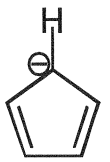
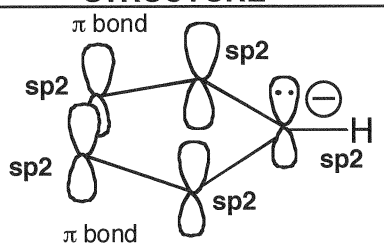
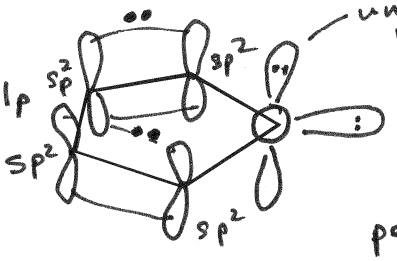
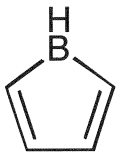
CHEM 5.12
PROBLEM SET #8 Due in Friday April 25th at 4 pm

1. (4points) For the following cyclic compounds:
a) Designate whether each is aromatic or not aromatic
b) Draw structures of the molecule (as illustrated in the box) labeling the hybridization state at each atom in the ring, the unhybridized p orbitals and any non-bonding electrons.

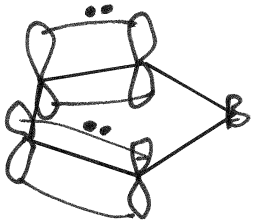
	AROMATIC	STRUCTURE
	yes	

6e⁻ 4 from c=c + 2 from Olp
yes

