

Remember:

Thiophene, pyrrole and Furan are all five membered heterocyclic aromatic compounds, with the hetero atom being sulfur (S), nitrogen (N) and oxygen (O) respectively. They are aromatic as they are planar ring systems, and resonance is possible due to delocalization of the two pi bonds and the lone pair of electrons of the heteroatom. However, if we compare the electronegativity of the heteroatoms, we will see that O is more electronegative as compared to N, S being the least electronegative. Hence, O will have the least tendency, among the three, to donate its lone pair of electrons for resonance, and will rather draw the electronic density of the ring towards itself. The concentration of electron density on the heteroatom makes it a good electron donor (Lewis base). Thus the order of basicity will be Furan > Pyrrole > Thiophene

Questions about basicity

- 1- What is basicity order of thiophene pyrrole and furan?
- 2- Why is pyridine more basic than common amines?
- 3- Pyridine is less basic than tertiary amine? Why?
- 4- What is the descending order of the basicity of piperidine, morpholine, pyridine and pyrrole?

Related Questions

- 1- Why is pyridine more basic than pyrrole?
- 2- Which is the most basic among pyrrole, pyridine and aniline? Why?
- 3- What is pyridine basicity?
- 4- What is the basicity order for Imidazoline, imidazole, and pyridine?

Questions

1- Draw the structure of the common aromatic heterocycles pyridine and pyrrole.

2- Use the Hückel $4n + 2$ rule to explain the aromaticity of each of pyridine and pyrrole.

2- Draw a diagram to show the orbitals involved in forming the conjugated six-pi-electron systems present in aromatic heterocycles such as pyridine, pyrrole, etc.

COMMENT

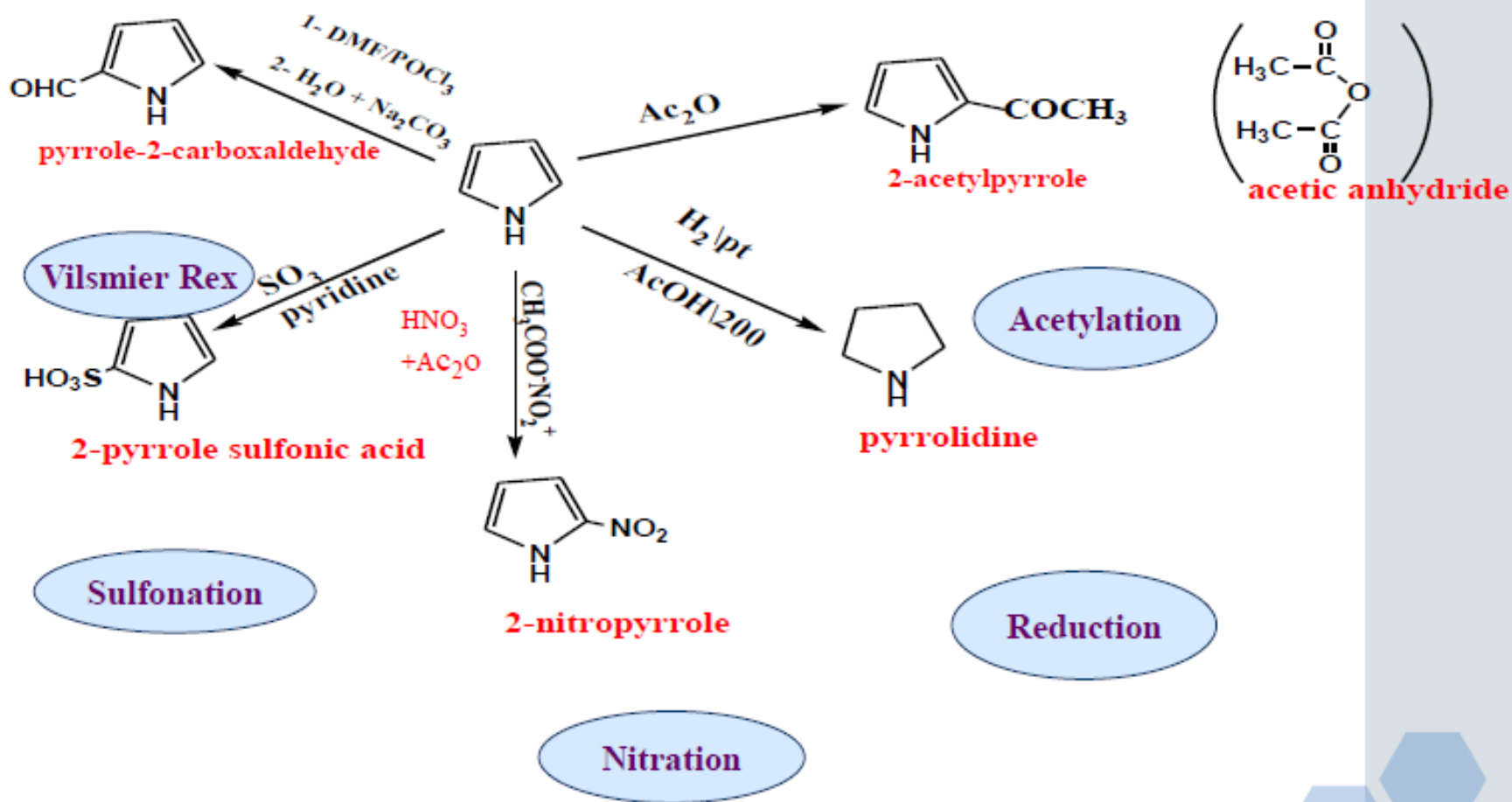
1- PYRIDINE IS MORE BASIC THAN PYRROLE.

