California State Polytechnic University, Pomona

Organic Chemistry II, CHM 3150, Dr. Laurie S. Starkey

Ch. 17-18 Summary (Klein): Aromaticity & Aromatic Substitution Reactions

I. Benzene (17.3)
  A) resonance stabilized (confirmed ΔH hydrogenation), 3-D sketch
II. Aromaticity
  A) definition and rules (17.1, 17.4) **SkillBuilder 17.2**
    i) cyclic and planar; contiguous p orbitals
    ii) (4n + 2) electrons in p orbitals (Hückel's rule, n = 0, 1, 2, etc.)
    iii) Molecular Orbital (MO) theory to explain aromatic stability
  B) common aromatic compounds (furan, naphthalene, etc.) (17.5) **SkillBuilder 17.3**
  C) nomenclature: *ortho (o-), meta (m-), para (p-)* positions, common names (17.2) **SB 17.1**
  D) special topics: buckminsterfullerene (C_{60}, Bucky Ball) as a "new" form of carbon
III. Electrophilic Aromatic Substitution (EAS) (18.2 – 18.6)
  A) mechanism: formation of E^+ (one or more steps) addition of E^+ (slow step), loss of H^+
IV. EAS on substituted benzenes (18.7 – 18.11) **SkillBuilder 18.1, SkillBuilder 18.3**
  A) three categories of substituents (18.10)
    i) electron-donating groups (EDG, 18.7)
    ii) electron-withdrawing groups (EWG, 18.8)
    iii) halogens (X = Cl, Br) (18.9)
  B) reactivity
    i) EDG are activating (electron-rich ring, good Nu:)
    ii) EWG/X are deactivating (electron-deficient ring, poor Nu:)
  C) regioselectivity (for *ortho*, *para* directors, *para* is usually major due to sterics)
    i) regioselectivity can be explained by looking at resonance forms for:
      a) starting material (Nu:) electron density (in certain cases only)
      b) carbocation intermediate stability (can be used for all cases)
    ii) EDG/X are *ortho*, *para* directors (because they stabilize adjacent carbocations)
    iii) EWG are *meta* directors (because EWG's destabilize adjacent carbocations)
  D) directing power for disubstituted benzenes (18.11) **SkillBuilder 18.2**
V. Electrophiles for EAS
  A) –X ($Br_2/FeBr_3$ or $Cl_2/FeCl_3$) (18.2)
  B) $-NO_2$ (HNO_3/H_2SO_4) (18.4)
  C) $-SO_3H$ (SO_3/H_2SO_4), reaction is reversible (18.3) **SkillBuilder 18.4**
  D) –R (Friedel-Crafts Alkylation, via carbocation which can rearrange) (18.5)
    i) RX + $AlCl_3$ *or* ROH + HA *or* ROH + BF_3 *or* alkene + HA
  E) –COR (Friedel-Crafts Acylation, $RCOX/AlCl_3$) (18.6)
    i) can then reduce carbonyl to give desired 1° alkyl side chain
VI. Diazonium Salts (ArN_2^+, 22.10, 22.11)
  A) two-step preparation from $ArNO_2$
    i) reduce nitro to amine: $-NO_2 \rightarrow -NH_2$ (H_2/Pd or Fe/Zn/Sn and HA)
    ii) add nitrous acid $-NH_2 \rightarrow -N_2^+$ (HONO = $NaNO_2$/HCl)
  B) uses: replace its good LG (N_2) with the following groups
    i) halogens: –Cl (CuCl), –Br (CuBr), –I (KI), –F (HBF_4)
    ii) cyanide: –CN (CuCN)
    iii) hydrogen: –H (H_3PO_2)
    iv) hydroxyl –OH (H_2O/H_2SO_4)
VII. Aromatic Synthesis (18.12) **SkillBuilders 18.4, 18.5, 18.6**
VIII. Nucleophilic Aromatic Substitution (S_NAr, 18.13, 18.15) **SkillBuilder 18.7**
  A) two-step mechanism: add Nu:, eject LG (Addition-Elimination)
  B) EWG substituents ($-NO_2$) required
IX. Reactions of Benzylic Carbons (17.6) **SkillBuilder 17.4**
  A) oxidation (Na_2CrO_7 or $KMnO_4$) to oxidize benzylic carbons → benzoic acids
  B) substitution (S_N1, S_N2) and free-radical halogenation ($Br_2/h\nu$)

SKIP: Spectroscopy (17.8), Benzyne "Elimination-Addition" (18.4), [ox] of ArOH (12.12)