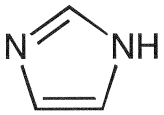




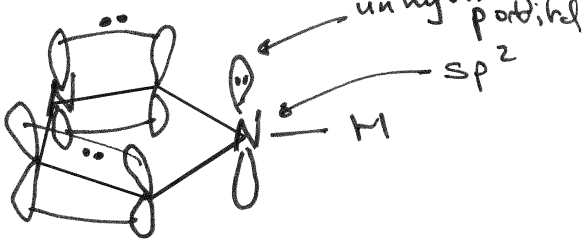
no 4e⁻
all sp²

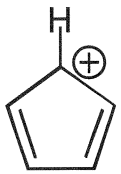


1 each

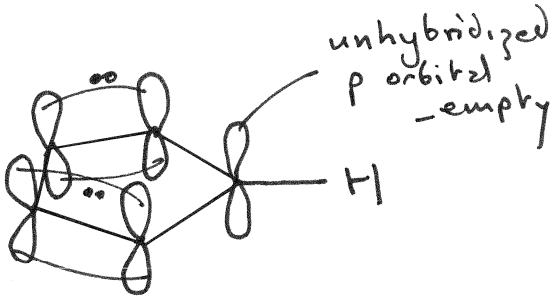


yes 6e⁻
all sp²





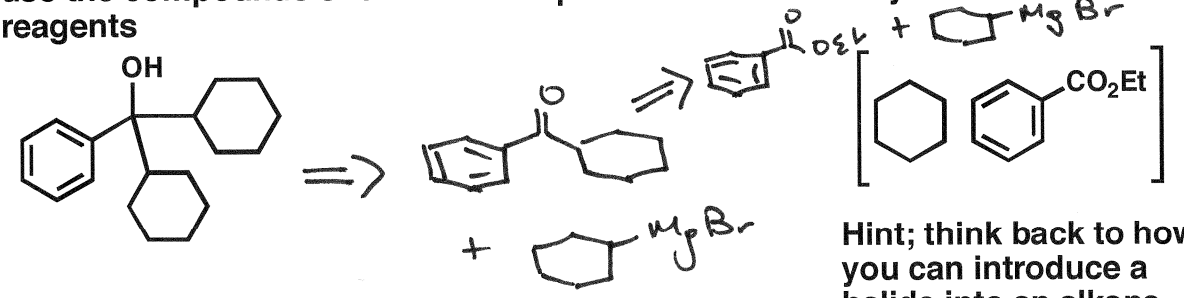
no 4e⁻



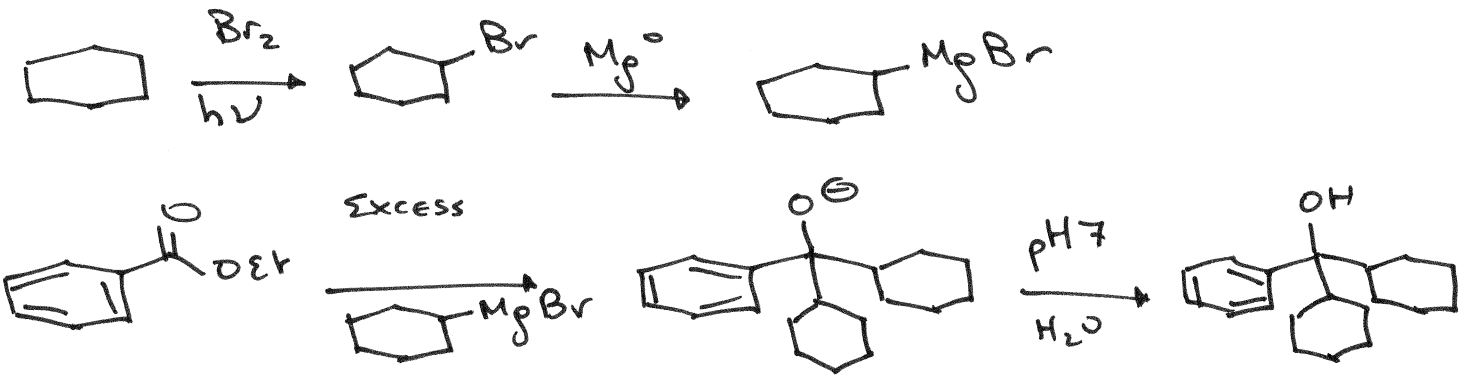
all sp²

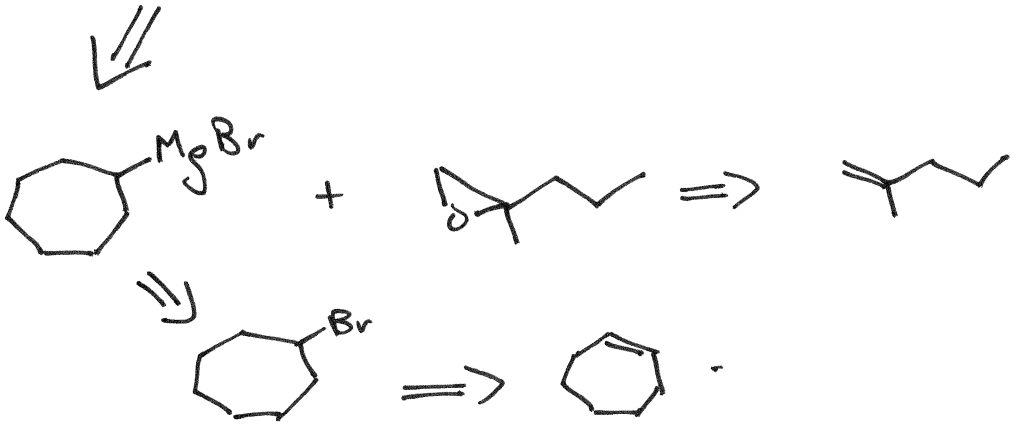
3. for each synthesis

2. (6 points)Design synthesis of the compounds shown on the left. You may use the compounds shown in the square brackets and any other standard reagents

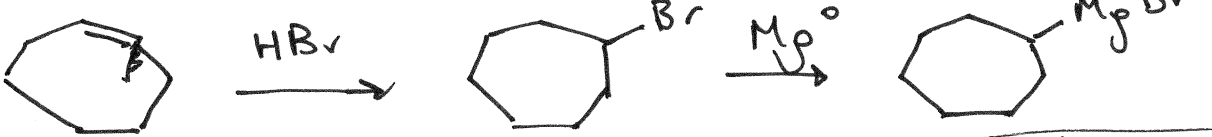


Hint; think back to how you can introduce a halide into an alkane.....

