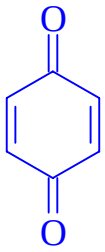
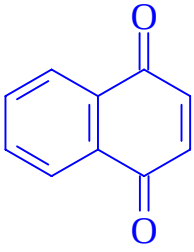
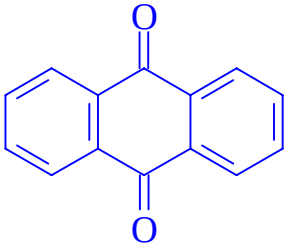
Anthrachinon



p-Benzochinon

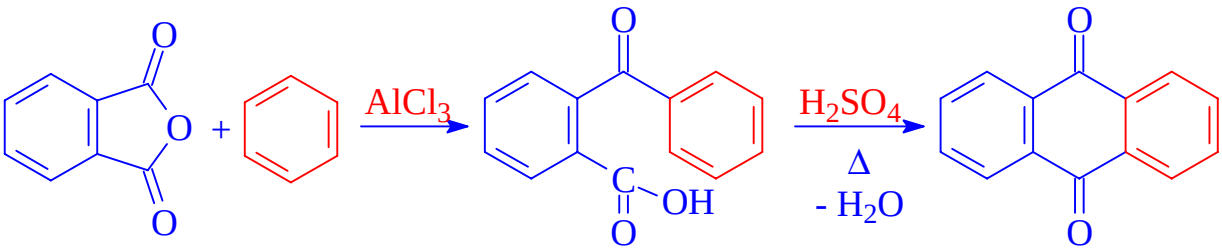


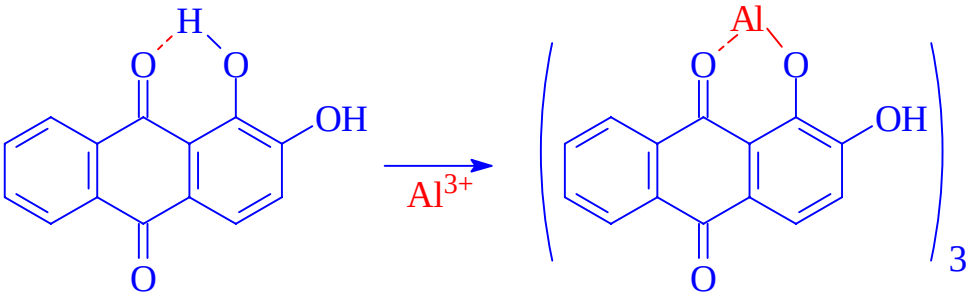
1,4-Naphthochinon



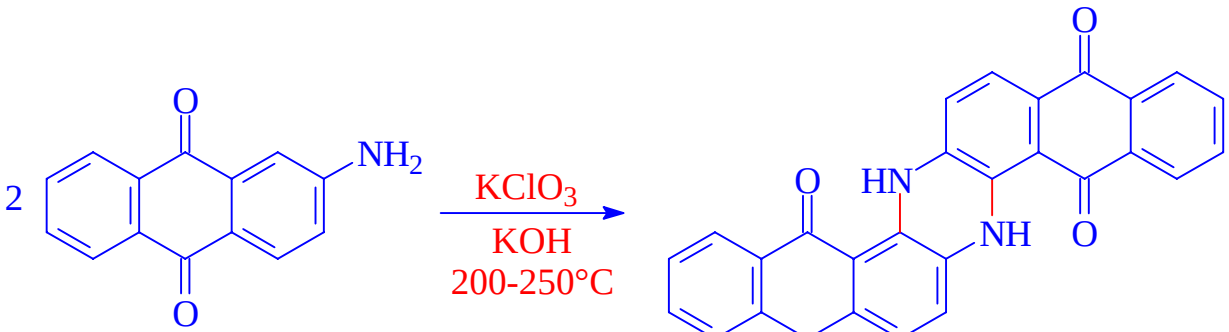
Anthrachinon

alle gelb





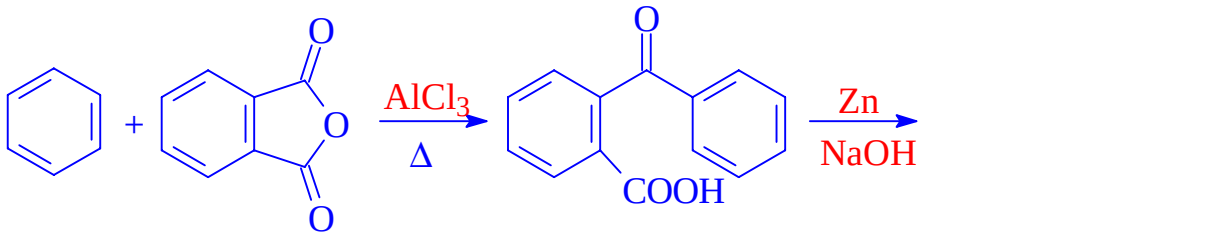
Chelat-Komplex, besonders gut haftbar auf Fasern.

