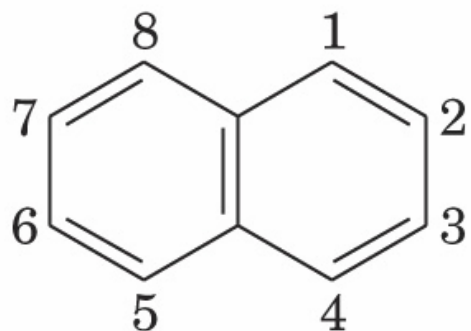


CHAPTER 19

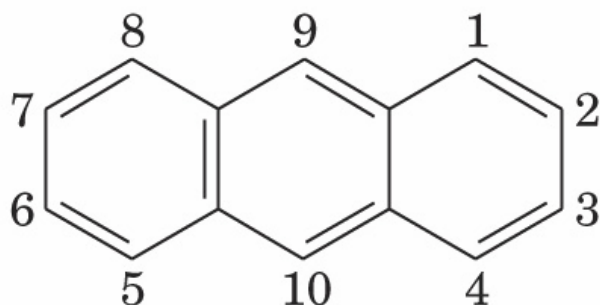
Polycyclic And Heterocyclic Aromatic Compounds

Nomenclature of Polycyclic Aromatic Compounds

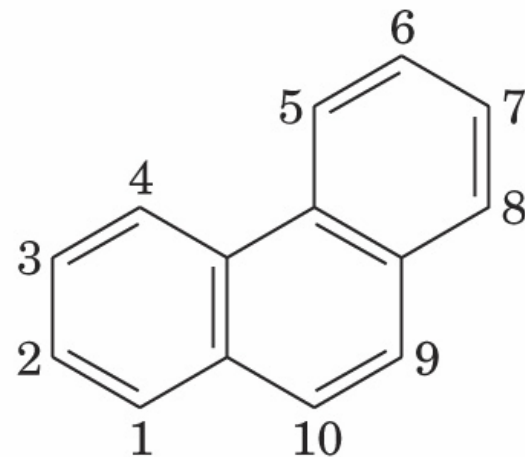
Polycyclic aromatic compounds have two or more benzene rings fused together



Naphthalene
 $C_{10}H_8$

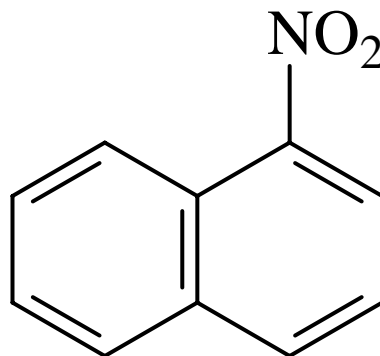
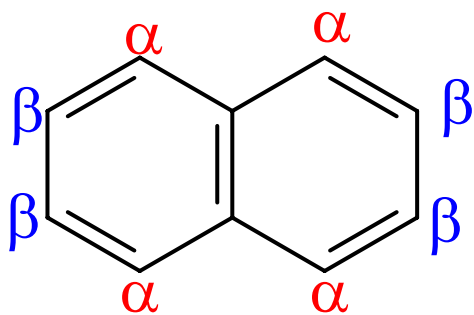


Anthracene
 $C_{14}H_{10}$

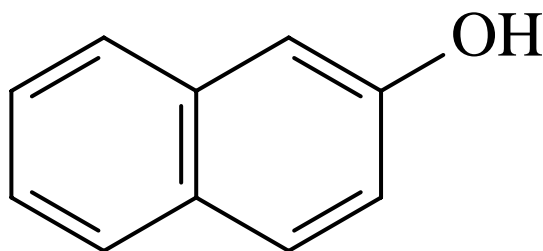


Phenanthrene
 $C_{14}H_{10}$

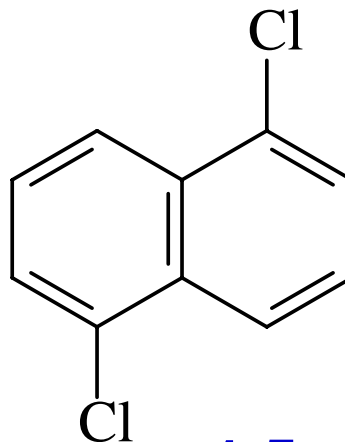
Monosubstituted Naphthalene is often designated by Greek Letter



1-nitronaphthalene
 β -nitronaphthalene

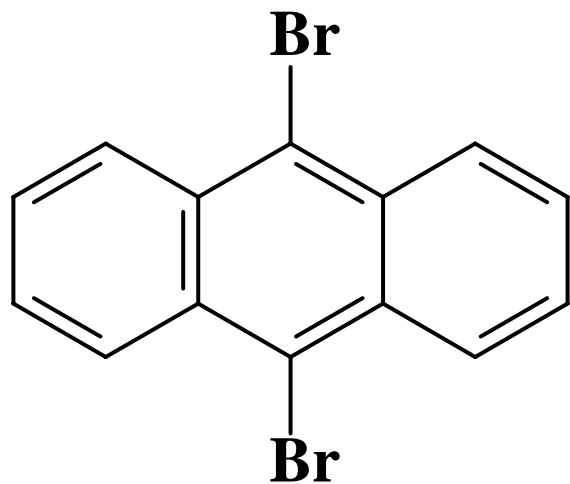


2-naphthol
 β -naphthol

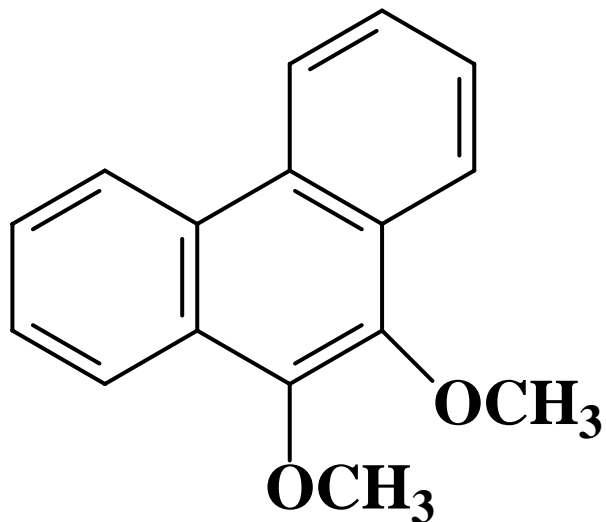


1,5-dichloronaphthalene

More Naming



9,10-dibromoanthracene

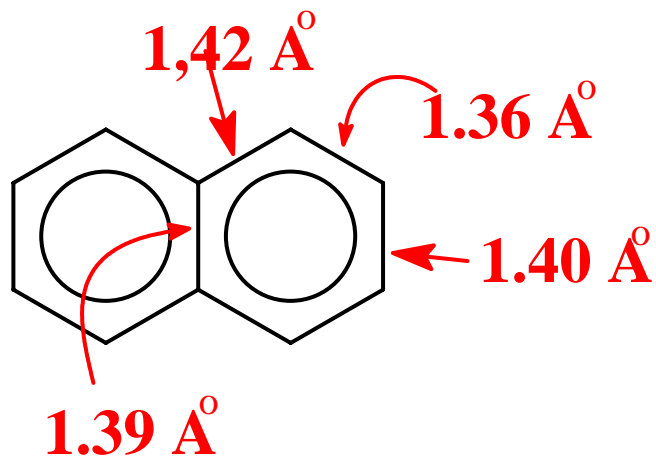


9,10-dimethoxy phenanthrene

Bonding in Polycyclic Aromatic Compounds

- In benzene, all C-C bond lengths are equal (equal distribution of *pi* electrons around the benzene ring).
- In the polycyclic aromatic compounds, the C-C bond lengths are **not** the same (e.g. the distance between carbon 1 and 2 = 1.36 Å in naphthalene is smaller than the distance between Carbon 2 and 3 = 1.40 Å) → there is no equal distribution of *pi* electrons around naphthalene

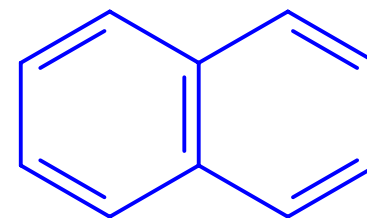
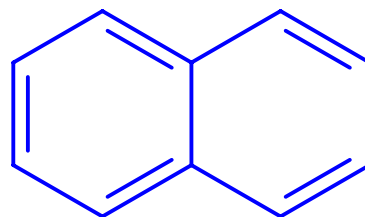
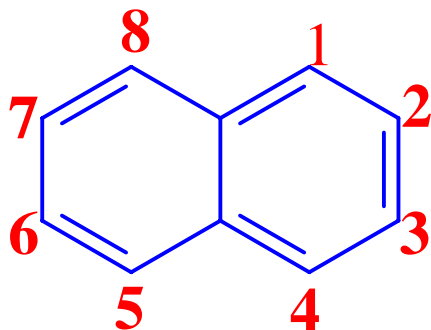
Comparison of bond lengths in Naphthalene



C-C in ethane: 1.54 Å

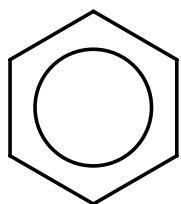
C-C in ethylene: 1.34 Å

C-C in benzene: 1.40 Å

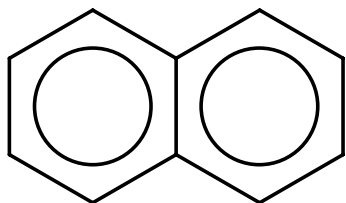


Two out of three resonance structures show a carbon 1 carbon 2 double bond

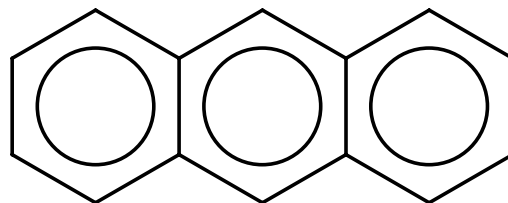
Resonance Energy of Polycyclic Aromatic Compounds



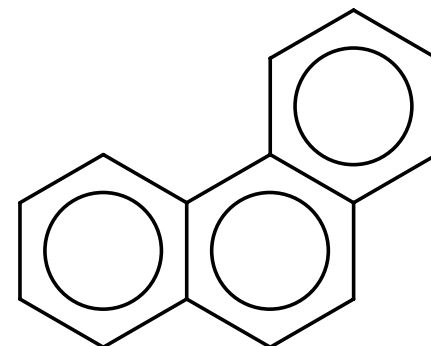
36



61



84

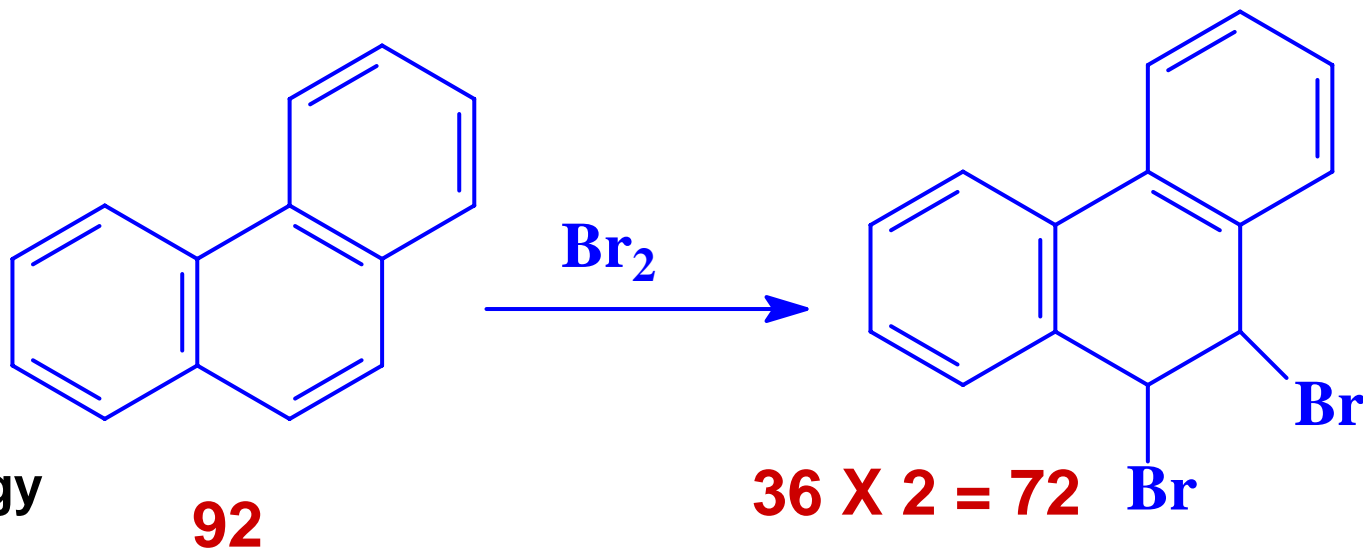


92 Kcal/mol

The resonance energy per ring is less than that of benzene → suggest

- the polycyclic aromatic compounds are more reactive than benzene.
- reaction at one ring loses less energy because the product still have one or more intact benzenoid rings.

