Chemistry 3B, Midterm 1

Tuesday, October 8, 2002

Student name: Answer Key

Student signature: _____

Write TA's name or Lecture Only: _____

1. Please make sure that the exam has 9 pages including this one.
2. Please write your answers in the spaces provided.
3. Write clearly; illegible or ambiguous answers will be considered incorrect.
4. Only writing implements are allowed **(No Calculators)**.

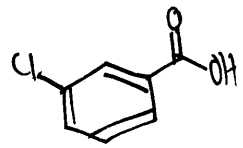
GOOD LUCK!

1.	8 points	_____
2.	30 points	_____
3.	50 points	_____
4.	37 points	_____
5.	35 points	_____
6.	20 points	_____
Total	**180 points**	_____

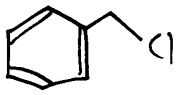
MINI-PERIODIC TABLE

I	II	III	IV	V	VI	VII	VIII
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr

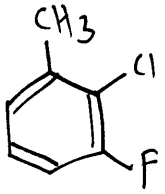
1. Provide structures for the following chemical names (8 points)



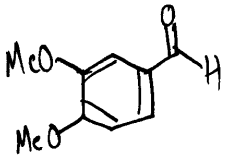
m-chlorobenzoic acid



benzyl chloride



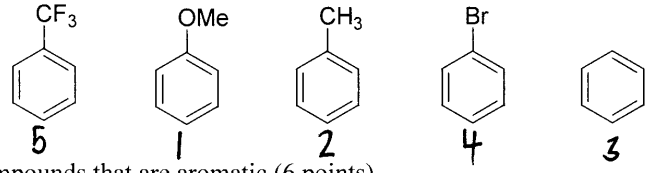
2-chloro-3-flourotoluene



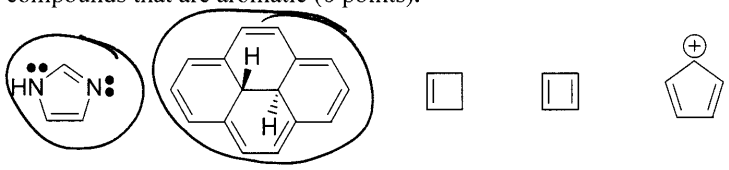
3,4-dimethoxybenzaldehyde

2. Answer the following questions. Every wrong answer cancels a correct answer (30 points).

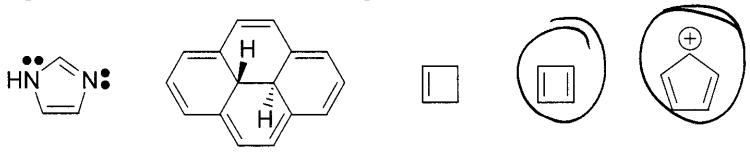
(a). Rank the compounds according to those that would react most rapidly with Br_2, $FeBr_3$ to those that would react the least rapidly [1 = **most** rapid, 5 = **least** rapid] (6 points).



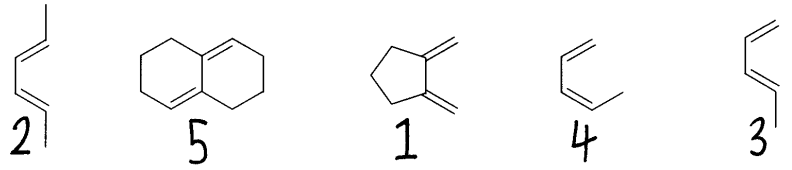
(b). Circle the compounds that are aromatic (6 points).



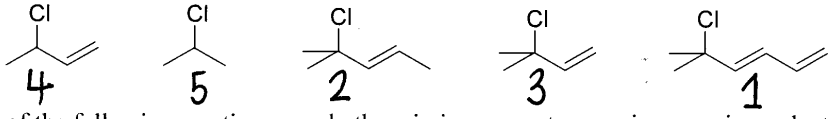
(c). Circle the compounds that are anti-aromatic (6 points).



(d). Rank the dienes according to those that would undergo a Diels Alder from most to least rapidly [1 = **most** rapid, 5 = **least** rapid] (6 points).

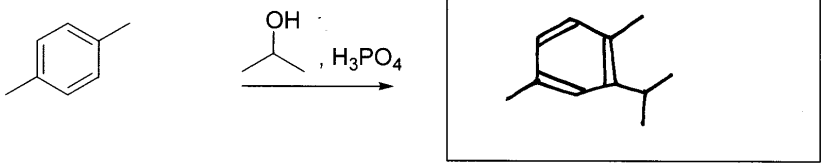


(e). Upon treatment with methanol, each of the following compounds produces methyl ether products with the rate-determining step being formation of a carbocation intermediate. Rank the compounds from 1 to 5 for rate of reaction [1 = **fastest** rate, 5 = **slowest** rate] (6 points).

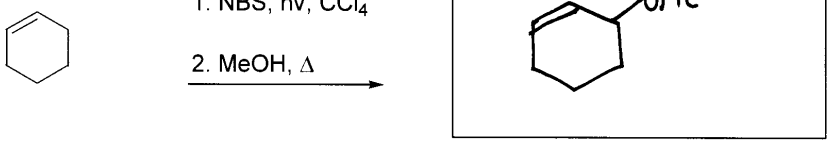


3. For each of the following reactions supply the missing reagents or major organic product in the space provided. If no reaction is expected indicate by N.R. (50 points total).