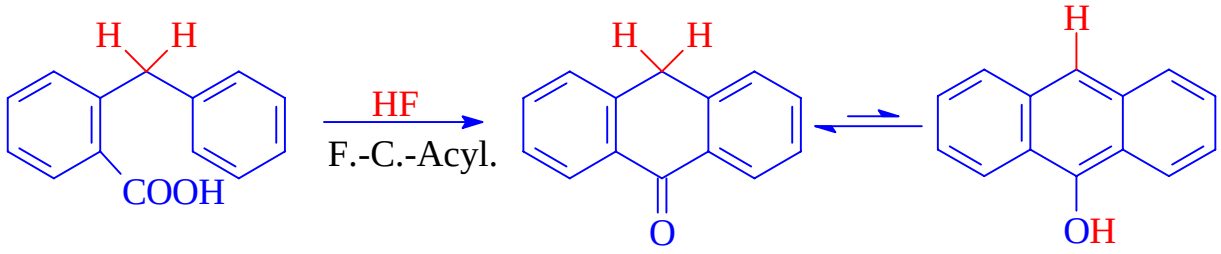


oxidative Dimerisierung

Indanthren-Blau RS

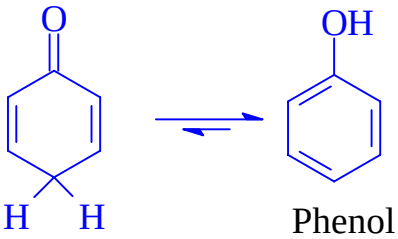
Synthese von Anthron





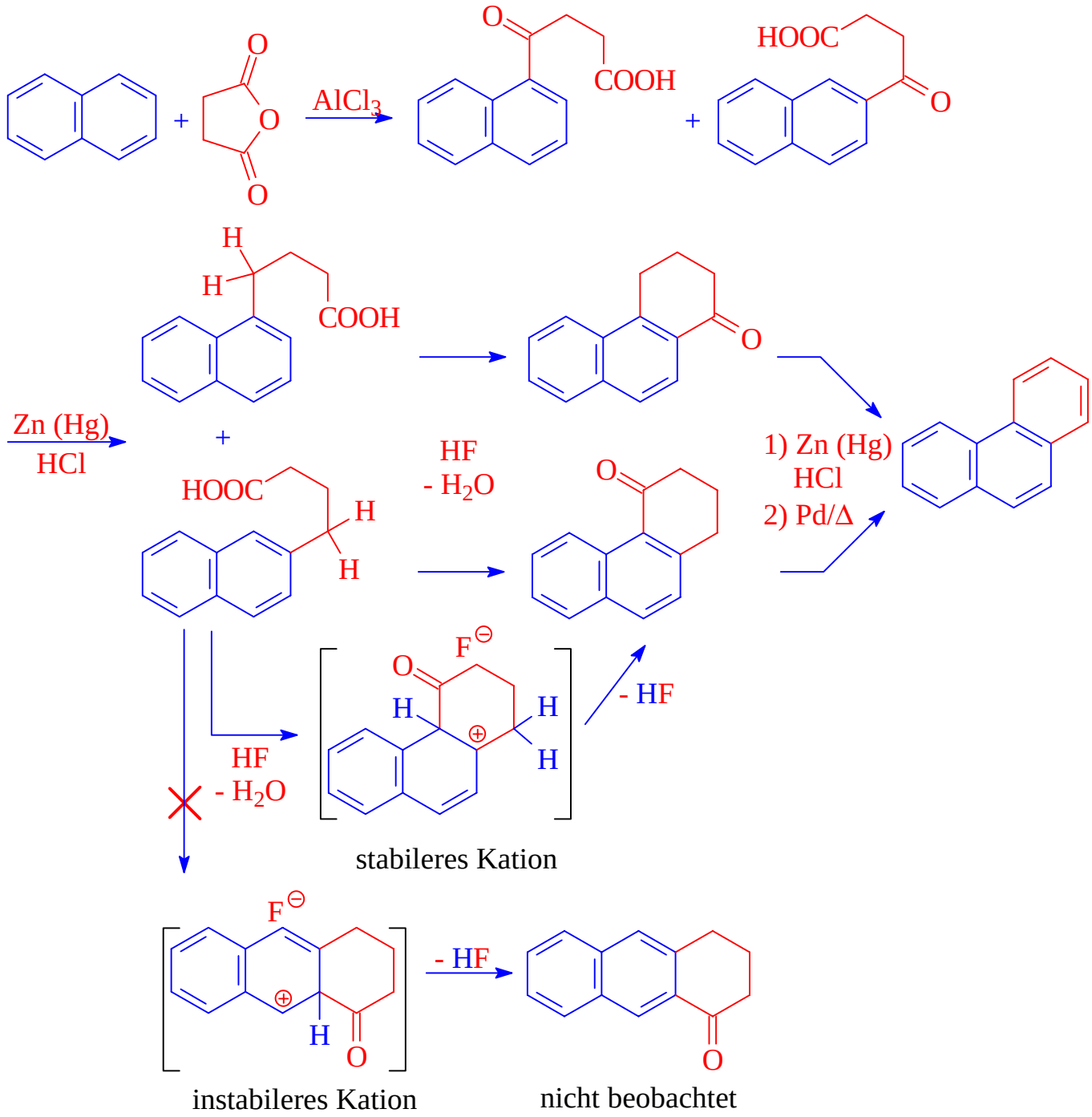
Anthron

9-Anthrol
(9-Anthracenol)

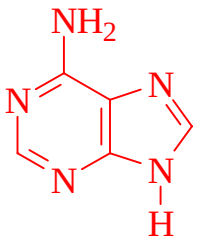


Phenol

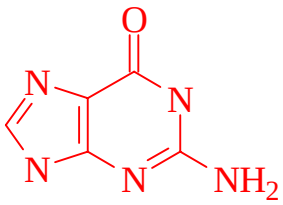
Synthese von Phenanthren



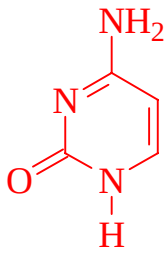
Basen, die in der DNA (Desoxyribonucleic Acid – Desoxyribonucleinsäure) vorkommen



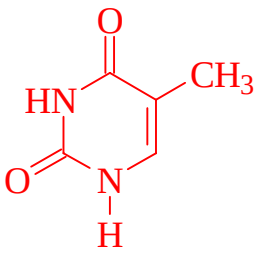
Adenin (A)



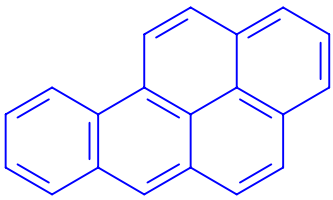
Guanin (G)



Cytosin (C)

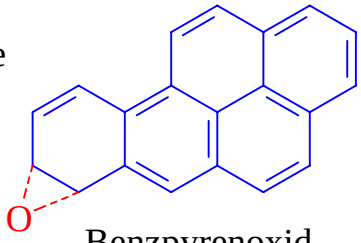


Thymin (T)



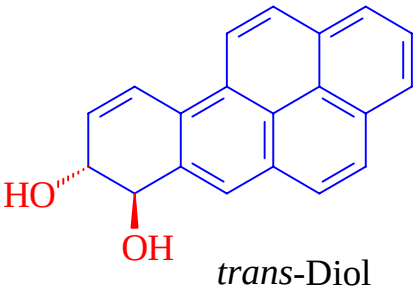
Benzpyren

enzymische Oxidation



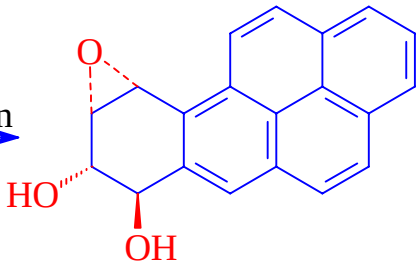
Benzpyrenoxid, ein Arenoxid

H_2O
enzymische Hydrolyse

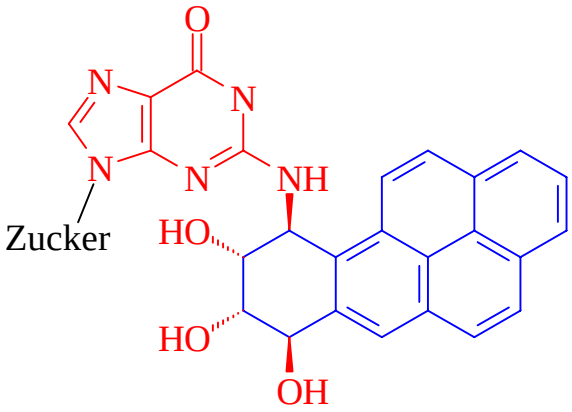


trans-Diol

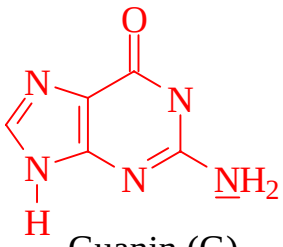
Oxidation



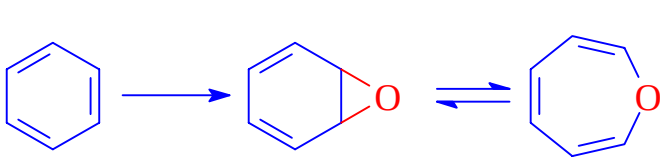
nucleophile Addition an den Epoxidring



Zucker

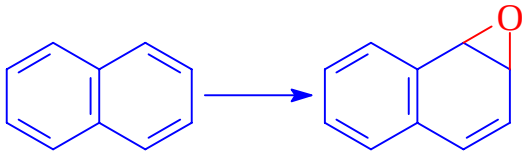


Guanin (G)

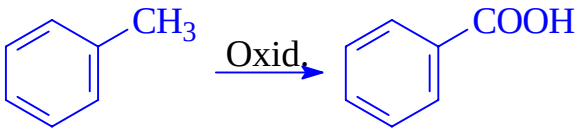


Benzoloxid

Oxepin

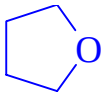
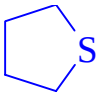
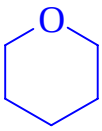
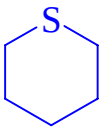
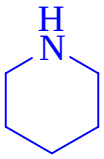


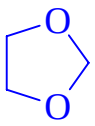
Naphthalinoxid

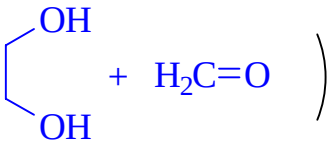


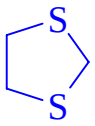
Oxid.

