B. Sc. III Year

Chapter-1

Heterocyclic Compounds

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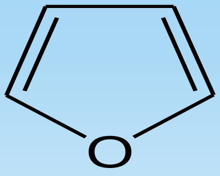
Heterocyclic Compounds

Cyclic compound containing at least one hetero atom other than carbon, such compounds are called as heterocyclic compounds.

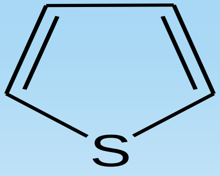
Generally N, O, S atoms are present as a hetero atoms.

Stable heterocyclic compounds are called as aromatic heterocyclic compounds.

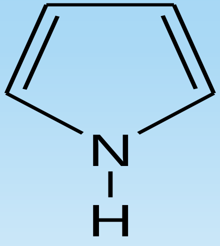
Ex.



Furan



Thiophene

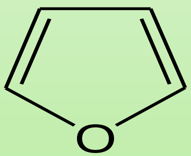


Pyrrole

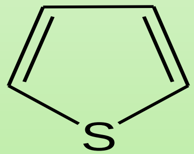
Classification of Heterocyclic Compounds

Heterocyclic compounds are classified on the basis of size of the ring and no. of hetero atoms present in a ring structure as follows.

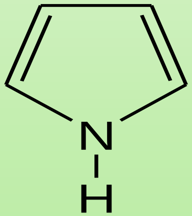
a) Five member heterocyclic compound containing one hetero atom. Ex.



Furan

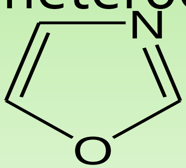


Thiophene

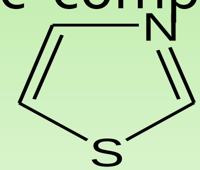


Pyrrole

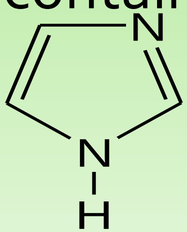
b) Five member heterocyclic compound containing two hetero atoms. Ex.



Oxazole



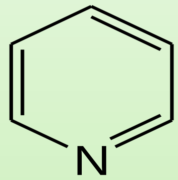
Thiazole



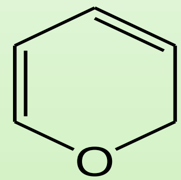
Imidazole

c) Six member heterocyclic compound containing one hetero atom.

Ex.



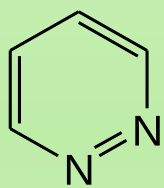
Pyridine



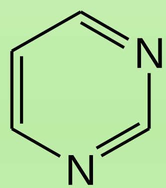
α-pyran

d) Six member heterocyclic compound containing two hetero atoms.

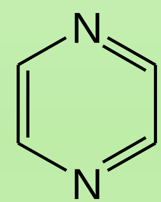
Ex.



Pyridazine



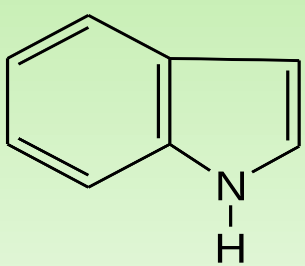
Pyrimidine



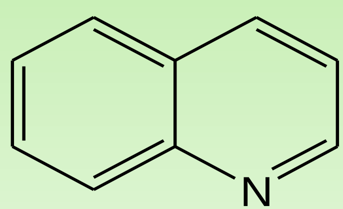
Pyrazine

e) Bicyclic compound containing one hetero atom.

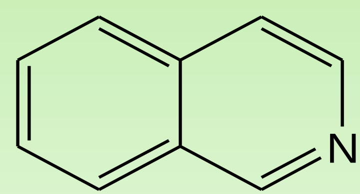
Ex.



Indole



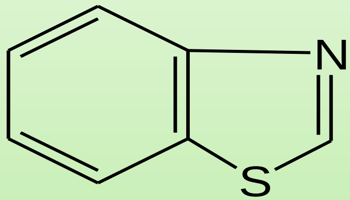
Quinoline



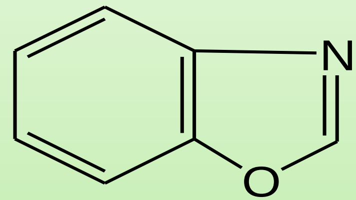
Isoquinoline

f) Bicyclic compound containing two hetero atoms.

Ex.



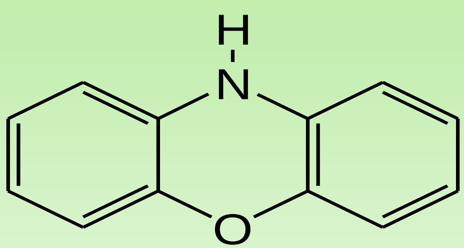
Benzothiazole



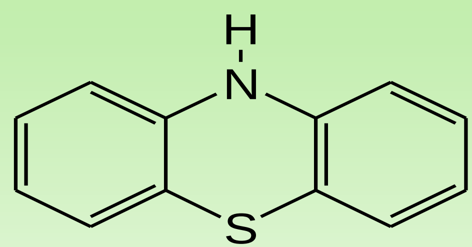
Benzoxazole

g) Polycyclic compound containing two or more than two hetero atoms.

Ex.



Phenoxazine



Phenothiazine

IUPAC Nomenclature of Heterocyclic Compounds

Following IUPAC rules are used for nomenclature of Heterocyclic compounds :

1) Following prefixes are used for hetero atoms

O = Oxa

S = Thia

N = Aza

Si = Sila

P = Phospha

2) Last vowel of prefixes are replaced by the respective name ending words, depending upon the size of the ring.

No. of atoms in ring	Name ending
3	irine
4	ete
5	ole
6	ine
7	epine

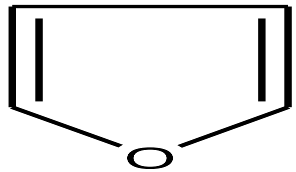
3) In monocyclic compound containing only one hetero atom, numbering start at this hetero atom.

4) When two or more same hetero atoms, then prefixes di, tri, tetra can be used.

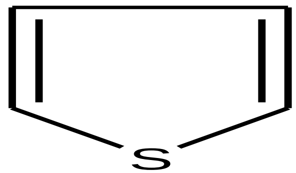
5) When ring contain more than one type of hetero atoms, then the preference is given to that hetero atom which having highest group no. in periodic table (Ex. Oxygen (Gr. VI) before Nitrogen (Gr. V) and Sulphur (Gr. VI) before Nitrogen (Gr.V).

6) When different element having same group, then preference is given to the element which having lowest atomic number. (Ex. preference is to O (Gr.VI, atomic No. 8) before S (Gr.VI, atomic No. 16).

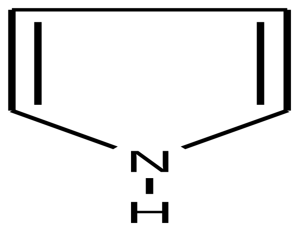
7) The direction of numbering around to the ring is such that the numbers are kept to a minimum.



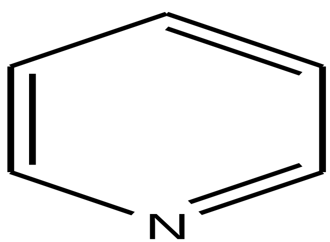
Oxole



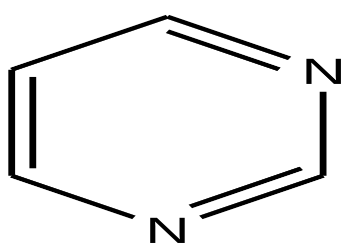
Thiole



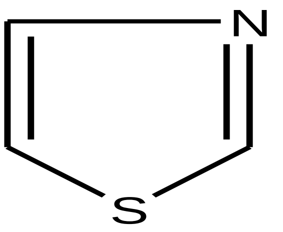
Azole



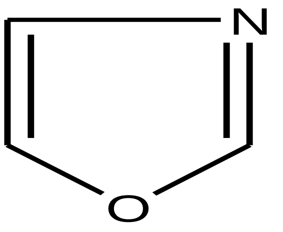
Azine



1,3-diazine



1,3-thiazole



1,3-oxazole

Molecular Orbital Structure of Furan (Oxole)

Furan is five member aromatic heterocyclic compound containing one oxygen and four carbon atoms in their cyclic structure. All four carbon atoms and one oxygen atom is SP^2 hybridized.

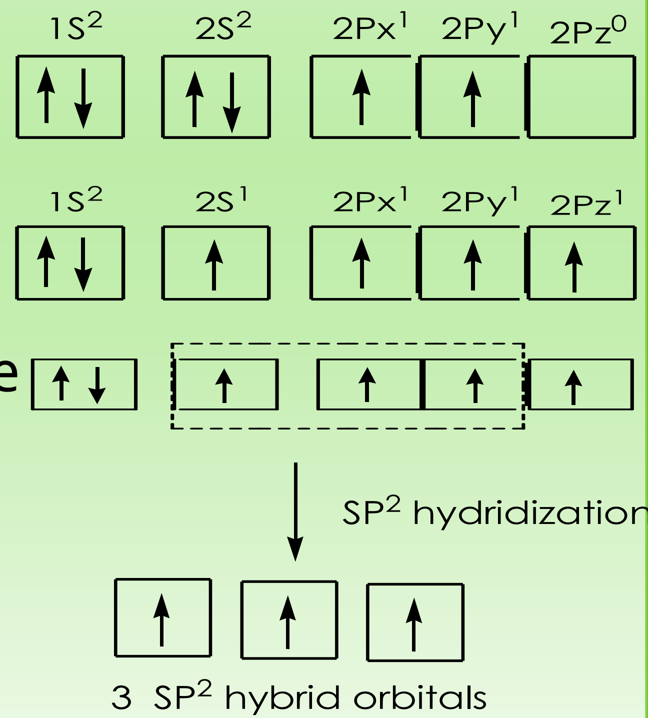
The electronic configuration of carbon is as follows :

Atomic no. of carbon atom is 6

Electronic conf. of Carbon in ground state

Electronic conf. of Carbon in excited state

Electronic conf. of Carbon hybridized state



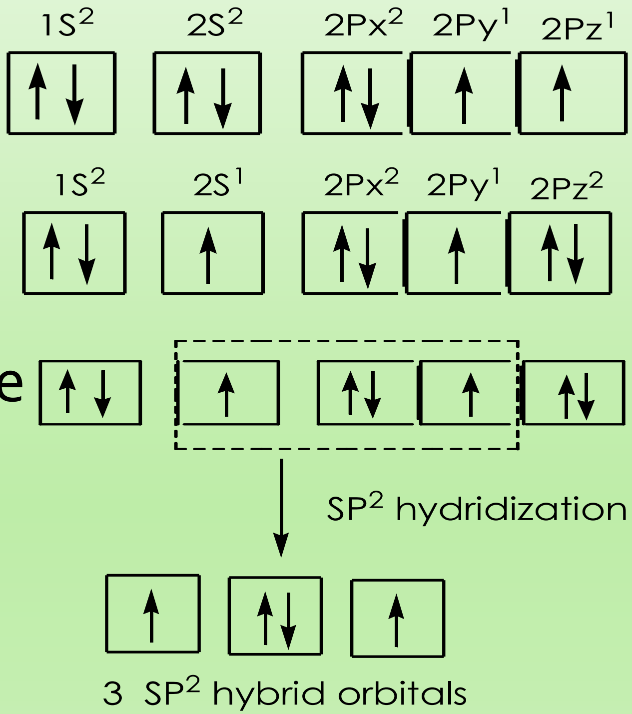
The electronic configuration of Oxygen is as follows :

Atomic no. of Oxygen atom is 8

Electronic conf. of Oxygen in ground state

Electronic conf. of Oxygen in excited state

Electronic conf. of Oxygen hybridized state



All four carbon atoms forms three SP^2 hybrid orbitals containing single electron. Each carbon atom forms three sigma bonds. Carbon-carbon sigma bond is formed by SP^2-SP^2 overlapping and carbon-hydrogen sigma bond is formed by SP^2-S overlapping and carbon –oxygen sigma bond is formed by SP^2-SP^2 overlapping.

Oxygen atom forms three SP^2 hybrid orbitals. One containing a pair of electron, this lone pair used for protonation. Two hybrid orbitals containing single electrons which take part in sigma bond formation. Oxygen atom forms two sigma bonds with adjacent carbon atoms by SP^2-SP^2 overlapping.

Each carbon atom having one unhybridized 2Pz orbital containing single electron which take part in pi bond formation.

Oxygen atom containing one unhybridized 2Pz orbital having a pair of electrons which take part in delocalization.

Formation of sigma bonds in Furan as follows :

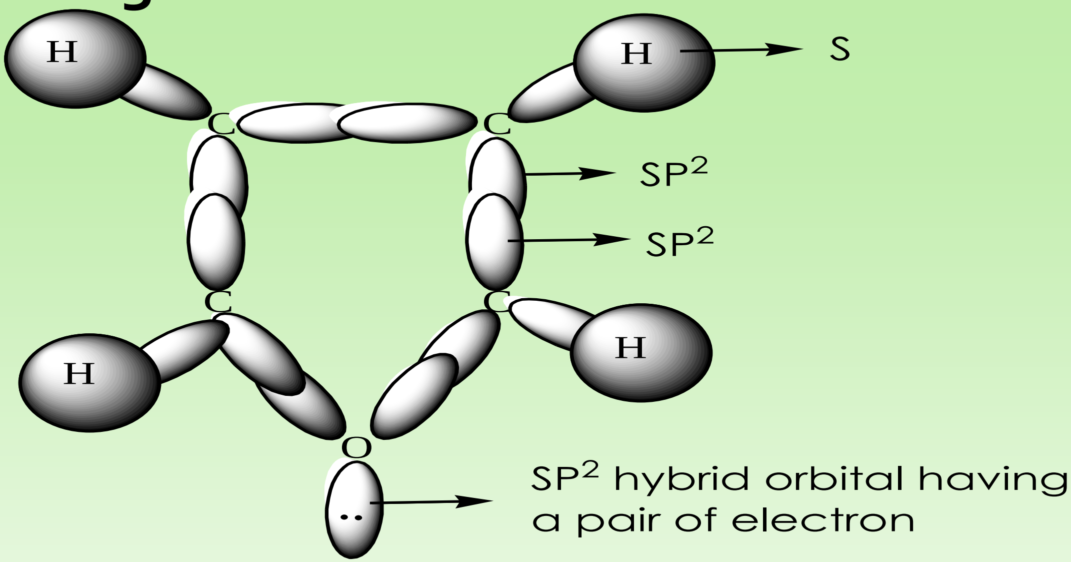


Fig : Formation of sigma bonds in Furan

Formation of π-bond in Furan as follows :

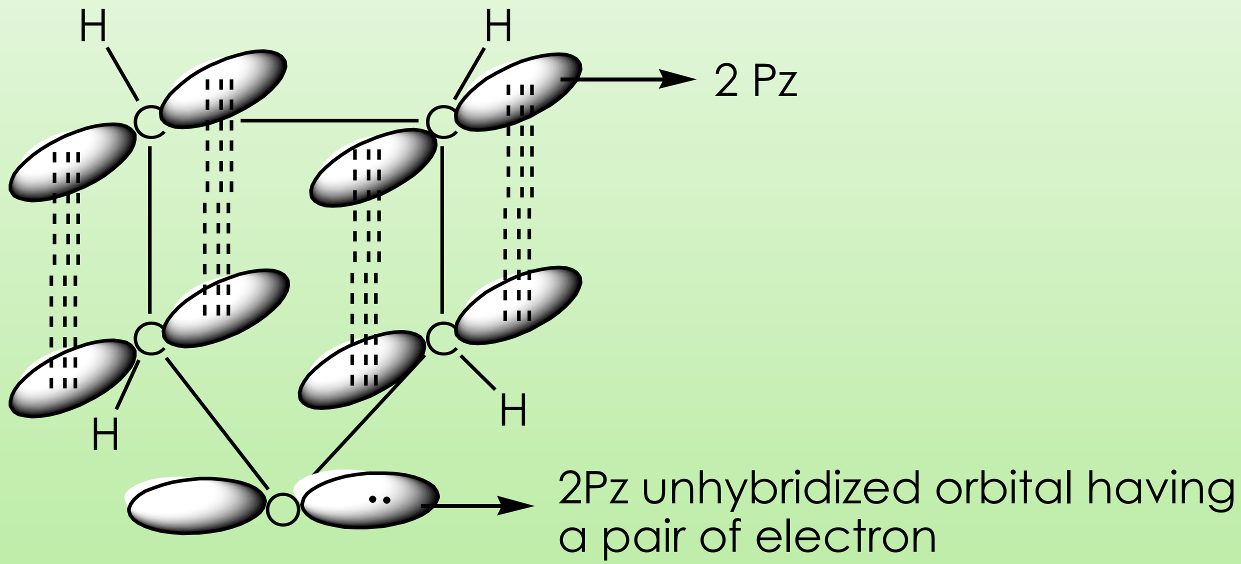


Fig : Formation of pi bonds in Furan

Structure of Furan as follows :

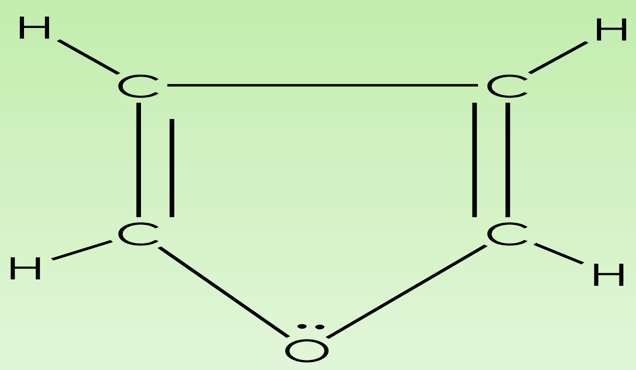


Fig : Structure of Furan

Molecular Orbital Structure of Thiophene (Thiole)

Thiophene is five member aromatic heterocyclic compound containing one sulphur and four carbon atoms in their cyclic structure. All four carbon atoms and one sulphur atom is SP^2 hybridized.