2- REASON LONE PAIR OF ELECTRONS ON N IN PYDRINE AND PYRROLE ARE DIFFERENT IN NATURE, THESE FORM A PART OR AROMATIC SEXTET IN PYRROLE, WHILE NOT IN PYRIDINE.

Again

Reactions of pyrrole

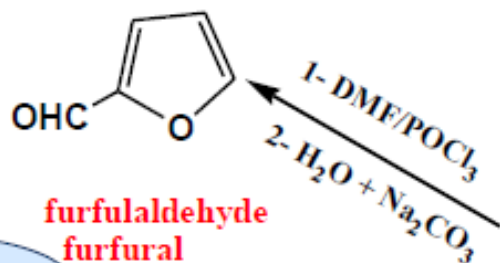
A. Five-membered Rings with one Heteroatom



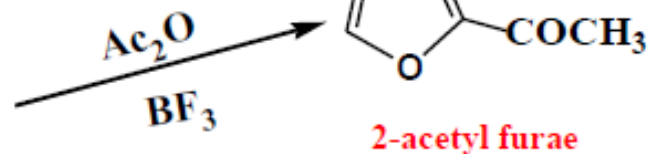
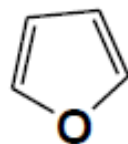


Reactions of Furan

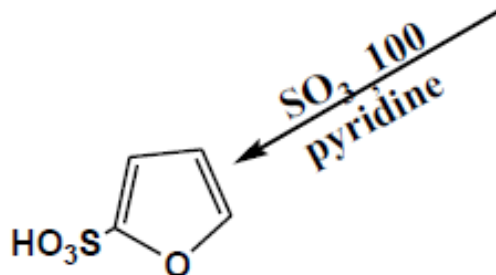
A. Five-membered Rings with one Heteroatom