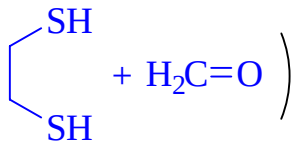
Nicht-aromatische Heterocyclen

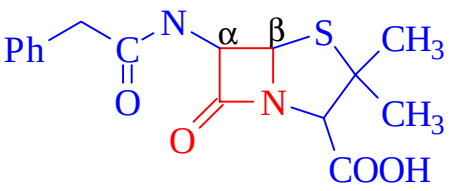
Cyclische Ether	Cyclische Thioether	Cyclische Amine
		
Oxivan (Ethylenoxid)	Thiiran (Ethylensulfid)	Aziridin (Ethylenimin)
		
Oxetan	Thiethan	Azetidin
		
Tetrahydrofuran	Tetrahydrothiophen	Pyrrolidin
		
Tetrahydropyran	Tetrahydrothiopyran	Piperidin



1,3-Dioxalan (Acetal aus )

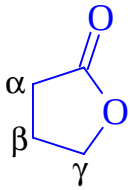


1,3-Dithian (Thioacetal aus )



Penicillin G

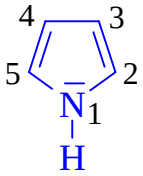
β-Lactamring



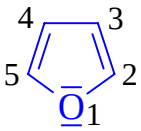
γ-Butyrolacton

Fünfgliedrige Ringe

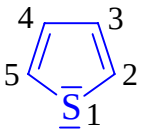
Aromatische 5-Ring-Heterocyclen:



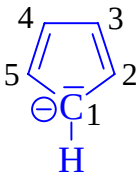
Pyrrol



Furan

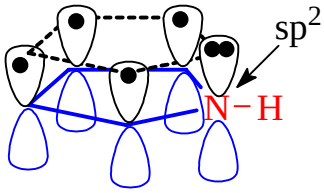


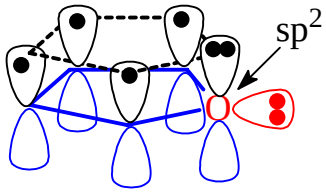
Thiophen



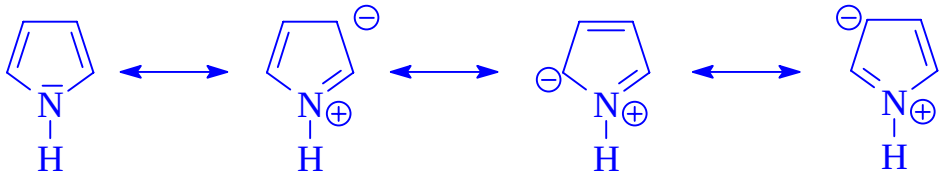
Cyclopenta-dienylanion

MO-Bild

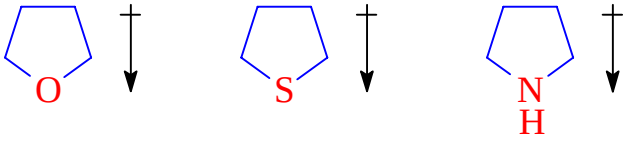




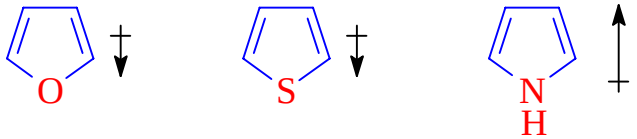
Resonanzstrukturen



Dipolmomente



1.73 D 1.90 D 1.58 D



0.70 D 0.51 D 1.81 D

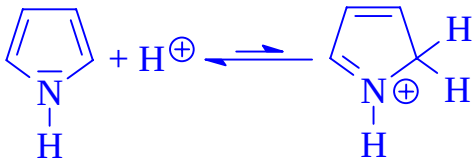
Basizitätskonstante $K_B = \frac{[B^+\text{-}H]\,[OH^-]}{[B]}$

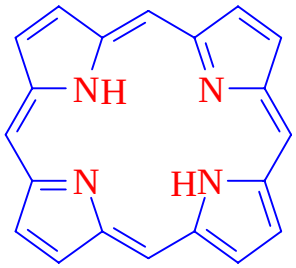
10^{-4} [M]

2.5×10^{-14} [M]

Resonanzenergie: R.E. ≈ 22-28 kcal/mol

Protonierung von Pyrrol:

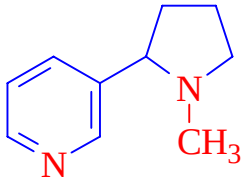




Porphin

(Grundkörper

sonst Porphyrine)



Porphyrin-Derivate:

Nicotin

Chlorophyll (grünes Pflanzenpigment)

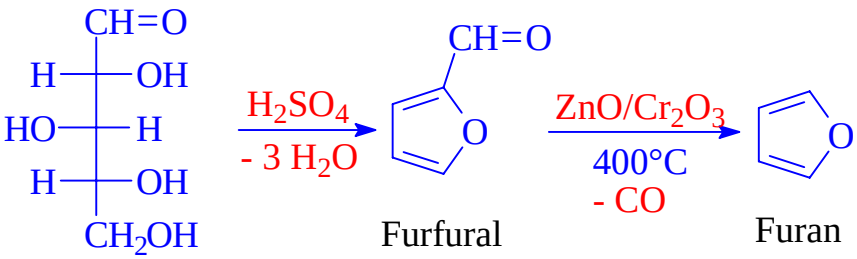
Hämoglobin (Sauerstoff-Transport im Blut) (Folie 378)

(Alkaloid des Tabaks)

