

HETROCYCLIC COMPOUND

B.Sc.-III Chemistry(H/S)

Organic chemistry

Paper- VII

Lecture-04



Estd.- 1962

By

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HETROCYCLIC COMPOUND

Key points:

- ❖ Heterocyclic compounds are cyclic compounds with the ring containing carbon and other element, such as oxygen, nitrogen and sulfur.
- ❖ Heterocyclic compounds have one or more hetero atoms in their structure
- ❖ These five membered ring contains single heteroatoms.
- ❖ They may be cyclic or non cyclic in nature.
- ❖ The simple five membered heterocyclic compounds are pyrrole, furan and thiophene

Note: The name of the heterocyclic ring is chosen as the parent compound and the name of the fused ring is attached as a prefix. The prefix in such names has the ending 'o', i.e., benzo, naphtho and so on.

HETROCYCLIC COMPOUND

Thiophene

- ⦿ **Chemical Formula: C₄H₄S**
- ⦿ **Molar mass 84.14 g/mol**
- ⦿ **Boiling point 84 °C**
- ⦿ **Density 1.05 g/cm³**
- ⦿ **Related thioethers Tetrahydrothiophene; Diethyl sulfide**
- ⦿ **Refractive index (n_D): 1.5287**

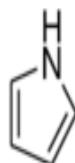
HETEROCYCLIC COMPOUND



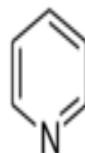
Furan



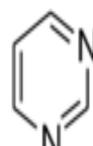
Thiophene



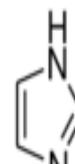
Pyrrole



Pyridine



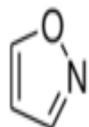
Pyrimidine



Imidazole



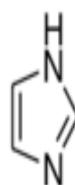
Oxadiazole



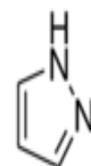
Isoxazole



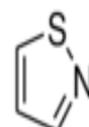
Oxazole



Imidazole



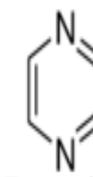
Pyrazole



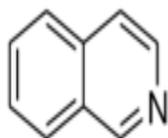
Isothiazole



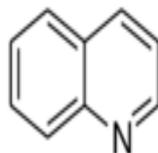
Thiazole



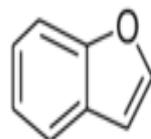
Pyrazine



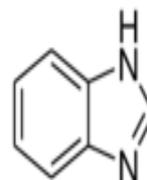
Isoquinoline



Quinoline



Benzofuran



Benzimidazole

Example of heterocyclic ring

HETEROCYCLIC COMPOUND

- ❖ Thiophene is a heterocyclic compound and its chemical formula is C_4H_4S .
- ❖ It is a planar five-membered ring.
- ❖ It is aromatic and follow $4n+2$ system
- ❖ It shows extensive substitution reactions.
- ❖ It is a colorless liquid with a benzene-like odor.
- ❖ It resembles benzene in most of its reactions.
- ❖ Analogous Compounds of thiophene like furan (C_4H_4O), selenophene (C_4H_4Se), pyrrole (C_4H_4NH), which each vary by the heteroatom in the ring.

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Properties and structure of Thiophene:

- ❖ Thiophene is a colorless liquid at room temperature
- ❖ It has mildly pleasant odor .
- ❖ The high reactivity of thiophene toward sulfonation is the basis for the separation of thiophene from benzene
- ❖ Thiophene are difficult to separate by distillation due to their similar boiling points (4 °C difference at ambient pressure). Like benzene, thiophene forms an azeotrope with ethanol.
- ❖ The molecule is flat due to aromaticity.
- ❖ The bond angle at the sulfur is around 93°, the C–C–S angle is around 109°, and the other two carbons have a bond angle around 114°.
- ❖ The C–C bonds to the carbons adjacent to the sulfur are about 1.34 Å, the C–S bond length is around 1.70 Å.

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Properties

- ❖ Stabilities of thiophene is very high
- ❖ Thiophenes comes from sulfur sources and hydrocarbons in many reactions , especially from unsaturated ones.
- ❖ The first synthesis of Thiophene by Meyer, in which he made acetylene and elemental sulfur.

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Paal-Knorr thiophene synthesis:

Thiophenes are classically prepared by the reaction of 1,4-diketones, diesters, or dicarboxylates with sulfidizing reagents such as P_4S_{10} in the Paal-Knorr thiophene synthesis.

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Reaction Of Thiophene

1. Oxidation

Oxidation can occur both at sulfur, giving a thiophene *S*-oxide, as well as at the 2,3-double bond, giving the thiophene 2,3-epoxide, followed by subsequent NIH shift rearrangement. Oxidation of thiophene by trifluoroacetic acid also demonstrates both reaction pathways.

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2 Alkylation

The sulfur atom is relatively unreactive and the flanking carbon centers, the c2- and c5-positions, are highly susceptible to attack by electrophiles.

Halogens give initially 2-halo derivatives followed by 2,5-dihalothiophenes; perhalogenation is easily accomplished to give C_4X_4S ($X = Cl, Br, I$).

3 Polymerization

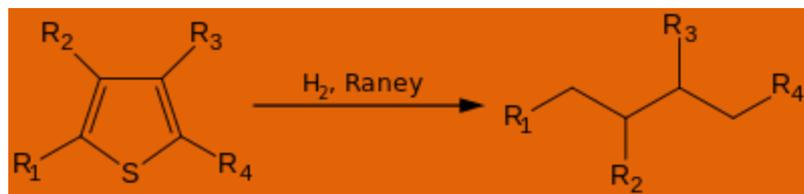
The polymer formed by linking thiophene through its 2,5 positions is called polythiophene. Polymerization is conducted by oxidation using electrochemical methods (electropolymerization) or electron-transfer reagents. An idealized equation is shown:



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Desulfurization by Raney nickel

Desulfurization of thiophene with Raney nickel affords butane. When coupled with the easy 2,5-difunctionalization of thiophene, desulfurization provides a route to 1,4-disubstituted butanes.



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Reactivity of Thiophene

- ⦿ Thiophene is considered as aromatic but theoretical calculations suggest that the degree of aromaticity is less than that of benzene.
- ⦿ The “Lone pairs” on sulfur are significantly delocalized in the pi electron system. As a result of its aromaticity, thiophene does not exhibit the properties seen for conventional sulfides. For example, the sulfur atom resists alkylation and oxidation.

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Problem for practice:

Q1. Which one is more aromatic and why ?

- a) **Furan**
- b) **Thiophene**

Q2. Which one is more basic and why ?

- a) **Furan**
- b) **Thiophene**