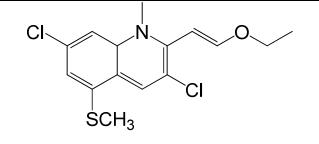
Spring 2017 (March 22)

1. Use the Woodward-Fieser table to estimate the λ_{max} observed in a UV spectra of the following cross-conjugated systems (6 pts)



Parent = 253 nm Extra conjugated C=C (3 x 30) 90 nm Exocyclic C=C 5 nm CI (2 x 5) 10 nm SCH₃ 30 nm N(Alkyl)₂ = 60 nm O-Alkyl 6 nm C-Alkyls (5 x 2) 10 nm

464 nm

Parent = 253 nm

Extra conjugated C=C (2 x 30) = 60 nm

Exocyclic C=C (2 x 5) = 10 nm

SCH₂CH₃ = 30 nm

N(Alkyl)₂ = 60 nm

O-Alkyl = 6 nm

C-Alkyls (4 x 5) = 20 nm

Acyclic	217 nm
Heteroannular	214 nm
Homoannular	253 nm

For each additional conjugated double bond	+ 30 nm
For each exocyclic double bond	+ 5 nm
For each substituent C-substituent CI Br O-Alkyl OCOCH ₃ N(alkyl) ₂ S-alkyl	+ 5 nm + 5 nm + 5 nm + 6 nm + 0 nm + 60 nm + 30 nm
Solvent correction	+ 0 nm

2. Name the following compounds $(3 \times 6 = 18 \text{ pts})$

(b)

$$O_{2N}$$

2-sec-butoxy-5-hydroxy-4-nitrobenzaldehyde

(c)

3-bromo-4-isopropylthio-6-methoxy-2-nitroaniline

(d)

7-methoxy-3-methyl-6-phenylnon-4-en-8-yne-2-thiol

(e)

2-bromo-6-hydroxy-4-isobutoxybenzoic acid

$$O_2N$$
 OH Br

4-bromo-6-sec-butyl-5-nitrobenzene-1,3-diol

3. Classify the following molecules as aromatic, anti-aromatic or non-aromatic (5 pts)

4. Predict the major product(s) expected from the following reaction sequences (3 x 14 = 42 pts)

(c)
$$SO_3$$
 O HNO_3 O I $I/_2 I_2$ I_2 SO_3H

$$\begin{array}{c|c}
\hline
Br \\
\hline
FeBr_3
\end{array}$$

$$\begin{array}{c|c}
\hline
O & N \\
\hline
Light
\end{array}$$

$$\begin{array}{c|c}
Br \\
Br \\
\hline
Br
\end{array}$$

$$CO_2Me$$

$$\begin{array}{c|ccccc}
 & OCH_3 & OCH_3 & OCH_3 \\
\hline
 & HNO_3 & Pe, HCI & Pr \\
\hline
 & Br & Br & Br
\end{array}$$

(i)

$$\frac{OH}{BF_3} \qquad \frac{CO + HCI}{CuCI/AICI_3} H$$

(k)
$$CI_2$$
 CI_2 CI_3 CI_4 CI_5 CI_6 CI_7 CI_8 $CI_$

$$\begin{array}{c} \text{HNO}_3 \\ \text{H}_2\text{SO}_4 \\ \text{O}_2\text{N} \end{array} \begin{array}{c} \text{Zn(Hg)} \\ \text{HCI} \\ \text{O}_2\text{N} \end{array}$$

MeO
$$CO + HCI$$
 MeO H_2SO_4 CO_2H CO_2H CO_2H

NO₂ NO₂ NH₂ O
$$Zn$$
 HCI BF_3

5. Show how you would synthesize each of the following compounds from the given starting material(s). You must draw keys intermediates to receive full credit $(3 \times 6 = 18 \text{ pts})$

$$\frac{\text{CO} + \text{HCI}}{\text{AlCI}_3, \text{CuCl}} \xrightarrow{\text{SO}_3} \xrightarrow{\text{O}} \xrightarrow{\text{SO}_3 \text{H}} \xrightarrow{\text{Br}_2} \xrightarrow{\text{BBr}_3} \xrightarrow{\text{O}} \xrightarrow{\text{SO}_3 \text{H}}$$

6. Propose a mechanism consistent with the following reactions (you must show all the intermediates to receive full credit) ($3 \times 3 = 9 \text{ pts}$)

(b)
$$CI: AICI_3 \longrightarrow CI-AICI_3 \longrightarrow O$$
 OH
 OH