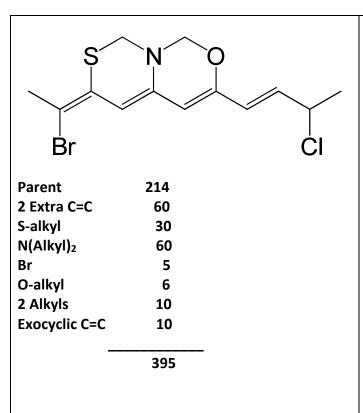
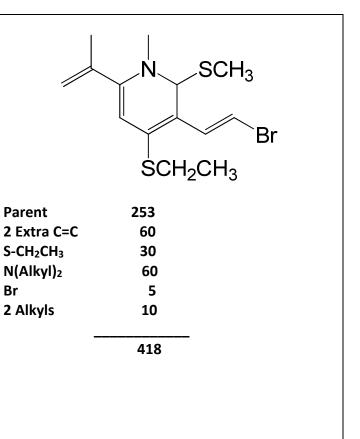
Fall 2017 (October 19)

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





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	+ 5 nm
Cl	+ 5 nm
Br	+ 5 nm
O-Alkyl	+ 6 nm
OCOCH₃	+ 0 nm
N(alkyl) ₂	+ 60 nm
S-alkyl	+ 30 nm
Solvent correction	+ 0 nm

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

(a)

7-methoxy-3,6-dimethyl-4-methylthio-2-phenylocta-2,5-diene

(b)

4-bromo-5-hydroxy-2-(isobutylthio)benzaldehyde

MeO NH₂

5-bromo-4-isopropoxy-3-methoxy-2-nitroaniline

HO NO₂ OCH₃

Вr

2-sec-butyl-4-methoxy-6-nitrophenol

OH O OH

2-bromo-6-hydroxy-4-(1-hydroxypropyl)benzoic acid

OH OH Br

ÓΗ

4-bromo-6-isopropyl-5-mercaptobenzene-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 ($3 \times 14 = 42 \text{ pts}$)

Br
$$O_2N$$
 O_2N O_2N

$$\begin{array}{c|c}
\hline
 & CO + HCI \\
\hline
 & CuCl, AlCl_3
\end{array}$$

$$\begin{array}{c|c}
\hline
 & HNO_3 \\
\hline
 & 1/_2 I_2
\end{array}$$

not take place

(h)
$$OCH_3$$
 OCH_3 OCH_3

$$\begin{array}{c|c} \text{(k)} & \text{HO}_3S & \text{D}_2O \\ \hline \\ O & AlCl_3 & \text{CI} \\ \end{array}$$

Br
$$NH_2$$
 NH_2 NH_3 , - 33°C +

NO2 NO2
$$\frac{NH_2}{BF_3}$$
 $\frac{Zn}{HCI}$

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 $(3 \times 6 = 18 \text{ pts})$

(a)
$$\frac{Br}{FeBr_3} \longrightarrow \frac{CO + HCI}{CuCI, AlCl_3} \longrightarrow \frac{Cl_2}{AlCl_3} \longrightarrow \frac{HNO_3}{H_2SO_4} \longrightarrow \frac{HNO_3}{OH}$$

(b)
$$\frac{HNO_3}{H_2SO_4} \qquad \frac{NO_2}{Fe, HCI} \qquad \frac{NH_2}{HCI} \qquad \frac{NaNO_2}{HCI} \qquad \frac{CuCN}{CuCN}$$

$$O_2N \qquad CN \qquad CN \qquad CN \qquad CN \qquad CN$$

$$Br_2 \qquad FeBr_3 \qquad H_2SO_4 \qquad CN$$

(e)
$$SO_3H$$
 SO_3H SO_3H SO_3H SO_3H SO_3H SO_3H SO_3H SO_4 SO_4 SO_4 SO_4 SO_4 SO_5 SO_8 SO

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)

(c)
$$CI$$
 $AICI_3$ CI CI $AICI_3$ CI CI $AICI_3$ CI CI $AICI_3$ CI $AICI_3$