Summary of CH 15 Unusual stability of the cyclic electron sextet

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

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

II. Nomenclature

- monosubstitiuted 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
- C_6H_5- named as substituent: "phenyl"
- annulene: [n]annulene, n = ring size

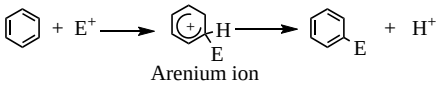
III. Structure of benzene

- ΔH^o, heat of hydrogenation, is an experimental measurement of the "resonance energy"
- sheilding/desheilding 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 orbital)

IV. Huckel's rule

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

V. Electrophilic aromatic substitution



Arenium ion

step I: generation of E^+ (usually assisted by a Lewis acid)
step II: electrophilic attack to yield an arenium into intermediate (rate-limiting)
step III: loss of H^+ by 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_2SO_4
• Sulfonation	SO_3	SO_3, H_2SO_4

- reversibility: sulfonation/desulfonation in organic synthesis
- Friedel-Crafts alkylation R^+ RX, $AlCl_3$; ROH, H^+, or ROH, BF_3; Alkene, H^+

-rearrangement of alkyationg agent

-polyalkylation

-intramolecular alkylation (fiveor 6 membered ring)

- Friedel-Crafts acylation RCO^+ RCOCl, $AlCl_3$; RCO-O-COR, $AlCl_3$

-more than one molar equivalent of $AlCl_3$ is required

-no rearrangement of acylating reagents

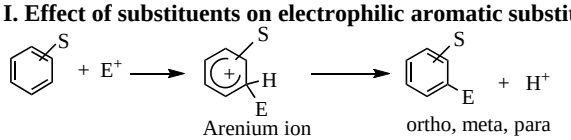
-no polyacylation

-intramolecular acylation (synthesis of 6 membered ring)

-acylation-Clemmensenreduction sequence to prepare alkylbenzenes

Summary of CH 16 Electrophilic Attack on Derivatives of Benzene

I. Effect of substituents on electrophilic aromatic substitution



Arenium ion ortho, meta, para

-relative reactivities [i.e. benzene vs substituted benzene (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 beaing full or partial positive charge have an electron withdrawing inductive effect
- resonance effect: resonance interaction between the nonbonding electron of S with the π system of the arenium ion
- groups bearing nonbonding electrons have an 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, $-NH_2$, -NHR, $-NR_2$, -NHCOR

- S = electron-withdrawing groups are called deactivating groups:

-X, -CN, $-SO_3H$, $-CO_2H$, $-CO_2R$, --CHO, --COR, $-NO_2$, $-N^+R_3$, $-CF_3$, $-CCl_3$

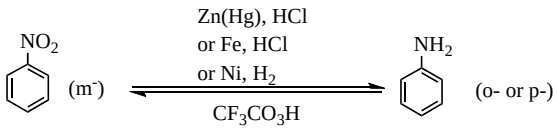
IV. Regioselectivities

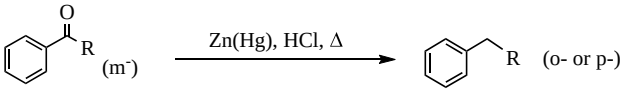
- activating groups are ortho- and para- directors
- deactivating groups are meta-directors
- halogens (X) are exception that they are deactivating groups but are ortho- and para- directors
- disubstituted benzenes
- doubly activated position is favored over a singly activated one
- the stronger activating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

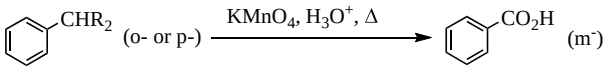
-between meta-substituents is sterically unfavored

V. Synthetic strategies

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

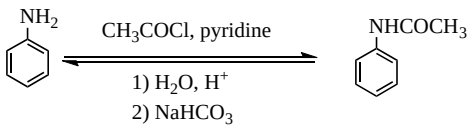


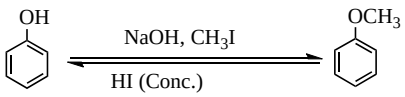




R = alkyl (1^o, or 2^o), alkenyl, alkynyl

- moderate the activating power of $-NH_2$ and -OH groups





- sulfonation/desulfonation for position blocking