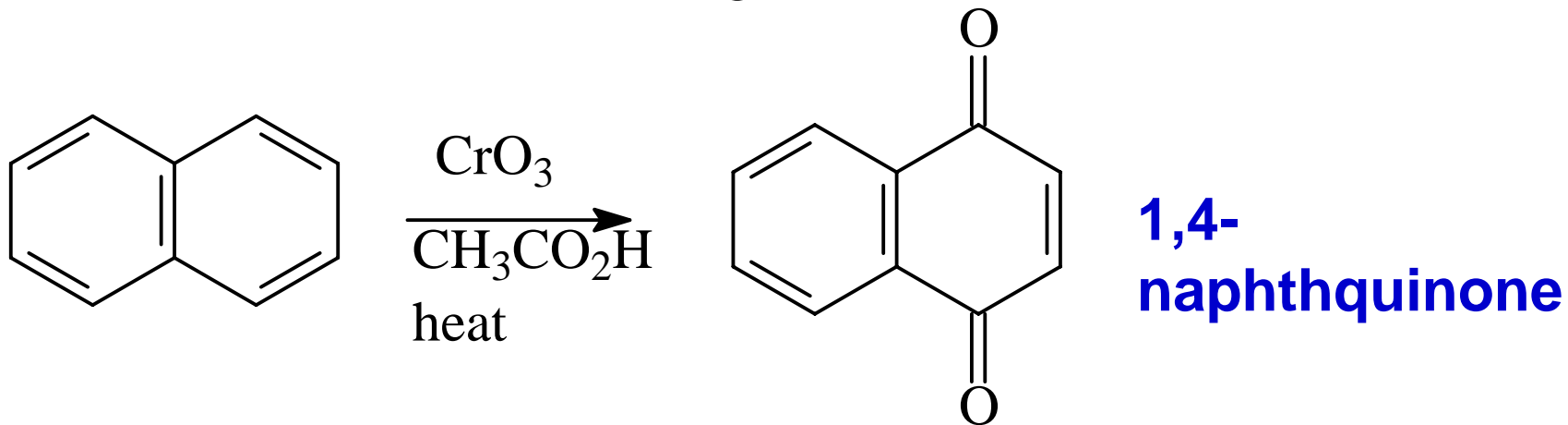
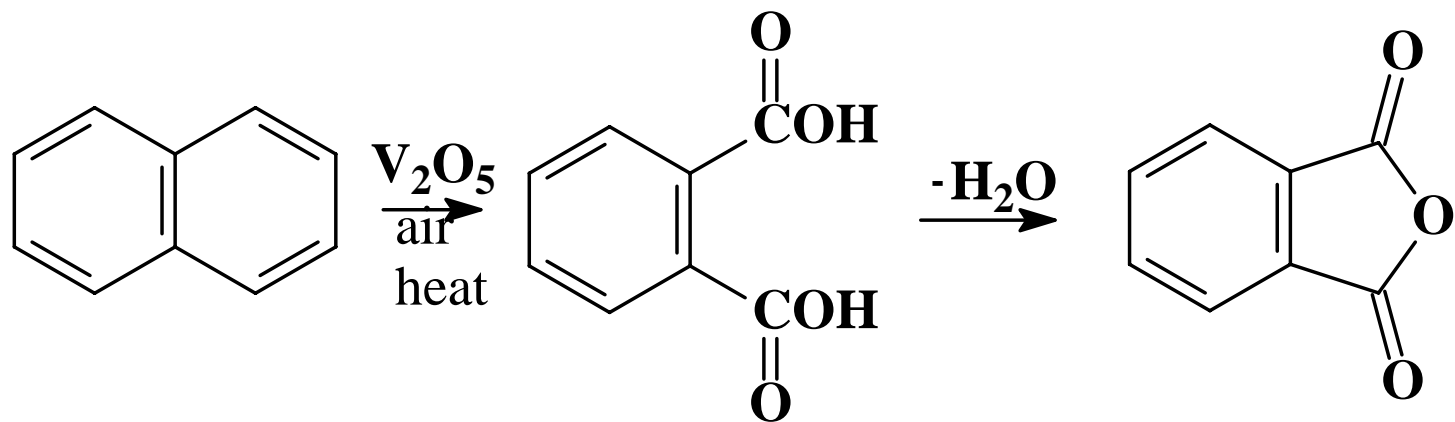
Example



The product still has two benzene rings ; it loses only 20 Kcal/mol

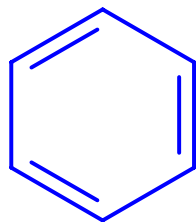
Oxidation of Naphthalene

- Naphthalene can be oxidized to products in which much of the aromaticity is retained.

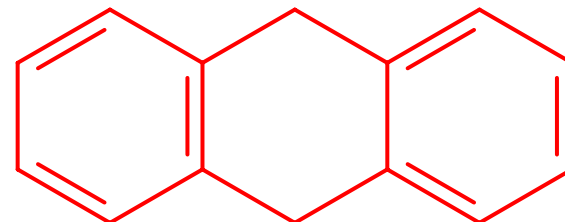
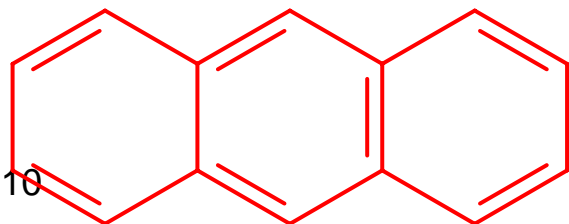
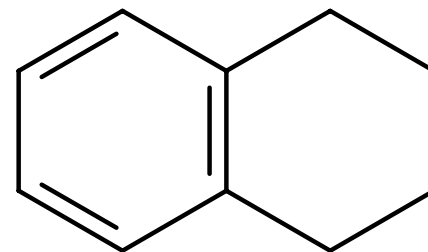
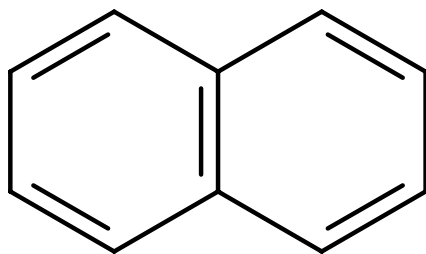


Reduction of Polycyclic Aromatic Compounds

The polycyclic aromatic compounds (unlike benzene) can be hydrogenated without heat or pressure, or they can be reduced with sodium and ethanol

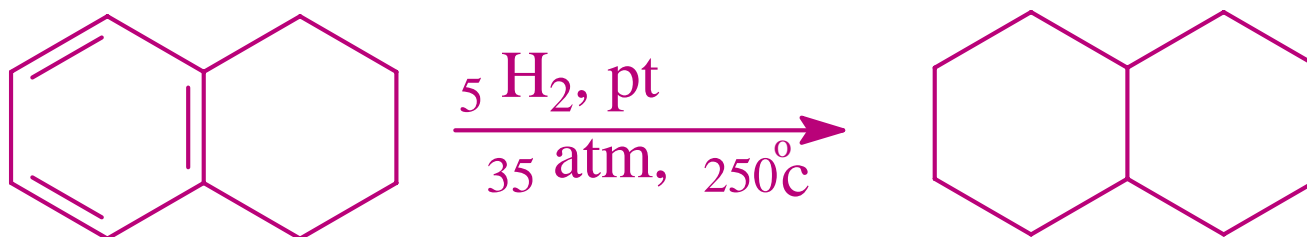
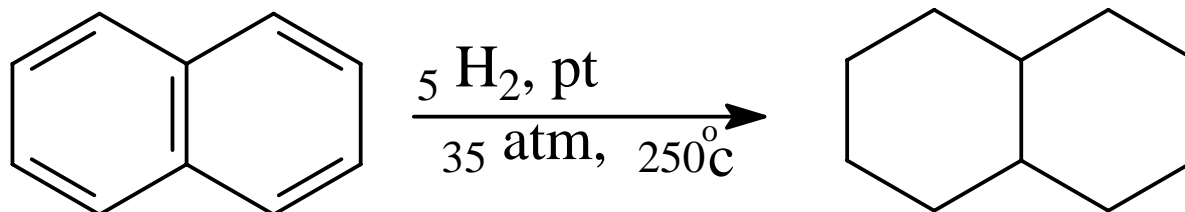


no reaction



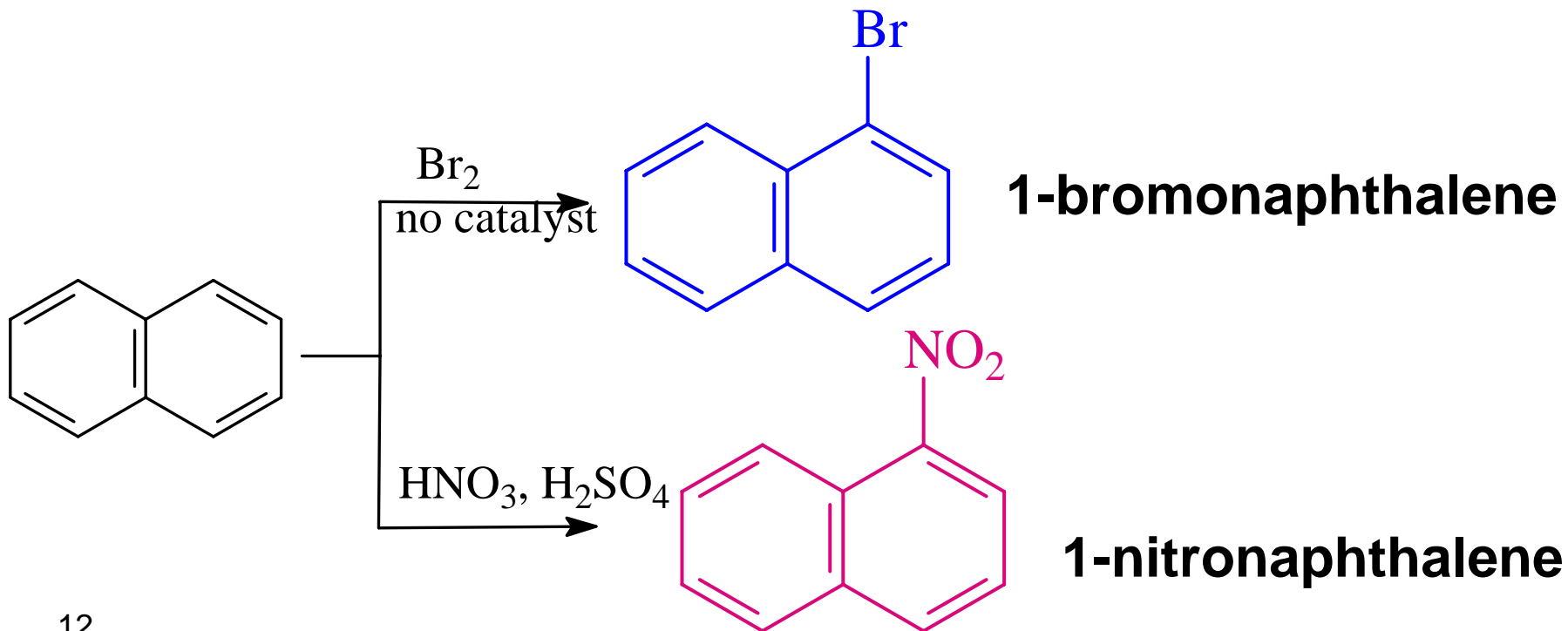
Hydrogenation of Polycyclic Aromatic Compounds

Hydrogenation of Polycyclic Aromatic Compounds requires heat and pressure just as it does for benzene

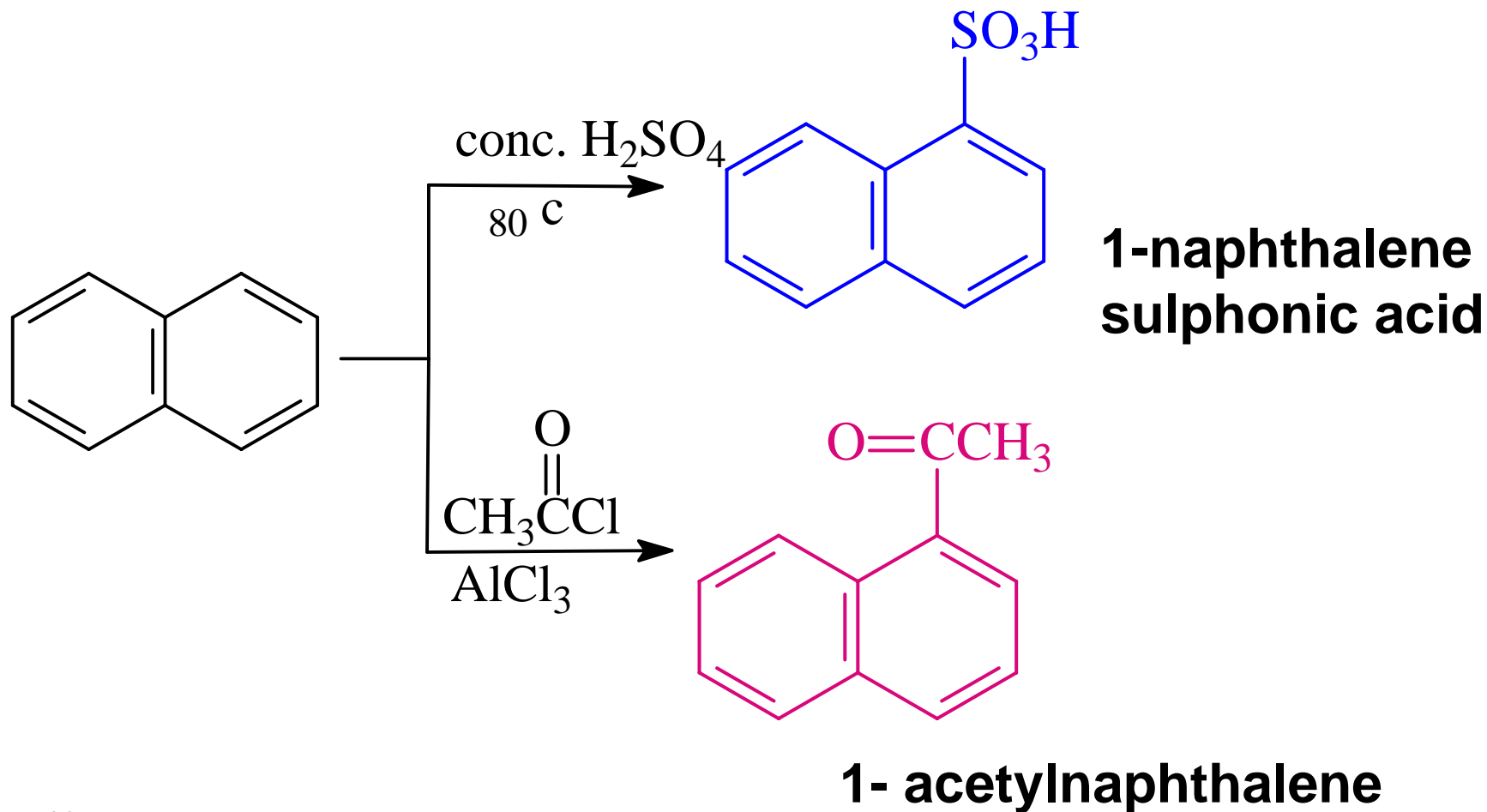


Electrophilic Aromatic Substitution of Naphthalene

Naphthalene undergoes electrophilic aromatic substitution predominately at the 1-position (α -position)