Vilsmier Rex

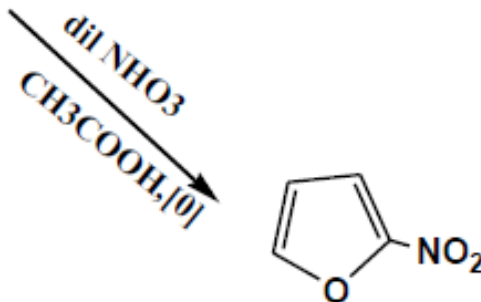


Acetylation



2-furan sulfonic acid

Sulfonation



2-nitrofuran

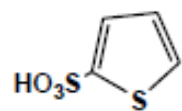
Nitration



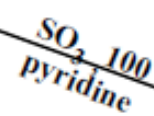
Reactions of Thiophene

A. Five-membered Rings with one Heteroatom

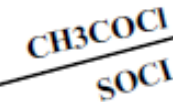
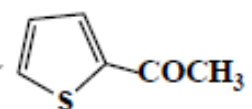
Sulfonation



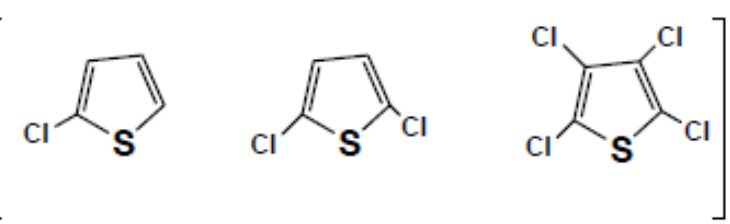
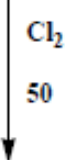
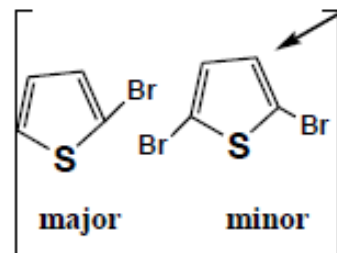
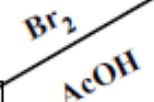
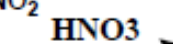
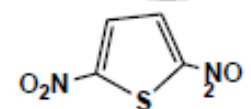
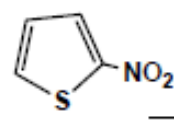
2-thiophene-2-sulfonic acid



Acetylation



Nitration

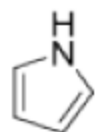


Halogenation

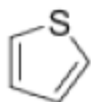


Answer the following questions to the best of your ability. Once you have completed the assignment, be sure to check your answers against the answer key.

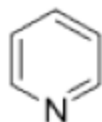
1. Name the following heterocyclic compounds:



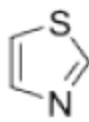
(a)



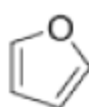
(d)



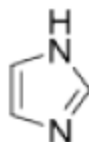
(c)



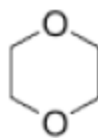
(d)



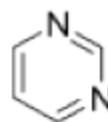
(e)



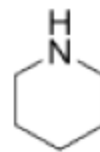
(f)



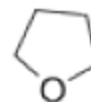
(g)



(h)



(i)



(j)

Answer:

- (a) pyrrole
- (b) thiophene
- (c) pyridine
- (d) thiazole
- (e) furan
- (f) imidazole
- (g) dioxane
- (h) pyrimidine
- (i) piperidine
- (j) tetrahydrofuran