Alkaloid ⇒ alkaliähnliche also basische Eigenschaften

Synthese von Furan, Thiophen und Pyrrol

1) Furan

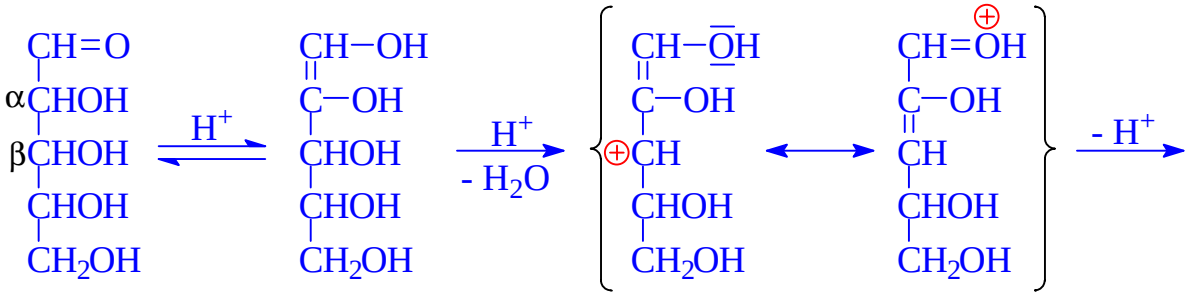


Furfural

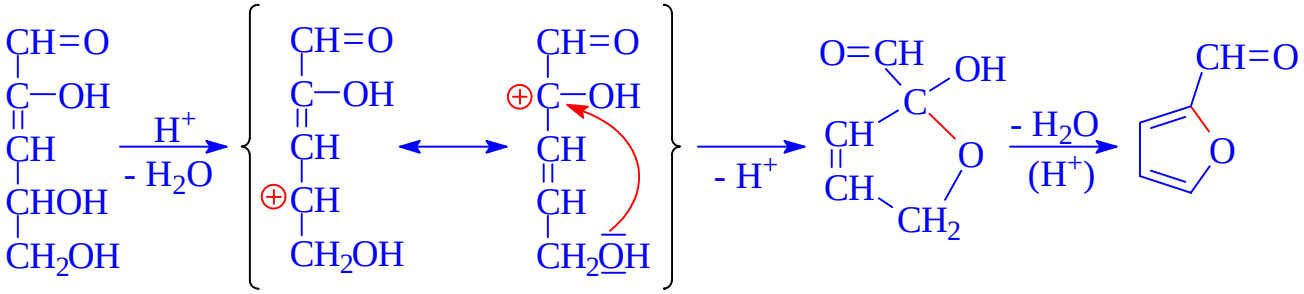
Furan

Pentose
(z.B. aus Kleie)

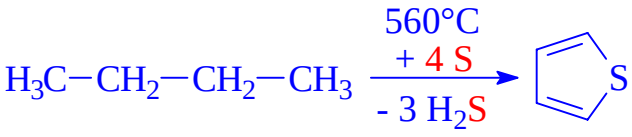
Mechanismus



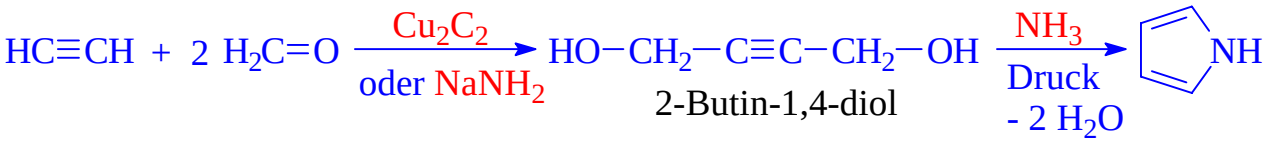
Keto-Enol-Tautomerie



2) Thiophen

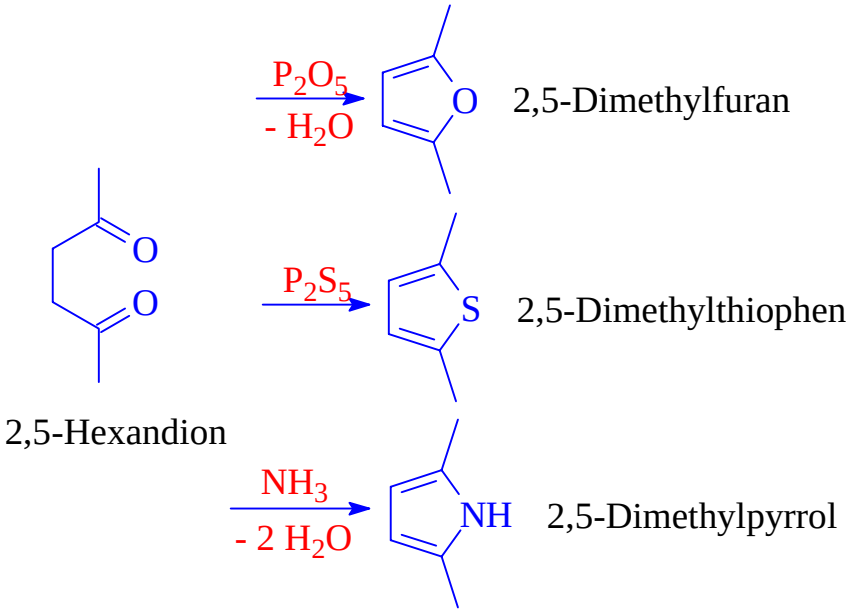


3) Pyrrol



(technische Synthese)

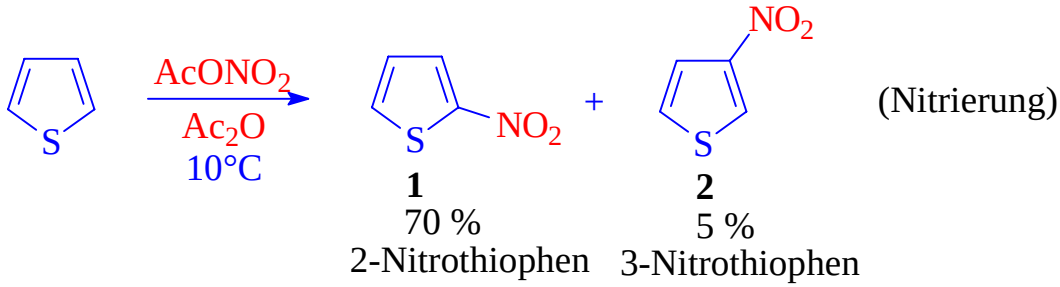
Substituierte Furane, Thiophene und Pyrrole aus 1,4-Diketone



Reaktionen

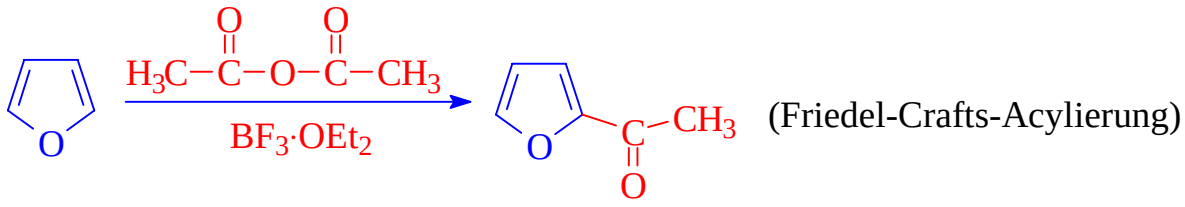
1) Elektrophile aromatische Substitution