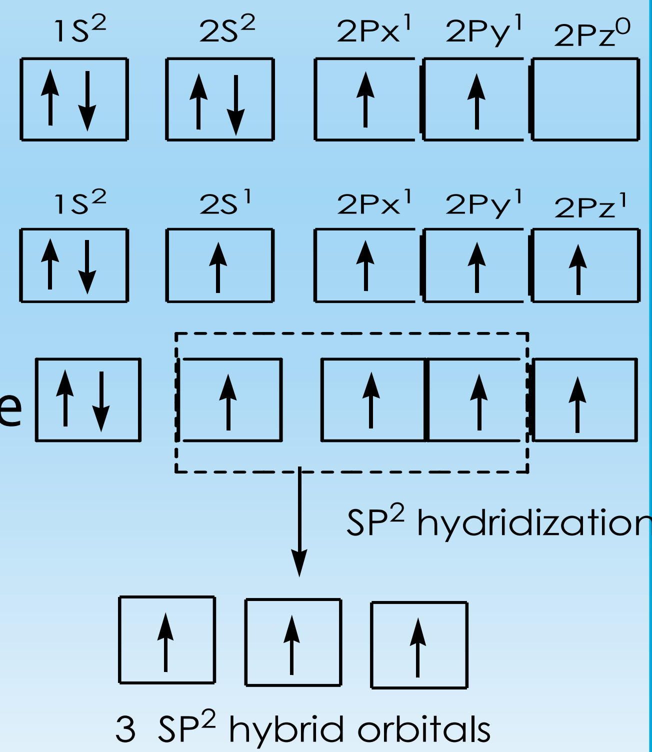
The electronic configuration of carbon is as follows :

Atomic no. of carbon atom is 6

Electronic conf. of Carbon in ground state

Electronic conf. of Carbon in excited state

Electronic conf. of Carbon hybridized state



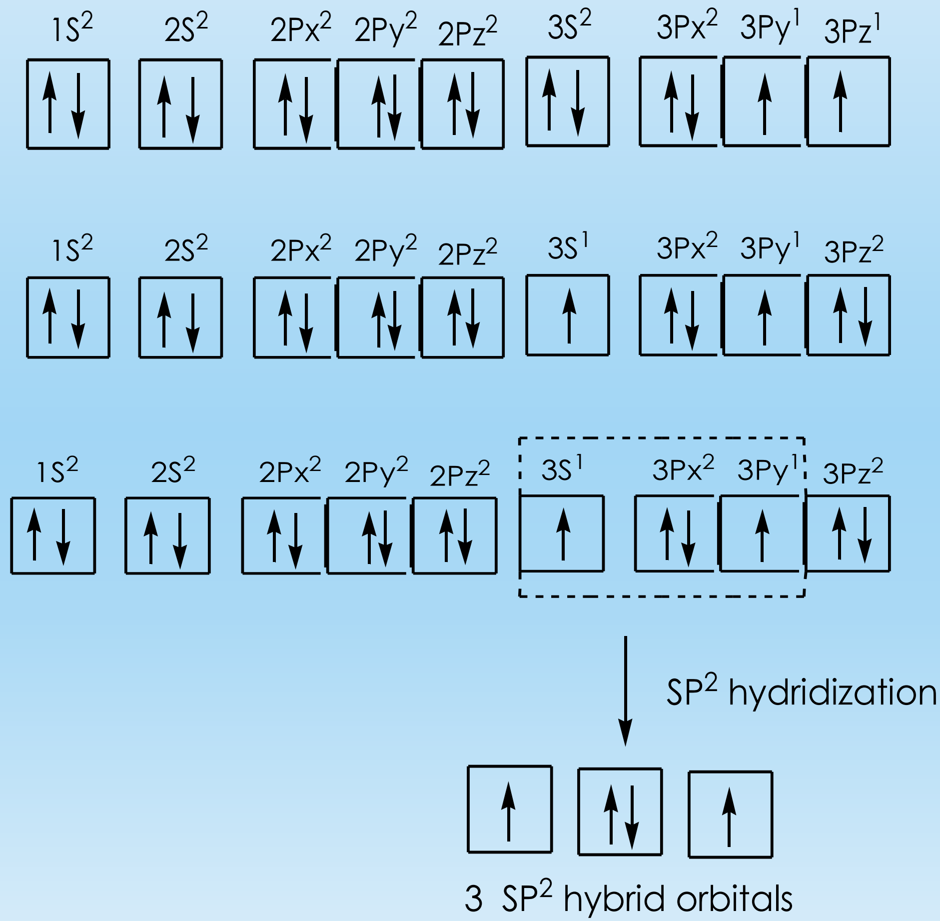
The electronic configuration of Sulphur is as follows :

Atomic no. of Sulphur atom is 16

Elec. conf. of S in gr. state

Elec. conf. of S in exci. state

Elec. conf. of S hybri. state



All four carbon atoms forms three SP^2 hybrid orbitals containing single electron. Each carbon atom forms three sigma bonds. Carbon-carbon sigma bond is formed by SP^2-SP^2 overlapping, carbon-hydrogen sigma bond is formed by SP^2-S overlapping and carbon-sulphur sigma bond is formed by SP^2-SP^2 overlapping.

Sulphur atom forms three SP^2 hybrid orbitals. One containing a pair of electron, which is used for protonation. Remaining two containing single electrons which take part in sigma bond formation. Sulphur atom forms two sigma bonds with adjacent carbon atoms by SP^2-SP^2 overlapping.

Each carbon atom having one unhybridized 2Pz orbital containing single electron which take part in pi bond formation.

Sulphur atom containing one unhybridized 3Pz orbital having a pair of electrons which take part in delocalization.

Formation of Sigma bonds in Thiophene as follows :

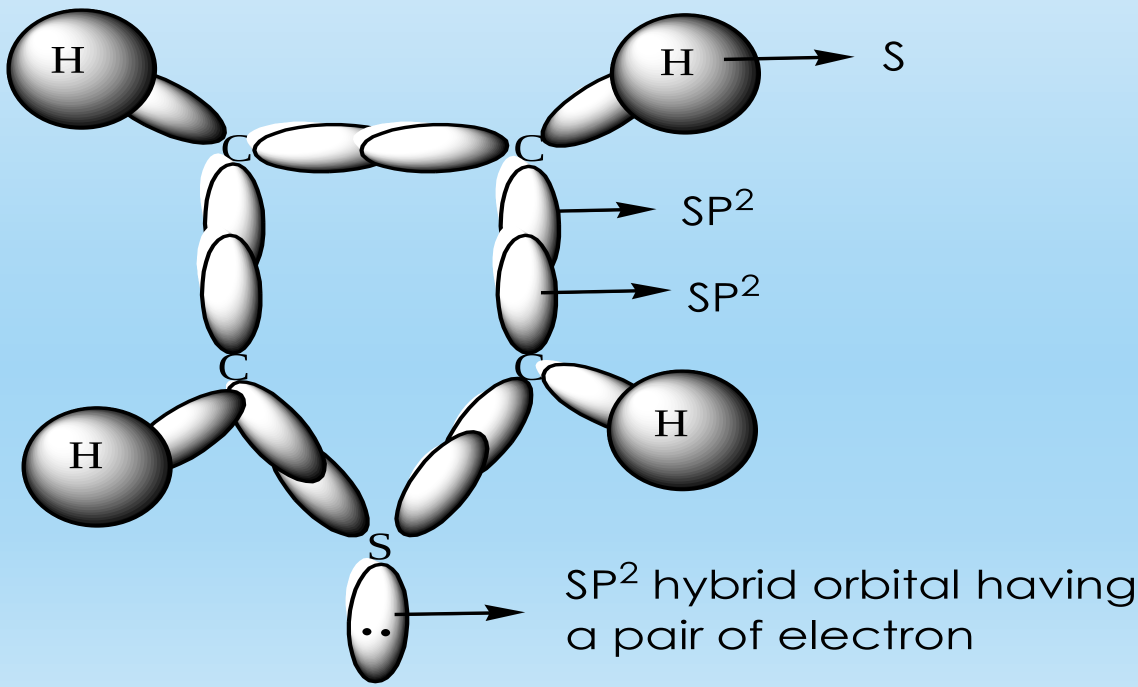


Fig : Formation of sigma bonds in Thiophene

Formation of π-bonds in Thiophene as follows :

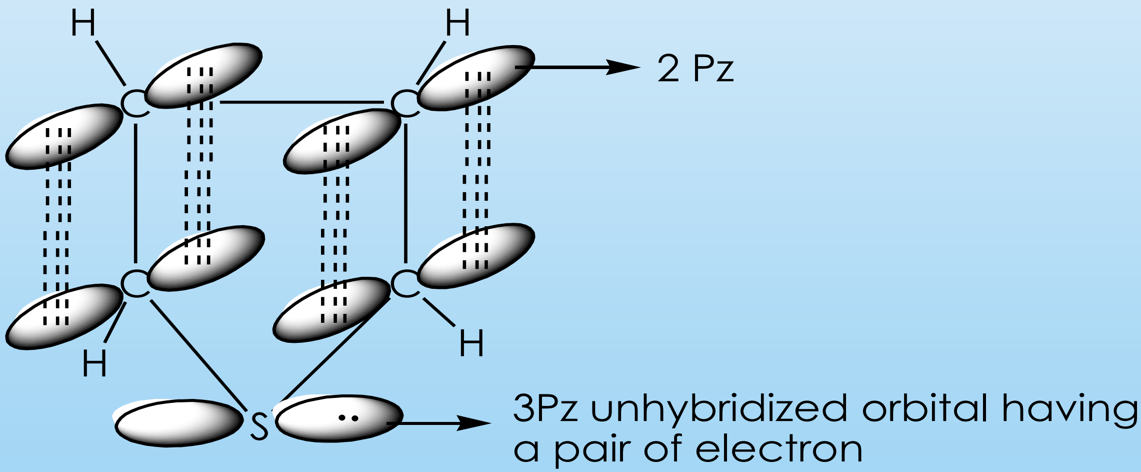


Fig : Formation of pi bonds in Thiophene

Structure of Thiophene as follows :

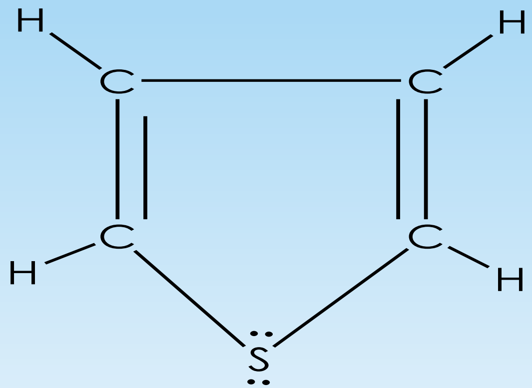


Fig : Structure of Thiophene

Molecular Orbital Structure of Pyrrole (Azole)

Pyrrole is five member aromatic heterocyclic compound containing one nitrogen and four carbon atoms in their cyclic structure. All four carbon atoms and one nitrogen atom is SP^2 hybridized.

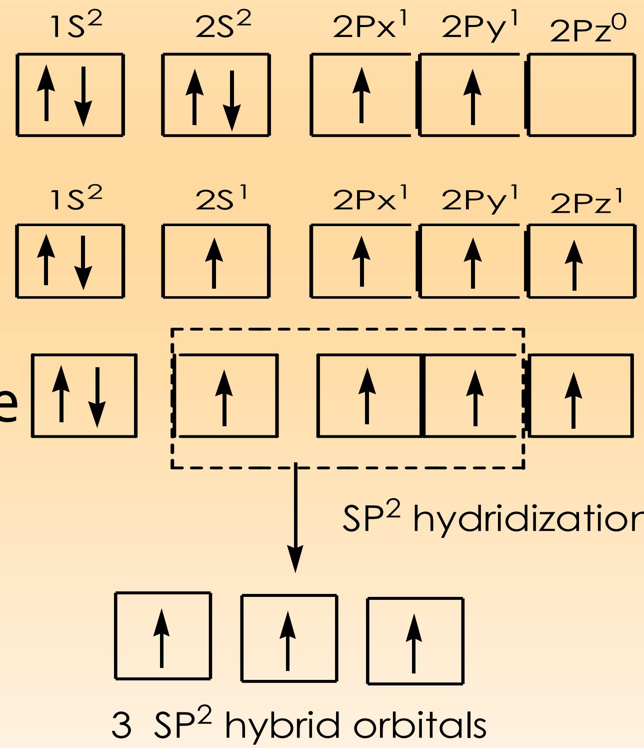
The electronic configuration of carbon is as follows :

Atomic no. of carbon atom is 6

Electronic conf. of Carbon in ground state

Electronic conf. of Carbon in excited state

Electronic conf. of Carbon hybridized state



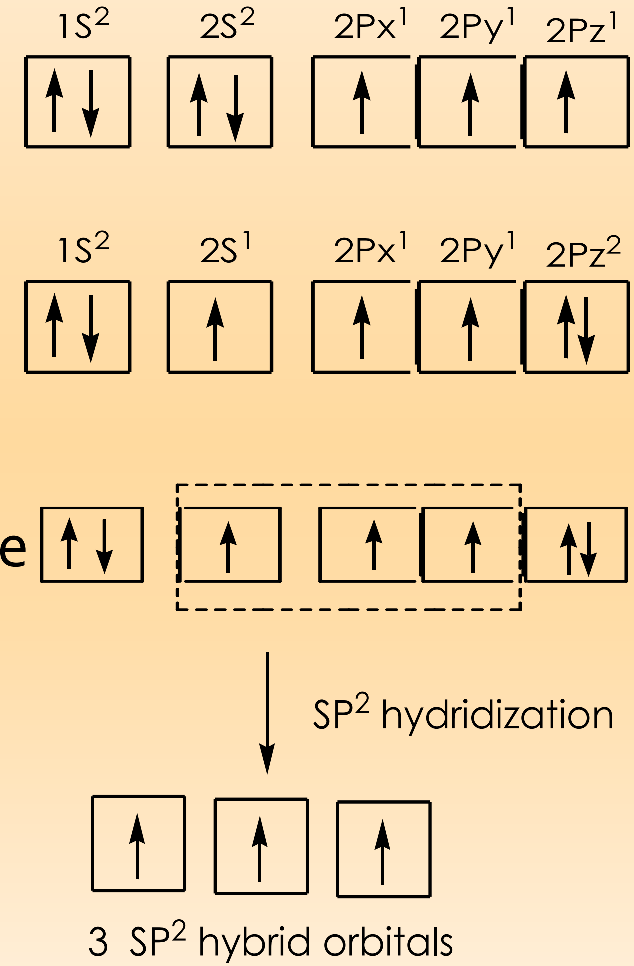
The electronic configuration of Nitrogen is as follows :

Atomic no. of Nitrogen atom is 7

Electronic conf. of Nitrogen in ground state

Electronic conf. of Nitrogen in excited state

Electronic conf. of Nitrogen hybridized state



All four carbon atoms forms three sigma bonds. Carbon-carbon sigma bond is formed by SP^2-SP^2 overlapping, carbon-hydrogen sigma bond is formed by SP^2-S overlapping and carbon-nitrogen sigma bond is formed by SP^2-SP^2 overlapping.

