

CHEM 20481 - Basic Organic Chemistry - Chapter 11 Review

Arenes and Aromaticity

Definitions

Aromatic: Cyclic compounds containing (1) p_π orbitals on all atoms in the ring, and (2) $4n+2$ π electrons (Hückel's Rule) which are delocalized around the ring. Lone pairs of electrons on sp^3 hybridized atoms contribute to the total number of π electrons. Aromatic compounds are more stable and less reactive than alkenes, and have very different chemistry. Aromatic ions also exist.

Benzene

Benzene (C_6H_6) is the probably the best example of an aromatic compound. It is unreactive toward HX, H_2/Pt (except under forcing conditions), Br_2 , and other typical reaction conditions for alkenes. The structure consists of a six-membered ring with identical C-C bond lengths (140pm) intermediate between typical C-C ($154pm$)¹ and C=C (135pm). The $\Delta H_{hydrogenation}$ is relatively small (less than 1,3-cyclohexadiene). Pictures of the valence molecular orbitals of benzene are available in your text and on the course web site.

Nomenclature

Common names: Benzene, benzaldehyde, benzoic acid, styrene, acetophenone, phenol, aniline.

Disubstituted compounds: ortho (*o*-) \equiv 1,2 meta (*m*-) \equiv 1,3 para (*p*-) \equiv 1,4

Common polycyclic aromatic hydrocarbons: Naphthalene, Anthracene

Common heterocyclics: pyridine, pyrrole, furan

'New' common substituents: NO_2 = nitro, OCH_3 = methoxy

Annulenes: Conjugated ring system containing >6 carbons. Named as [#]annulene, where # is the number of carbon atoms in the ring.

Reactions

- toluene $\xrightarrow[\text{alcohol}]{Na, NH_3}$ 1-methyl-1,4-cyclohexadiene Birch Reduction
- toluene $\xrightarrow[\Delta \text{ or } h\nu]{X_2}$ benzyl halide ($C_6H_5-CH_2X$) Radical halogenation
- toluene $\xrightarrow[H_2O, H_2SO_4, \Delta]{Na_2Cr_2O_7}$ benzoic acid Side-chain Oxidation (Any R except 3°)
- $C_6H_5-CH_2X \xrightarrow[\text{aprotic solvent}]{\text{Nucleophile}}$ S_N2 substitution product
- $C_6H_5-CR_2X \xrightarrow[\text{protic solvent}]{\text{Nucleophile}}$ S_N1 substitution product
- Other side chain reactions also occur. Text illustrates formation of alkenes and addition reactions of alkenes.

¹Your text correctly notes that the typical sp^2-sp^2 C-C bond length is only 146pm.