Reaktivität: **Pyrrol > Furan > Thiophen >> Benzol**

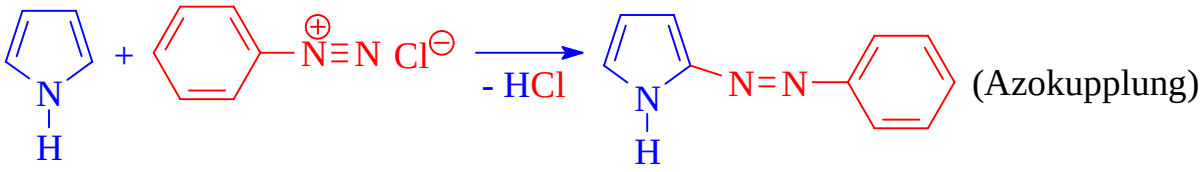


1
70 %
2-Nitrothiophen

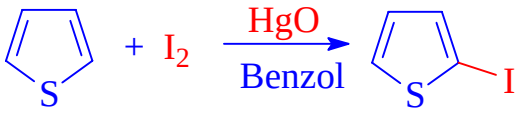
2
5 %
3-Nitrothiophen



75-92%
2-Acetylfuran

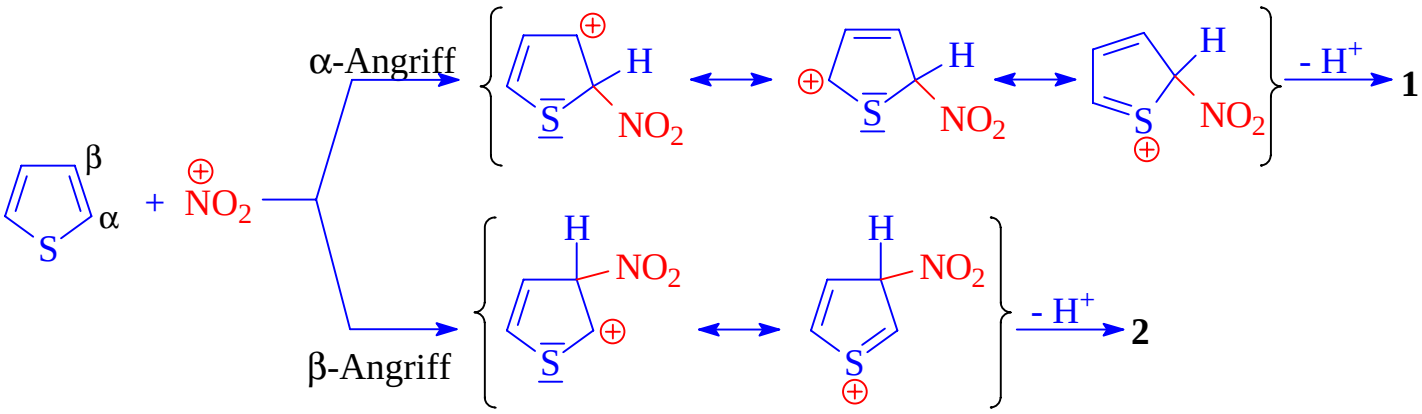


2-(Phenylazo)pyrrol



75 %
2-Iodthiophen

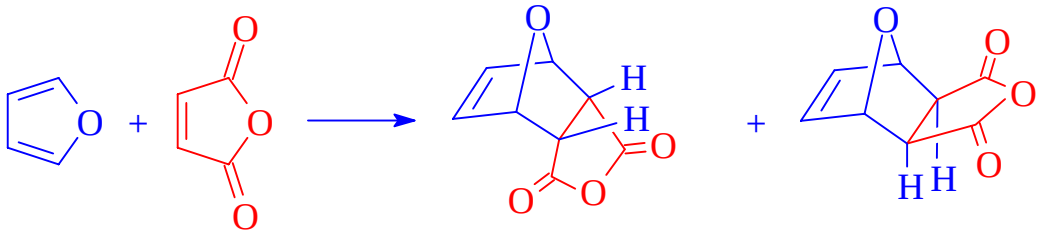
Orientierung bei der Substitution



weniger stabil
ungünstiger als α-Angriff

2) Diels-Alder-Reaktionen

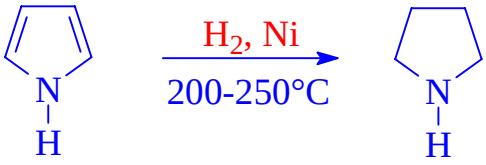
Reaktivität: **Furan > Pyrrol > Thiophen**



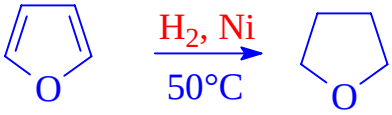
endo-Addukt
Hauptprodukt

exo-Addukt
Nebenprodukt

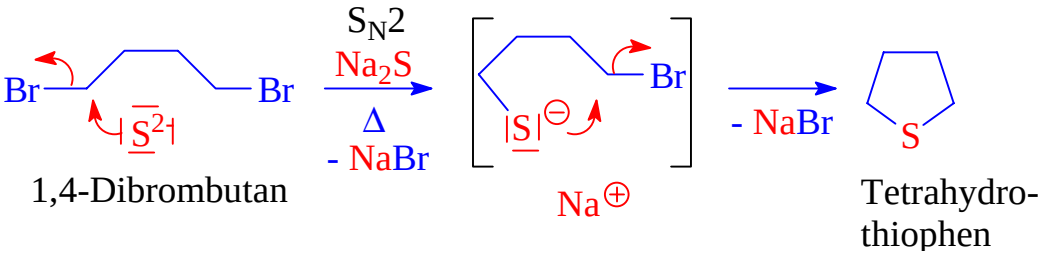
3) Hydrierung (gesättigte Systeme)



Pyrrol Pyrrolidin



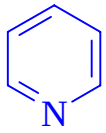
Furan THF



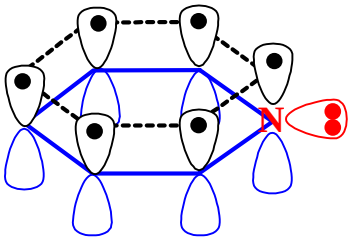
1,4-Dibrombutan

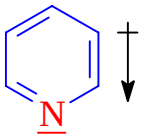
Tetrahydro-
thiophen

Sechsgliedrige Ringe (Sechring-Heteroaromaten)

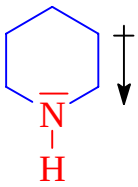
Pyridin: 

Dipolmoment



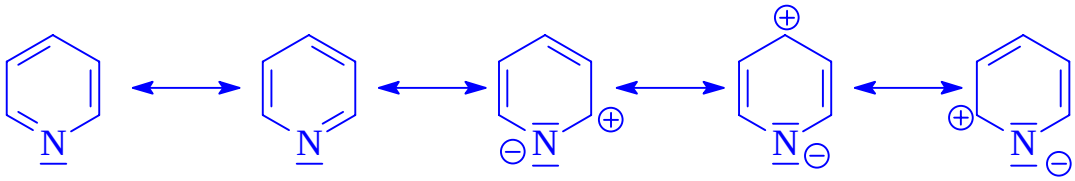


2.26 D

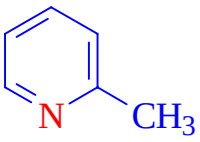


1.17 D

Kekule-Strukturen

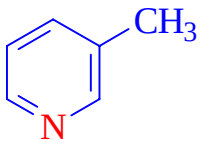


Pyridin-Derivate



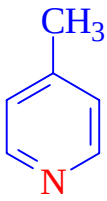
2-Methylpyridin

α-Picolin



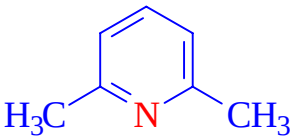
3-Methylpyridin

β-Picolin



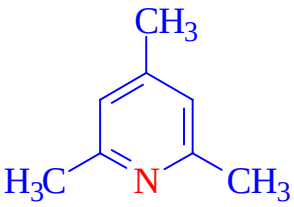
4-Methylpyridin

γ-Picolin



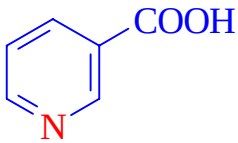
2,6-Dimethylpyridin

2,6-Lutidin



2,4,6-Trimethylpyridin

(Collidin)

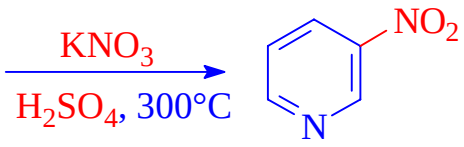


Nicotinsäure

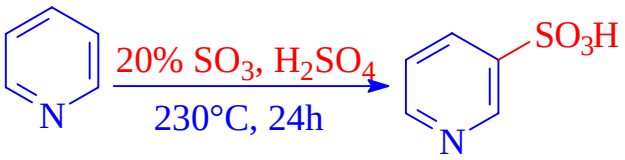
(3-Pyridincarbonsäure)