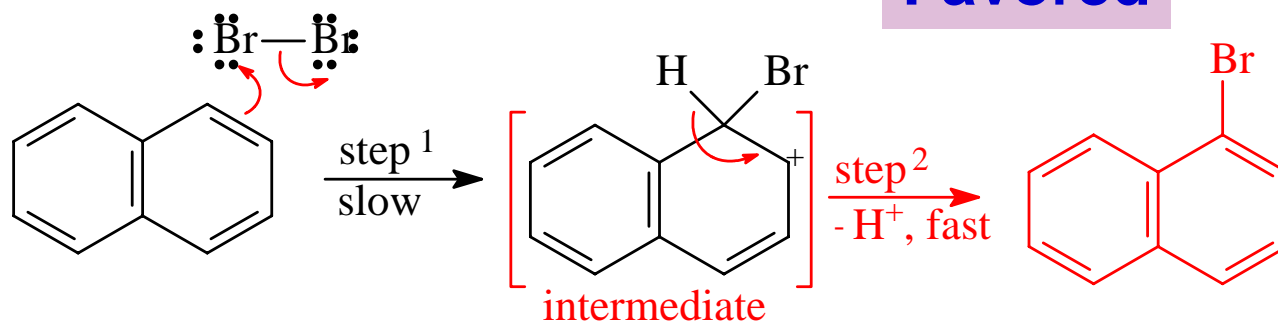


More Electrophilic Aromatic Substitution Reactions

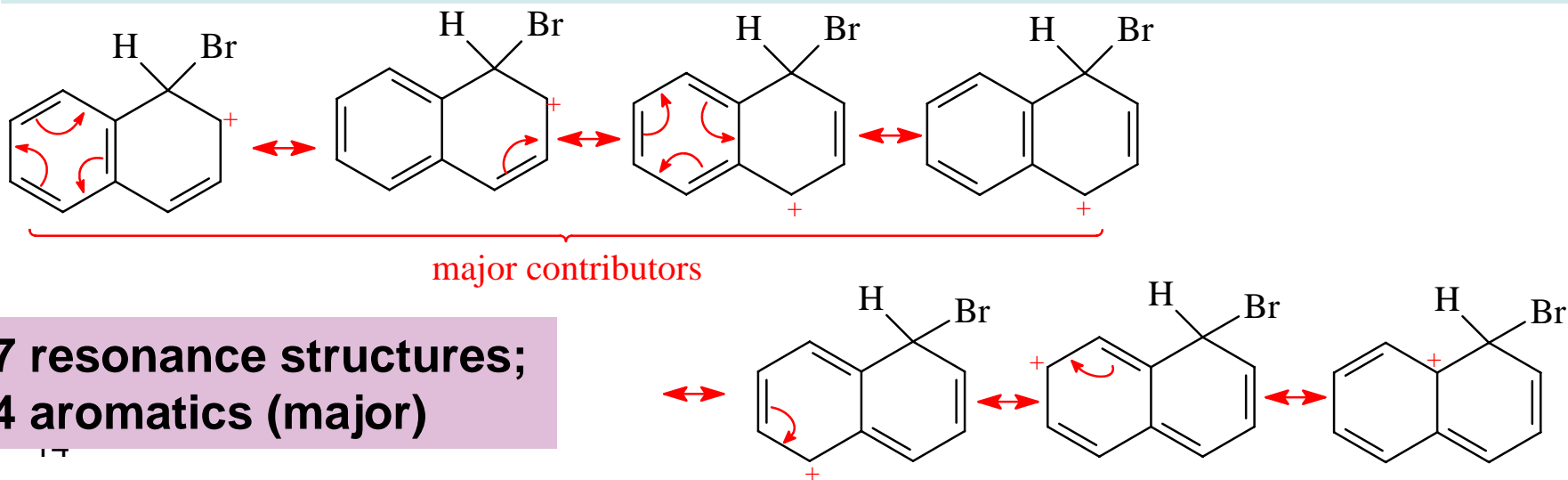


Position of Substitution of Naphthalene

1-substitution Mechanism

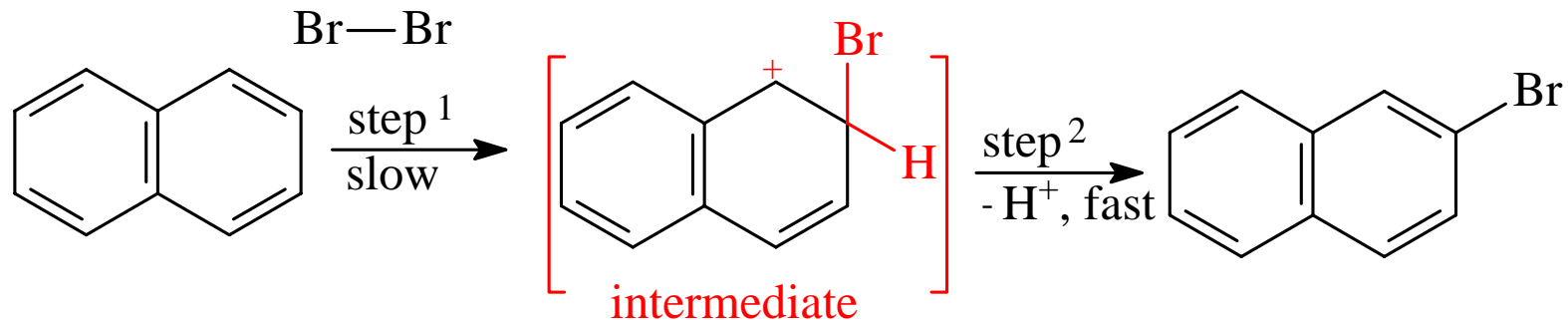


Resonance structures for the 1- substitution intermediate



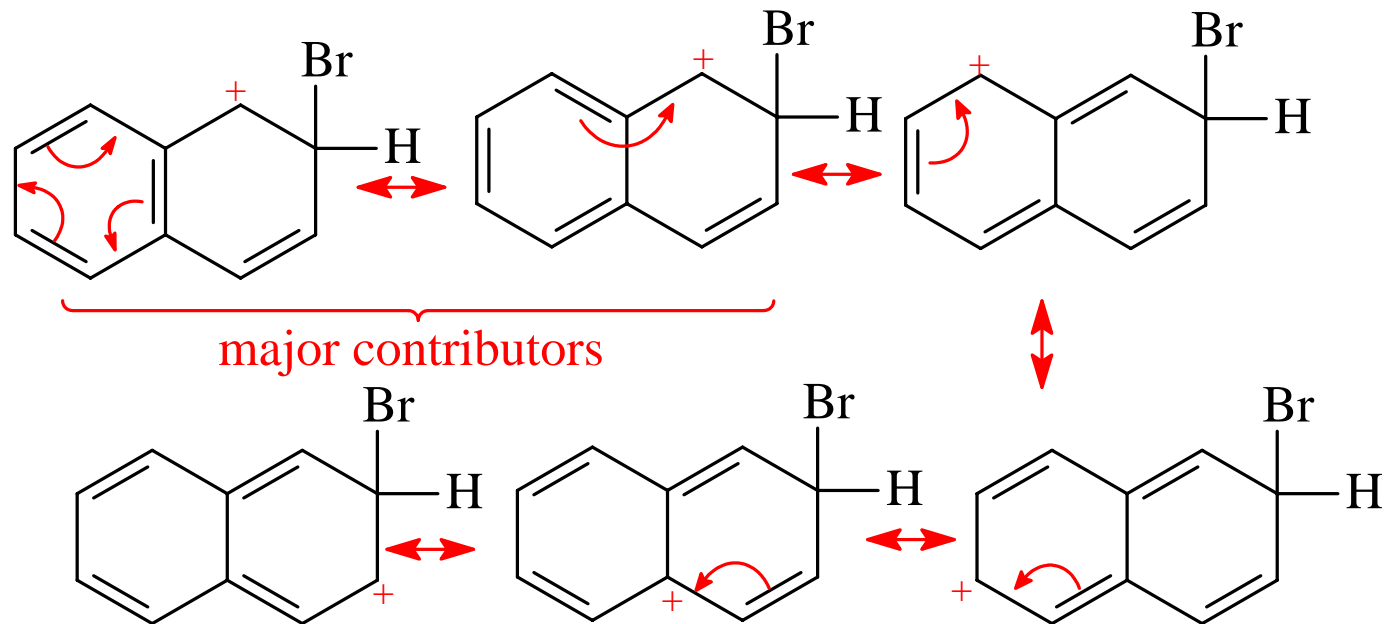
2-position mechanism

Not favored

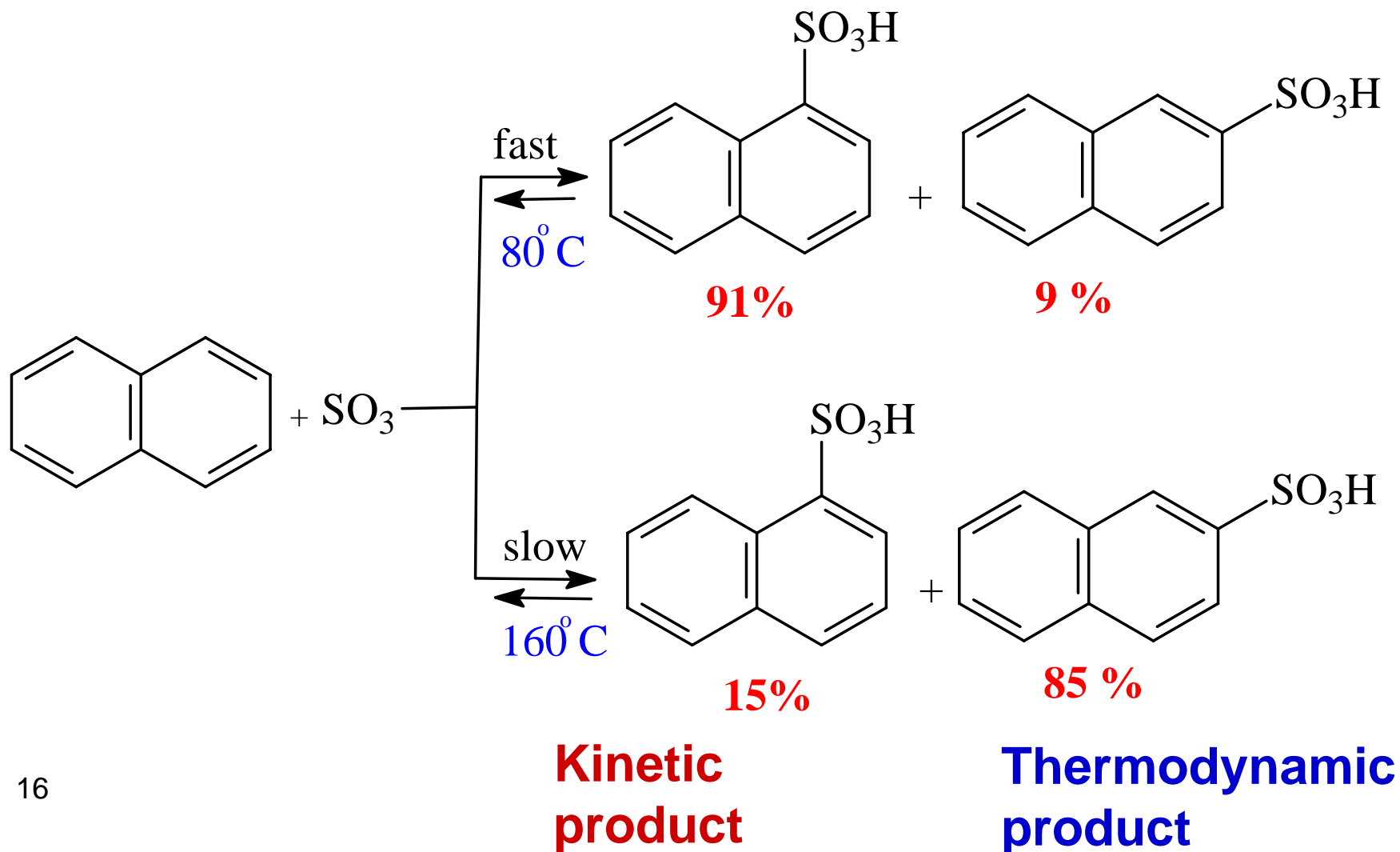


Resonance structures for the 2- substitution intermediate

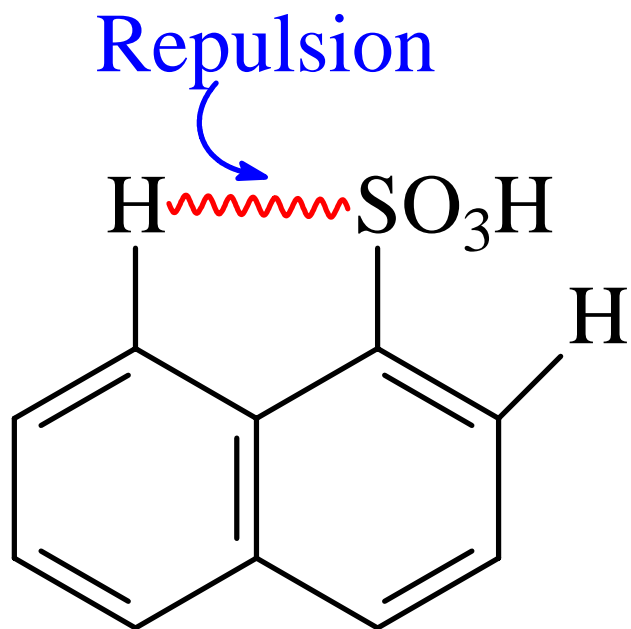
Only 6
resonance
structures;
2 aromatics