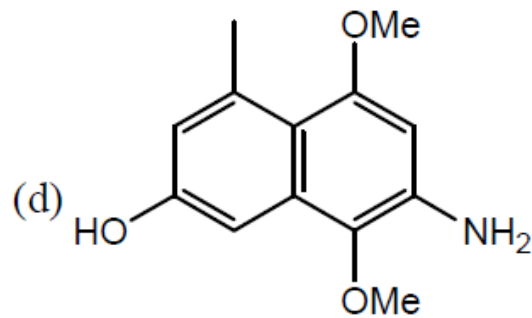
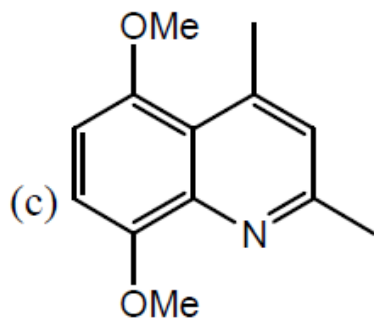
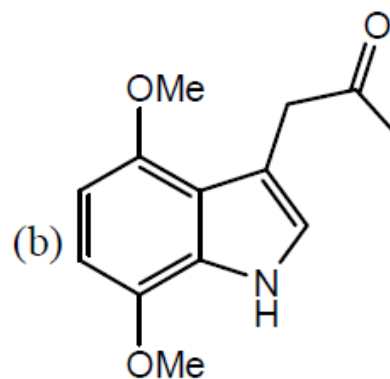
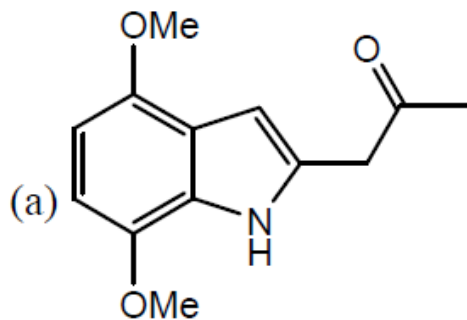
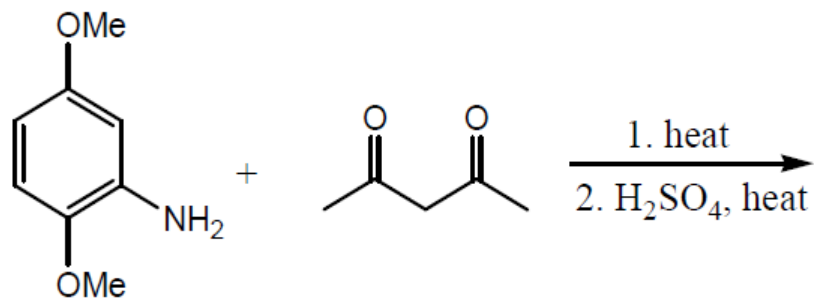
2. Compare the reactivity of pyridine to that of Benzene in electrophilic aromatic substitution.

Answer: Pyridine is less reactive, than benzene toward electrophilic aromatic substitution, because nitrogen is more electronegative, than carbon and acts like an electron withdrawing group. As a result, the meta hydrogen is substituted.

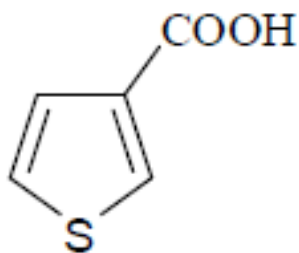
3. Compare the reactivity of pyridine to that of Benzene in nucleophilic aromatic substitution.

Answer: Pyridine is more reactive than benzene because the presence of nitrogen enables pyridine to react with nucleophiles. Nitrogen is an electron withdrawing substituents enables the aromatic ring to participate in such reactions and the substitution happens in the ortho and meta positions.

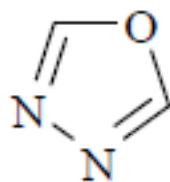
The major product formed in the following reaction is



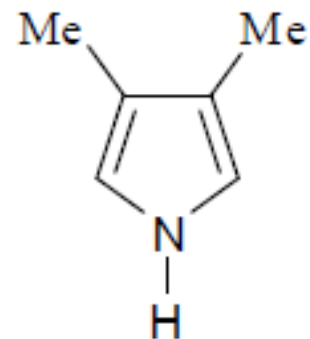
a. Suggest the Hantzsch-Widman name for compounds a-f shown below:



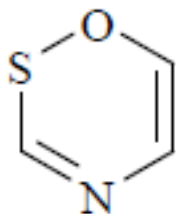
a



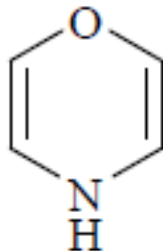
b



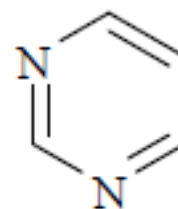
c



d



e



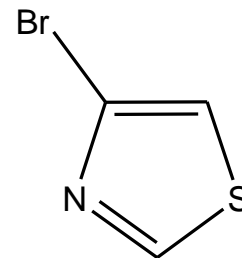
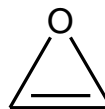
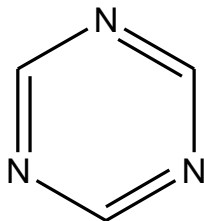
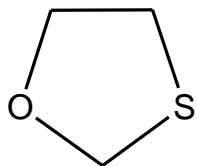
f

b.

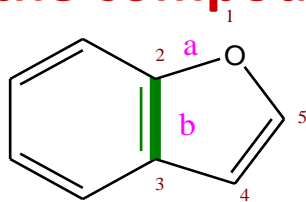
Outline using a scheme the synthesis of a 1,3-thiazole from a bromoketone and a thioamide.

Exercise:

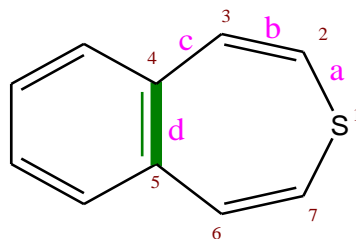
Explain how can you name the following heterocycles.



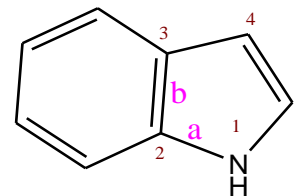
Name the compounds which have the following structures



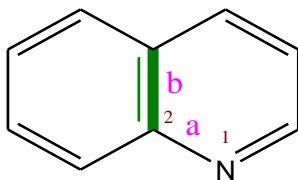
Benzo[b]furan



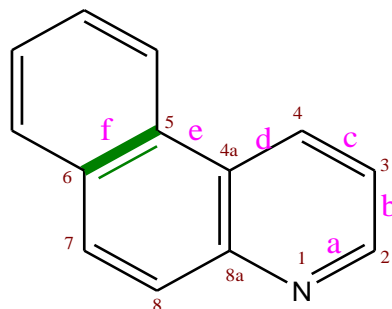
Benzo[d]thiophene



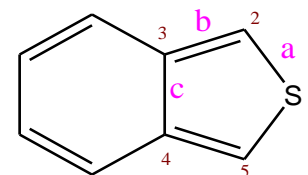
Benzo[b]pyrrole
Indole



Benzo[b]pyridine
Quinioline

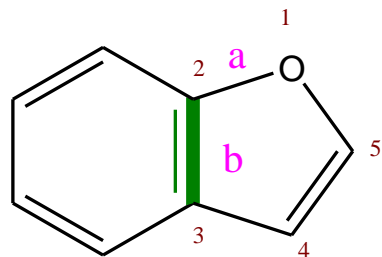


Benzo[f]quinoxaline

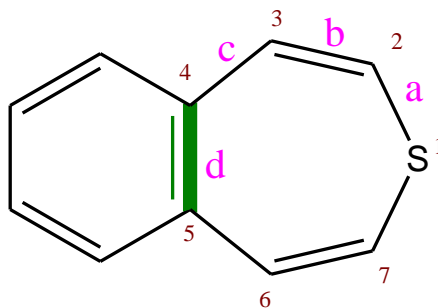


Benzo[c]thiophene

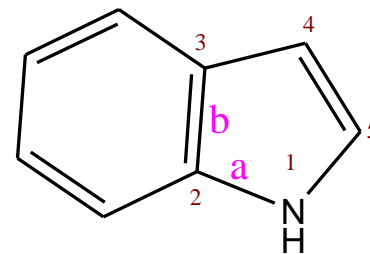
Name the compounds which have the following structures



