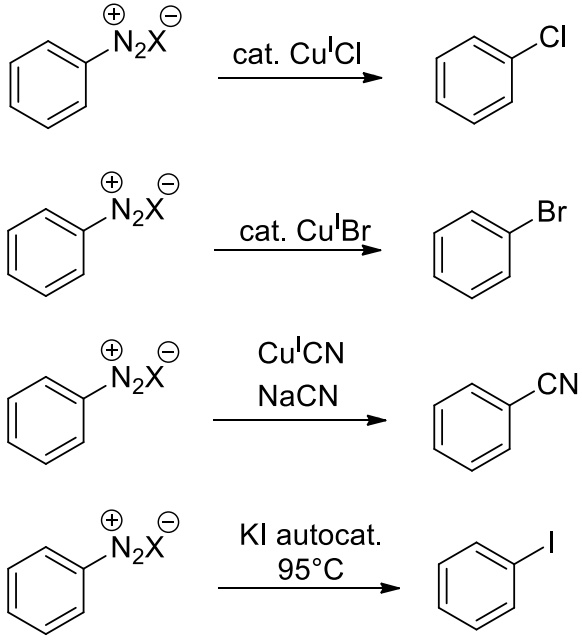
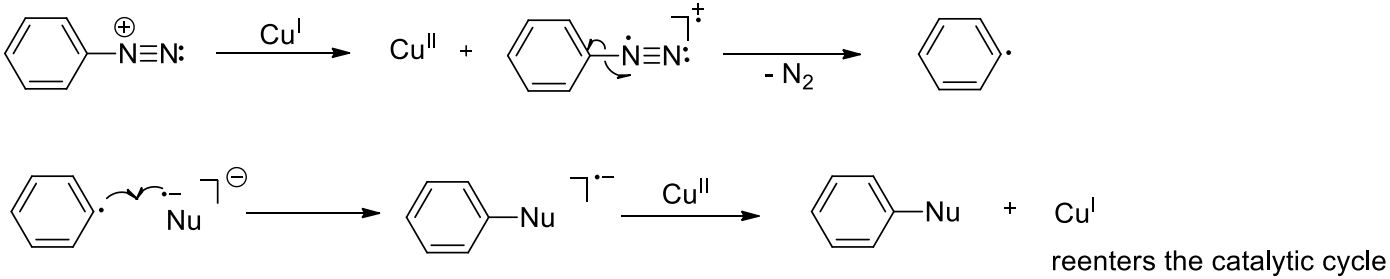
1.7. Reaction of diazonium salts

- Sandmeyer reaction



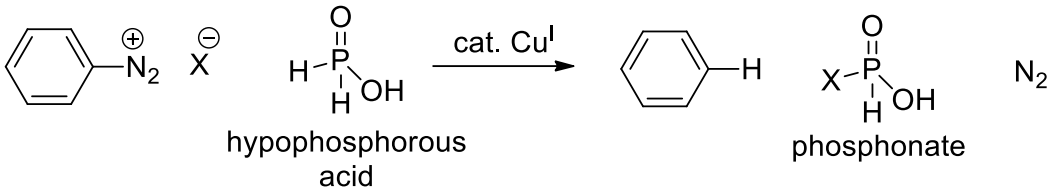
- General mechanism:



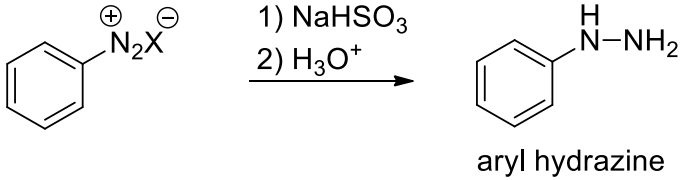
Exception: no copper needed with iodide, iodide act as a redox catalyst itself

1.7. Reaction of diazonium salts

- Meerwein reduction: removal of the diazonium group



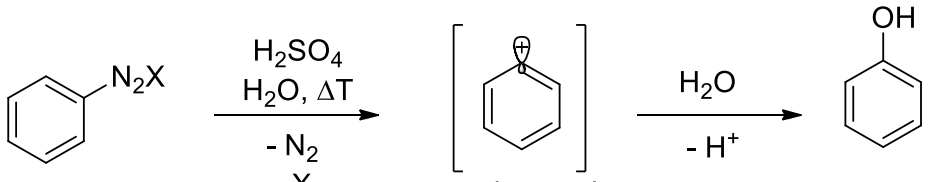
- Reduction of a diazonium salt maintaining the N-N single bond: preparation of aromatic hydrazines