Sulfonation of Naphthalene

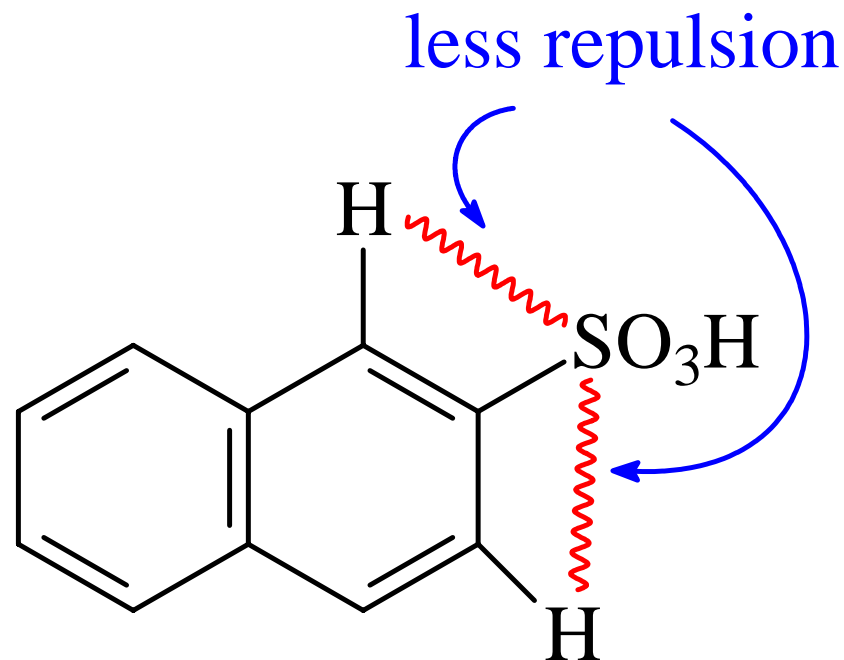


1-naphtalenesulphonic acid **vs** 2-naphtalenesulphonic acid



1-naphtalenesulphonic acid

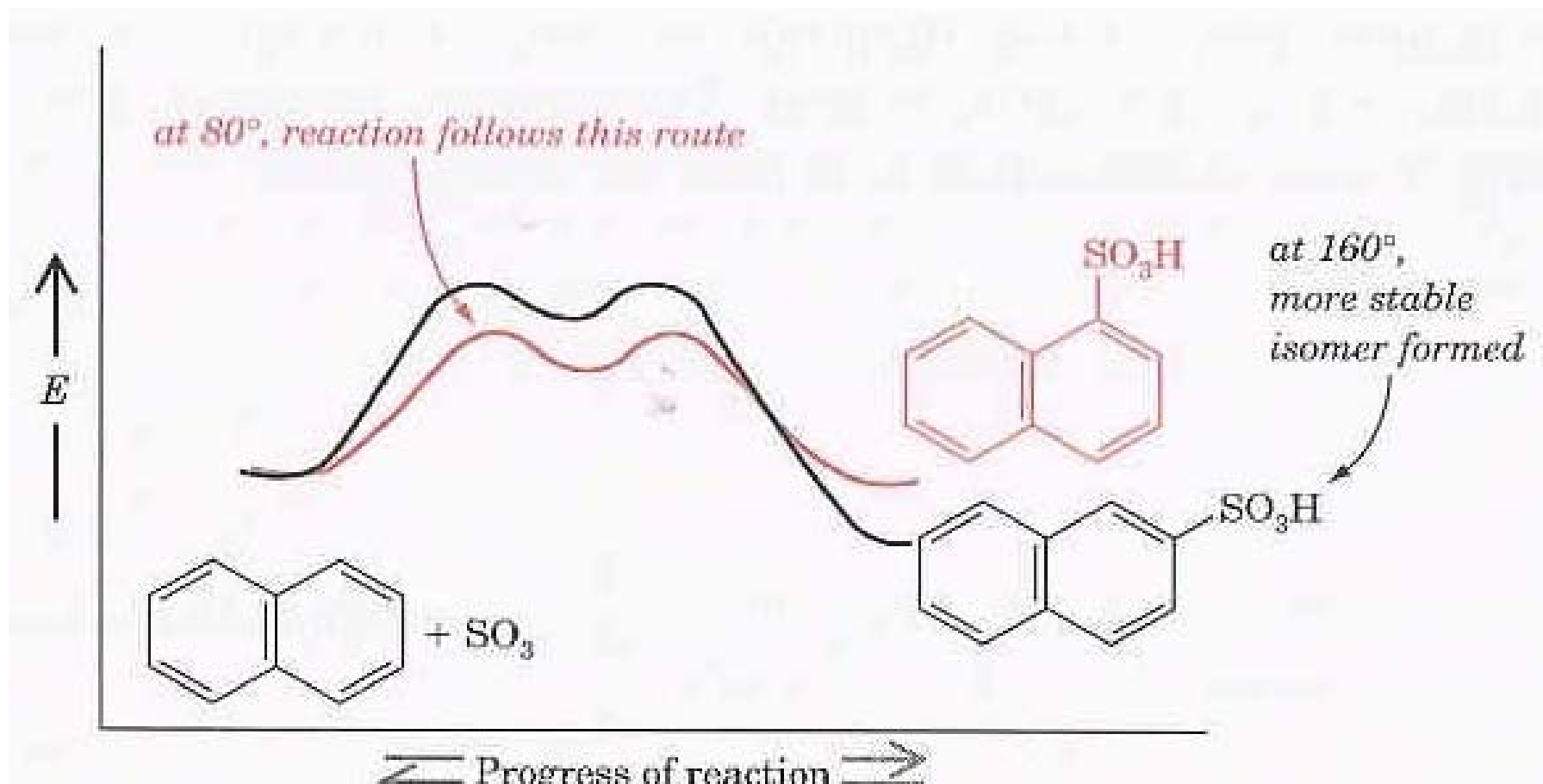
Less stable



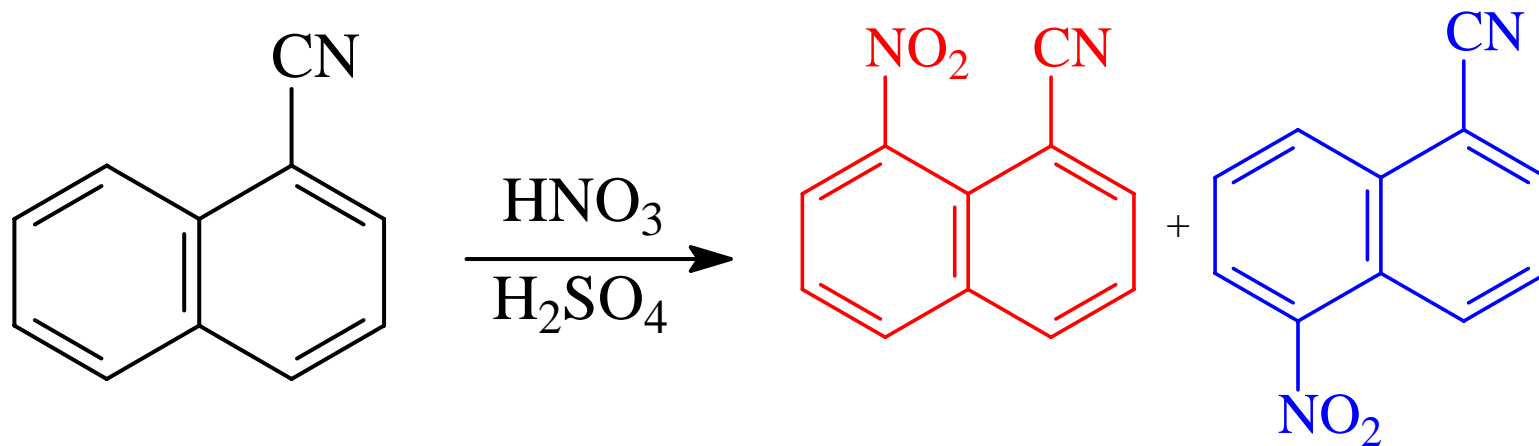
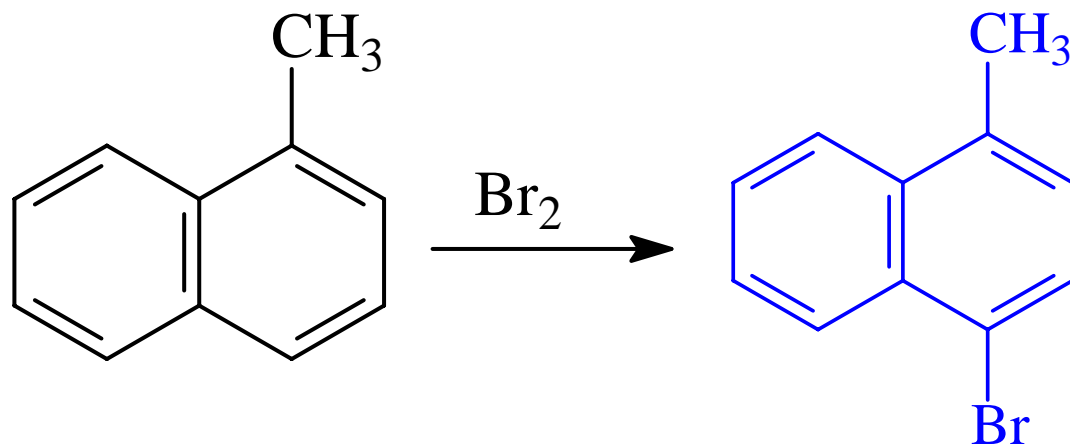
2-naphtalenesulphonic acid

More stable

Kinetic vs Thermodynamic Control

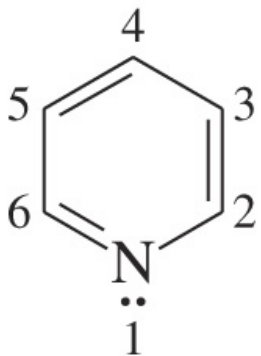


Reactions Examples

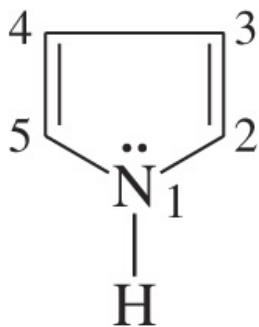


Heterocyclic Aromatic Compounds

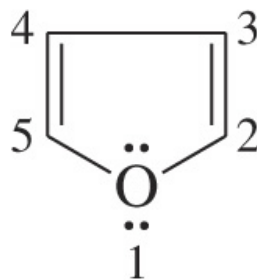
- Heterocyclic compounds have an element other than carbon as a member of the ring
- Example of aromatic heterocyclic compounds are shown below
 - **Numbering always starts at the heteroatom**



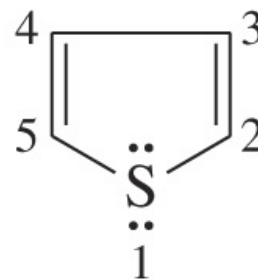
Pyridine



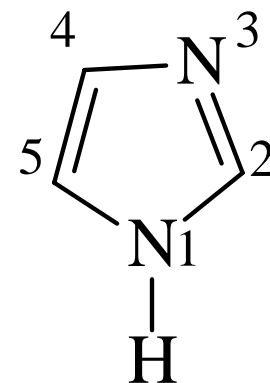
Pyrrole



Furan



Thiophene

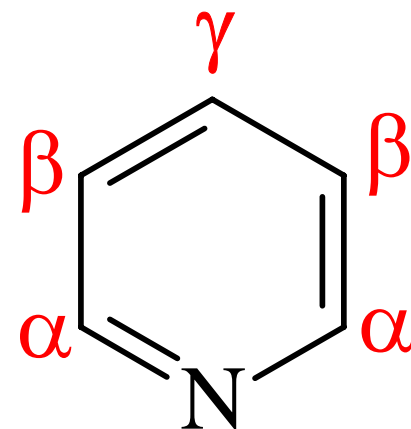
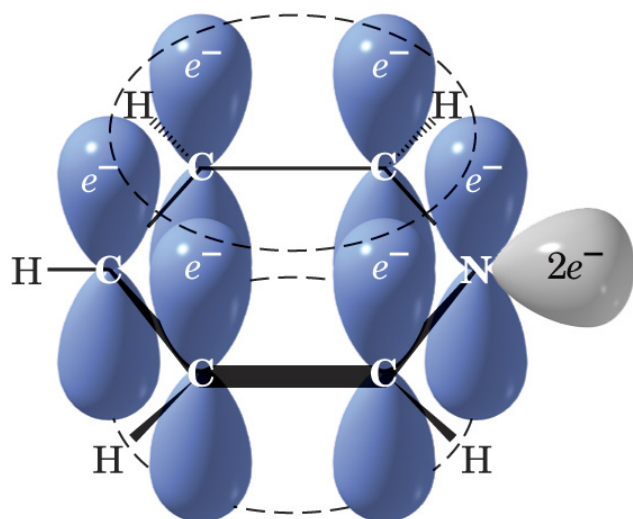


imidazole

Pyridine, a Six-Membered Aromatic Heterocycle

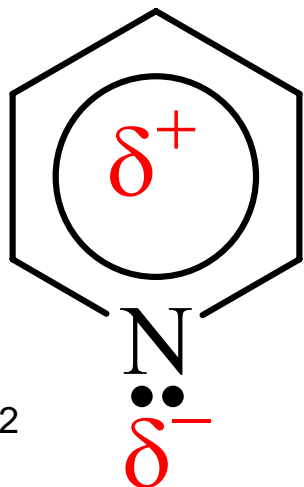
- Pyridine has an sp^2 hybridized nitrogen.
- The p orbital on nitrogen is part of the aromatic π system of the ring.
- The nitrogen lone pair is in an sp^2 orbital orthogonal to the p orbitals of the ring; these electrons are not part of the aromatic system.
- The lone pair on nitrogen is available to react with protons and so pyridine is basic

Pyridine



aromatic

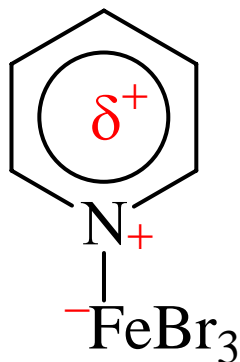
Pyridine contain an electronegative nitrogen \rightarrow polar



Because the nitrogen is more electronegative than carbon, the rest of pyridine ring is electron deficient \rightarrow carbon atoms on the ring carry a partial positive charge \rightarrow pyridine has a low reactivity toward electrophilic substitution compared to benzene

Reactions of Pyridine

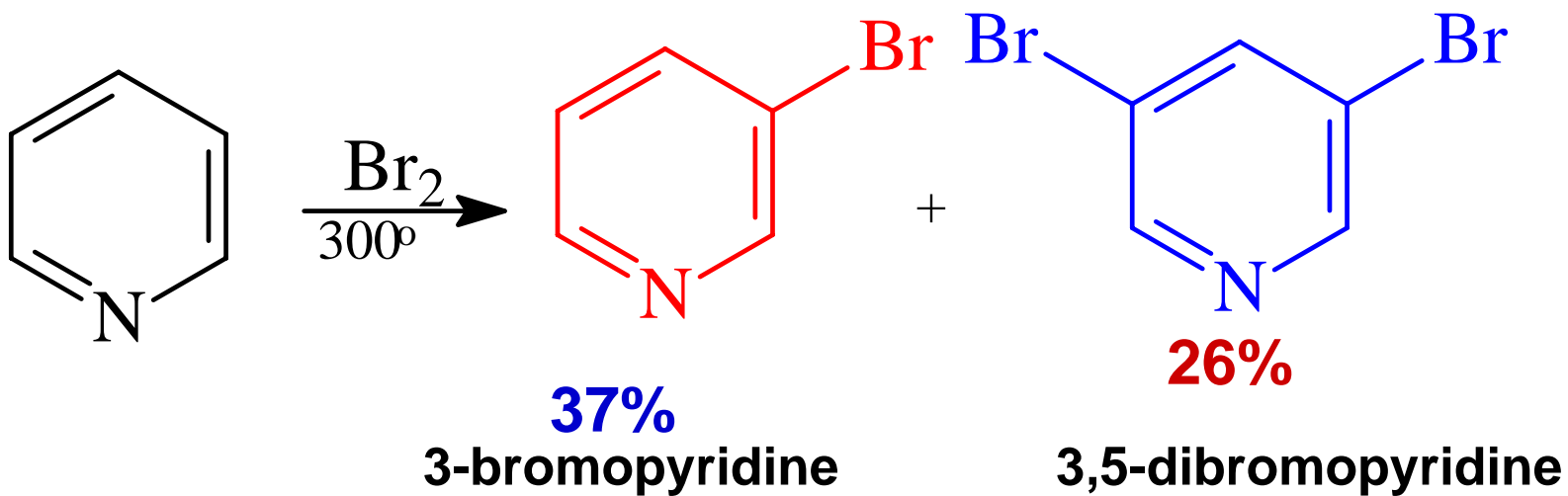
- Pyridine forms a cation with Lewis acids → the ring becomes even more electron deficient.



