

# Test 2 Topic Summary – Chapters 15, 16, 19

## Chapter 15: Benzene and Aromaticity

- Structure and stability of benzene (resonance and molecular orbital explanations)
- Aromaticity rules (Hückel  $4n+2$  rule)

## Chapter 16: Chemistry of Benzene: Electrophilic Aromatic Substitution

- Halogenation of benzene rings (Lewis Acid catalyst needed, e.g.  $\text{FeBr}_3$ ) **Mech**
- Nitration of benzene rings (Lewis Acid catalyst needed –  $\text{H}_2\text{SO}_4$ ) **Mech**
- Sulfonation of benzene rings (no Lewis acid) **Mech**
- Friedel–Crafts Alkylations (Lewis Acid catalyst needed, e.g.  $\text{AlCl}_3$ ) **Mech**
- Problems with F–C Alkylations
- Friedel–Crafts Acylations (Lewis Acid catalyst needed, e.g.  $\text{AlCl}_3$ ) **Mech**
- Reduction of F–C acylation products to give alkylated benzenes
- Activation (strong and weak) and Deactivation (strong and weak) of Benzene rings
- Substituent effects and regioselectivity of Electrophilic Aromatic Substitutions (ortho, para directors and meta directors)
- Substituent effects are cumulative
- Better activators direct better (strong better than weak and both better than deactivator)
- Nucleophilic Aromatic Substitution reactions – Activating and Deactivating substituents are reversed. **Mech**
- Making phenol from aryl halides (benzyne intermediate) **Mech**
- $\text{KMnO}_4$  oxidations of alkyl benzenes to carboxylic acids
- Benzylic Brominations – analogous to allylic brominations
- Reduction of benzene compounds
  - benzene to cyclohexane with  $\text{H}_2$  and Rh/C
  - $\text{NO}_2$  to  $\text{NH}_2$  with  $\text{H}_2$  and Pd/C
  - $\text{ArCOR}$  to  $\text{ArCH}_2\text{R}$  with:  $\text{H}_2$ , Pd/C and heat
    - or
    - Wolff-Kishner ( $\text{NH}_2\text{NH}_2$ , KOH, water)
    - or
    - Clemmensen Reduction ( $\text{Zn(Hg)}$ , HCl, heat)
    - or
    - Make thioketal, reduce (1:  $\text{CH}_3\text{SH}$ ,  $\text{BF}_3$  2: Raney Ni)

## Chapter 19: Ketones and Aldehydes

- Naming Aldehydes and Ketones
- Synthesis of Aldehydes and Ketones
  - Aldehydes from Hydroboration of terminal alkynes
  - Ketones from Mercuric Ion Hydration of terminal alkynes
  - Ketones and aldehydes from alkene cleavage reactions (ozonolysis, potassium permanganate)
  - Oxidation of alcohols with PCC (1° or 2° alcohols) or Jones' Reagent (2° alcohols)
  - Friedel-Crafts Acylations of benzene compounds
  - Reduction of Esters with DIBAL (diisobutylaluminum hydride)
  - Ketone from acid chloride and Gilman Reagent ( $R_2CuLi$ )
- Reactions of Aldehydes and Ketones
  - Oxidation of aldehydes to carboxylic acids – Jones Reagent **or** Tollens' Reagent ( $Ag_2O$ ,  $NH_4OH$ ,  $H_2O$ ,  $EtOH$ ) **or** by cleavage with 1)  $KMnO_4$ ,  $H_2O$ ,  $NaOH$  2)  $H_3O^+$
  - Addition of water to aldehydes or ketones under acidic *or* basic conditions to form geminal diols – **mechanisms**
  - Cyanohydrin formation with  $HCN$  – **mechanism**
    - Conversion of cyanohydrin to 1° amine with 1)  $LiAlH_4$  and 2) water
    - Conversion of cyanohydrin to carboxylic acid under acidic or basic conditions
  - Grignard Additions to aldehydes and ketones – **mechanism**
  - Hydride Reductions of aldehydes and ketones to alcohols with 1)  $NaBH_4$  2) water – **mechanism**
  - Addition of 1° amines to aldehydes or ketones to form imines - **mechanism**
  - Addition of 2° amines to aldehydes or ketones to form enamines – **mechanism**
  - Reduction of ketones or aldehydes to alkanes with hydrazine – Wolff-Kishner Reaction ( $H_2NNH_2$ ,  $KOH$ ) – **mechanism**
  - Reduction of ketones or aldehydes to alkanes with  $Zn(Hg)$ ,  $H_3O^+$  (Clemmensen reduction)
  - Acetal formation from aldehydes or ketones with  $ROH$  and acid – **mechanism**
  - Wittig Reaction – **mechanism**
  - Conjugate (1, 4) Additions to  $\alpha,\beta$ -unsaturated ketones and aldehydes – amines or copper (Gilman's **or** Grignards with  $CuI$ ) nucleophiles – **mechanism**