1.7. Reactions proceeding by arenium cations

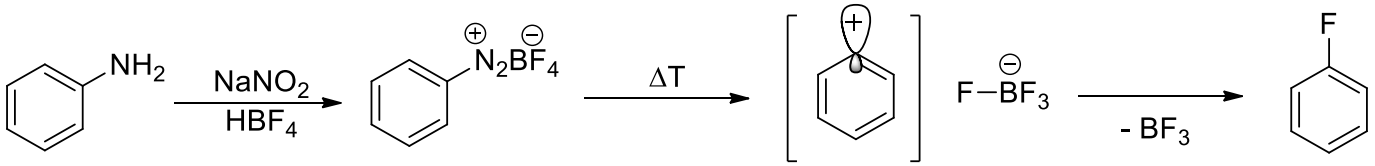
Only possible with the very best leaving group: N_2

- Generation of arene cations: “Phenol cooking”



arenium cation
orthogonal to π-system
unstabilized and very reactive

- Balz-Schiemann reaction: introduction of a fluorine substituent

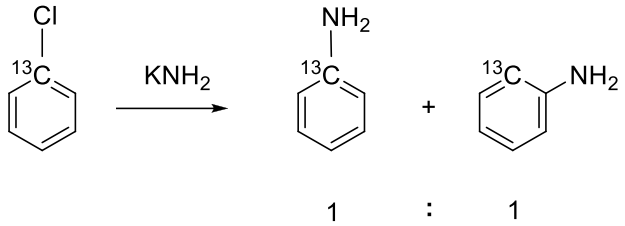


isolated salt

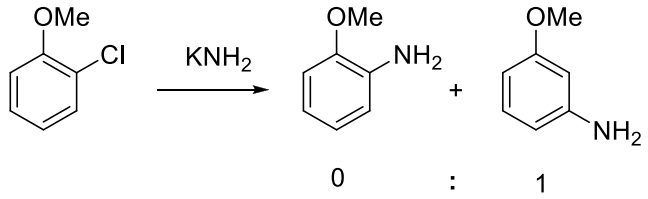
1.8. Substitution by the aryne mechanism

Experimental observations:

A)

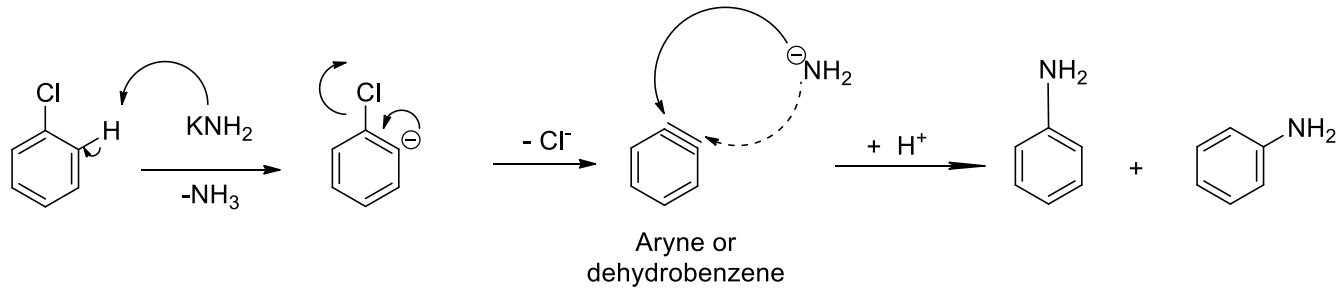


B)

