

Benzofused Five-Membered Aromatic Heterocyclic Compounds

Classification of Aromatic Heterocycles

Aromatic heterocycles contain hetero atoms such as nitrogen, oxygen, or sulfur and obey Huckel's rule. Benzofused five-membered heterocycles include indole, benzofuran, and benzothiophene.

Nomenclature

Indole is also called benzopyrrole, benzofuran contains oxygen, and benzothiophene contains sulfur as hetero atoms. Numbering starts from the hetero atom.

Benzopyrrole (Indole)

Structure: Pyrrole ring fused with benzene. Nitrogen lone pair participates in aromaticity.

Synthesis: Fischer indole synthesis, Madelung synthesis.

Reactions: Electrophilic substitution at C-3, oxidation to isatin, reduction to indoline.

Reaction Mechanism (Indole)

Electrophilic substitution occurs at C-3 due to formation of stable sigma complex and retention of benzene aromaticity.

Benzofuran

Structure: Benzene fused with furan containing oxygen.

Synthesis: Cyclodehydration of o-hydroxy ketones.

Reactions: Electrophilic substitution at C-2, oxidation and reduction reactions.

Reaction Mechanism (Benzofuran)

Electrophilic attack at C-2 forms a resonance stabilized sigma complex followed by deprotonation.

Benzothiophene

Structure: Benzene fused with thiophene containing sulfur.

Synthesis: Cyclization of o-mercapto phenyl derivatives.

Reactions: Electrophilic substitution at C-2, oxidation to sulfoxide and sulfone.

Reaction Mechanism (Benzothiophene)

Sulfur stabilizes carbocation during electrophilic substitution at C-2 followed by restoration of aromaticity.

Comparative Reactivity

Indole > Benzothiophene > Benzofuran

Conclusion

Benzofused heterocycles are aromatic, biologically important compounds widely used in pharmaceuticals and materials science.