Nitrogen atom forms three SP^2 hybrid orbitals, containing single electrons which take part in sigma bond formation. Nitrogen atom forms three sigma bonds. Two sigma bonds are formed by Nitrogen and adjacent carbon atoms by SP^2-SP^2 overlapping. Third sigma bond is formed by Nitrogen and Hydrogen atom by SP^2-S overlapping.

Each carbon atom having one unhybridized 2Pz orbital containing single electron which take part in pi bond formation.
Nitrogen atom containing one unhybridized 2Pz orbital having a pair of electrons which take part in delocalization.

Formation of sigma bonds in Pyrrole as follows :

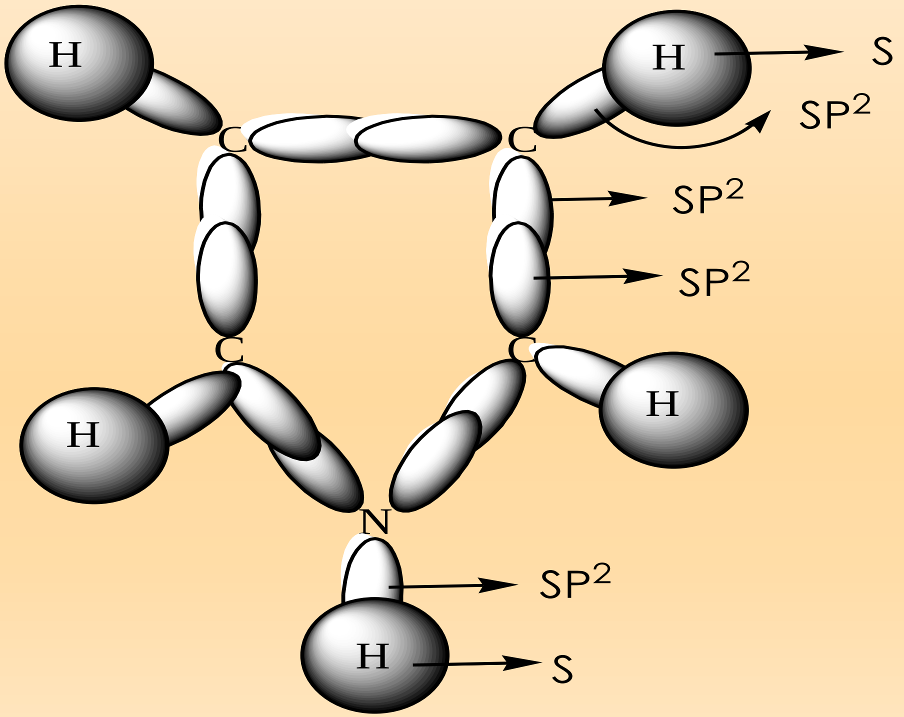


Fig : Formation of sigma bonds in Pyrrole

Formation of π-bonds in Pyrrole as follows :

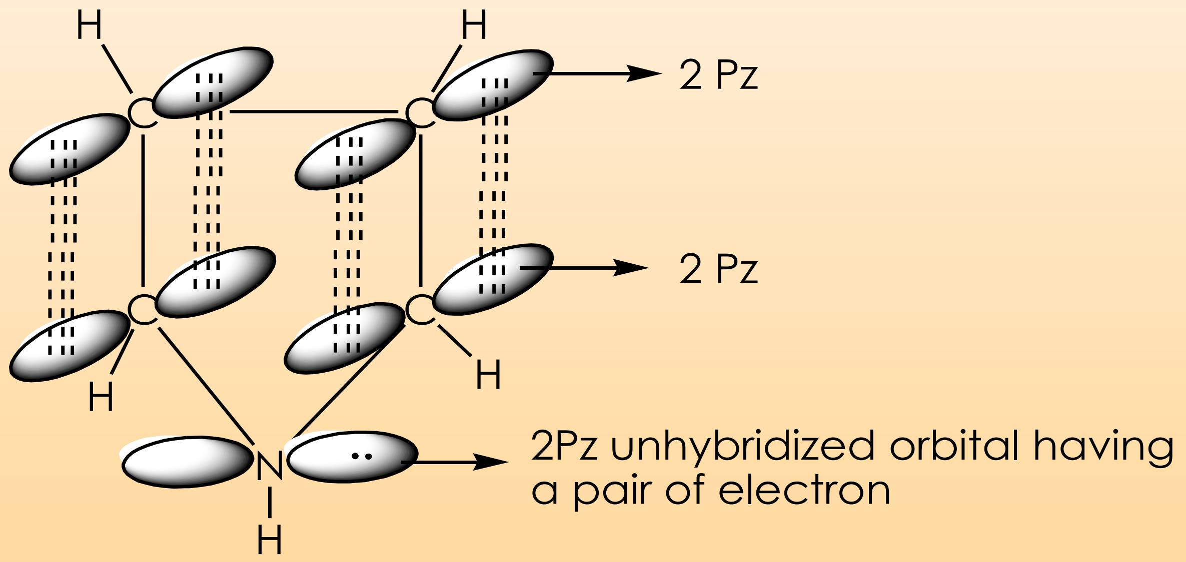


Fig : Formation of pi bonds in Pyrrole

Structure of Pyrrole as follows :

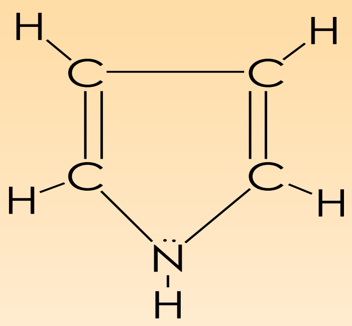


Fig : Structure of Pyrrole

Molecular Orbital Structure of Pyridine (Azine)

Pyridine has six member aromatic heterocyclic compound containing one nitrogen and five carbon atoms in their cyclic structure. All five carbon atoms and one nitrogen atom is SP^2 hybridized.

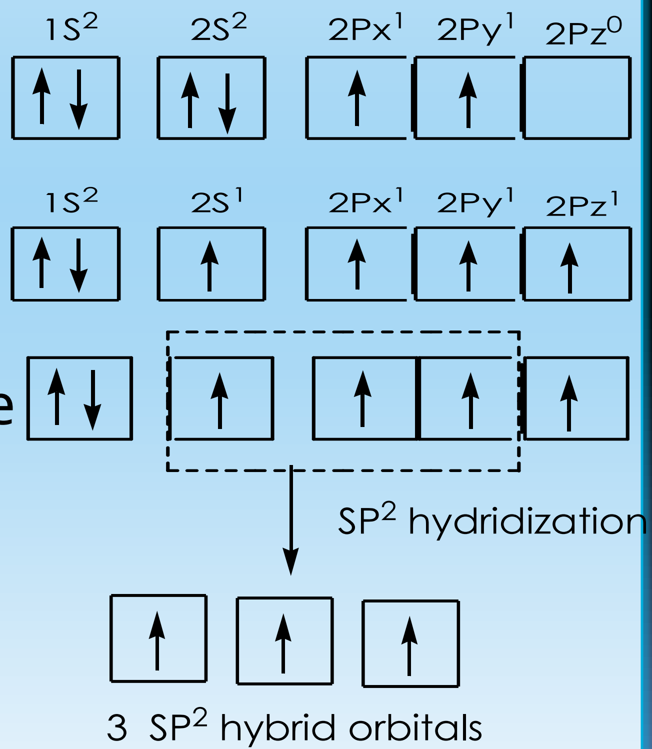
The electronic configuration of carbon is as follows :

Atomic no. of carbon atom is 6

Electronic conf. of Carbon in ground state

Electronic conf. of Carbon in excited state

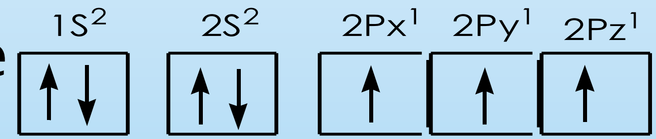
Electronic conf. of Carbon hybridized state



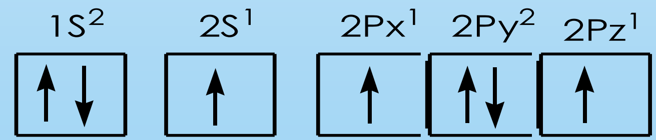
The electronic configuration of Nitrogen is as follows :

Atomic no. of Nitrogen atom is 7

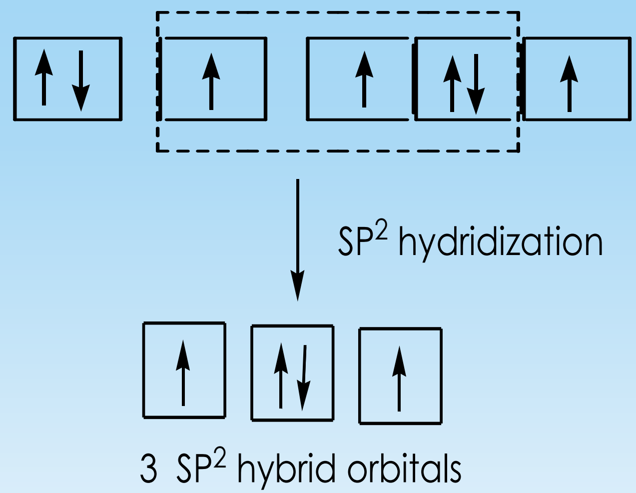
Electronic conf. of Nitrogen in ground state



Electronic conf. of Nitrogen in excited state



Electronic conf. of Nitrogen hybridized state



All five carbon atoms forms three sigma bonds. Carbon-carbon sigma bond is formed by SP^2-SP^2 overlapping, carbon-hydrogen sigma bond is formed by SP^2-S overlapping and carbon-nitrogen sigma bond is formed by SP^2-SP^2 overlapping.

Nitrogen atom forms three SP^2 hybrid orbitals, one SP^2 hybrid orbital containing two electrons which is used for protonation. Remaining two SP^2 hybrid orbitals containing single electrons which take part in sigma bond formation. Nitrogen atom forms two sigma bonds. Two sigma bonds are formed by SP^2-SP^2 overlapping of Nitrogen and adjacent carbon atoms.

All five carbon atoms and one nitrogen atom having one unhybridized 2Pz orbital containing single electron which take part in pi bond formation.

Formation of sigma bonds in Pyridine as follows :

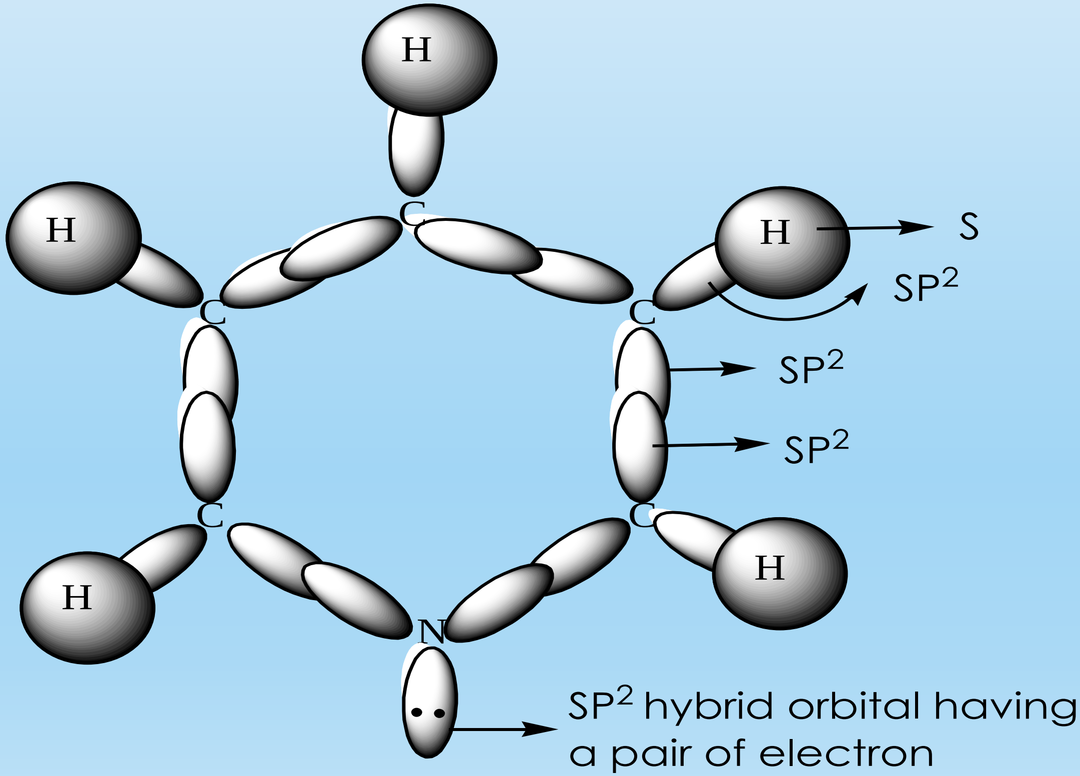


Fig : Formation of sigma bonds in Pyridine

Formation of π-bonds in Pyridine as follows :

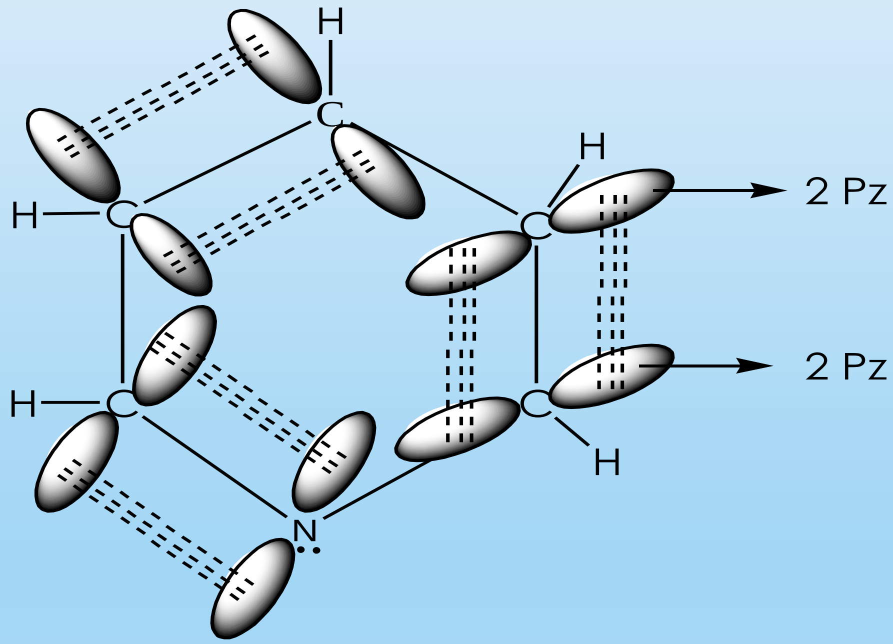


Fig : Formation of pi bonds in Pyridine

Structure of Pyridine as follows :