Reaktionen des Pyridins

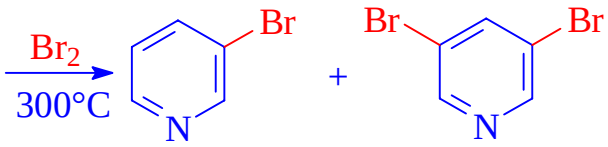
1) Elektrophile Substitution



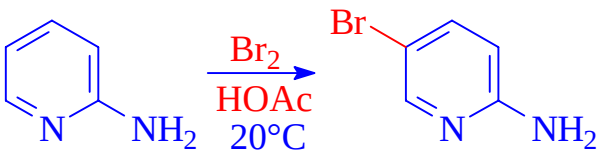
3-Nitropyridin
(22%)



3-Pyridinsulfonsäure
(71%)



3-Brompyridin 3,5-Dibrompyridin

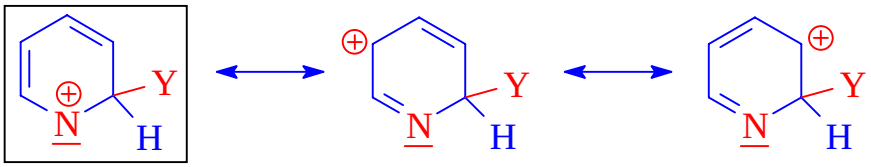


5-Brom-2-aminopyridin

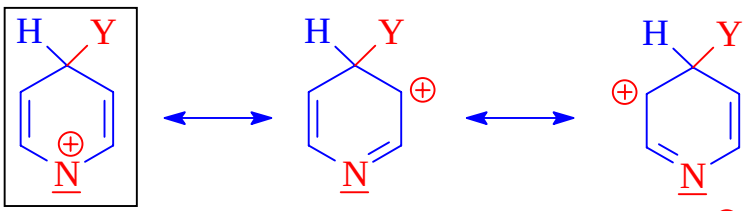
2-Aminopyridin

Erklärung der Orientierung des Substituenten in die m- bzw. 3-Position

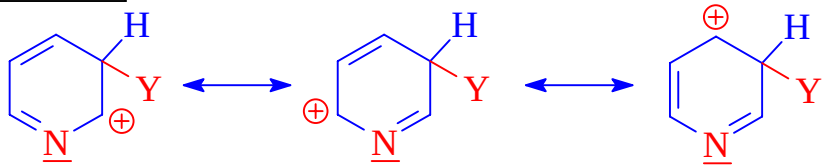
Elektronensextett und positive Ladung am N-Atom ⇒ besonders ungünstig



o-Substitution



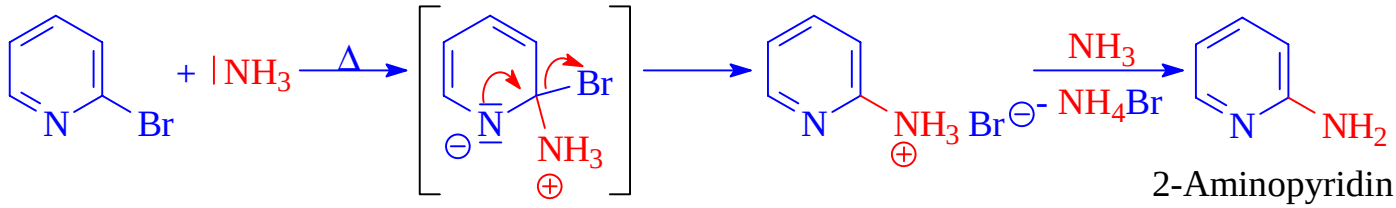
p-Substitution



m-Substitution

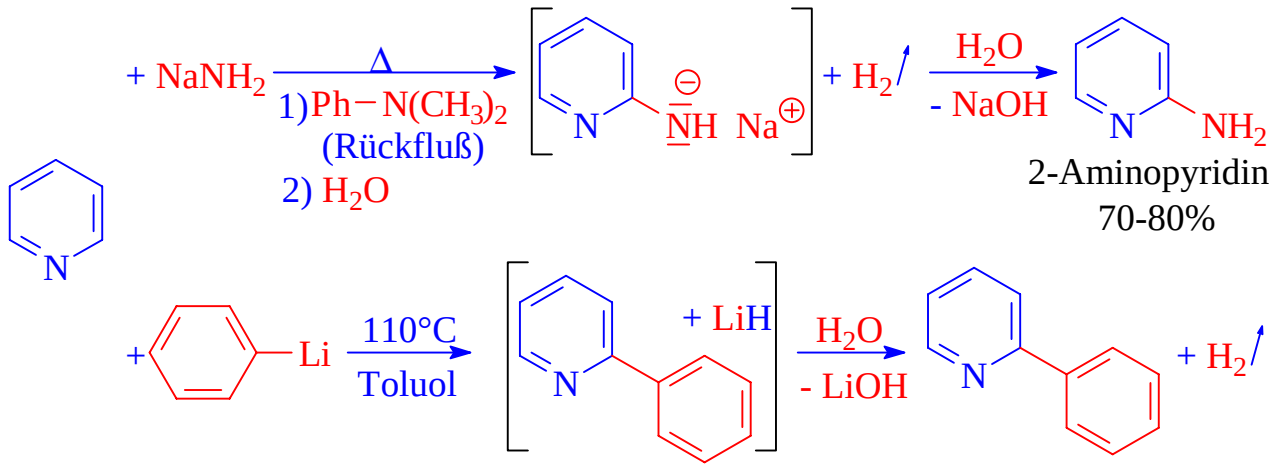
2) Nucleophile Substitution

a)

