**Supplement#5 Organic Chemistry II CHEM 4524 SUNY Alfred State**

**Reactions of ArR (Aromatic-Aliphatics) Summarized**

 *CHEMISTRY 4524 ORGANIC CHEMISTRY II Spring*

**A) Extreme Reactions (Oxidation, Hydrogenation, Radical Substitution)**

 **reaction name reagents products COMMENTS**

1 Oxidation of ArR KMnO4 or K2Cr2 O7 or HNO3(dilute) **ArCOOH**  think *Vasectomy* (SNIP, CUT, OUCH ...)

 HCrO4 (chromic acid) (Benzoic acid) {R side chain cut to COOH}



2 Reduction of ArR Na,NH3/CH3OH lobotomy… aromaticity is gone

 (Birch reduction)

 **cyclic diene**

**3 Free Radical hv/Cl2 or Br2 or NBSAr-CHR’-X** think*Radical Surgery*

 Halogenation {as with allylic radical additions...radical X goes for allylic site...}

**B) Easy Reactions (Additions, Substitutions, Polymerizations)**

# **reaction name reagents products COMMENTS**

4a) ArCH2X N: =nucleophile/non-polar solvent **ArCH2N**  S N2 substitution

 (1o aryl halide) (**=OH-, OR- , H2O , NH3 , CN-, RCOO-)**

4b) ArCH(R)-X or ArC(R2)X N: (as above)/polar solvent **ArCH(R)N or ArC(R2)N** SN1 substitution (carbocation)

(2 or 3o aryl halide)

5) ArCH=CH2 H2O, HX, X2 ,H2/Pt **ArCHOH-CH3, ArCHX-CH­3  (no peroxide) ArCHX-CH2X, ArC2H5**

 (styrene) HX **ArCH2-CH2X**  (peroxides)

6) ArCH=CH2 radical initiator (HO-OH/uv) **polystyrene**  *radical polymerization*



Radical initiation

 Chain propagation

 Etc… polystyrene

**C) Reactions to important aromatic-aliphatics**

**1) routes to styrene**

 **industrial**

 ZnO/60o

1.1) ArCH2CH3 ArCH=CH2

 **laboratory**

1.2) Dehydrohalogenation of benzene alkenyl halides:

 KOH/EtOH

 ArCCl-CH3 ArCH=CH2

1.3) Dehydration of benzene alkenols

 acid/heat

 ArCOH-CH3  ArCH=CH2

**2) Routes to ArR:Friedel-Krafts**

 *2.1)* One-Step Friedel-Krafts (DIRECT ALKYLATION)

 R-Cl/AlCl3

 Ar ------------> Ar-R ...BUT R+ can rearrange

 *2.2)* Two-Step Friedel-Krafts (ACYLATION, THEN ACYL REDUCTION)

 **Zn-Hg amalgam /HCl & heat (Clemmensen)**

 **{use when ArCOR is base sensitive...note that R can also be substituted}**

 **RCO-Cl/AlCl3**

 **Ar------------------> ArCOR ------> Ar-CH2 R ...R doesn’t rearrange**

 **...insures CH­2 alllylic to aryl**

 **hydrazine (N2H2) / OH- & heat (Wolff-Kishner)**

  **{use when ArCOR is acid sensitivenote that R can also be substituted}**

 *Miscellaneous Remarks*

 Can also go Friedel Krafts on activated, substituted rings...except .... when NH - groups are substituent (these bind Lewis acid and prevent insertion)