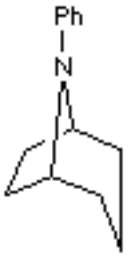
ORGANIC CHEMISTRY **CH 386, Spring 2010**

WORKSHOP, Chapters 22 - 24

Nitrogen Functional Groups, Aryl Halides, and Phenols

1. Treatment of the compound shown below with iodomethane led to the formation of two isomeric products, **A** and **B**. When each of these was treated first with Ag_2O/H_2O followed by heating, there was formed the same mixture of compounds **C** and **D**. Compound **C** could be resolved into enantiomers but **D** could not.



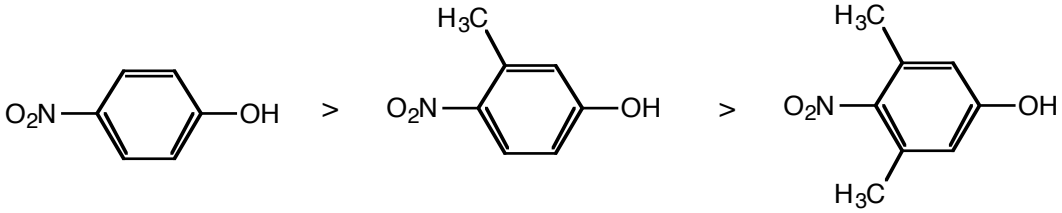
a. Provide structures for **A** and **B** and indicate the structural relationship between them.

b. Provide structures for **C** and **D**.

2. Compound **A**, $C_7H_{15}NO$, was neutral and exhibited strong absorption in the infrared spectrum at 1652 cm^{-1} but none in the 3200-3400 cm^{-1} region. Extended heating of **A** with $H_3O^{\oplus}/H_2O$ gave compound **B** and, after addition of NaOH, a nitrogen-containing compound **C**. **B** exhibited strong absorption in the infrared spectrum at 1712 cm^{-1} and a very broad absorption over the range 2500-3500 cm^{-1}. The ^1H NMR spectrum of **B** consisted of the following absorptions: δ 1.20 (d, rel. area 6, J = 7.0 Hz), 2.41 (septet, rel. area 1, J = 7.0 Hz), and 12.40, s, rel. area 1). Compound **C** exhibited a single absorption at 3335 cm^{-1} in the infrared spectrum and reacted with nitrous acid at 0 °C to give a yellow oil. Compound **C** was synthesized by treating ethyl amine first with formic acetic anhydride and then with $LiAlH_4$ ($H_3O^{\oplus}$ work up). Provide structures for **A**, **B**, and **C** which are consistent with this evidence.

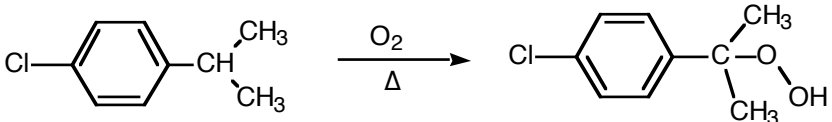
3. Compounds **A**, **B**, and **C** all have a molecular formula of $C_{10}H_{12}O_2$ and their IR and NMR spectra show that they are all *p*-disubstituted benzenes. All of these compounds are water insoluble. Compound **A** is insoluble in both NaOH and $NaHCO_3$. Compound **B** is soluble in both NaOH and $NaHCO_3$, and compound **C** is soluble in NaOH but insoluble in $NaHCO_3$. Give structures for **A**, **B**, and **C**, consistent with this information.

4. Explain the relative acidities of the phenols shown below.



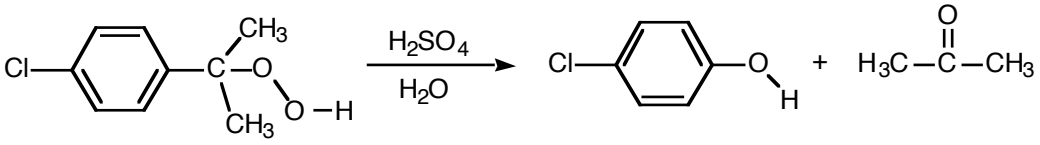
5. Give a reasonable mechanism for each the following reactions. Use curved arrows to show movement of electron pairs and "fish hooks" to show the movement of single electrons.

a.

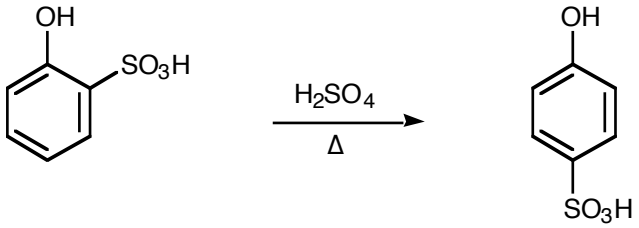


(Hint: Consider the structure of O_2.)

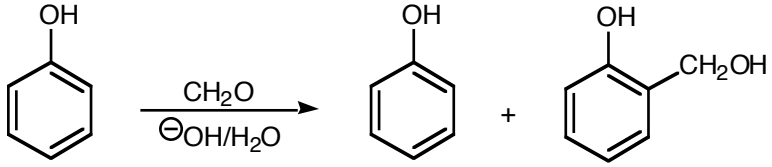
b.



c.



d.



e.