- Pyridine does not undergo Friedel- Crafts alkylation or Acylation.
- It does not undergo coupling with diazonium salts.

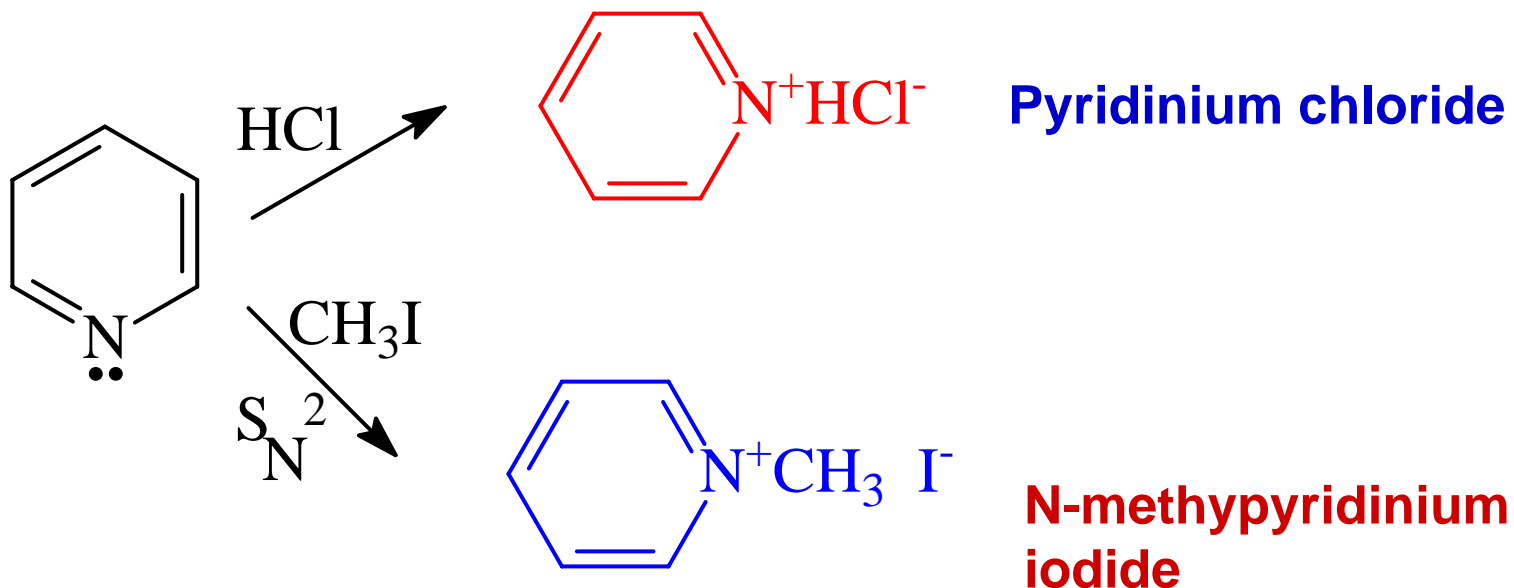
Bromination of Pyridine

- Bromination proceeds only at a high temperature in the vapor phase by free radical path → substitution occurs at the 3-position



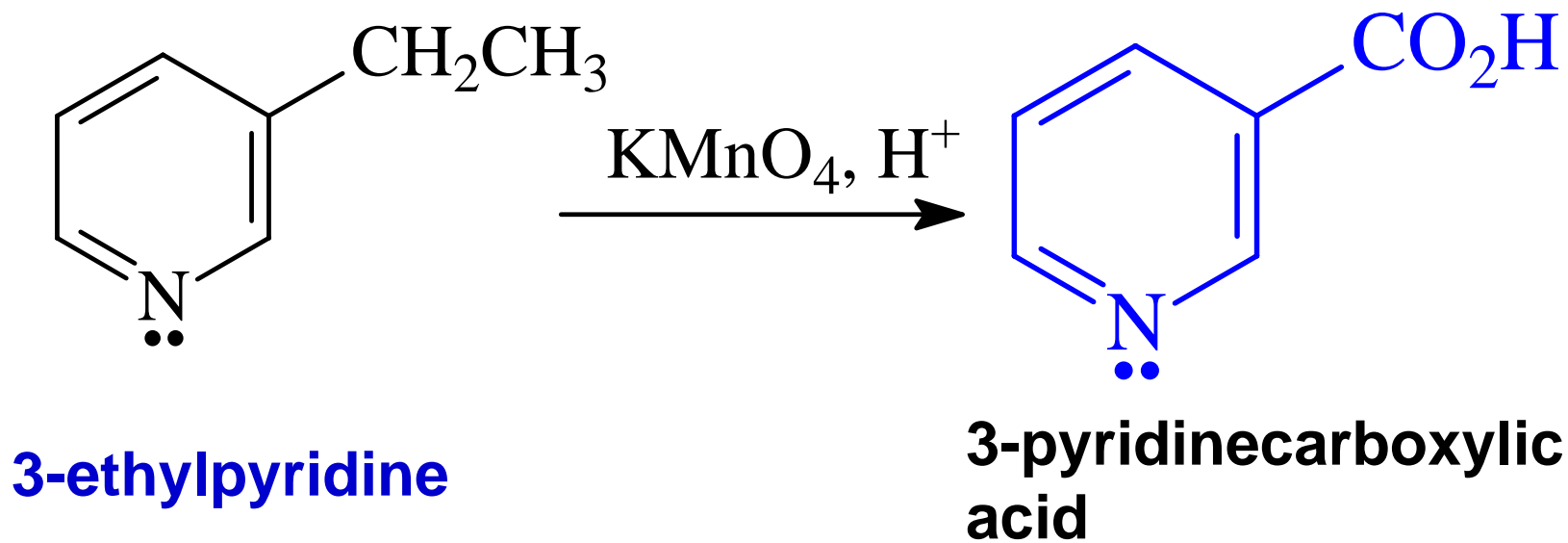
Pyridine is basic

- pK_b of pyridine = 8.75 . It is less basic than aliphatic amine (why?).
- It undergoes many reactions typical of amines



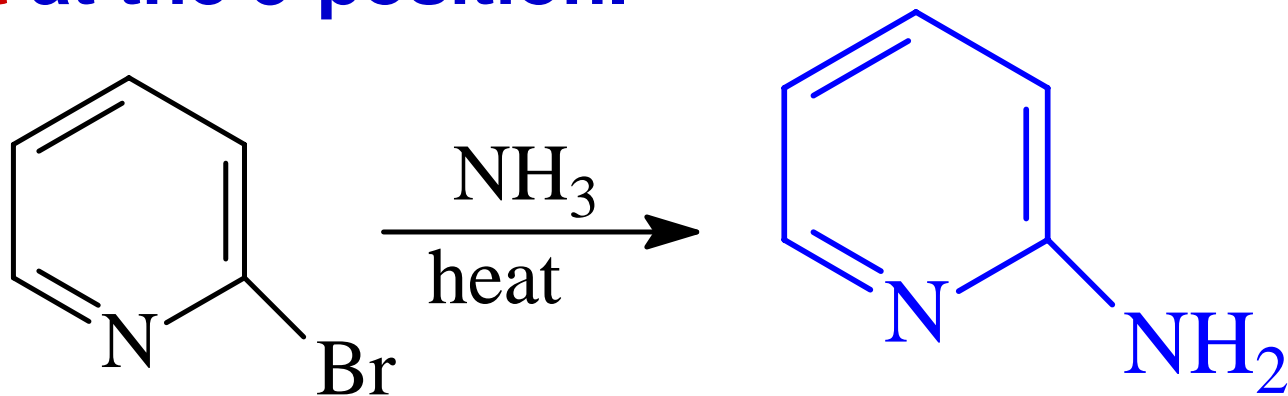
Oxidation of alkyl pyridine

- The side chains in pyridine can be oxidized to carboxyl groups similar to alkyl benzene.



Nucleophilic Substitution on the Pyridine Ring

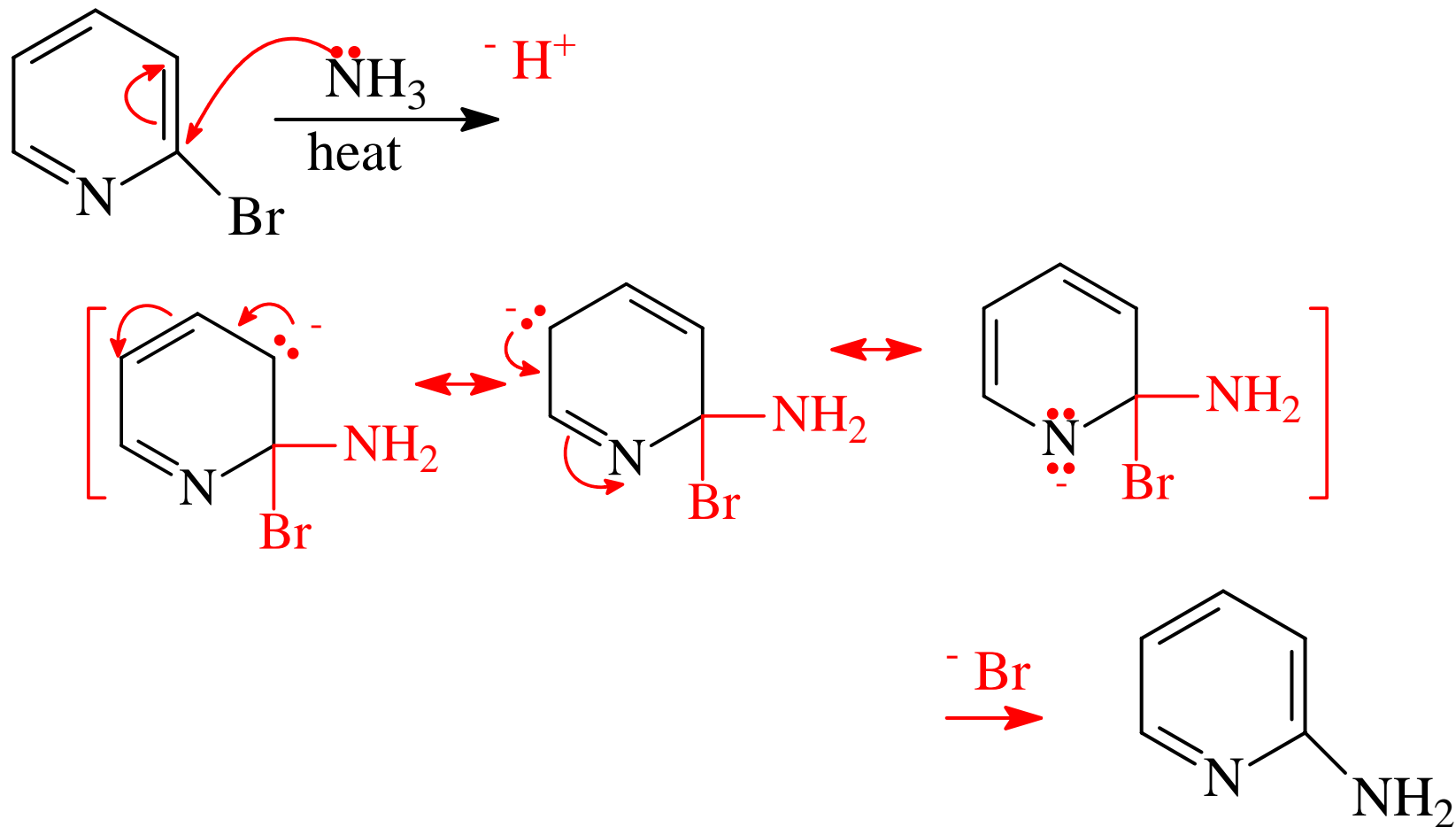
- Pyridine ring is electron deficient → it is susceptible to nucleophilic attack.
- Nucleophilic substitution proceeds readily at the 2-position followed by the 4-position but **not** at the 3-position.