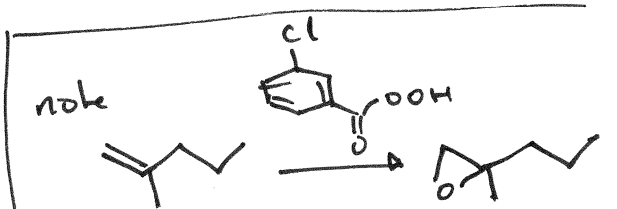




Synthesis

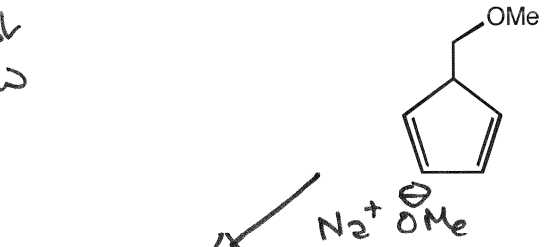


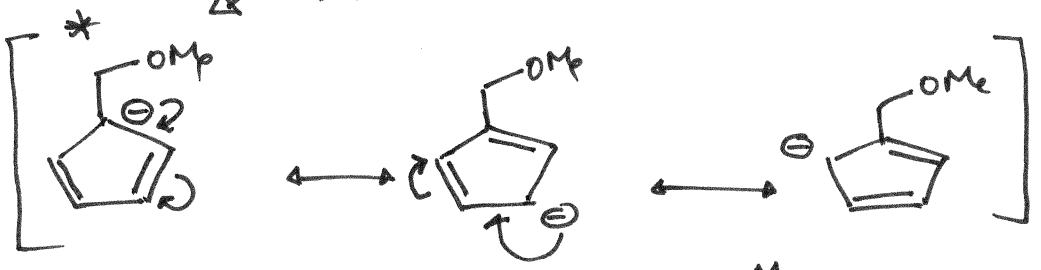
1. 
2. H_2O



3. (3 points) When compound I is treated as shown below, a mixture of isomeric products of identical molecular formula are obtained. EXPLAIN

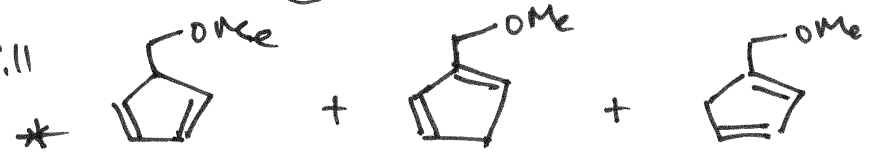
Must show





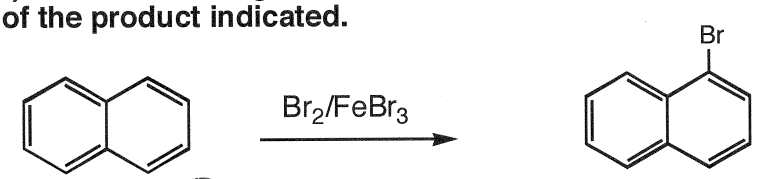
Explanation
Cyclopentadiene is quite acidic (anion is aromatic)
On forming anion charge is delocalized around ring.
Reprotonation at various sites gives a mixture of prods

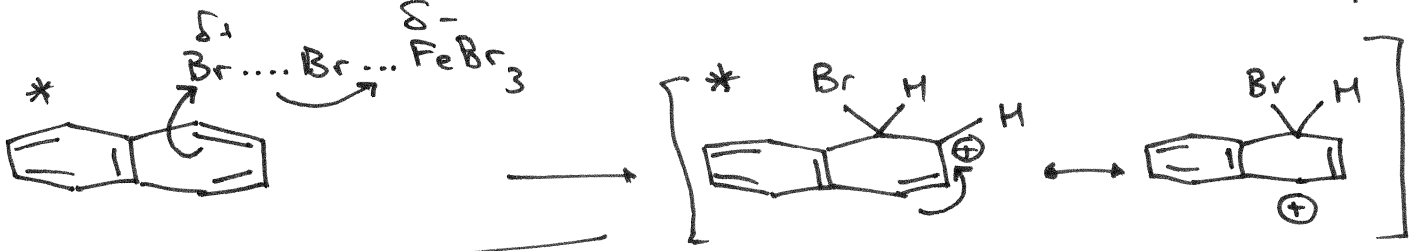
on neutralizing will get.

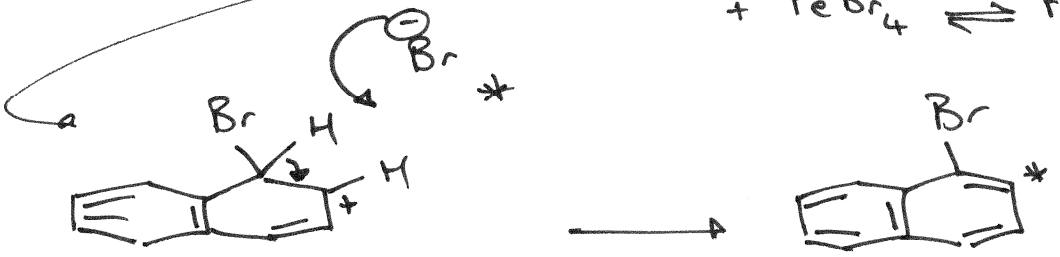


4. (3 points) For the following reactionshow the stepwise mechanism leading to the formation of the product indicated.

