CHEM 20482 - Basic Organic Chemistry - Chapter 24 Review
Phenols

Properties

Polar and high-melting due to hydrogen-bonding.

The OH group in phenols ($pK_a \sim 10$) is much more acidic than the OH of alcohols ($pK_a \sim 16$).

Synthesis

Several industrial preparations of phenols are used, but these reactions typically involve high temperatures and reaction conditions that are not easily understood by the mechanisms we have studied in this course. The most common laboratory preparation is through a diazonium salt.

- $C_6H_5\text{-}NH_2 \xrightarrow[H_2O,\ 0\text{-}5°C]{NaNO_2,\ H_2SO_4} [C_6H_5\text{-}N{\equiv}N]^+ \xrightarrow[\Delta]{H_2O} C_6H_5\text{-}OH$

Reactions

- **Electrophilic aromatic substitution.** The OH group in phenols is a strongly activating, ortho/para-directing group. Electrophilic aromatic substitution reactions often proceed without requiring a catalyst.
  - $C_6H_5\text{-}OH \xrightarrow[\text{non-polar solvent}]{Br_2 \text{ or } Cl_2} HO\text{-}C_6H_4\text{-}X$ Substitution on para position preferred
  - $C_6H_5\text{-}OH \xrightarrow{HNO_3} HO\text{-}C_6H_4\text{-}NO_2$
  - $C_6H_5\text{-}OH \xrightarrow{H_2SO_4} HO\text{-}C_6H_4\text{-}SO_3H$
  - $C_6H_5\text{-}OH \xrightarrow[\text{acid}]{ROH} R\text{-}C_6H_4\text{-}OH + H_2O$
  - $C_6H_5\text{-}OH \xrightarrow[AlCl_3]{RC(=O)Cl} R\text{-}C(=O)\text{-}C_6H_4\text{-}OH$ With $AlCl_3$, Friedel-Crafts occurs
  - $C_6H_5\text{-}OH \xrightarrow{RC(=O)Cl} C_6H_5\text{-}O\text{-}C(=O)\text{-}R$ OH of phenol substitutes at acid chloride
  - $C_6H_5\text{-}OH \xrightarrow{C_6H_5N{\equiv}N^+} C_6H_5\text{-}N{=}N\text{-}C_6H_4\text{-}OH$ Coupling of diazonium salts
- Preparation and Cleavage of Aryl ethers
  - $Ar\text{-}O\text{-}H \xrightarrow{\text{base}} Ar\text{-}O^- \xrightarrow{R\text{-}X} Ar\text{-}O\text{-}R$ RX either $1°$ or CH_3X
  - $Ar\text{-}O\text{-}R \xrightarrow{HI} Ar\text{-}OH + RI$
- Claisen Rearrangement
  - $Ar\text{-}O\text{-}CH_2CH{=}CH_2 \xrightarrow{HI} HO\text{-}Ar\text{-}CH_2\text{-}CH{=}CH_2$ *ortho*
- Oxidation of diphenols to quinones
  - $HO\text{-}C_6H_4\text{-}OH \xrightarrow{[O]} O{=}C_6H_4{=}O$