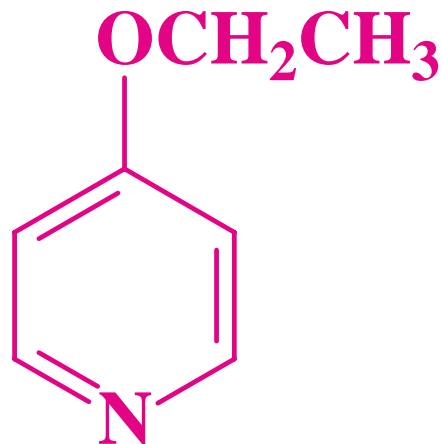
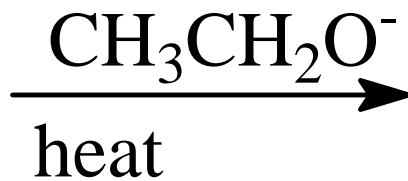
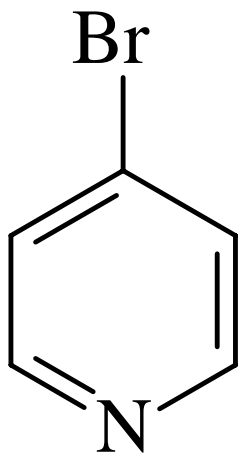
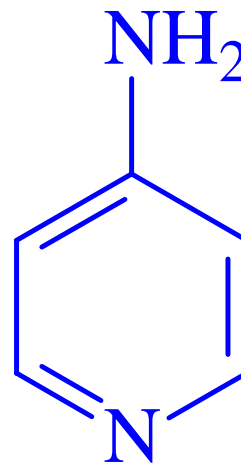
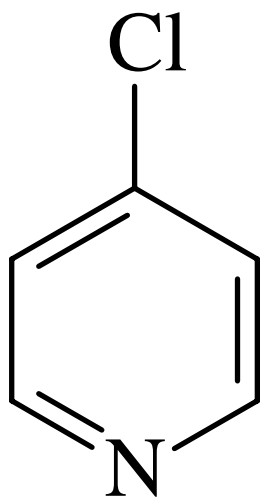
2-bromopyridine

2-aminopyridine

Mechanism of substitution at the 2-position

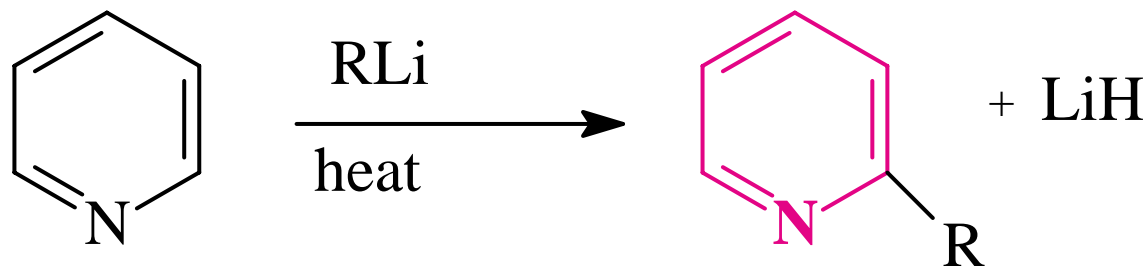
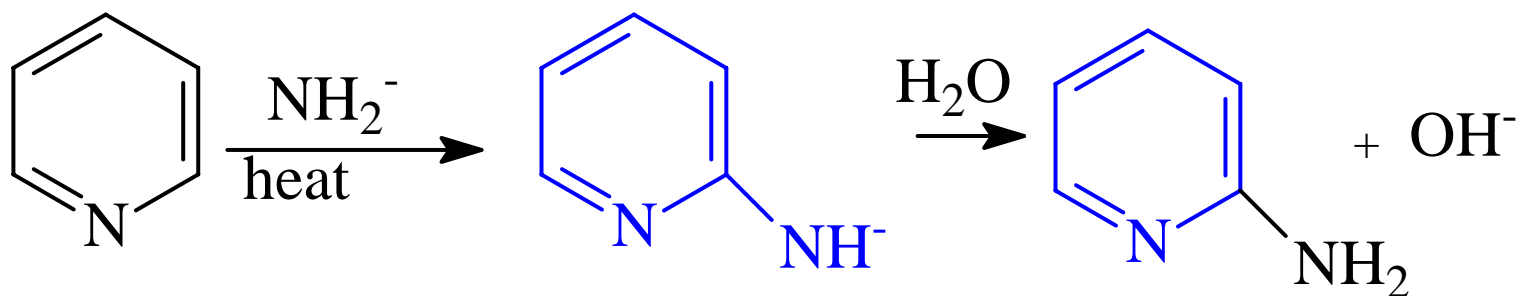


Substitution at the 4-position

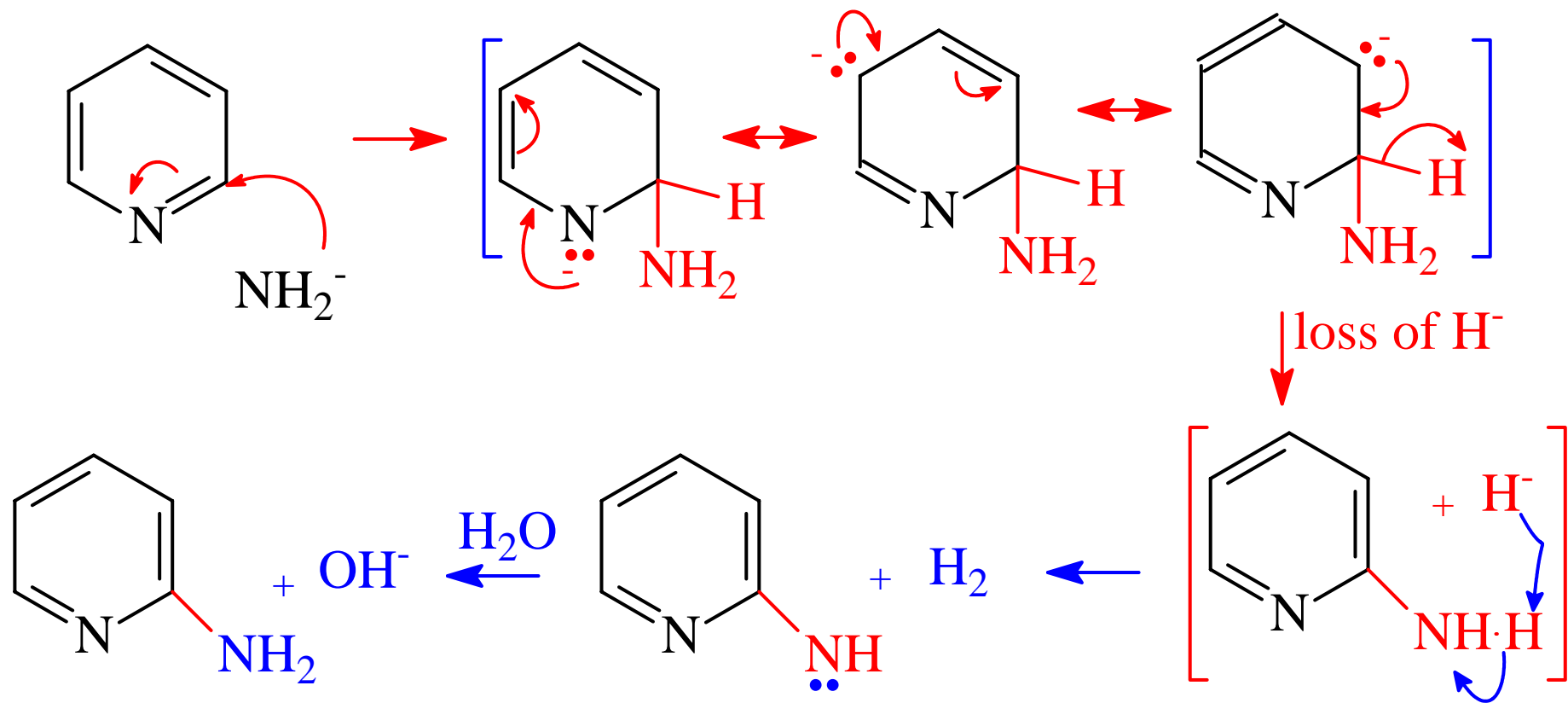


Nucleophilic Substitution of pyridine

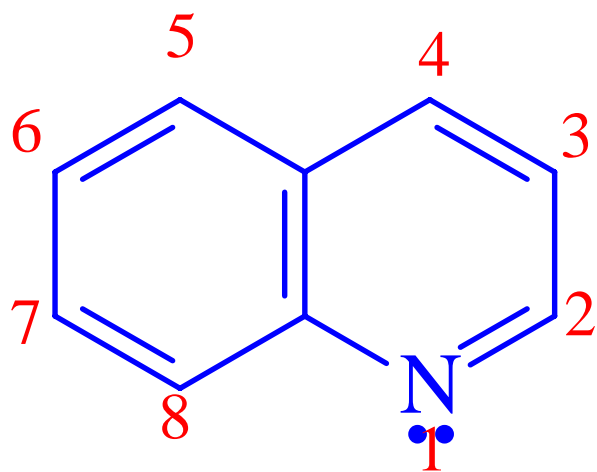
- Pyridine undergo nucleophilic substitution at the **2-position** with extremely strong bases e.g. **RLi** or **NH₂⁻**



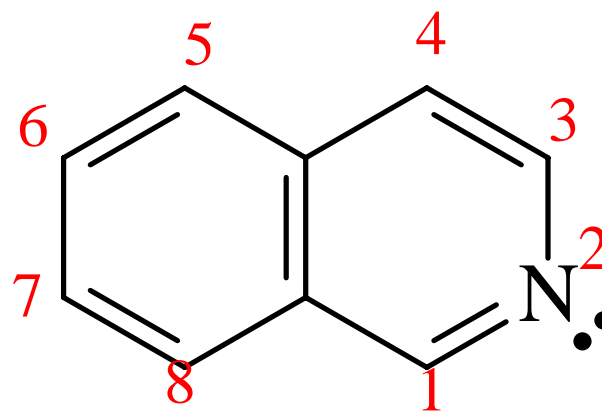
Mechanism



Quinoline and Isoquinoline



quinoline



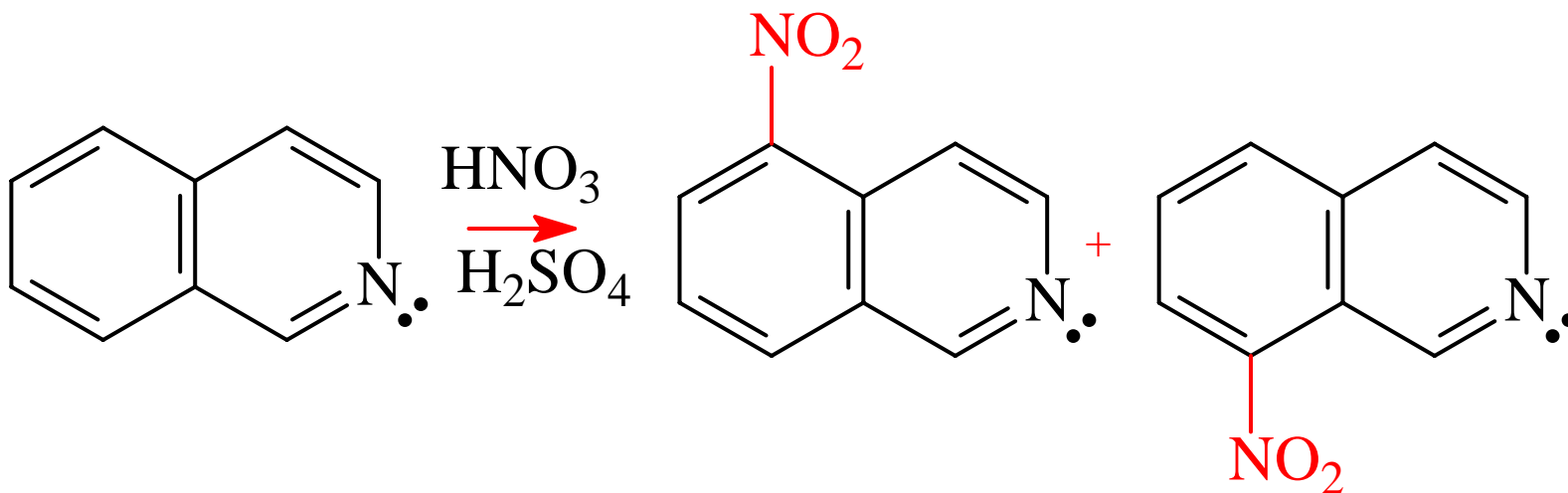
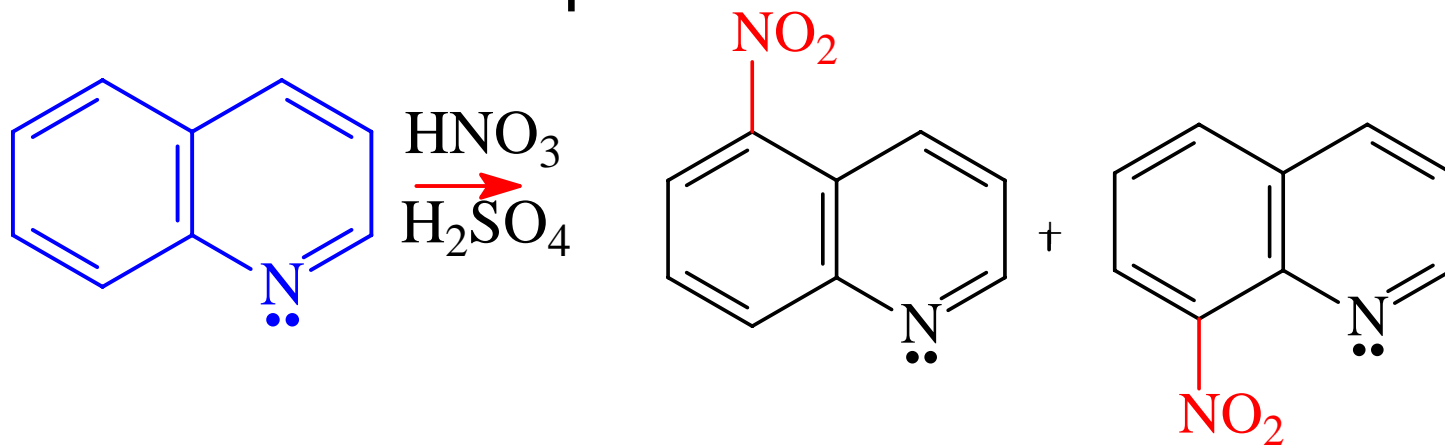
isoquinoline