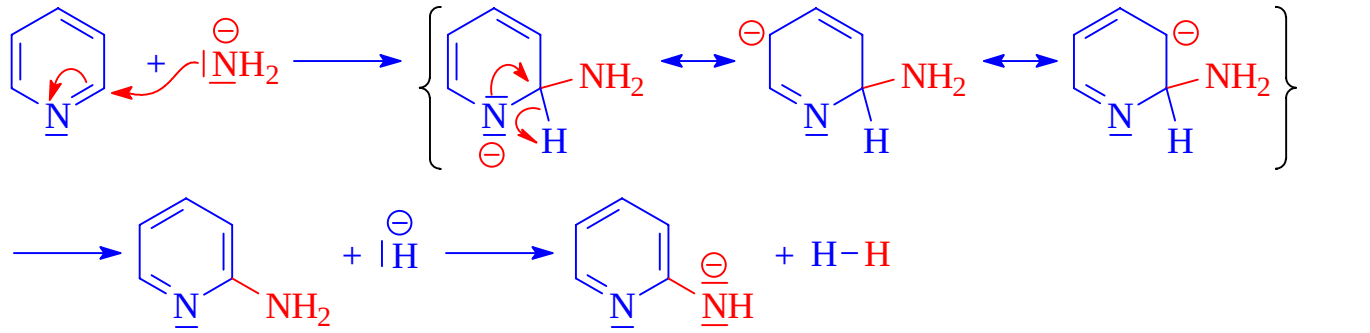


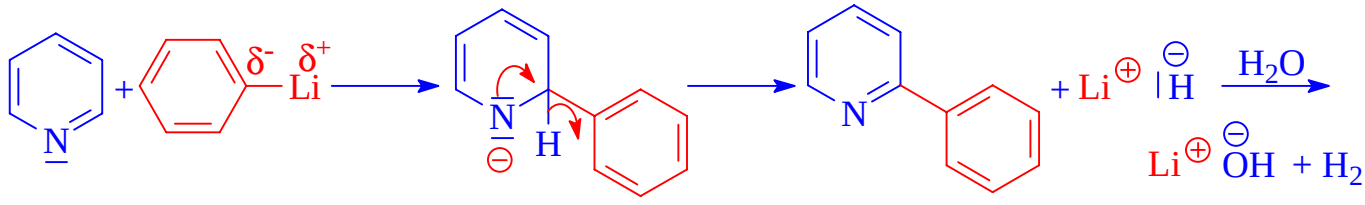
2-Aminopyridin

b) Tschitschibabin-Reaktion und Ziegler-Reaktion

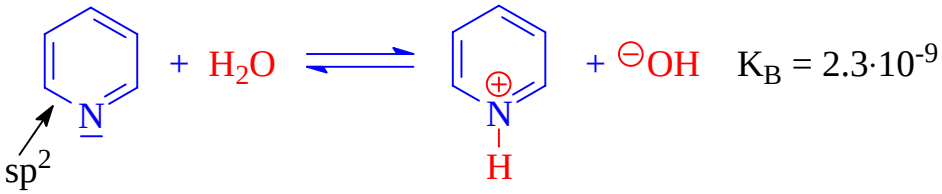


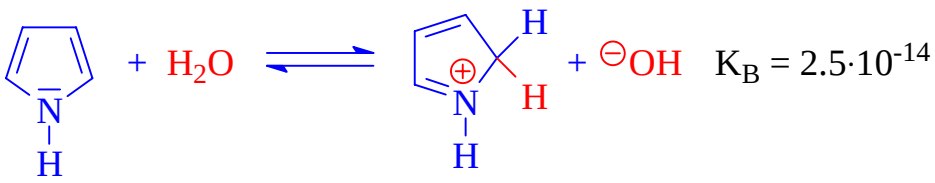
Mechanismus

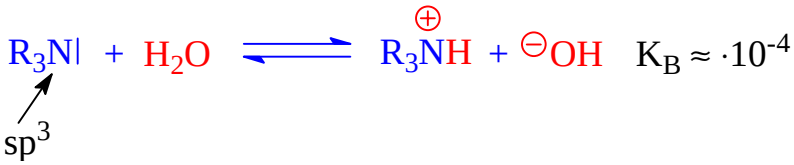




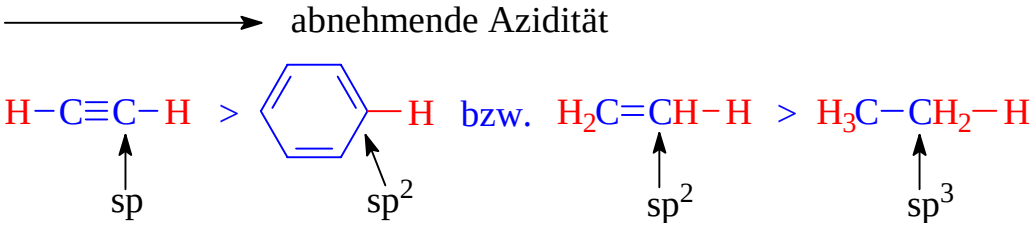
3) Basizität



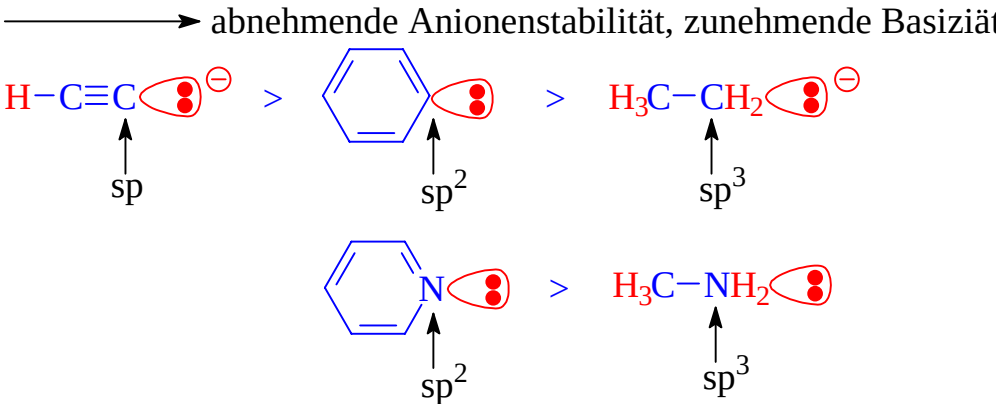


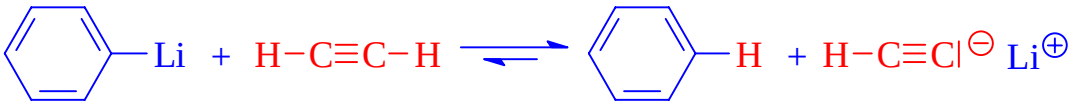


Relative Azidität

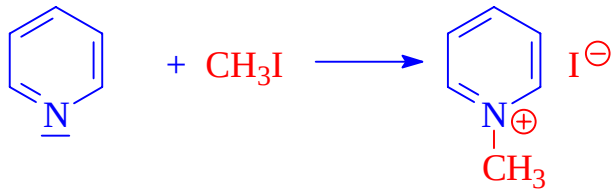


Stabilität der Anionen



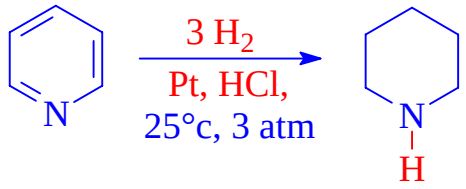


4) Alkylierung von Pyridin (S_N2-Reaktion)



N-Methyl-pyridiniumiodid

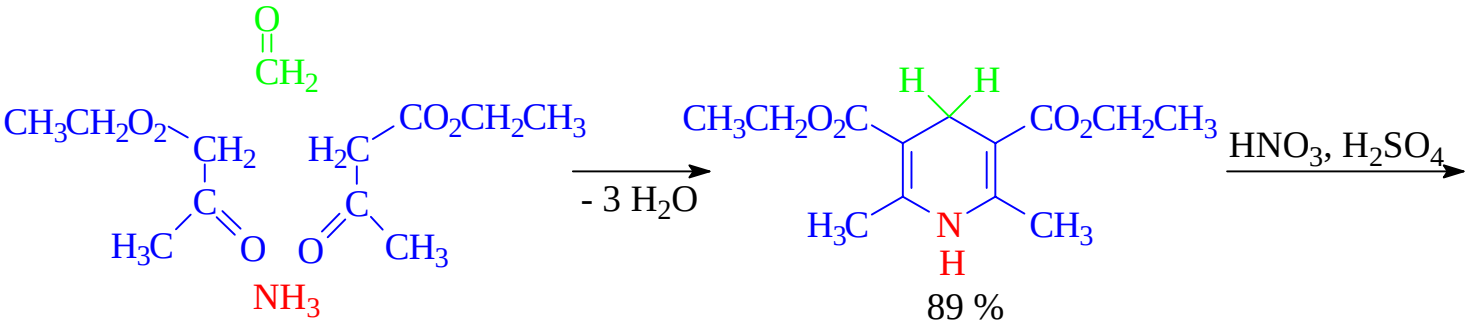
5) Reduktion



Piperidin

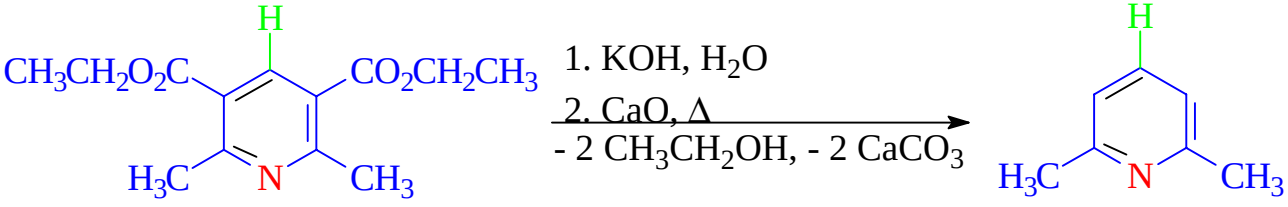
$K_B = 2 \cdot 10^{-3}$ [M]