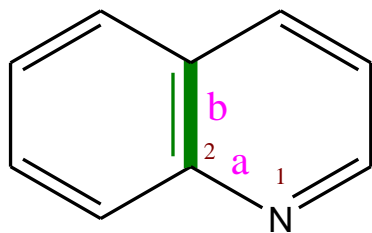
Benzo[b]furan



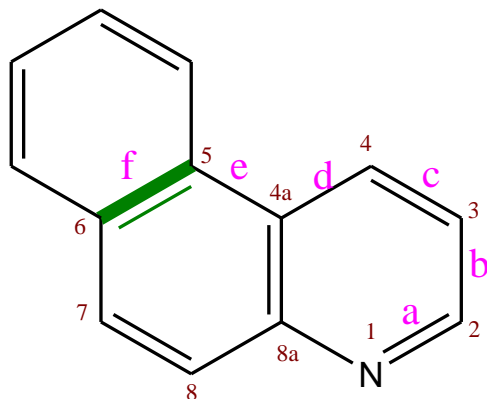
Benzo[d]thiepine



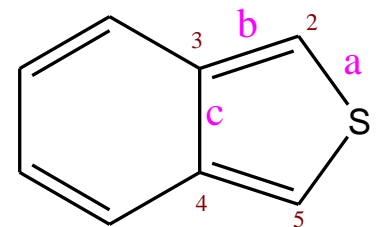
Benzo[b]pyrrole
Indole



Benzo[b]pyridine
Quinoline

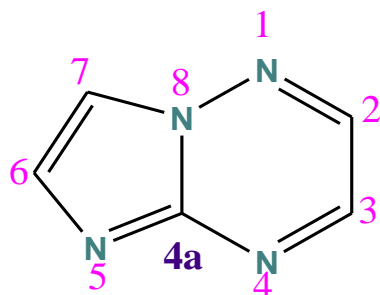


Benzo[f]quinoline

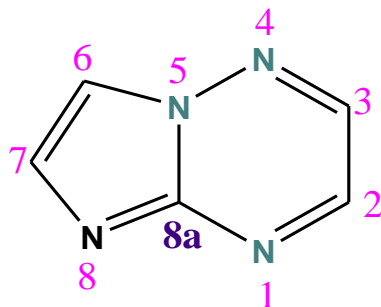


Benzo[c]thiophene

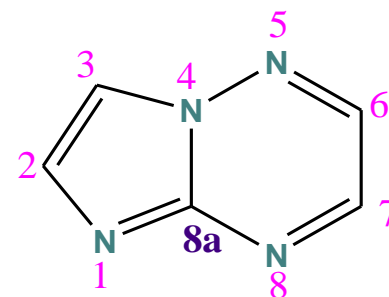
Name the compounds which have the following structures



Not

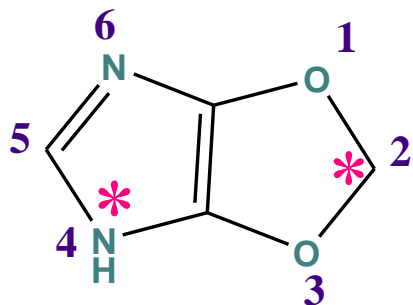


Not

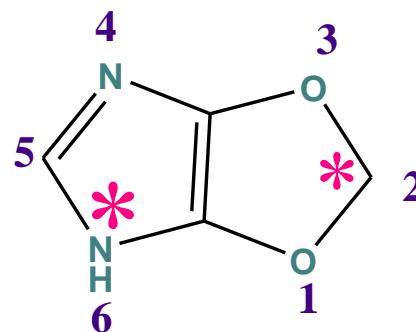


Imidazo[1,2-*b*][1,2,4]triazine

fusion C -4a is preferred to 8a



Not



2*H*,4*H*-[1,3]dioxol[4,5-*d*]imidazole

Indicated hydrogens 2,4 not 2,6