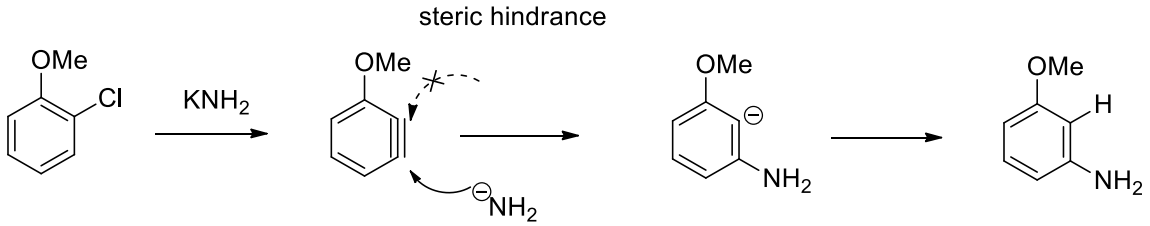


Explanation by a new mechanism:

A)



B)



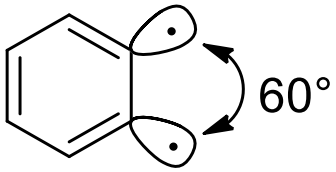
- σ- acceptor stabilizes the negative charge
- Attack on meta position due to less steric hindrance

1.8. Substitution by the aryne mechanism

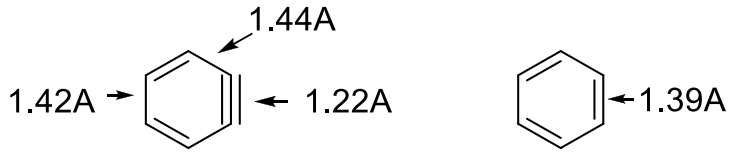
General properties of the arynes

- Are not real/normal triple bond with two sp-hybridized carbon atoms
- Only a partial orbital overlap possible, remain mostly sp^2-hybridized

- Arynes are reactive singulett species

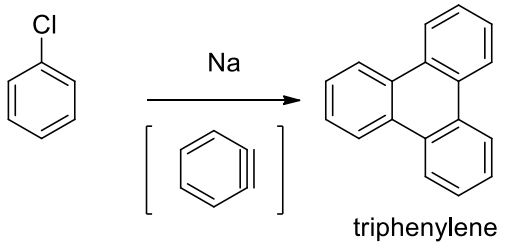


- Bond lengths in comparison to benzene



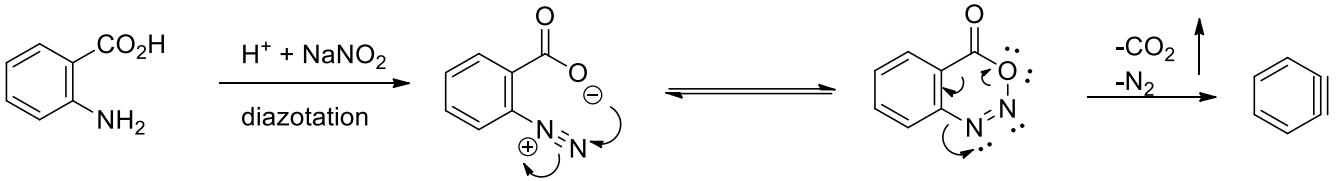
1.8. Substitution by the aryne mechanism

Other reactions of arynes:

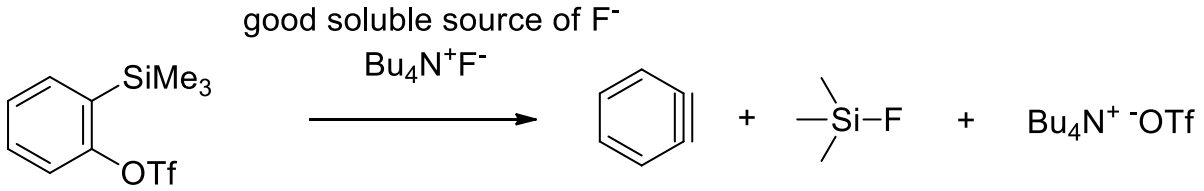


Trimerization in higher concentration and absence of reaction partner

Additional methods for their preparation:



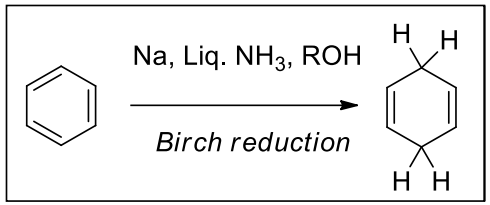
Modern method:



Tf= Triflat, Trifluoromethane sulfonyl $^{-}O_3SCF_3$

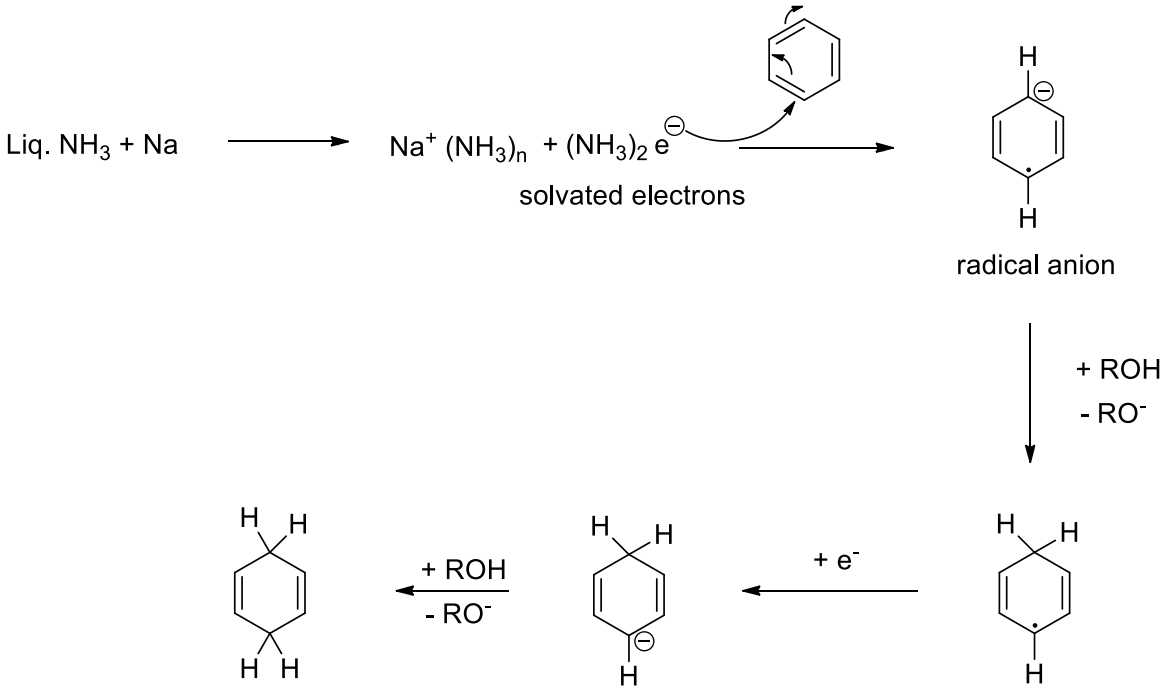
1.9. Reduction of the aromatic ring

Birch reduction: reduction of the aromatic ring to give 1,4-cyclohexadienes



Solvent: liquid ammonia
Reaction below -31°C

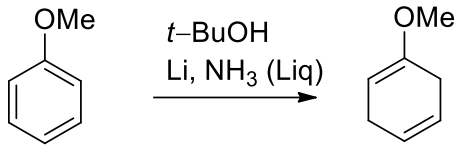
Mechanism:

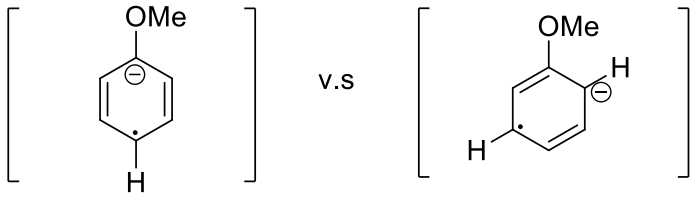


1.9. Reduction of the aromatic ring

Regioselectivity of the reduction:

Case 1: Electron-donating substituents

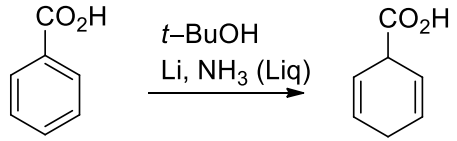


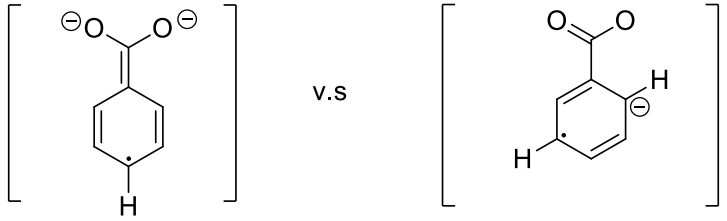


less stable intermediate not formed

more stable intermediate preferred

Case 2: Electron-withdrawing substituents





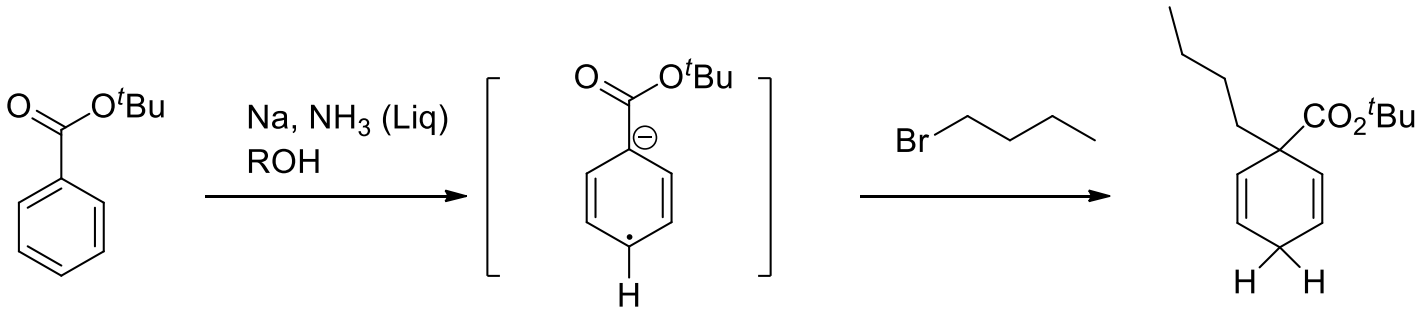
better stabilization of the negative charge

not formed

1.9. Reduction of the aromatic ring

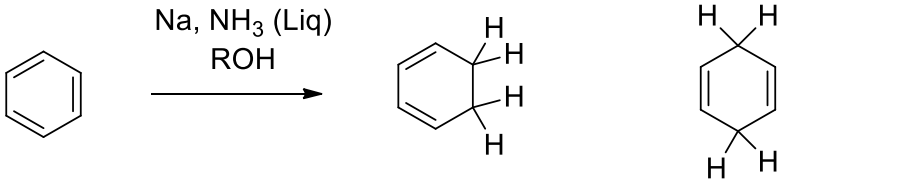
Example for a Birch alkylation:

interception of the carbanion by an electrophile, e.g. alkylhalide instead of proton

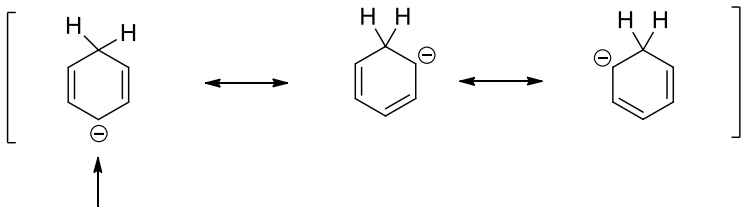


1.9. Reduction of the aromatic ring

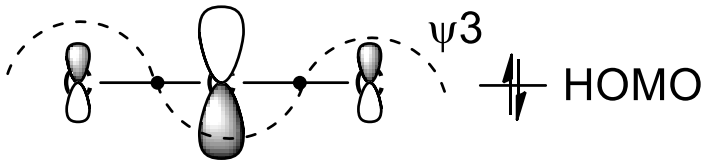
The Birch reduction yields selectively 1,4-Cyclohexadienes.
Why are 1,3-Cyclohexadienes not formed?

