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It's Important to Know!

BP301T — Pharmaceutical Organic Chemistry II

B.Pharm Semester 3 · Unit 1 — Benzene and its derivatives

Unit I: Benzene and its derivatives

Aromatic character

Benzene is a planar cyclic system with six delocalised pi electrons. Aromaticity requires a cyclic, approximately planar, continuously conjugated system with 4n + 2 pi electrons. This rule is a useful model, but its application to unusual systems should be checked against the prescribed text.

Evidence for the structure of benzene came from its formula, substitution pattern, equal carbon-carbon bond lengths and characteristic reactions. Resonance descriptions represent electron delocalisation, not rapidly switching structures. The orbital model describes overlap of p orbitals above and below the ring.

Electrophilic aromatic substitution

In nitration, an electrophile is generated in a strongly acidic medium and the aromatic ring forms a sigma complex before losing a proton. Sulphonation is reversible under suitable conditions. Halogenation requires activation of the halogen by a Lewis acid. Friedel-Crafts alkylation forms a carbon-carbon bond but can suffer from rearrangement and polyalkylation. Friedel-Crafts acylation forms an acylated aromatic compound and usually avoids carbocation rearrangement.

Orientation and reactivity

An existing substituent changes both the rate and position of a second substitution. Electron-donating groups generally activate the ring and direct incoming electrophiles to ortho and para positions. Strong electron-withdrawing groups generally deactivate the ring and direct to the meta position. Halogens are an important exception: they deactivate the ring but direct mainly to ortho and para positions. The exact behaviour of a substituted system should be checked against the prescribed text when more than one group is present.

Named compounds in the syllabus

The syllabus includes DDT, saccharin, BHC and chloramine. Study their verified names, functional groups, preparation or manufacture where prescribed, properties, hazards and approved uses from a current monograph. Compound-specific uses and safety classifications

should be taken from a current monograph.

Unit I: Frequently asked questions

Q: Why does benzene usually undergo substitution rather than addition?

A: Substitution can restore aromaticity after the electrophile is introduced, whereas addition would permanently reduce aromatic stabilisation.

Q: What is the sigma complex?

A: It is the temporary cationic intermediate formed when an electrophile bonds to the aromatic ring before proton loss restores aromaticity.

Q: Why are halogens unusual directing groups?

A: Halogens withdraw inductively and deactivate the ring, but their lone-pair donation stabilises ortho and para sigma-complex forms relative to meta forms.

Unit I: Key takeaways

- Aromaticity depends on cyclic conjugation, approximate planarity and the 4n + 2 rule.
- Electrophilic aromatic substitution proceeds through a sigma complex.
- Substituents affect both ring reactivity and orientation.
- Halogens deactivate but are mainly ortho and para directing.
- Compound-specific claims require verified monographs.

Unit I: Practical correlation

Practical correlation: reaction planning. A substitution experiment requires controlled reagent addition, temperature, ventilation and work-up. The exact hazard controls for a named reagent are set out in the laboratory manual.