Both quinoline and isoquinoline contain a pyridine ring fused to a benzene ring

**The nitrogen containing ring behaves like the pyridine ring.
The other ring behaves like naphthalene**

Electrophilic Substitution of Quinoline and Isoquinoline

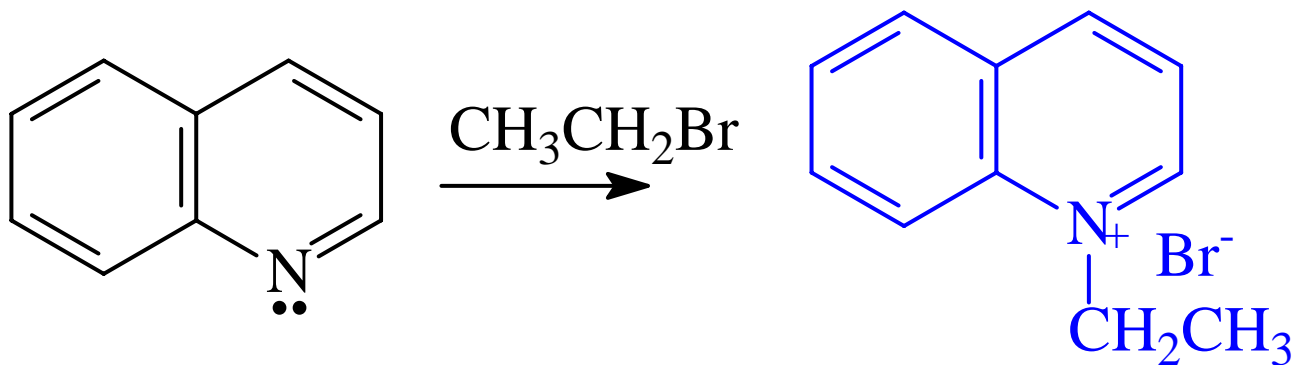
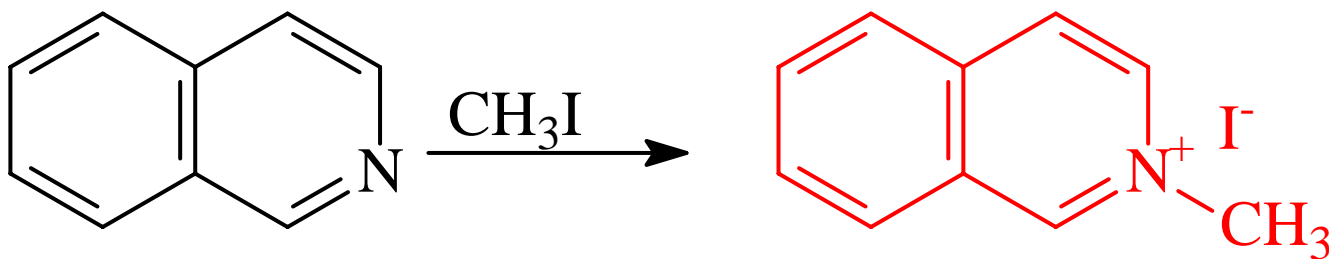
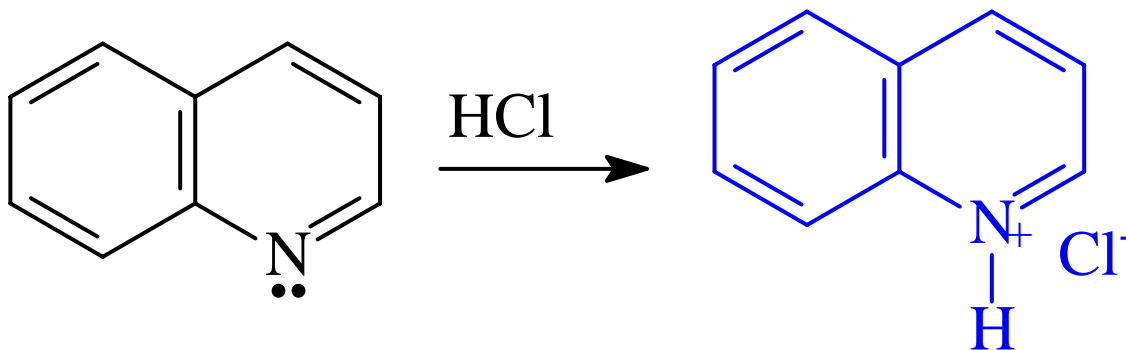
- Both compounds undergo electrophilic substitution but in positions 5 and 8.



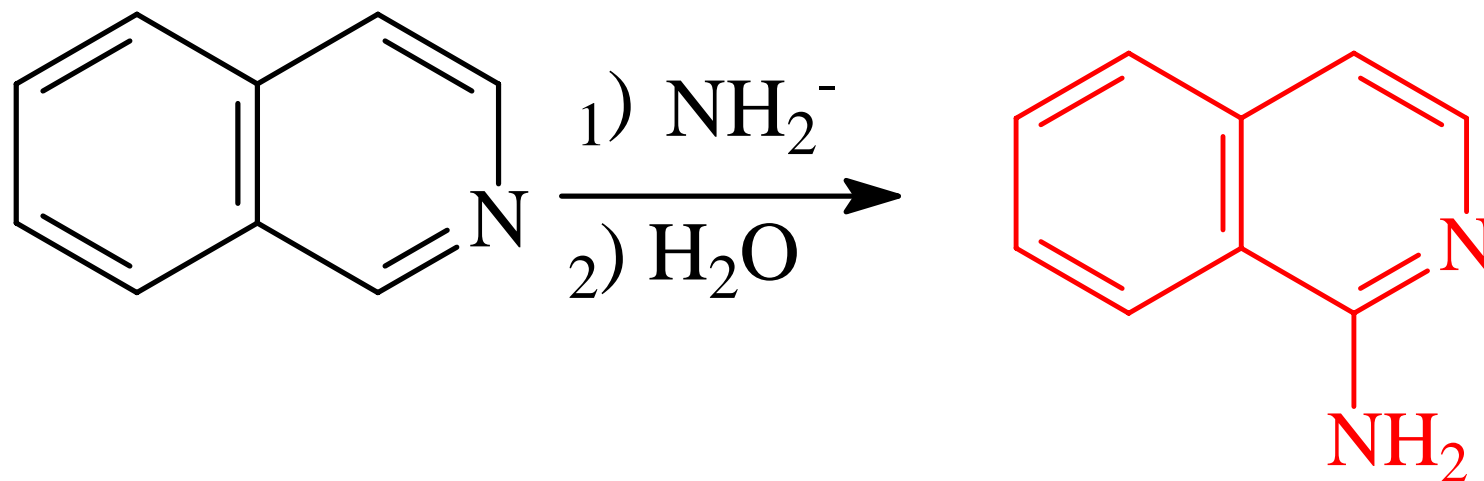
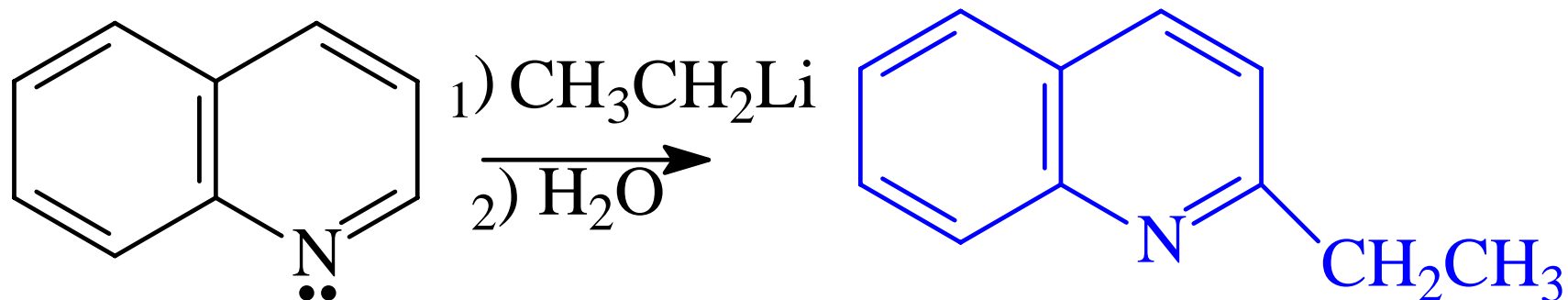
Reaction at the Nitrogen-Containing Ring of Quinoline and Isoquinoline

- 1. Both quinoline and isoquinoline (like pyridine) are weak bases ($pK_b = 9.1$ and 8.6 respectively).**
- 2. Both compounds (like pyridine) undergo nucleophilic substitution at the position α to the nitrogen.**

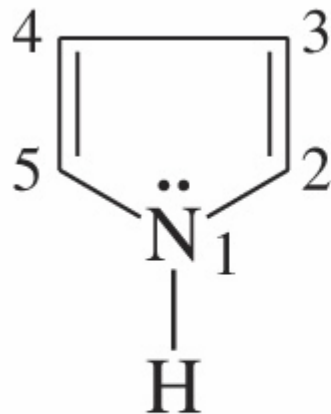
Examples



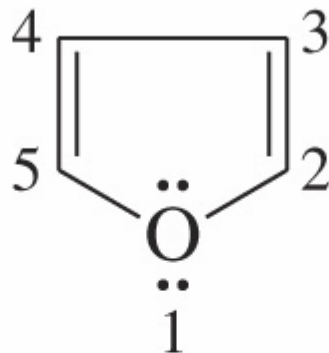
More Examples



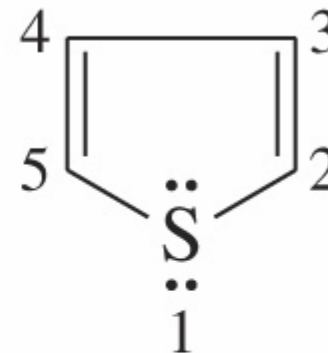
Five-membered Aromatic Heterocycle



Pyrrole



Furan

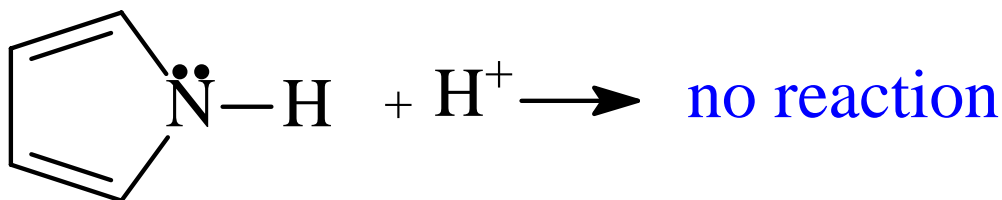
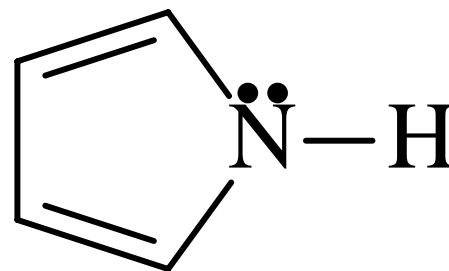
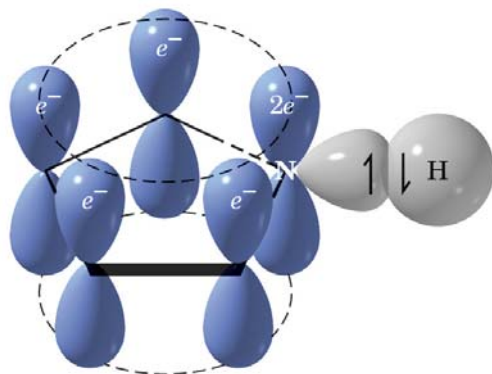


Thiophene

In furan and thiophene an electron pair on the heteroatom is in a p orbital which is part of the aromatic system

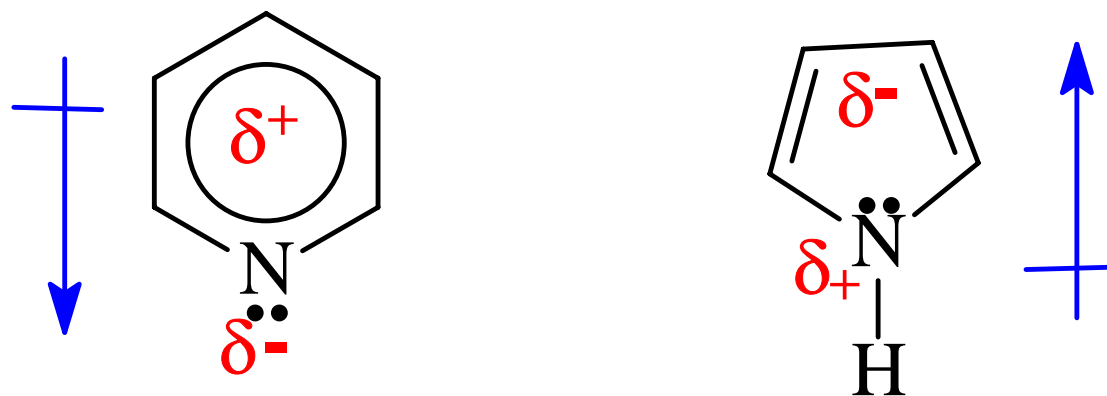
Pyrrole

- * This p orbital contains two electrons and participates in the aromatic system
- * The lone pair of pyrrole is part of the aromatic system and not available for protonation; pyrrole is therefore not basic



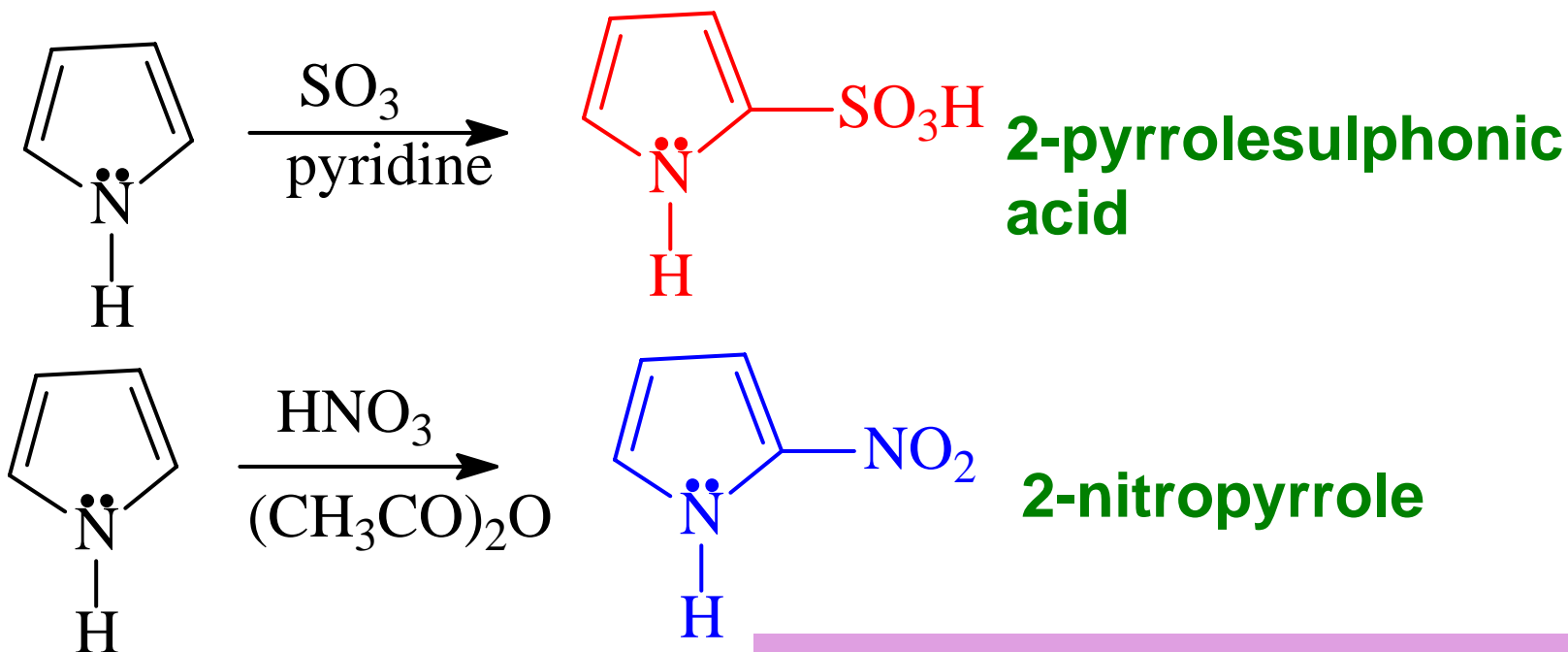
Pyrrole Ring is Polar

- The nitrogen atom in pyrrole contributes two electrons to the aromatic pi cloud → the nitrogen is electron deficient (not basic).
- The pyrrole ring is electron-rich → partial negative (opposite to pyridine ring)