Hantzsch-Synthese von 2,6-Dimethylpyridin



89 %

Diethyl-1,4-dihydro-2,6-dimethyl-3,5-pyridincarboxylat

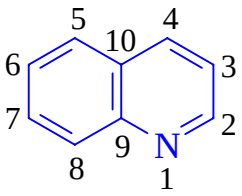


65 %

Diethyl-2,6-dimethyl-3,5-pyridincarboxylat

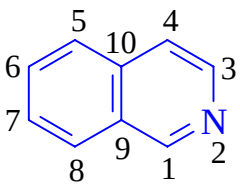
65 %

2,6-Dimethylpyridin



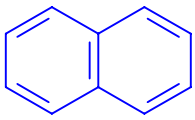
Chinolin

$K_B = 3 \cdot 10^{-10}$ [M]

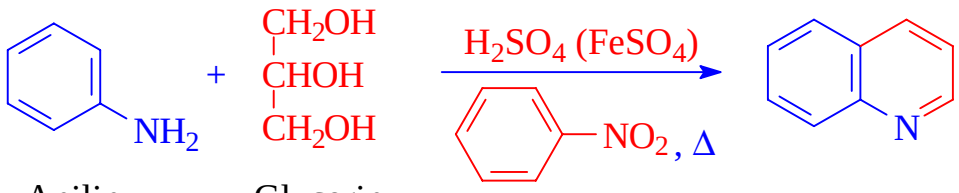


Isochinolin

$K_B = 1.1 \cdot 10^{-9}$ [M]

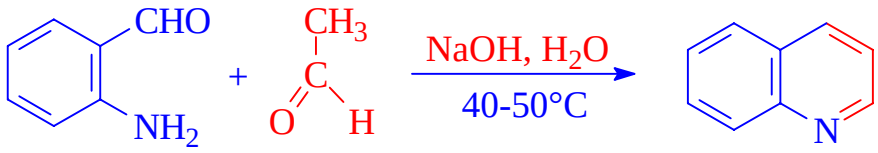


a) Skraup-Synthese von Chinolin



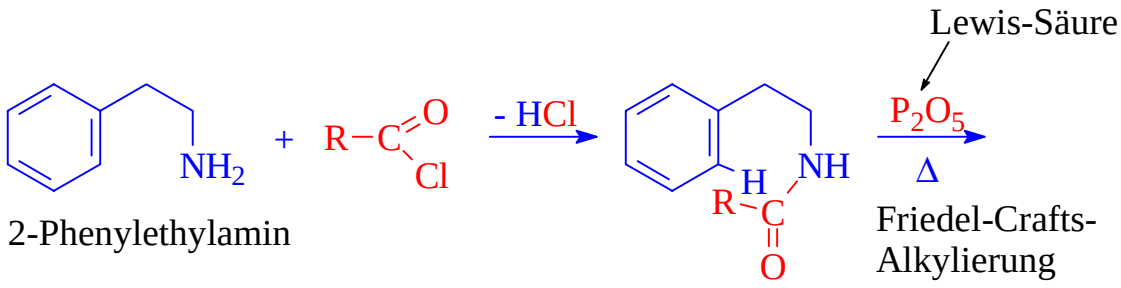
Anilin Glycerin

b) Friedländer-Synthese



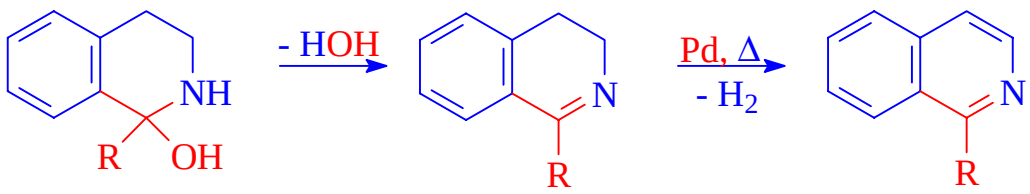
Aldol-Kondensation
nucleophile Addition

c) Bischler-Napieralski-Synthese von Isochinolin-Derivaten



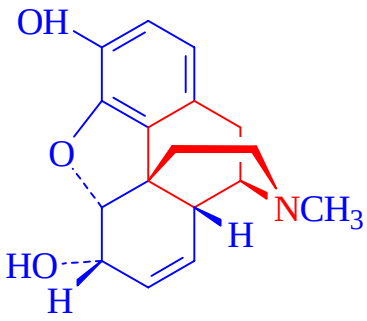
2-Phenylethylamin

Friedel-Crafts-
Alkylierung

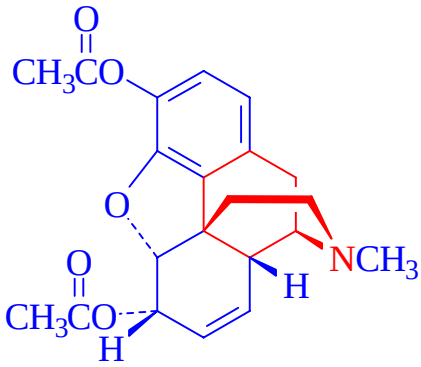


R = CH_3 : 1-Methylisochinolin

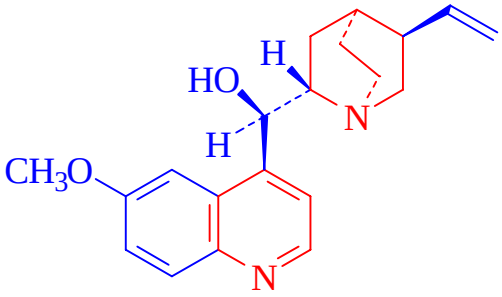
Alkaloide: Physiologisch wirksame Heterocyclen der Natur



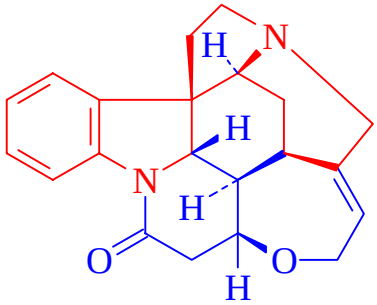
Morphin



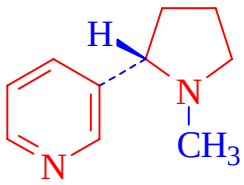
Heroin



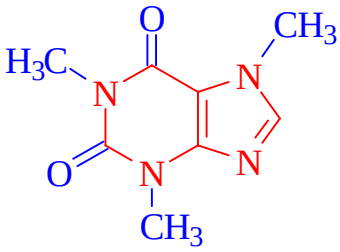
Chinin



Strychnin



Nicotin



Coffein