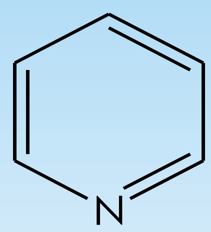
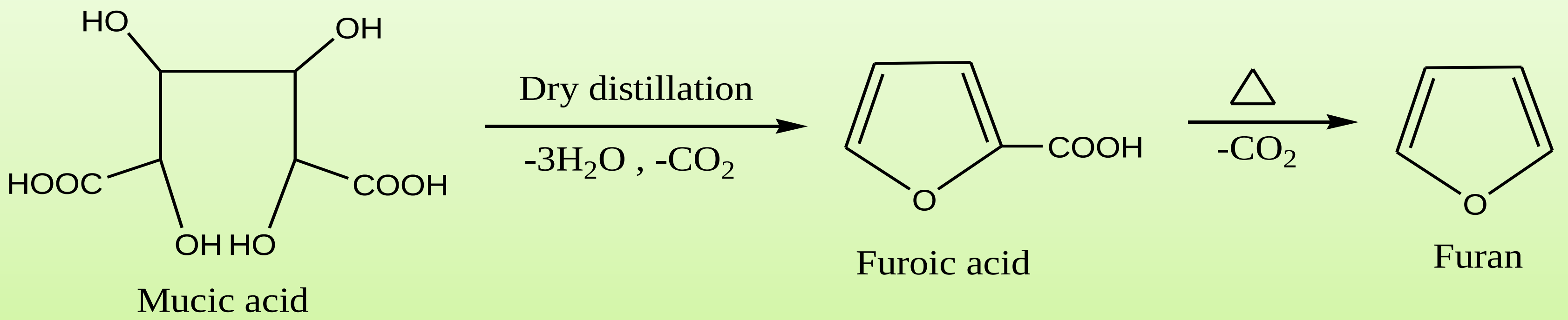


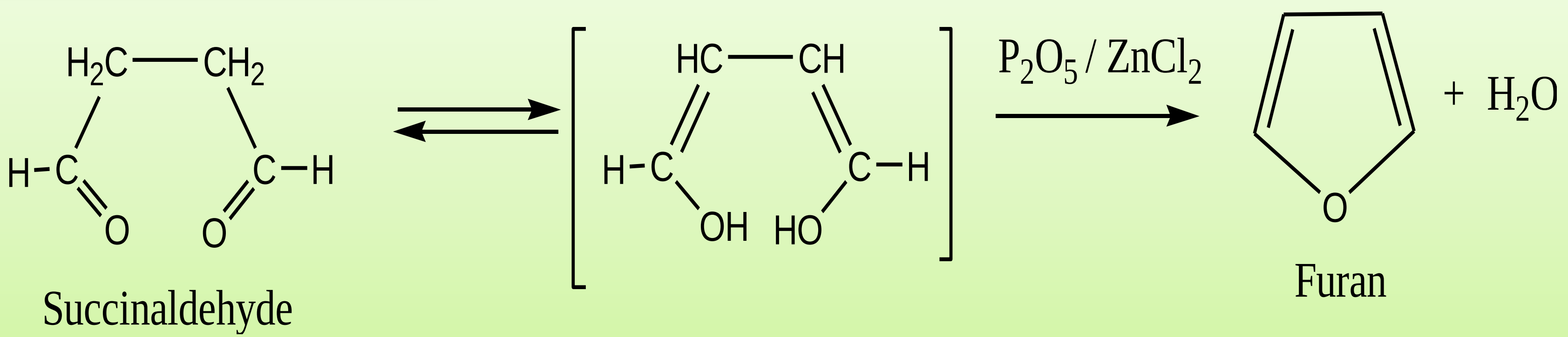
Fig : Structure of Pyridine

Synthesis of Furan (Oxole)

1) Mucic acid :

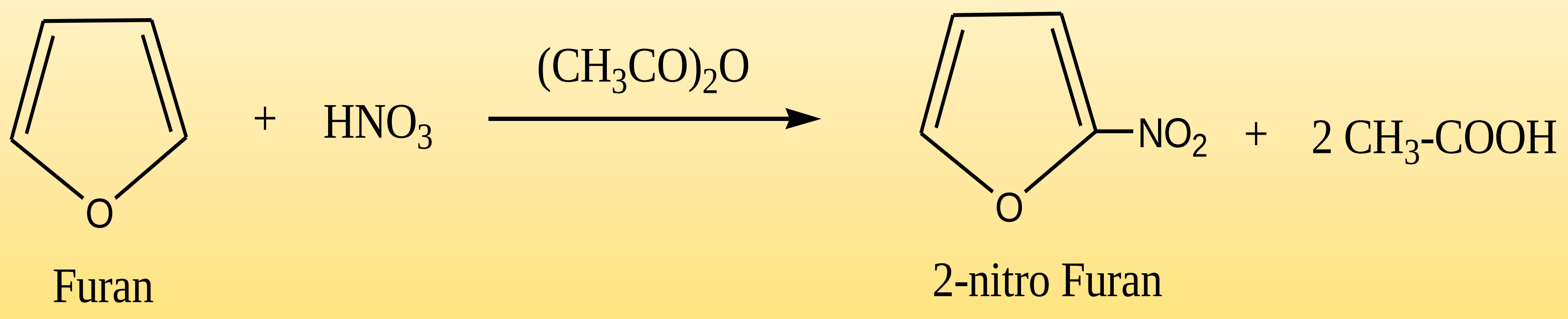


2) Succinaldehyde :

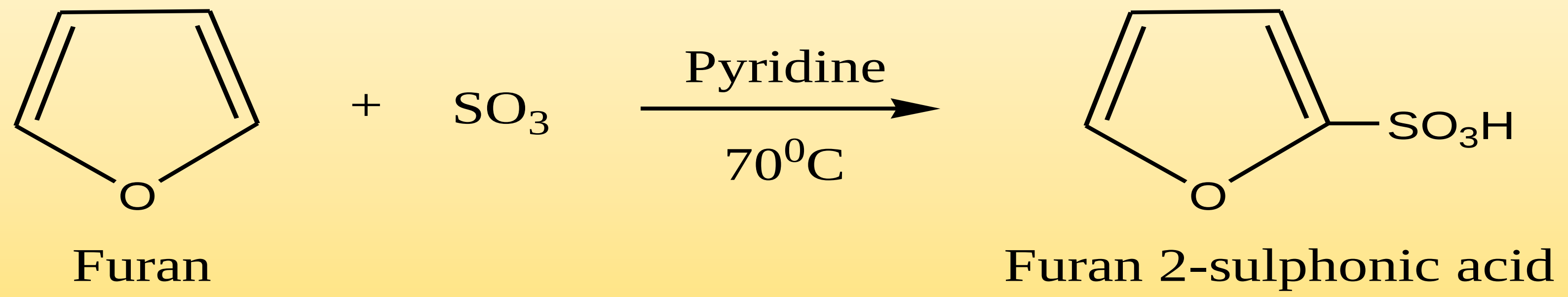


Chemical reactions of Furan

1) Nitration :

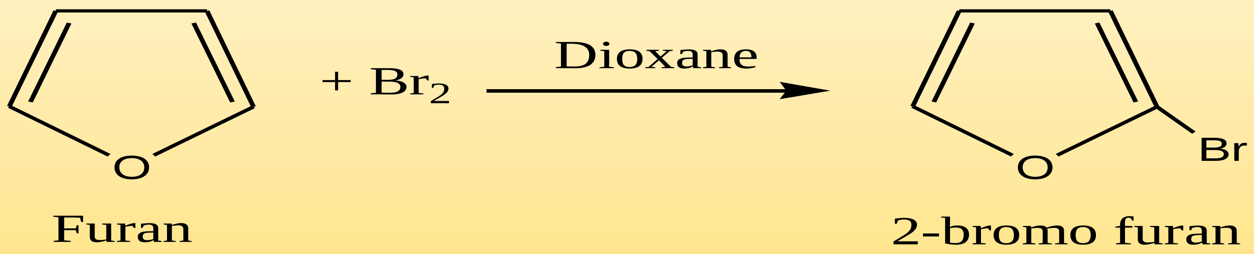


2) Sulphonation :

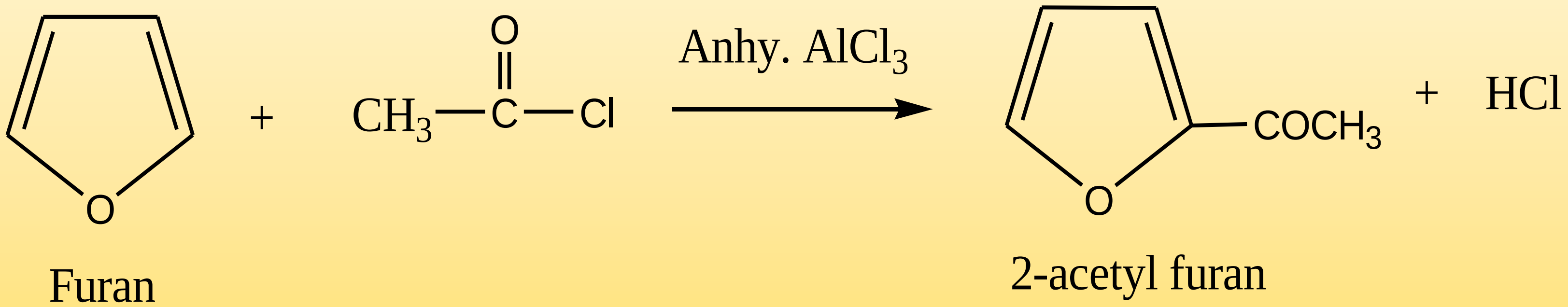


Chemical reactions of Furan

3) Halogenation :

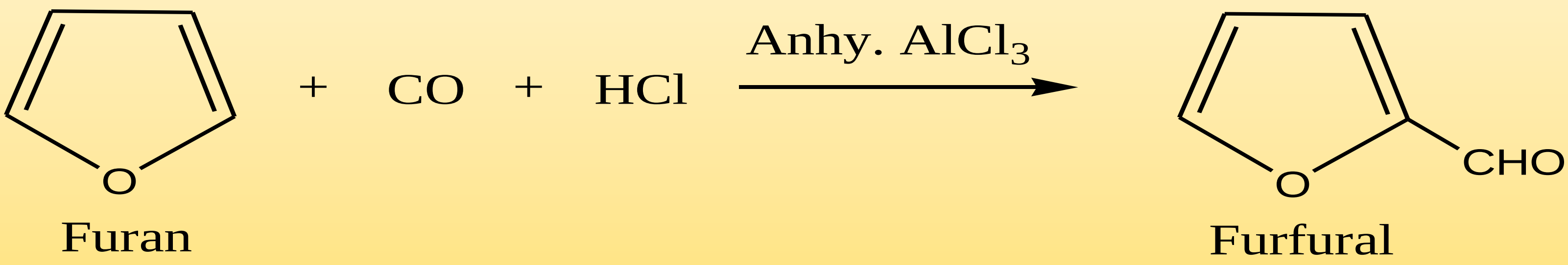


4) Friedel Craft Reaction :

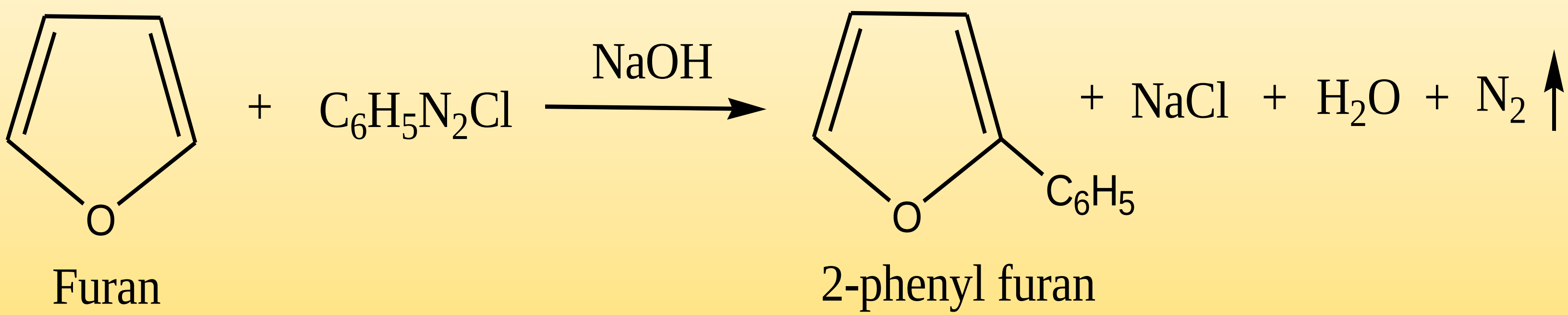


Chemical reactions of Furan

5) Gattermann Koch synthesis :

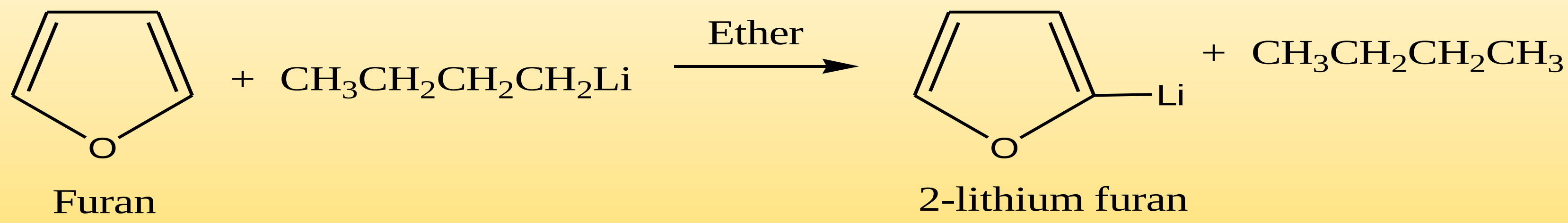


6) Gomberg Reaction :

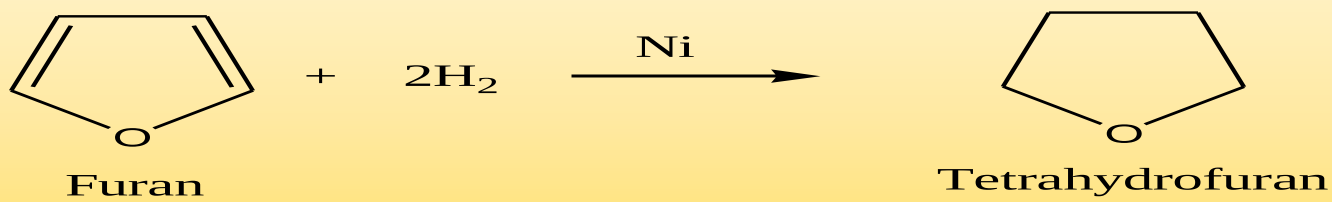


Chemical reactions of Furan

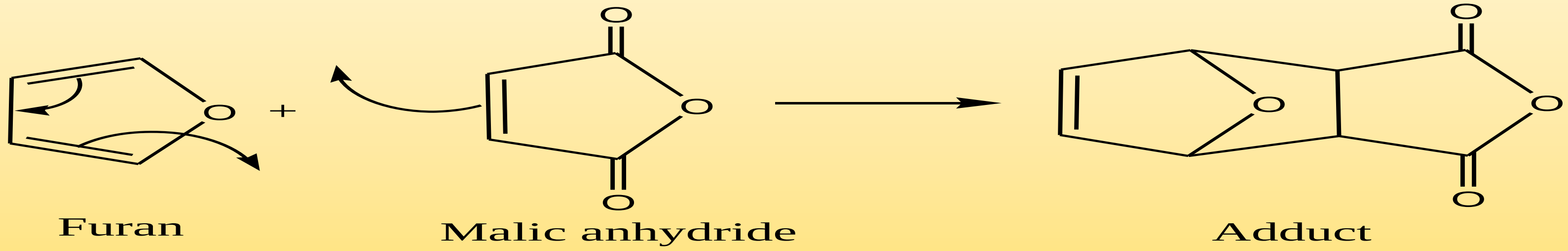
7) Reaction with n-butyl lithum :