Electrophilic Substitution on the Pyrrole Ring

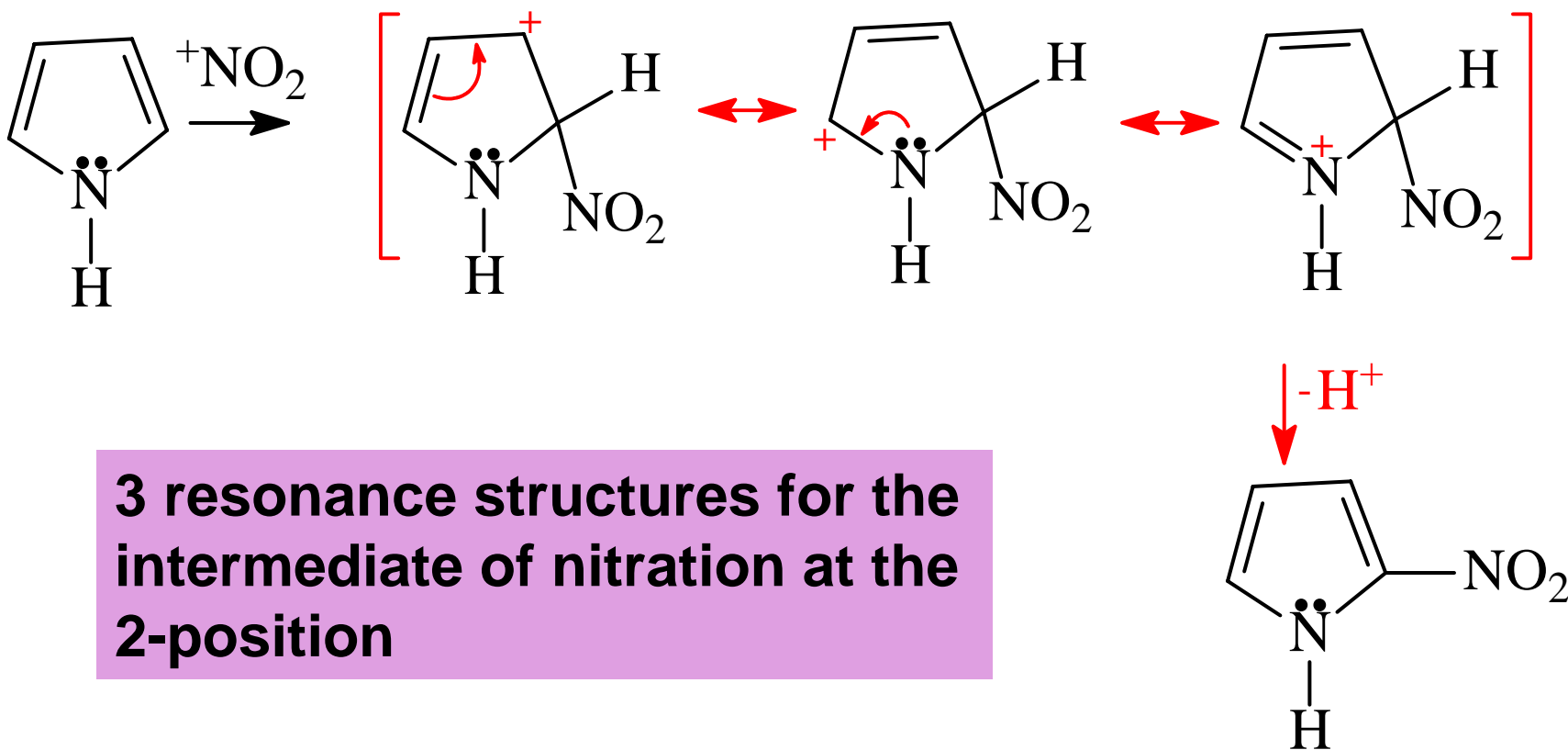
- Because the ring carbon are the negative part
→ the carbon are activated toward electrophilic attack (pyrrole is more reactive than benzene)



Substitution occurs at the 2-position

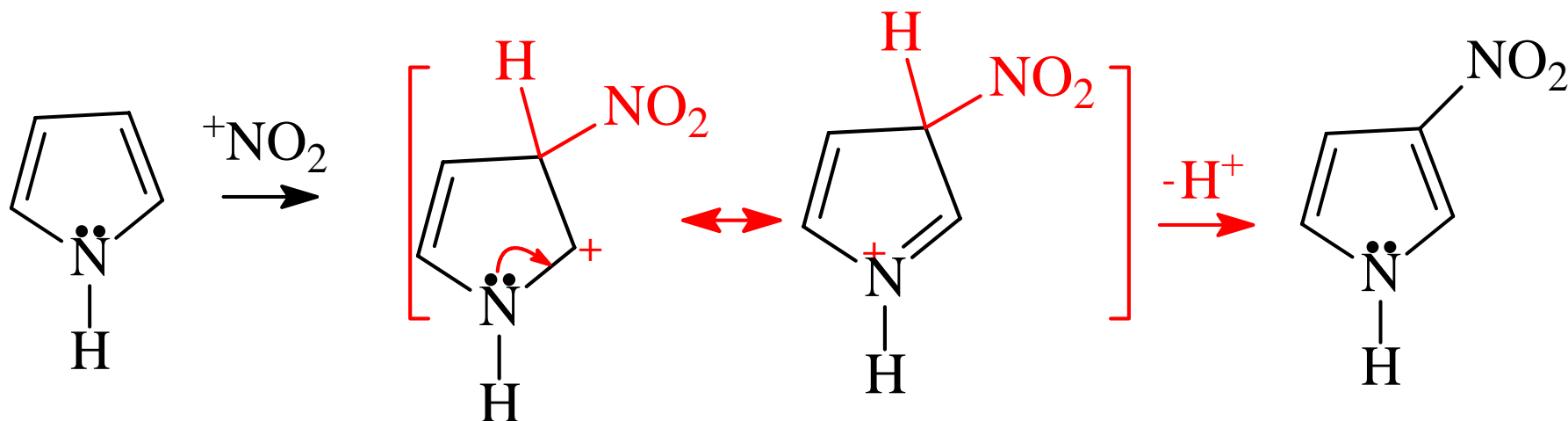
Substitution at the 2-position is Favored over the 3-position

2-nitration



3 resonance structures for the intermediate of nitration at the 2-position

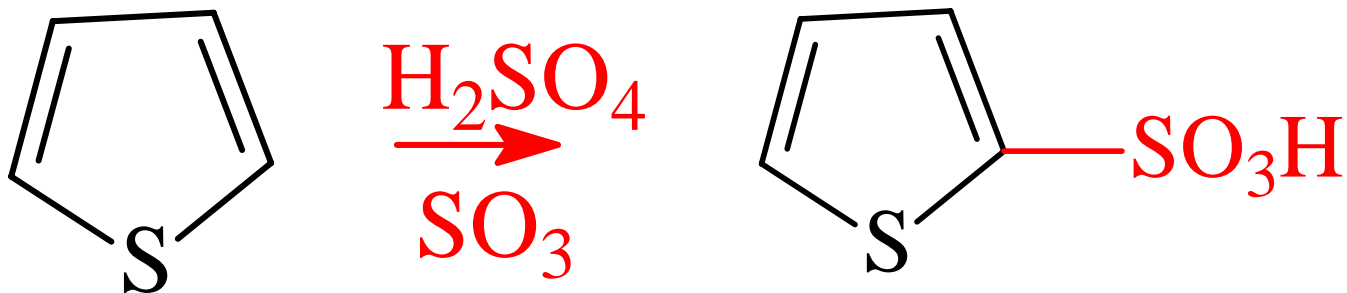
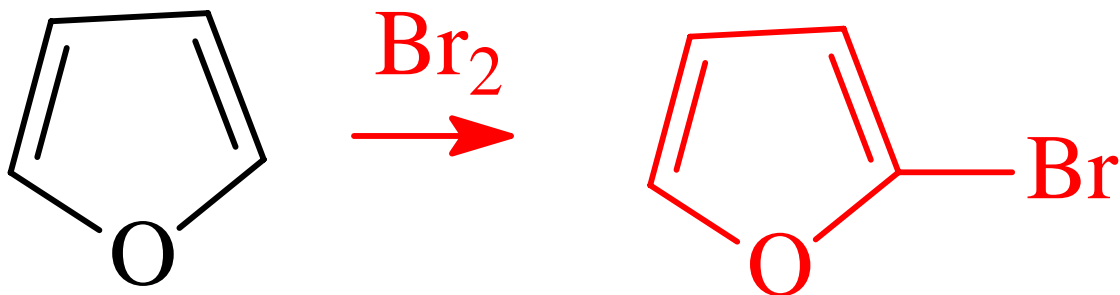
Nitration at the 3-position



The are only 2 resonance structures for the intermediate of nitration at the 3-position as compared to 3-resonance structures at the 2-position → substitution at 2-position is favored.

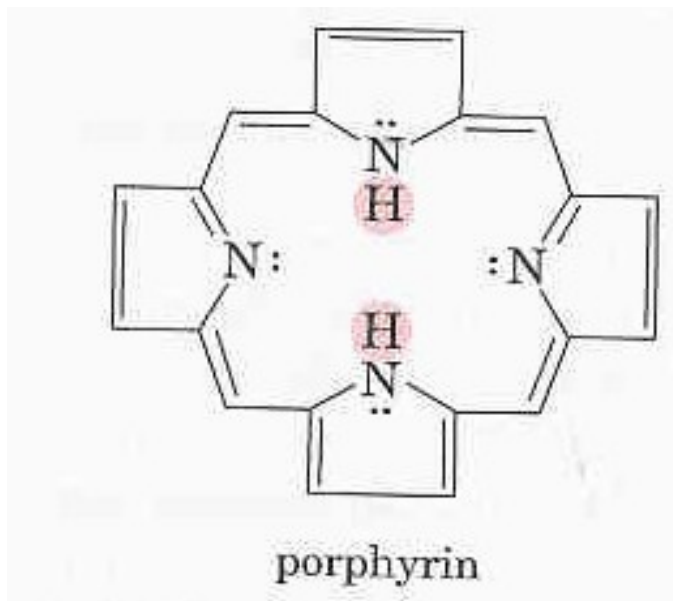
Other five-membered Heterocyclic Aromatic Compounds

- Furan and thiophene behave like pyrrole toward electrophilic substitution,

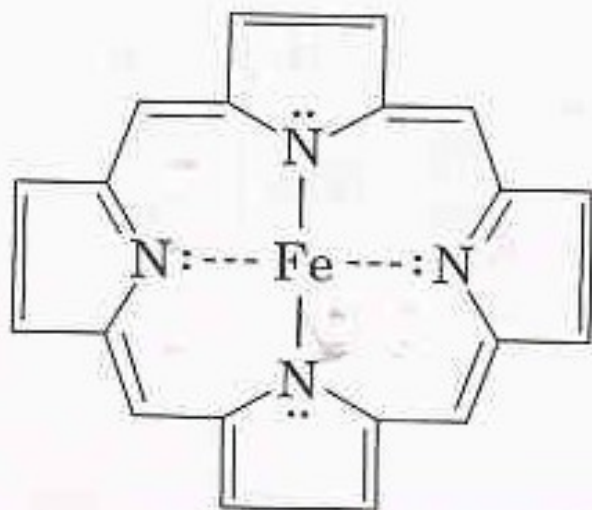


Porphyrins

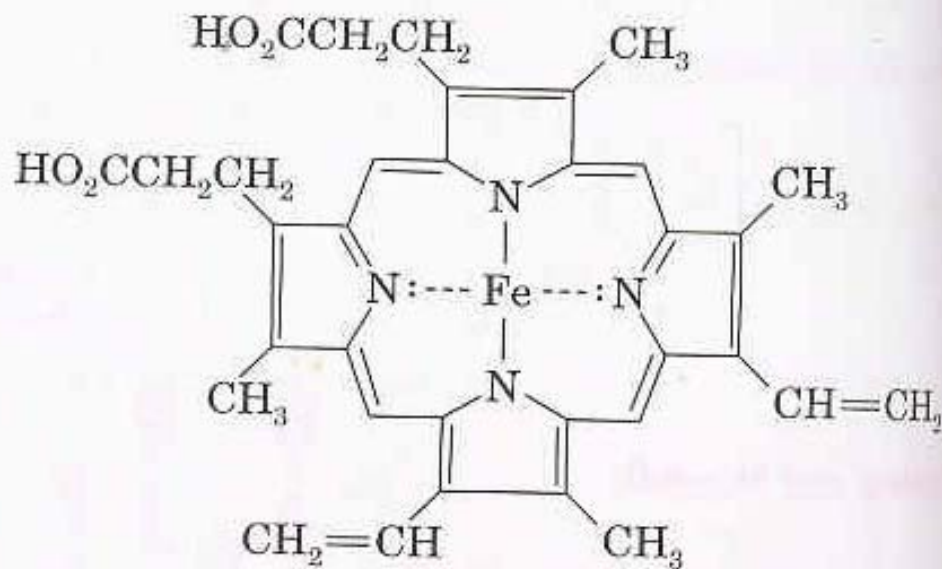
- The porphyrin ring system is aromatic planar compound contains four pyrrole rings joined by =CH- groups.
- They are biologically important unit.



The highlighted hydrogen atoms can be replaced by metal ions



*planar and
resonance-stabilized*



heme

