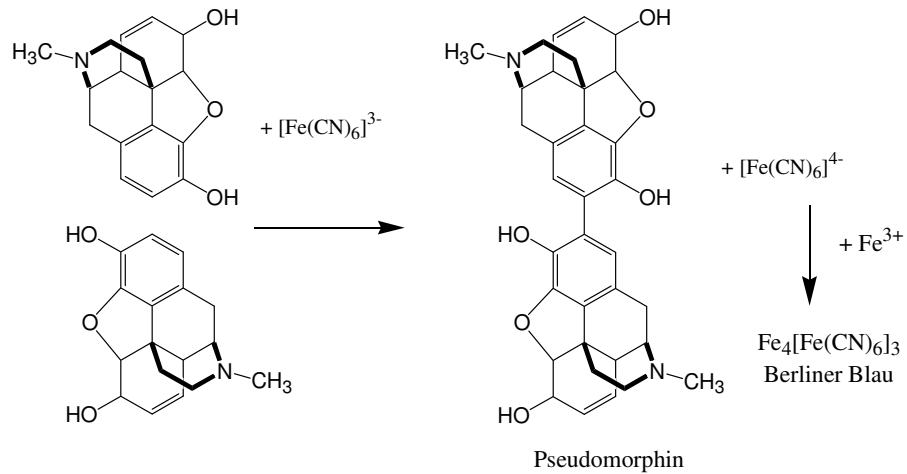
3.3 Apomorphin-Umlagerung -Morphin-Derivate-