8) Reduction :

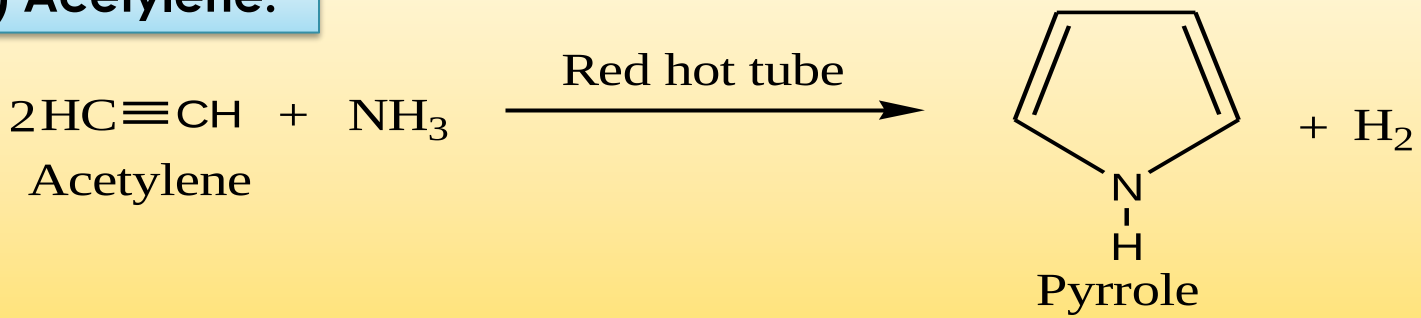


9) Diels Alder Reaction :

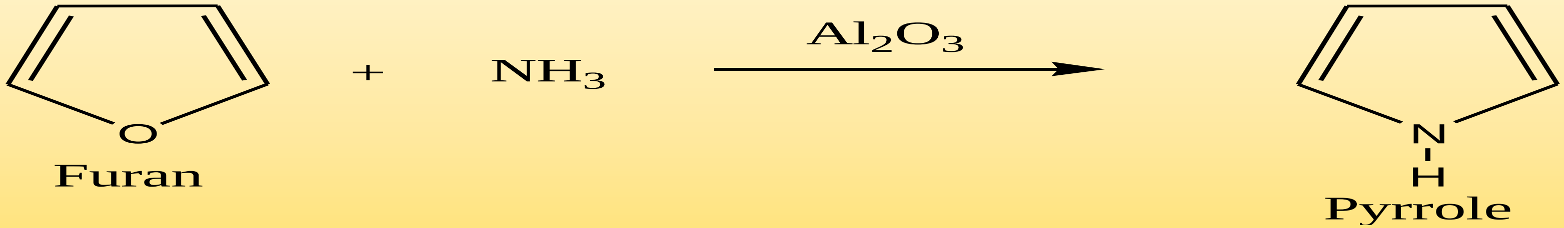


Synthesis of Pyrrole (Azole)

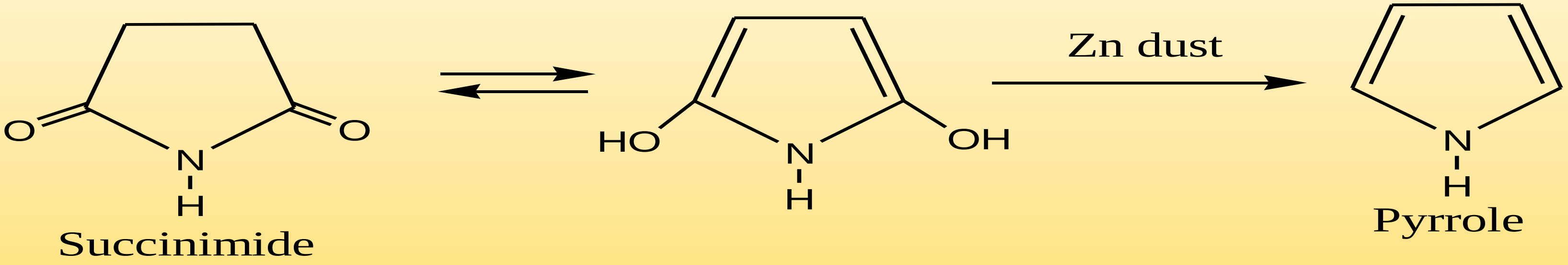
From : 1) Acetylene:



2) Furan :

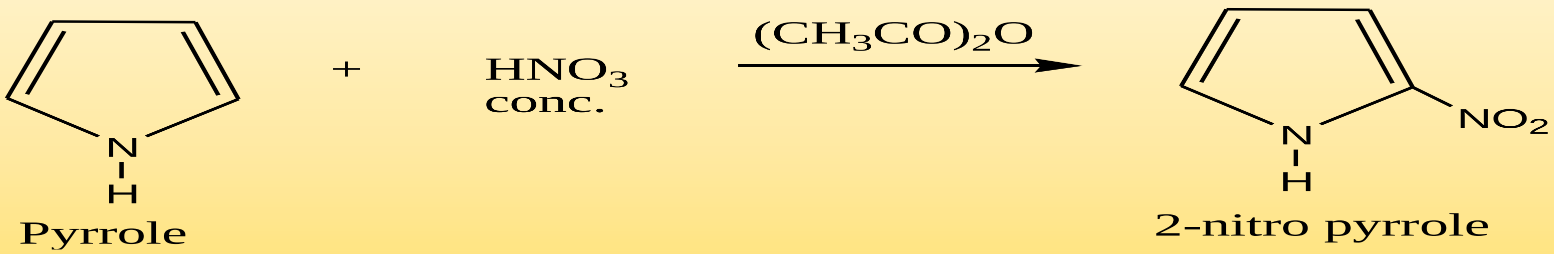


3) Succinimide :

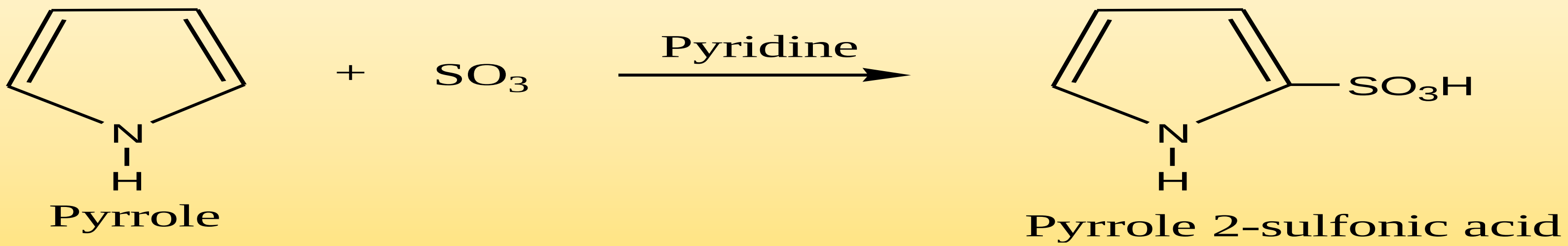


Chemical reactions of Pyrrole

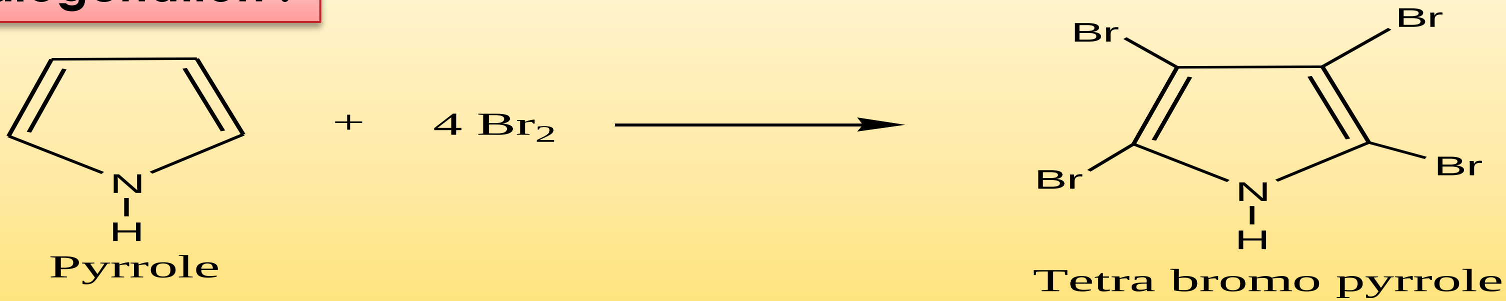
1) Nitration:



2) Sulphonation :

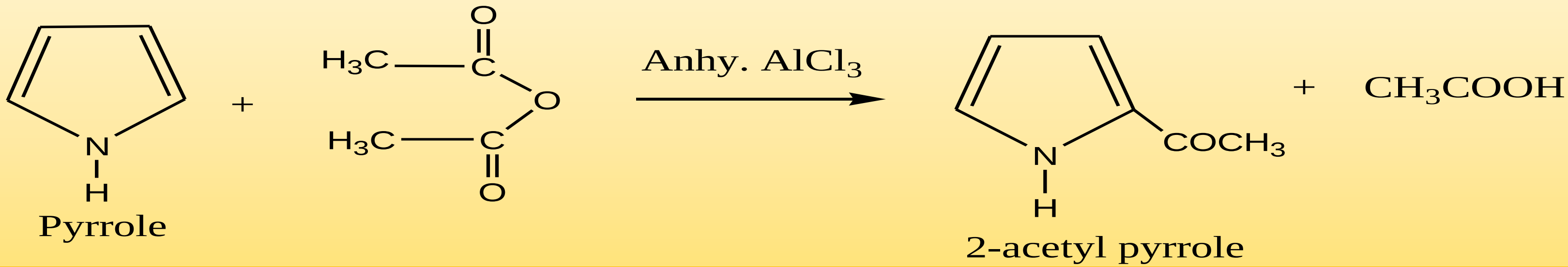


3) Halogenation :

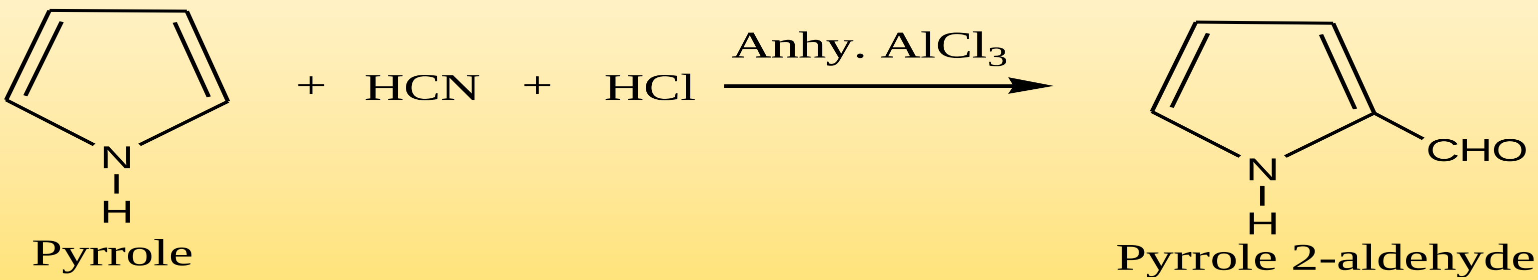


Chemical reactions of Pyrrole

4) Friedel craft acylation:



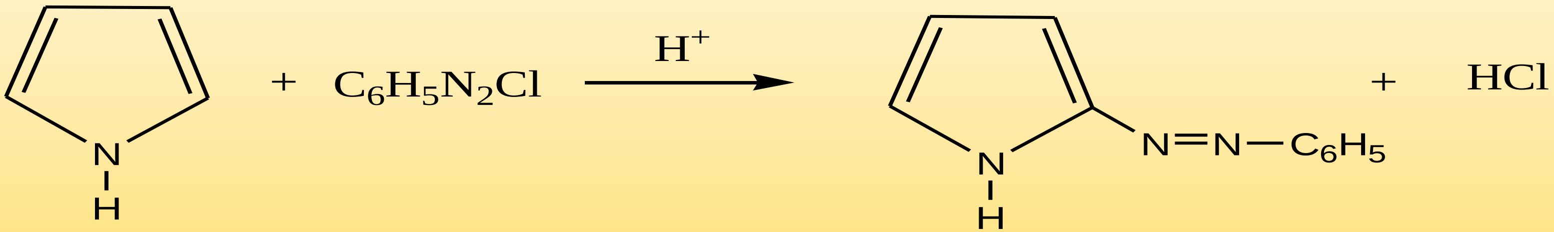
5) Gattermann Reaction :



6) Reimer Tiemann Reaction :

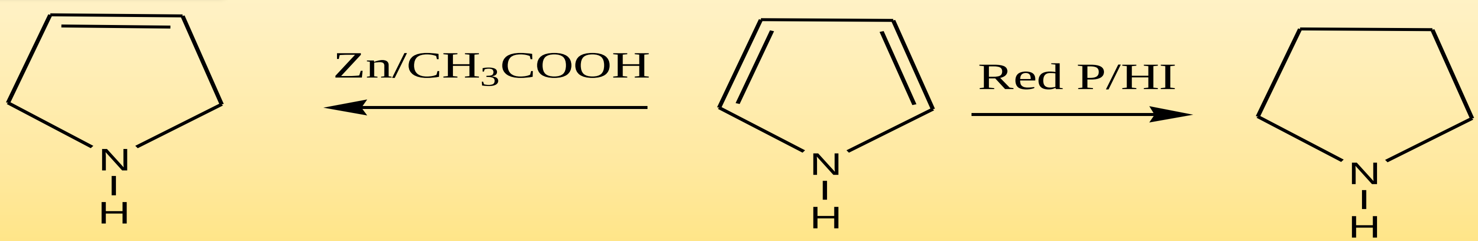
Chemical reactions of Pyrrole

7) Coupling Reaction :



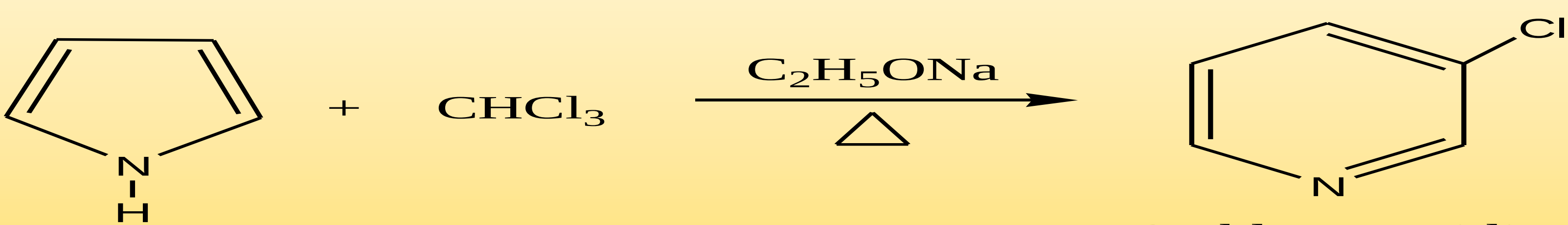
Pyrrole → 2-phenyl azo pyrrole

8) Reduction :