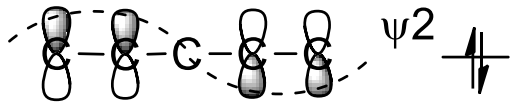


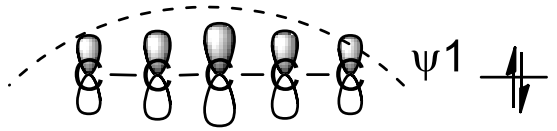
Explanation by the electron densities of the pentadienyl anion



MO scheme:

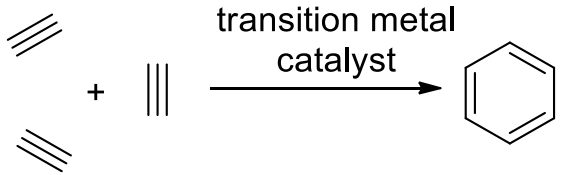






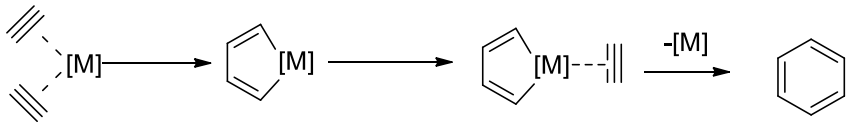
Relevant HOMO: the electron density is highest at central carbon atom C3

1.10. Construction of the aromatic ring: metal-catalyzed [2+2+2]-cyclization

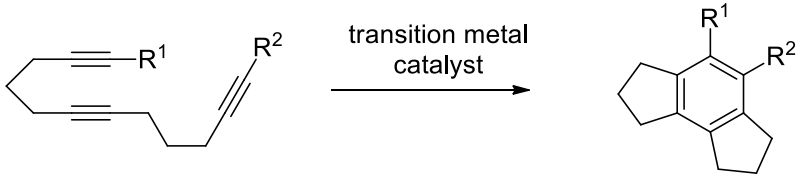


Several different metal complexes of Ni^0, Rh^I, Ir^I, Ru, Co, Pd are known for this reactivity.

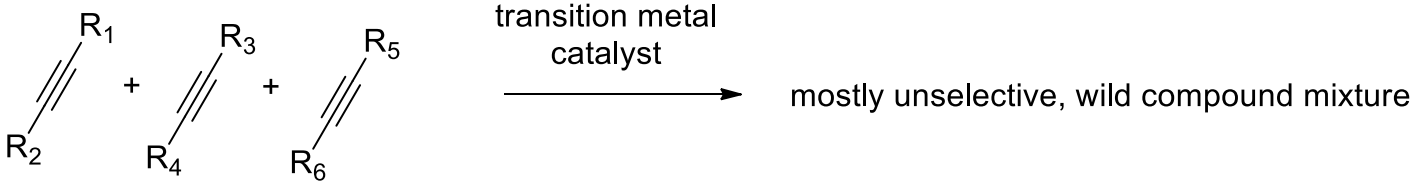
Simplified mechanism:



Well suited and excellent for intramolecular reactions



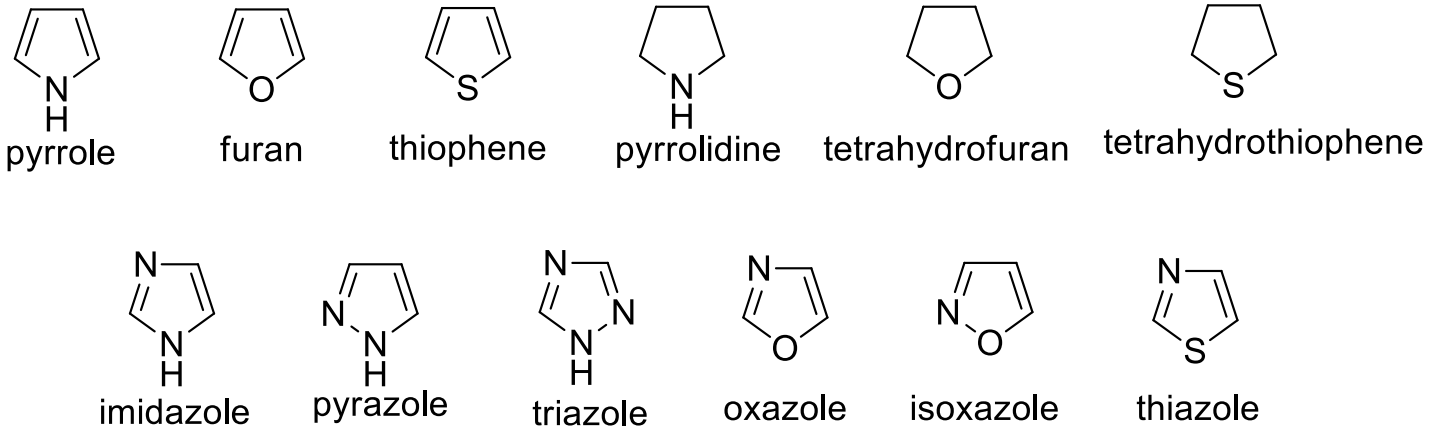
Problems of regioselectivity and chemoselectivity with different substituted alkynes