50



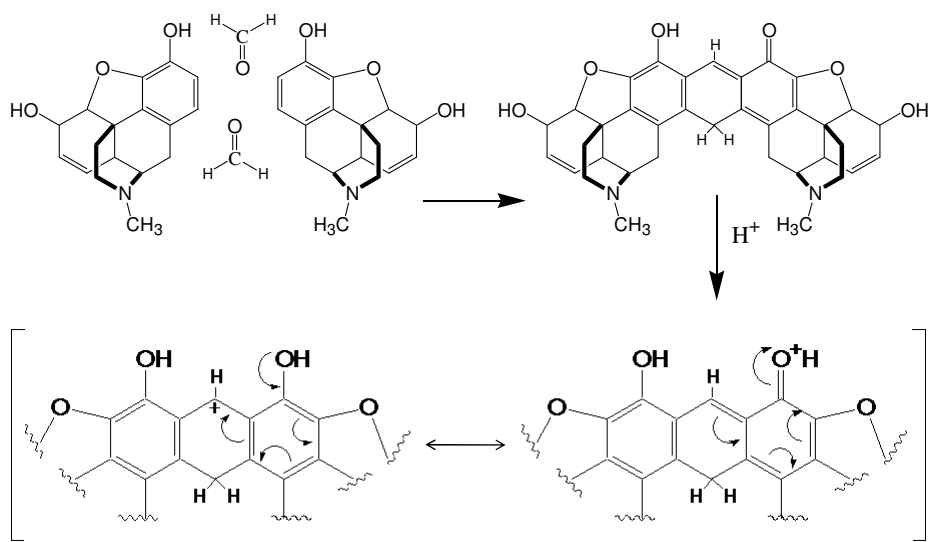
3.3 Morphin- Nachweis nach Kiefer

51



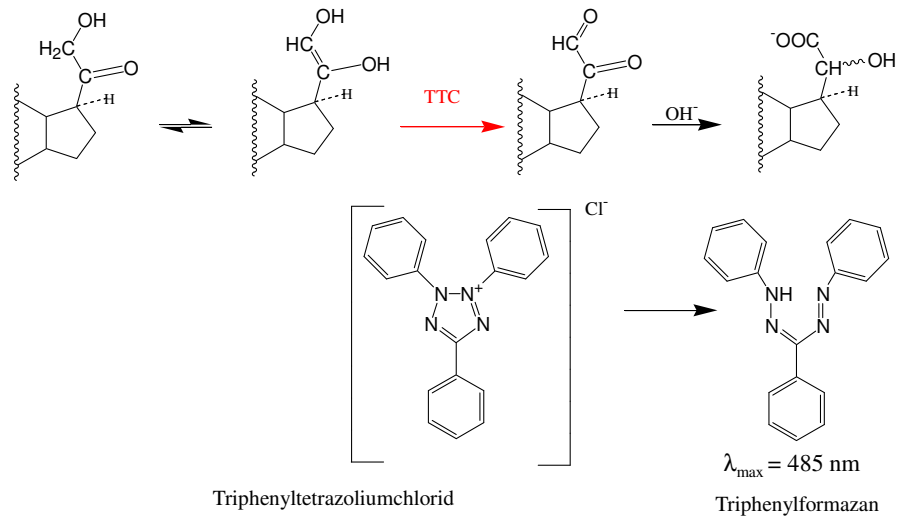
3.3 Morphin- Nachweis nach Marquis

52



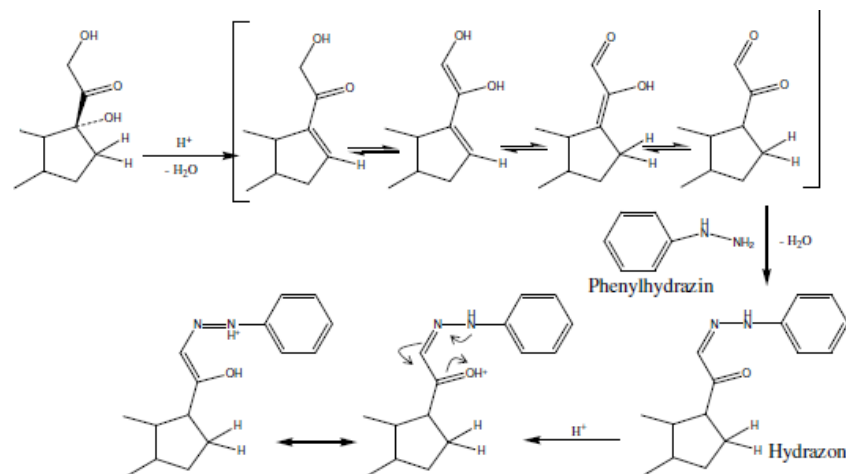
3.4 TTC - Reaktion - α - Ketol- Steroide -

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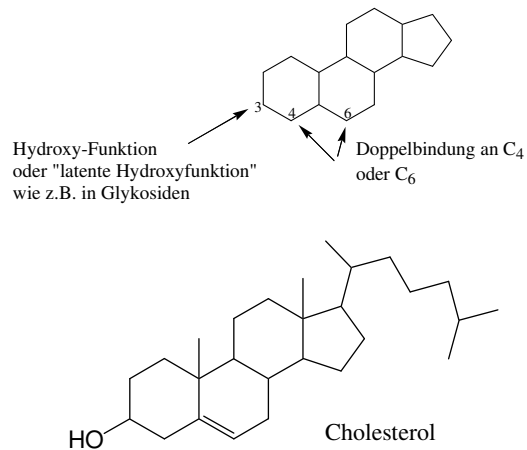
3.4 Porter-Silver Reaktion AS mit Dihydroxyacetonstruktur

54



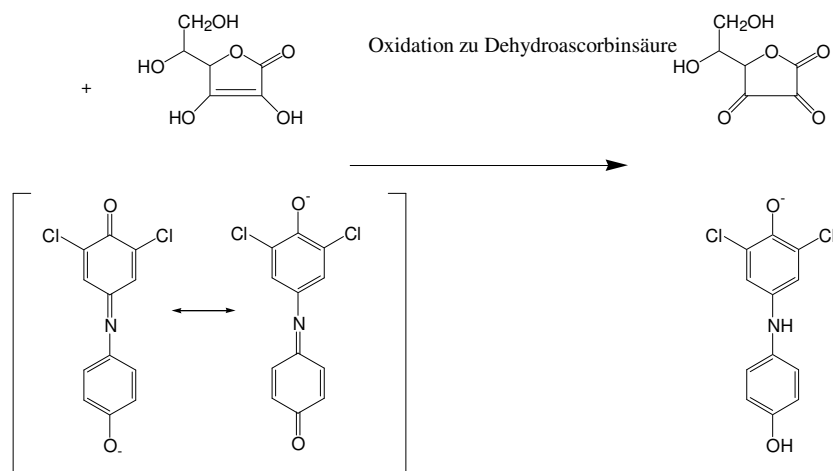
3.4 Liebermann - Burchard - „Steroide“ -

55



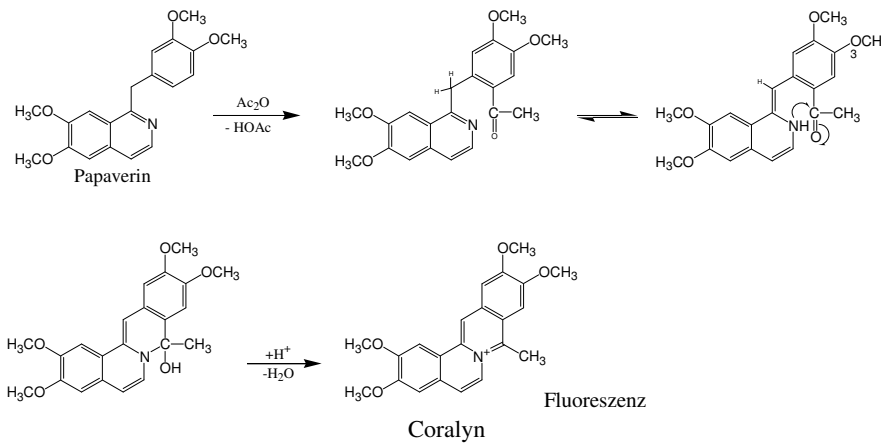
3.5 Tillmanns Reagenz - Ascorbinsäure -

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3.6 Coralyn - Reaktion - Papaverin -

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Vielen Dank für die Aufmerksamkeit!

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