2,5-dihydro pyrrole ← Pyrrole → Pyrrolidine

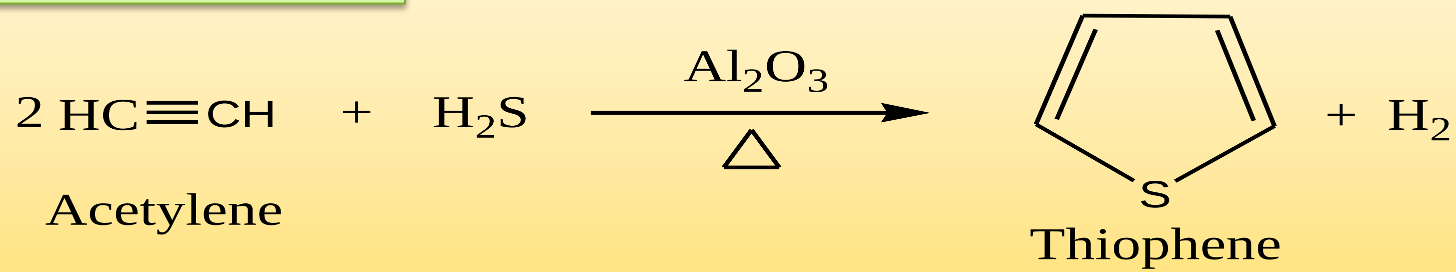
9) Ring Expansion :



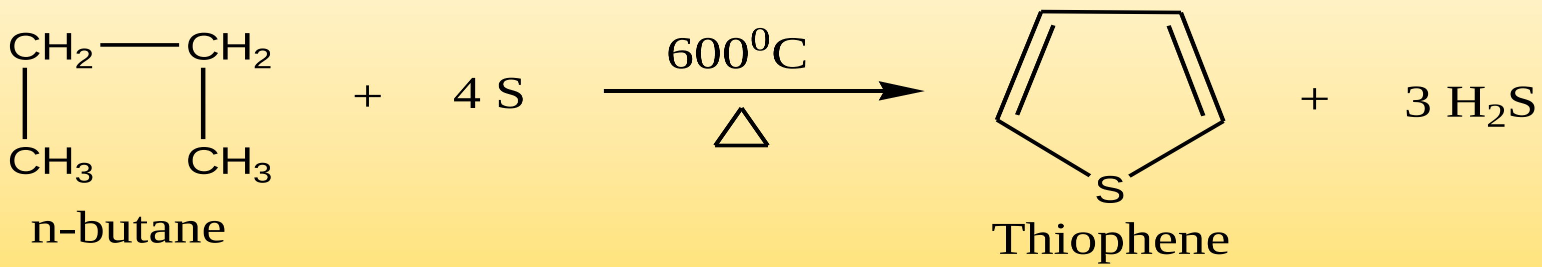
Pyrrole → 3-chloro pyridine

Synthesis of Thiophene (Thiole)

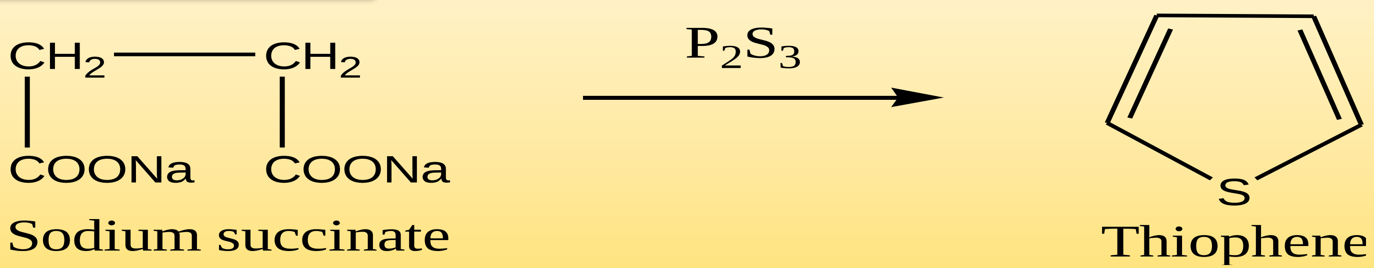
From : 1) Acetylene :



2) n-butane :

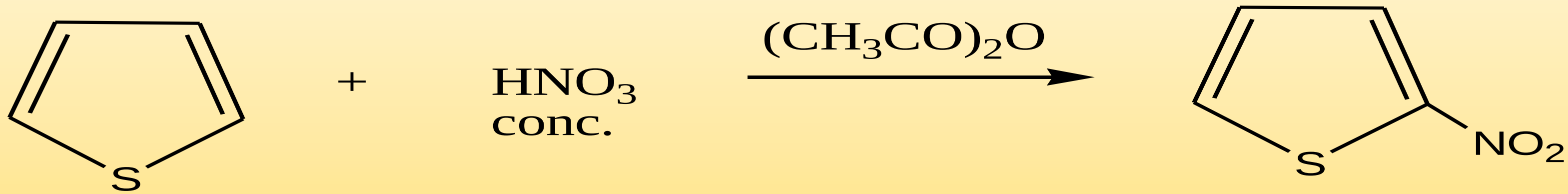


3) Sodium succinate :



Chemical reactions of Thiophene

1) Nitration :

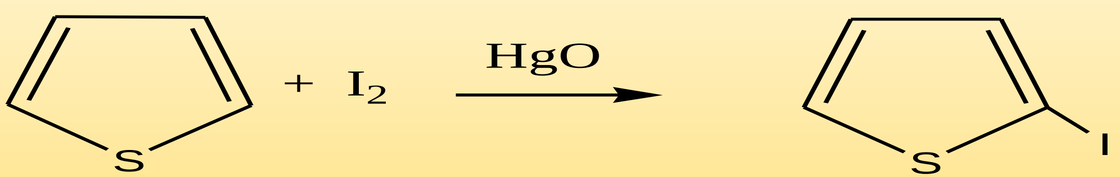


Thiophene 2-nitro thiophene

2) Sulphonation :

Thiophene Thiophene 2-sulphonic acid

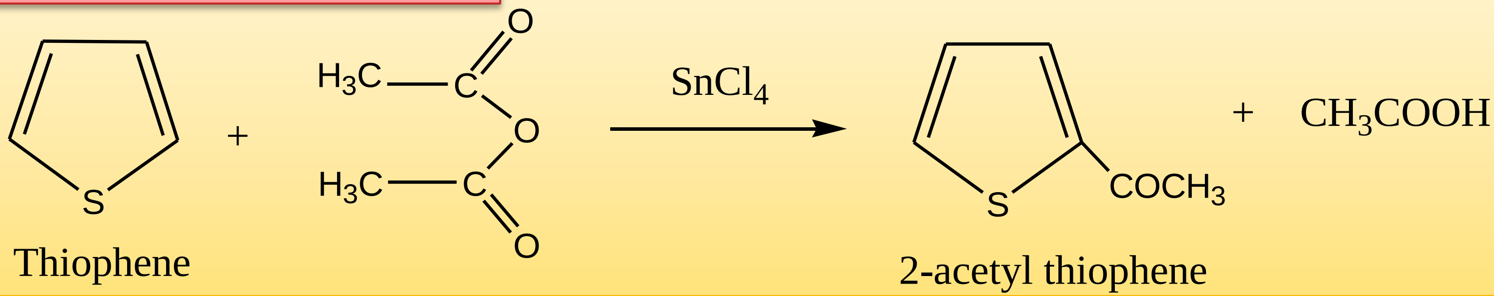
3) Halogenation :



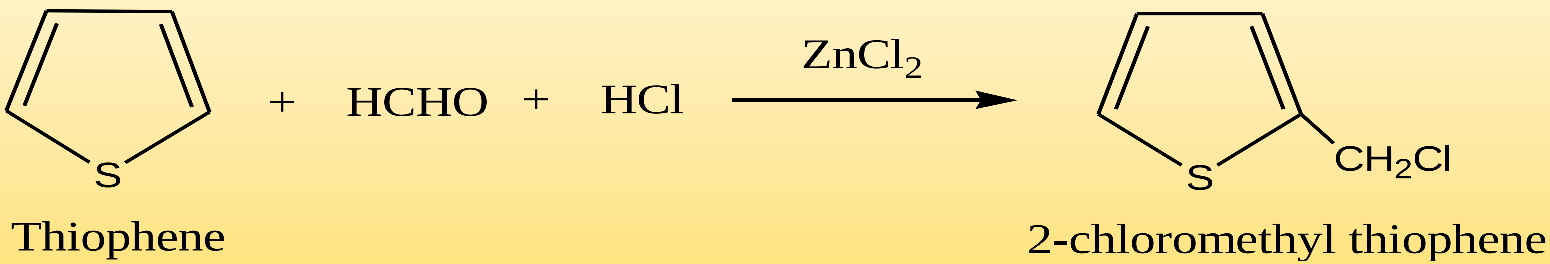
Thiophene 2-iodothiophene

Chemical reactions of Thiophene

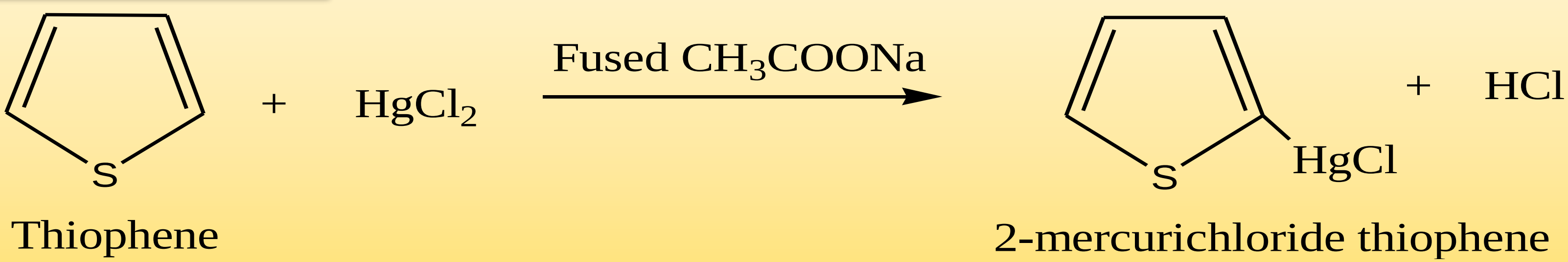
4) Friedel Craft acylation :



5) Chloromethylation :

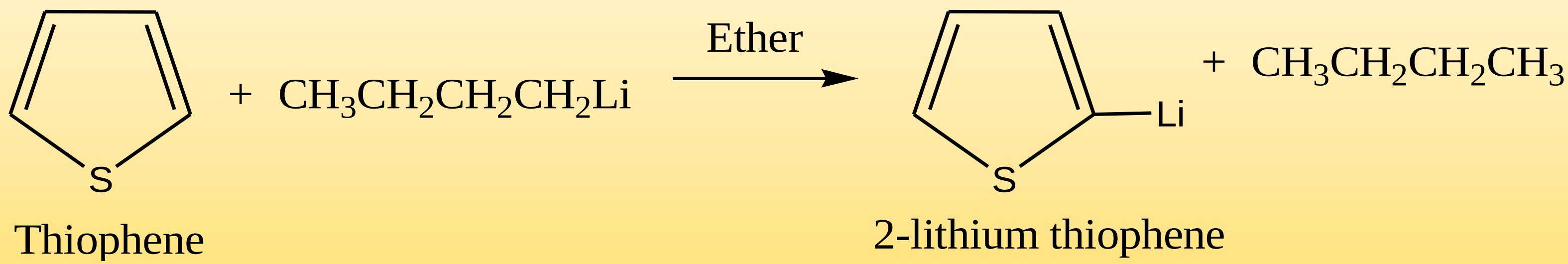


6) Mercuration :

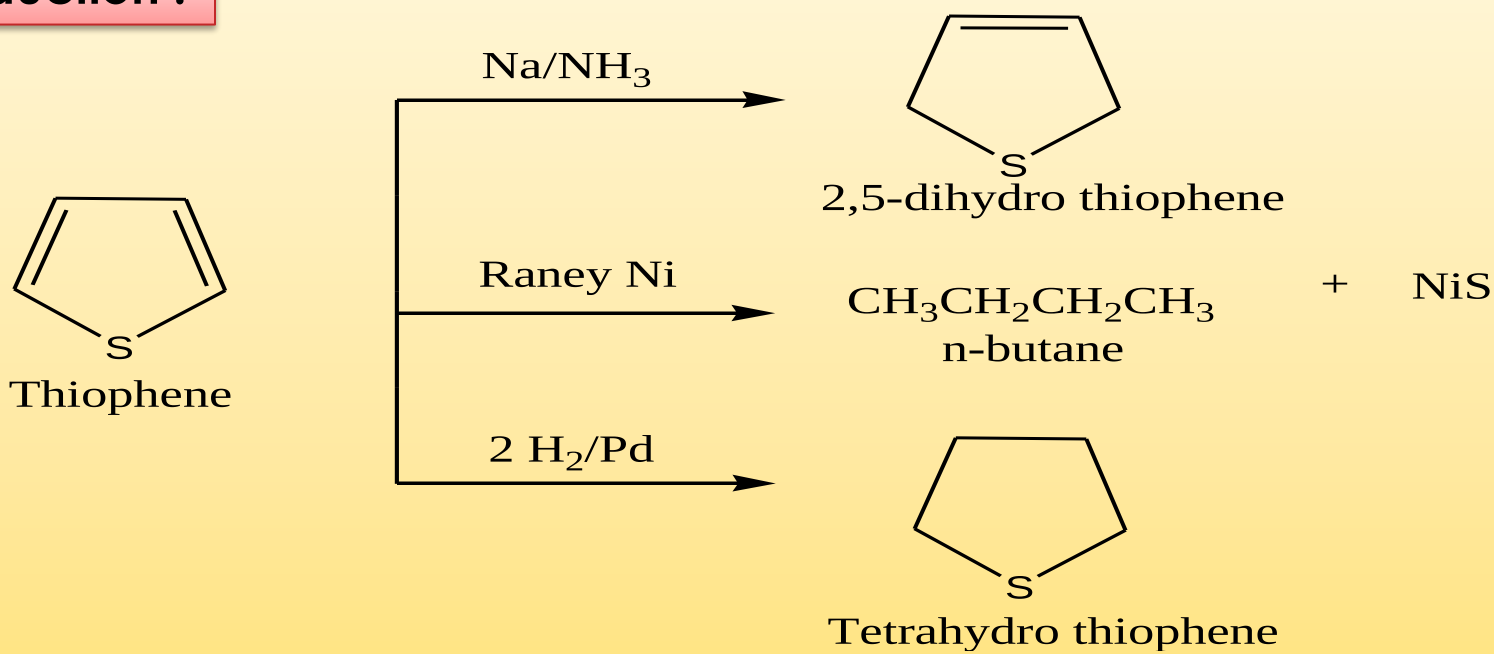


Chemical reactions of Thiophene

7) Reaction with n-butyl lithium :



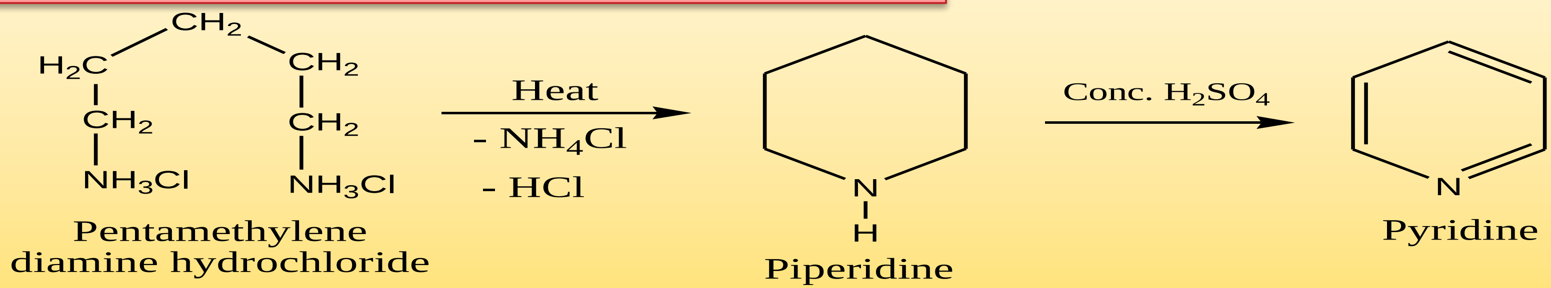
8) Reduction :