Must show *

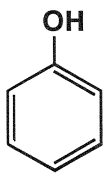




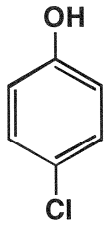


Bromination can also occur at *
but it is less favorable — think about why....

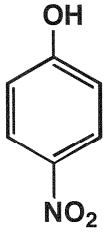
5. (4 points) Below are listed five different phenols and the pKa of the phenolic -OH proton. Explain why the pKa values are so different using resonance and inductive effect arguments (AND DRAWING STRUCTURES TO ILLUSTRATE THESE) as necessary.



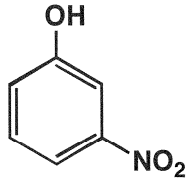
pKa 10



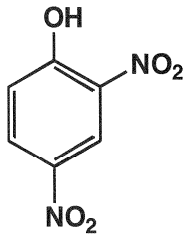
9.38



7.15



8.4

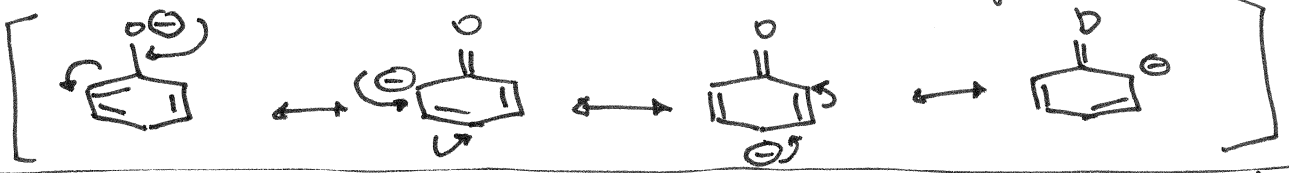


0.4

Hint - write out the full structure of the $-NO_2$

Differences in pka from resonance & inductive effects.

phenol - least acidic - Consider structures of conjugate base

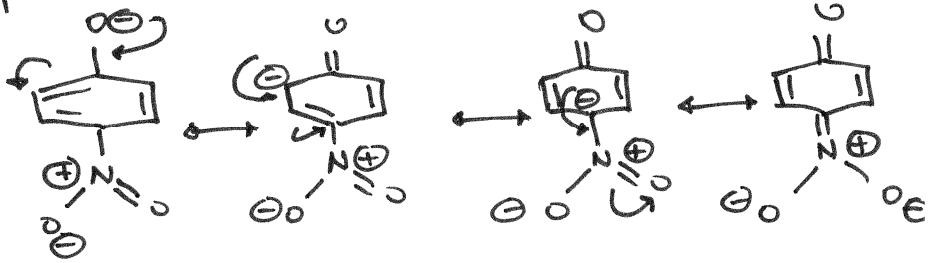


for Chlorosubstituent - Cl. helps stabilize -ve at para position by inductive effects.

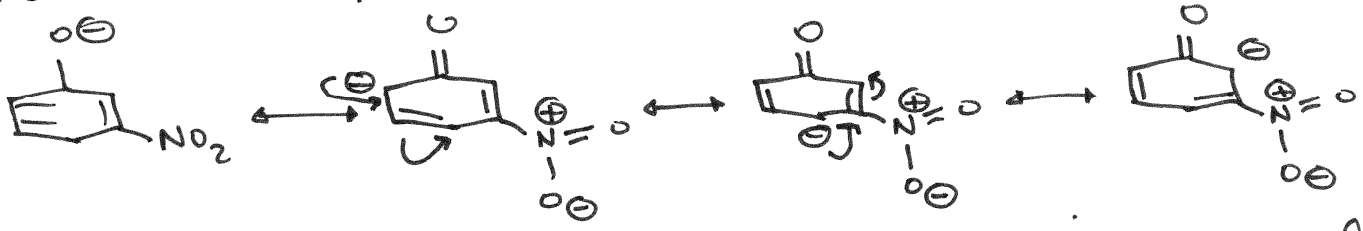
Eg

so slightly more acidic

For para-nitro phenol - extra resonance on $-NO_2$



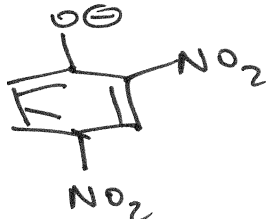
For meta-nitrophenol.



no extra resonance but nitro stabilizes -ve by strong inductive effs

Extra problems from the book: 10.10, 10.13, 10.38, 10.42, 10.44, 16.5, 16.7, 16.5, 16.34, 16.36.

for



most acidic
extra resonance structures with charge on both $-NO_2$