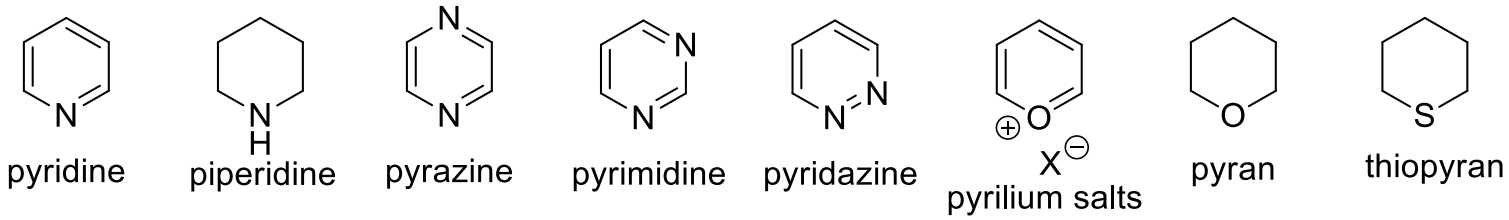
2.1.1. Nomenclature: trivial names

- Most important heterocycles:

– 5-membered ring series:



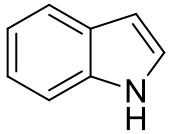
– 6-membered ring series:



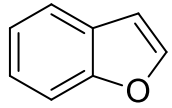
2.1.1. Nomenclature: trivial names

- Most important heterocycles:

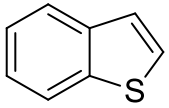
– Condensed series:



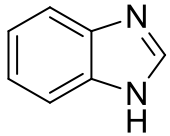
indole



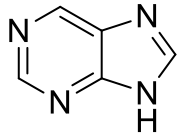
benzofuran



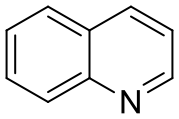
benzothiophene



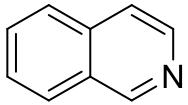
benzimidazole



purine



quinoline



isoquinoline

2.1.2. Nomenclature: The Hantsch-Widman system

- the essentials:

– Name is composed by number + prefixe(s) + suffix

– Numbering rules:

1) heteroatom is always number 1

2) If multiple heteroatoms priority: O > S > N

3) The smallest numbering combination for the heteroatoms is then correct

– Prefix originates from the heteroatom: N = az(a)

O = ox(a)

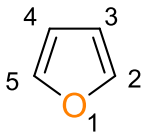
S = thi(a)

2.1.2. Nomenclature: The Hantsch-Widman system

– Suffix determines the ring size:

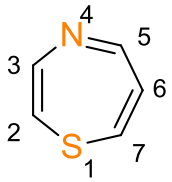
Ring size	Unsaturated ring	Saturated ring	N-Saturated ring
3	irene	irane	iridine
4	ete	etane	etidine
5	ole	olane	olidine
6	ine	inane	
7	epine	epane	
8	ocine	ocane	
9	onine	onane	

– Examples:

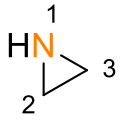


1-oxole

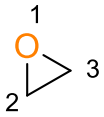
trivial name:
furane



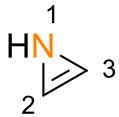
1,4-thiazepine



aziridine



oxirane



azirene