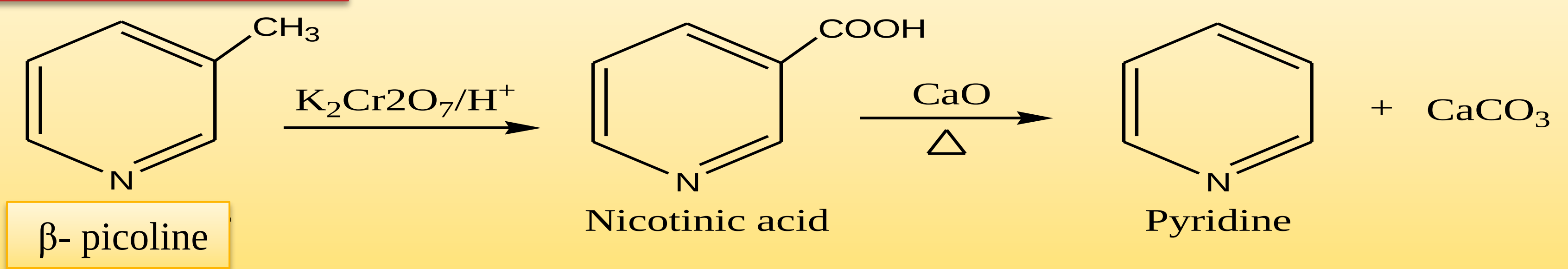
Synthesis of Pyridine (Azine)

From : 1) Acetylene :

2) Pentamethylene diamine hydrochloride :

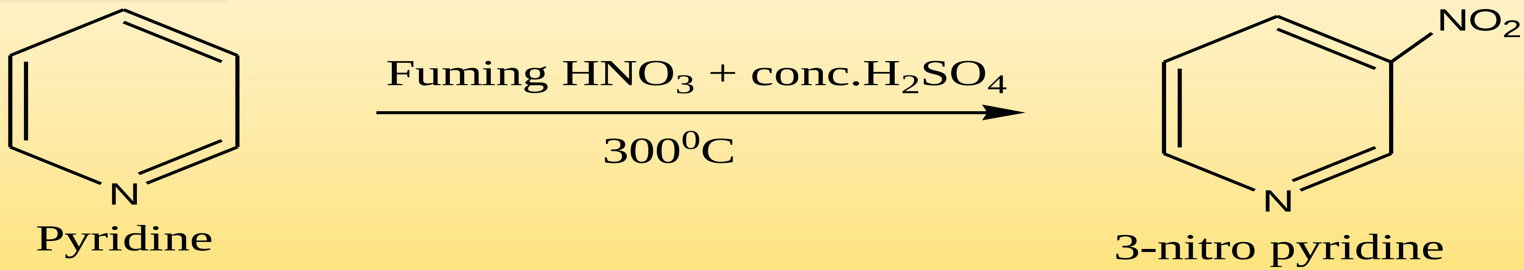


3) β- picoline :

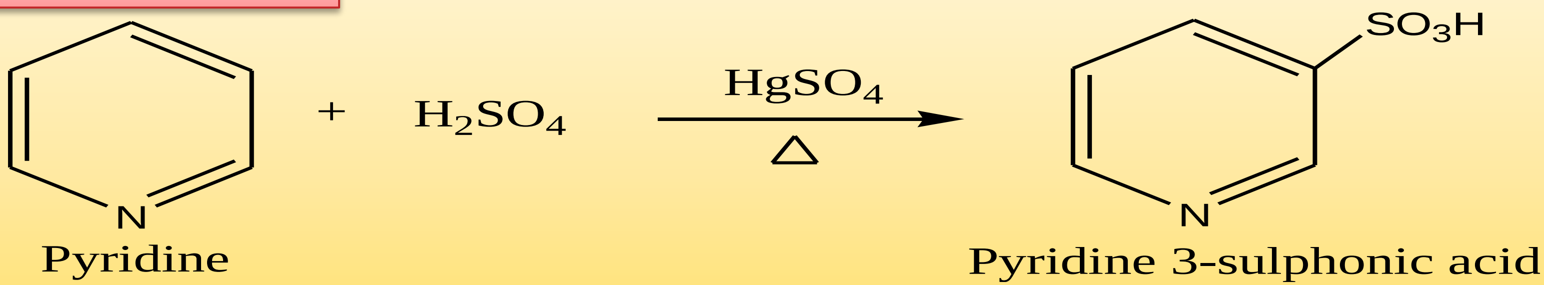


Chemical reactions of Pyridine

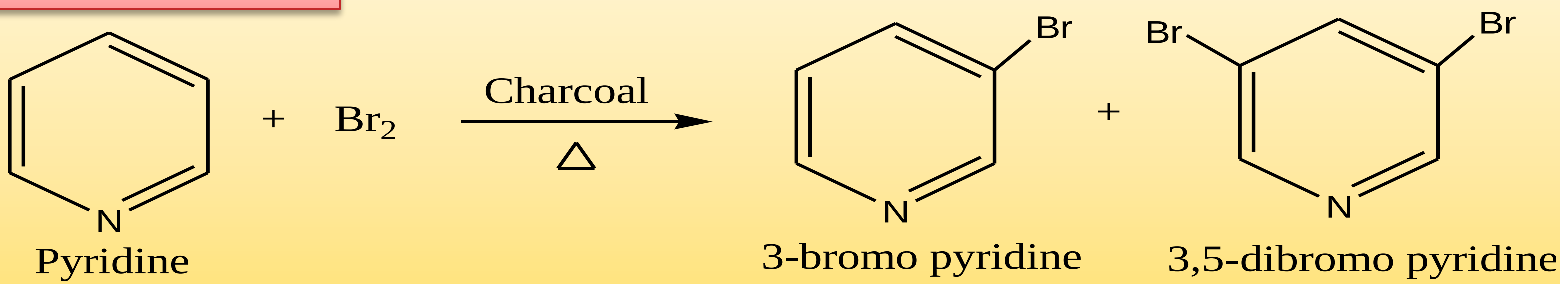
1) Nitration :



2) Sulphonation :

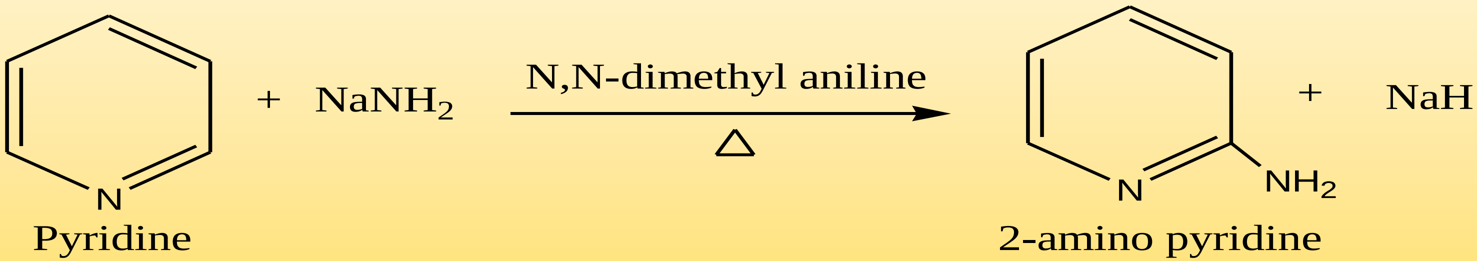


3) Bromination :

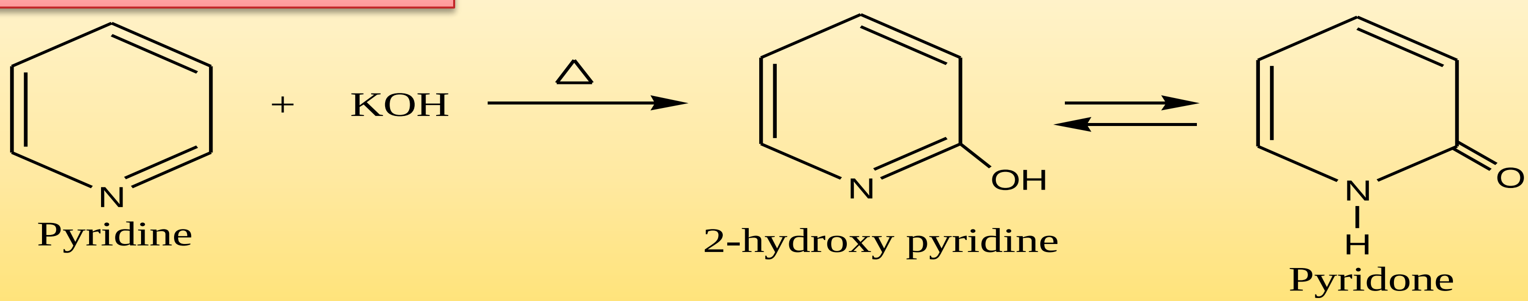


Chemical reactions of Pyridine

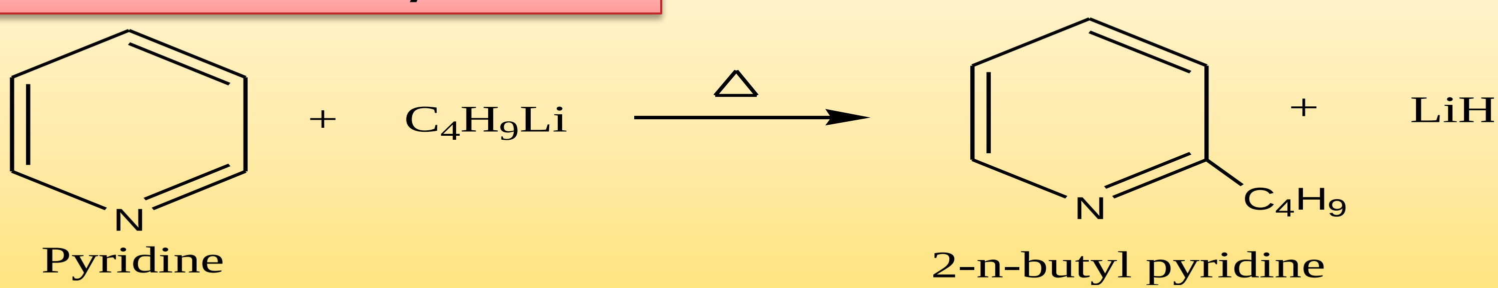
4) Amination :



5) Reaction with KOH :

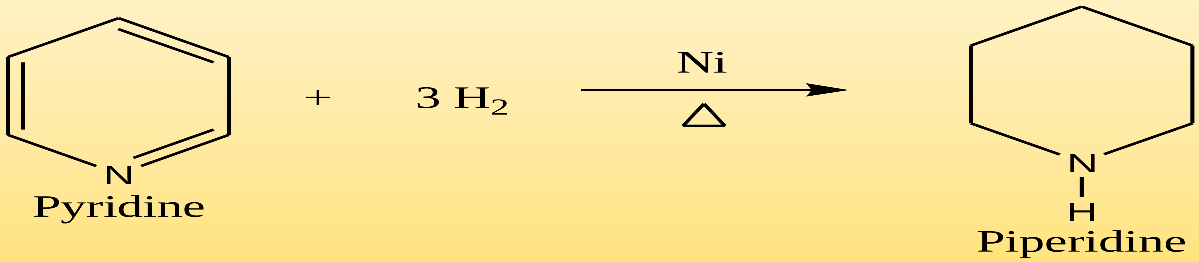


6) Reaction with n-butyl lithium :



Chemical reactions of Pyridine

7) Reduction :

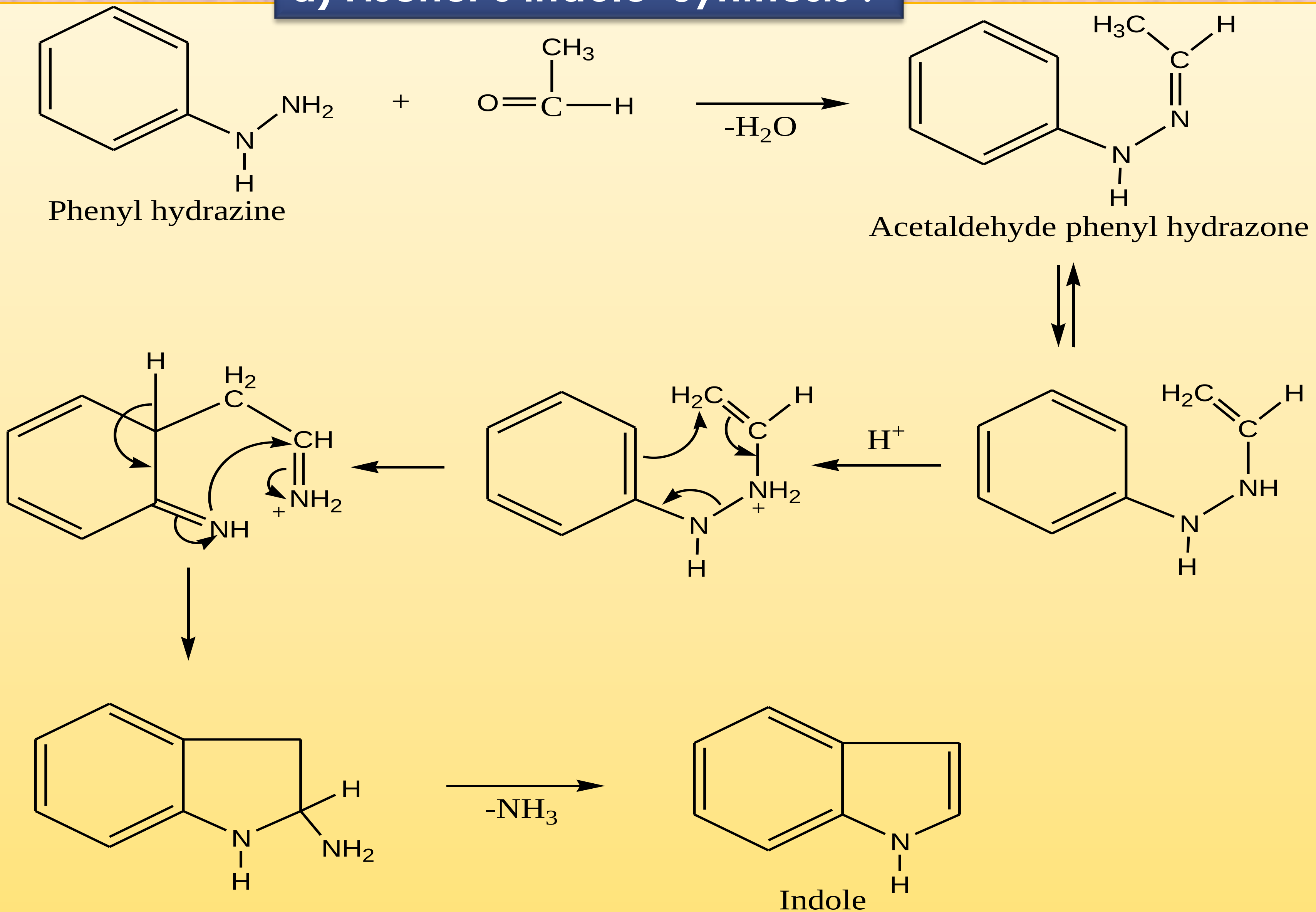


8) Oxidation :

