

Summary of CH15 Unusual Stability of the Cyclic Electron Sextet

I. Characteristics of aromatic compounds (i.e. aromaticity)

- large resonance energies
- ring current (shielding/deshielding effect in NMR)
- react by substitution rather than addition

II. Nomenclature

- monosubstituted benzenes
 - use "benzene" as parent name
 - use "substituted benzene" as parent name:
- IUPAC recognizes: phenol, benzaldehyde, benzoic acid
- disubstituted benzenes
 - use "benzene" as parent name: 1,2- (ortho-), 1,3- (meta-), 1,4- (para-)
 - use "monosubstituted benzene" as parent name
 - use "disubstituted benzene" as parent name
- more than two substituents
 - use either "benzene, monosubstituted benzene, or disubstituted benzene" as parent name
- C₆H₅- named as substituent: "phenyl"
- annulene: [n]annulene, n = ring size

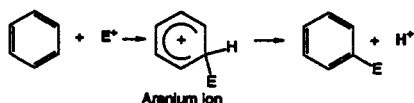
III. Structure of benzene

- ΔH₀, heat of hydrogenation, is an experimental measurement of the "resonance energy"
- shielding/deshielding effect in NMR is an experimental measurement of the "ring current"
- resonance explanation of benzene (review resonance theory)
- MO theory explanation of benzene (review the basic rule to construct MOs from p atomic orbitals)

IV. Huchel's rule

- planar, monocyclic, completely conjugated hydrocarbons will be aromatic when the ring contains (4n+2) π electrons
- MO theory basis of Huchel's rule
 - know how to determine the relative energies of MOs for a planar, monocyclic, completely conjugated molecule or ion
 - molecules or ions having (4n+2) π electrons have a closed-shell electron configuration (stable)
 - molecules or ions having 4n π electrons have unpaired electrons in nonbonding or antibonding MOs (unstable)

V. Electrophilic aromatic substitution

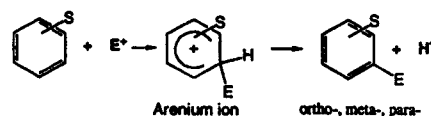


- step I: generation of E⁺ (usual assisted by a Lewis acid)
 step II: electrophilic attack to yield an arenium into intermediate (rate-limiting)
 step III: loss of H⁺ by the arenium ion (usually assisted by a base, fast)

	E ⁺	Reagents
• Halogenation	X ⁺	X ₂ , FeX ₃ (X=Cl, Br)
• Nitration	NO ₂ ⁺	HNO ₃ , H ₂ SO ₄
• Sulfonation	SO ₃	SO ₃ , H ₂ SO ₄ conc. H ₂ SO ₄
- reversibility: sulfonation/desulfonation in organic synthesis		
• Friedel-Crafts alkylation	R ⁺	RX, AlCl ₃ ROH, H ⁺ or ROH, BF ₃ Alkene, H ⁺
- rearrangement of alkylating reagents		
- polyalkylation		
- intramolecular alkylation (favor 6 membered ring)		
• Friedel-Crafts acylation	RCO ⁺	RCOCl, AlCl ₃ RCO-O-COR, AlCl ₃ RCO ₂ H (via RCOCl)
- at least one molar equivalent of AlCl ₃ is required		
- no rearrangement of acylating reagents		
- no polyacylation		
- intramolecular acylation (synthesis of 6 membered ring)		
- acylation-Clemmensen reduction sequence to prepare alkylbenzenes		

Summary of CH 16 Electrophilic Attack on Derivatives of Benzene

I. Effect of substituents on aromatic electrophilic substitution



- relative reactivities [i.e. benzene vs substituted benzenes (S≠H)]
- regioselectivity (orientation of the incoming E⁺)

II. Theories for electron-donating or electron-withdrawing properties of groups

- inductive effect: the electrostatic interaction between S and the π system of the arenium ion
 - groups bearing full or partial positive charge have a electron-withdrawing inductive effect
- resonance effect: resonance interaction between the nonbonding electrons of S with the π system of the arenium ion
 - groups bearing nonbonding electrons have a electron-donating resonance effect
- hyperconjugation: σ-bonding electrons delocalize into the π system of the arenium ion
 - alkyl groups are electron-donating by hyperconjugation
- π electron delocalization: phenyl group is electron-donating by π electron delocalization

III. Relative reactivities

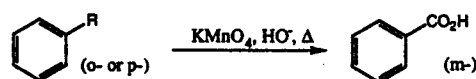
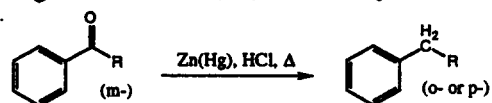
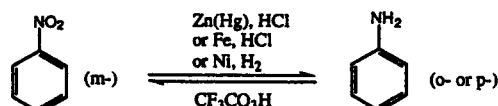
- S = electron-donating groups are called activating groups: -R, -Ph, -OH, -OR, -NH₂, -NHR, NR₂, -NHCOR
- S = electron-withdrawing groups are called deactivating groups: -X, -C≡N, -SO₃H, CO₂H, CO₂R, CHO, COR, -NO₂, -N⁺R₃, -CF₃, -CCl₃

IV. Regioselectivities

- activating groups are ortho- and para- directors
- deactivating groups are meta- directors
- halogens (X) are exception that they are deactivating groups but are ortho- and para- directors
- disubstituted benzenes
 - doubly activated position is favored over a singly activated one
 - the stronger activating group determines the outcome of the reaction
 - between meta-substituents is sterically unfavored

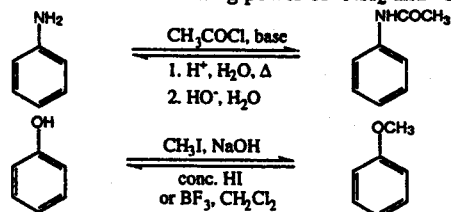
V. Synthetic strategies

- interconversions between a meta-directing groups and an ortho- and para-directing groups



R = alkyl, alkenyl, alkynyl

- moderate the activating power of -NH₂ and -OH groups



- sulfonation/desulfonation for position blocking