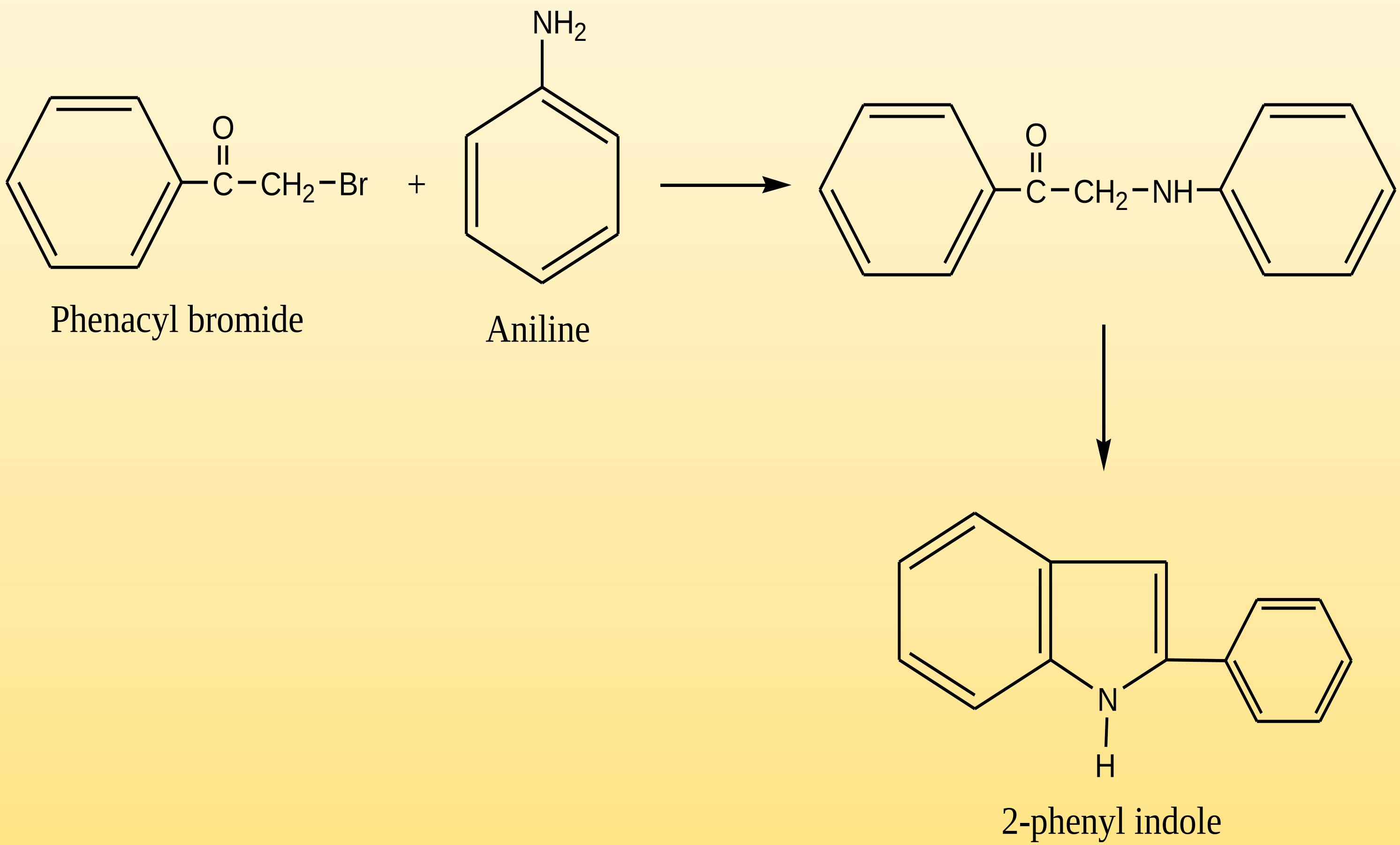
Condensed Heterocycles

Indole (Benzopyrrole)

a) Fischer's Indole Synthesis :



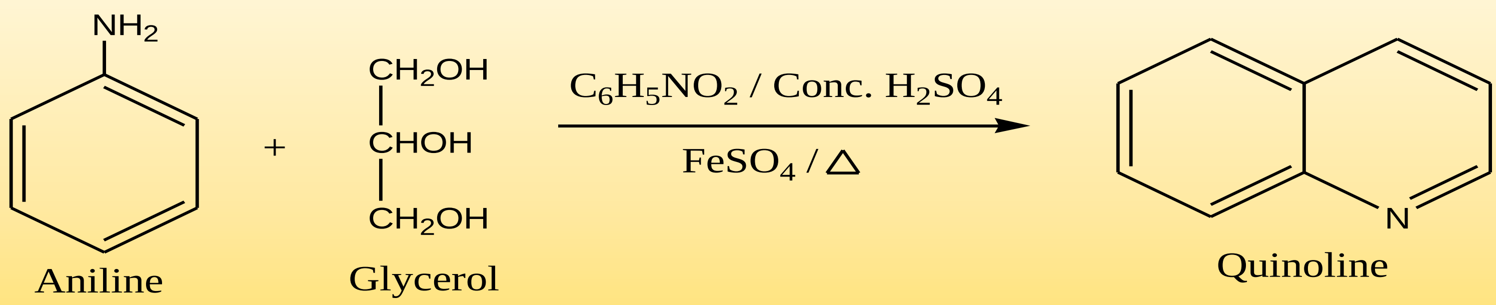
b) Bischler's Indole synthesis :



Quinoline (Benzopyridine)

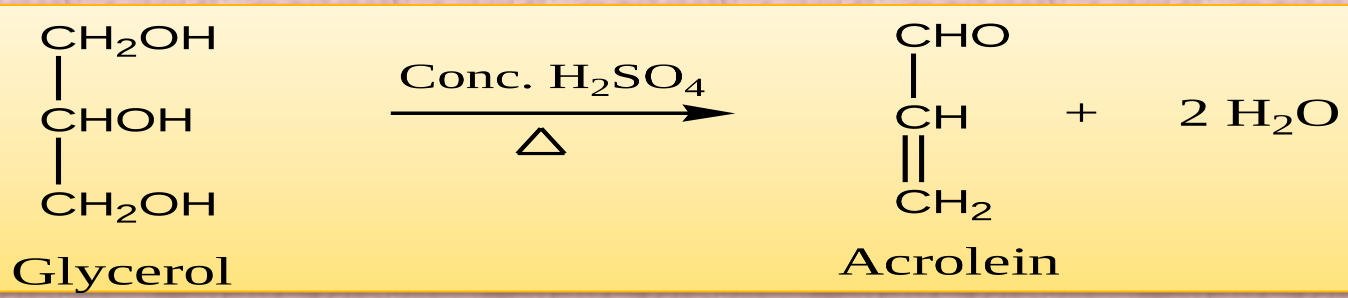
a) Skraup Synthesis :

Mixture of aniline , glycerol, nitrobenzene is heated in the presence of conc. H_2SO_4 and ferrous sulphate for 6 hours to give quinoline. Nitrobenzene act as oxidizing agent and ferrous sulphate makes the reaction less violent.

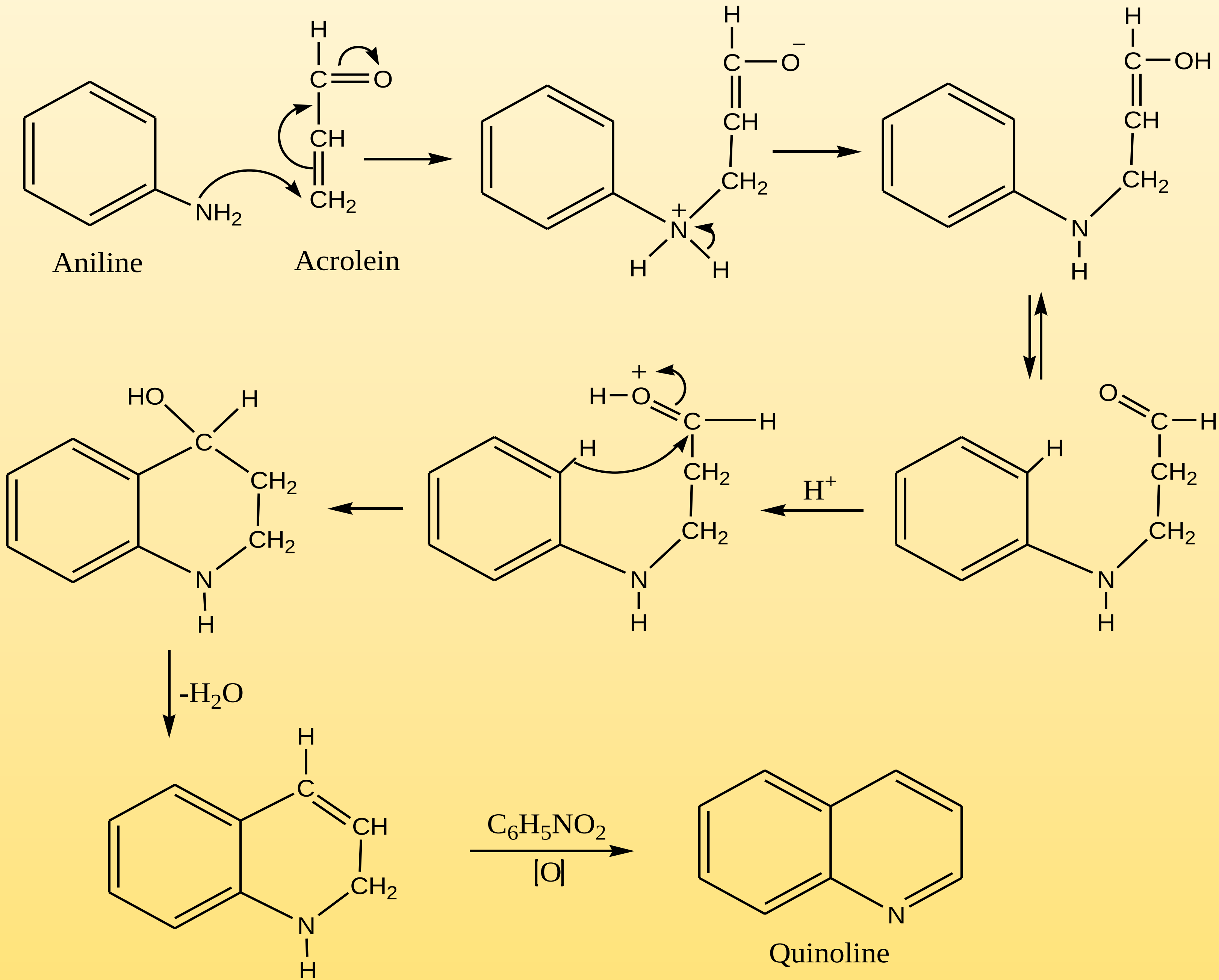


Mechanism :

Step -1 : Glycerol undergoes dehydration with H_2SO_4 to give acrolein.

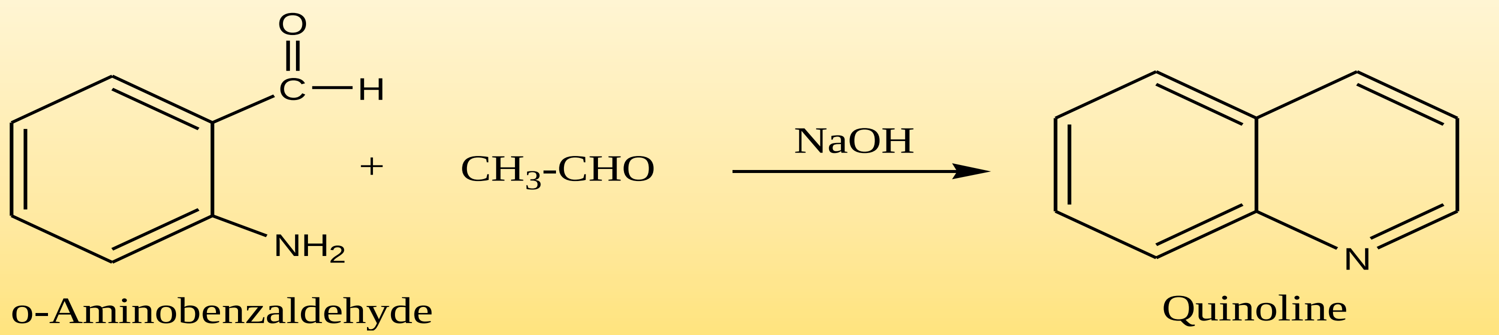


Step -2 : Addition of aniline to acrolein gives quinoline.

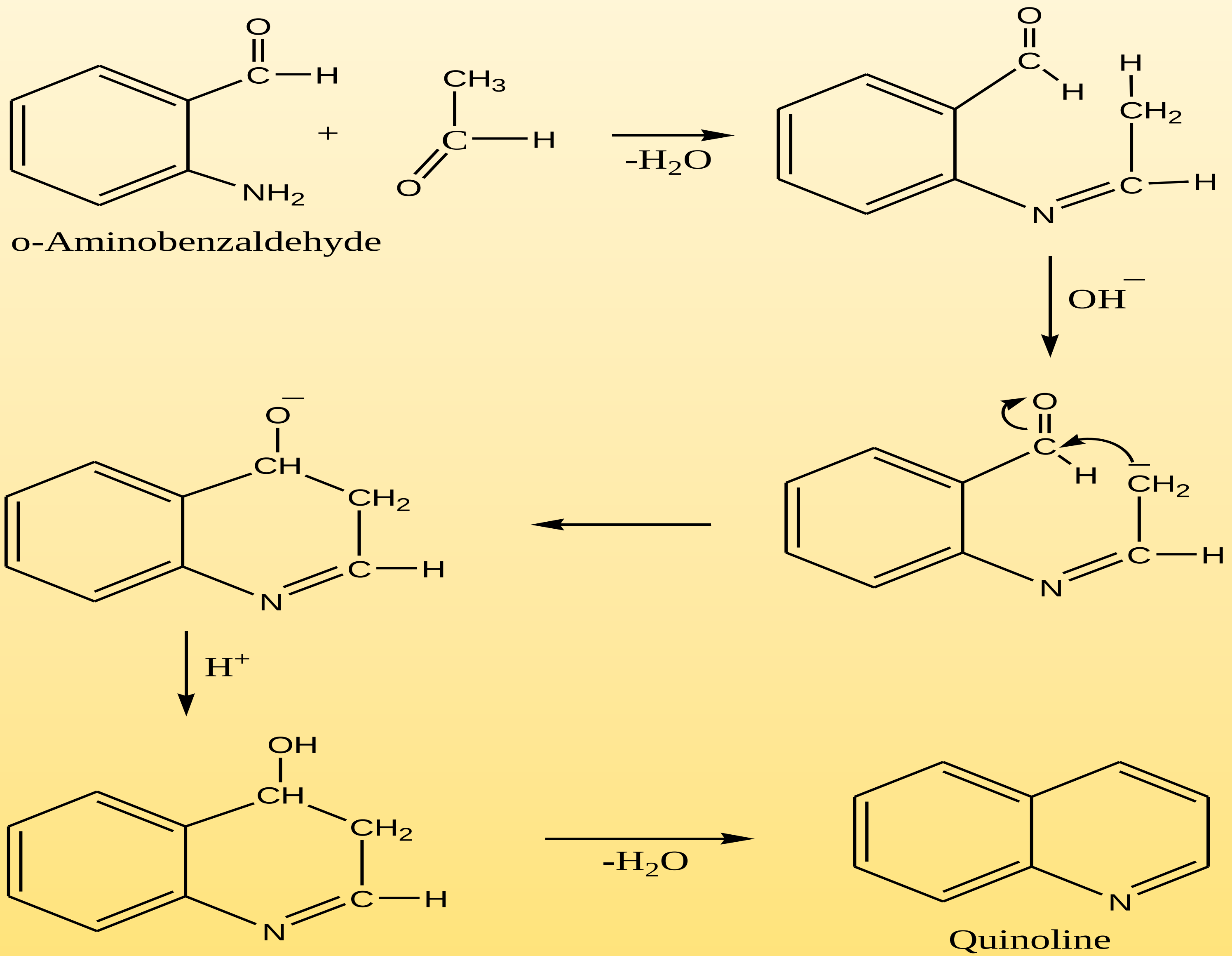


b) Friedlander Synthesis of Quinoline :

O-amino benzene on condensation with acetaldehyde in the presence of NaOH solution gives quinoline.



Mechanism :


O
C
H
NH2
+
CH3
C
H
O
-H2O
o-Aminobenzaldehyde
O
C
H
H
CH2
N
C
H
OH
O
C
H
CH2
N
C
H
O
CH
CH2
N
C
H
H+
OH
CH
CH2
N
C
H
-H2O
N
Quinoline

Thank You ……