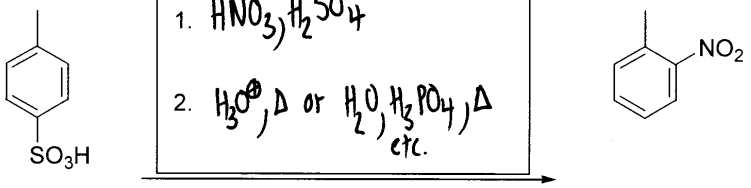
(a)



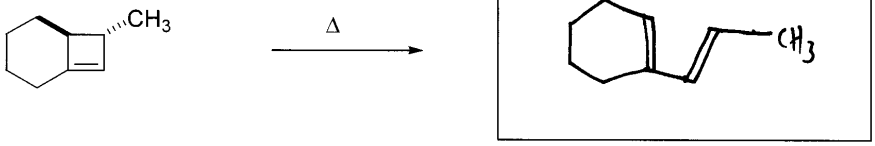
(b)

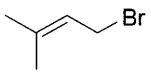


(c)



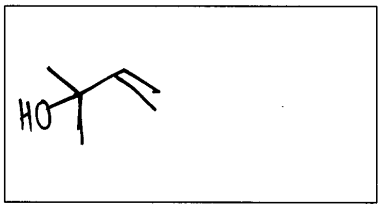
(d)

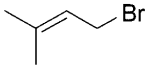


(e) 

H_2O

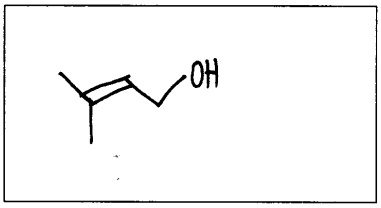
(under kinetic control, i.e., low temp)

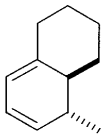


(f) 

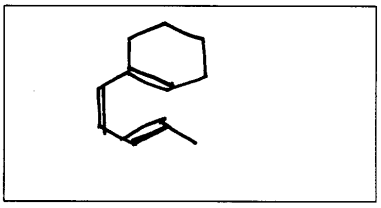
H_2O

(under thermodynamic control, i.e., high temp)

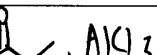


(g) 

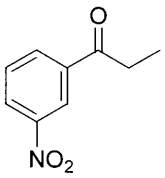
hv

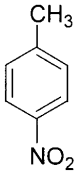


(h) 

1. 

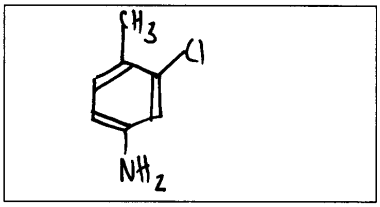
2. HNO_3, H_2SO_4

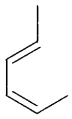


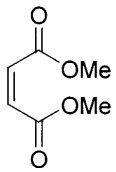
(i) 

1. Cl_2, $FeCl_3$

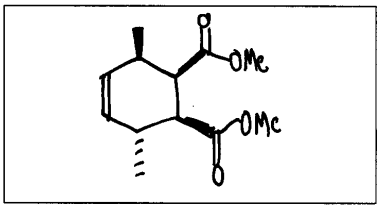
2. Fe, HCl



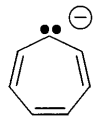
(j) 

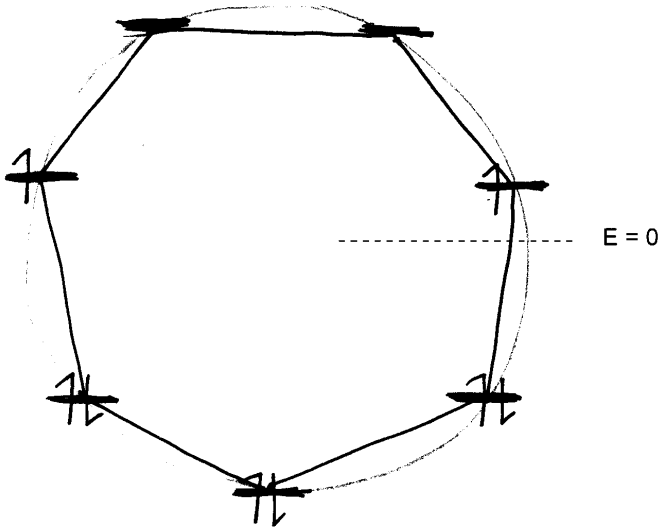
+ 

Δ



4. 35 points total.
(a) Show an energy level diagram for the molecular orbitals of the tropylium anion drawn below (10 points).

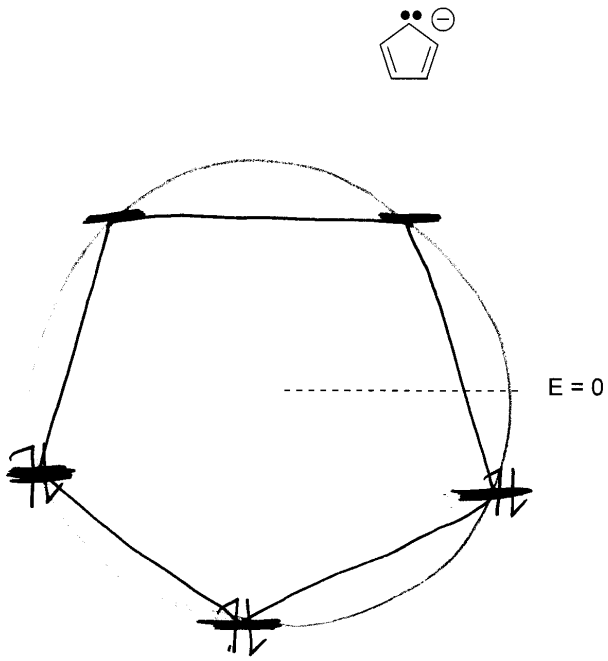




(b) Place the electrons in the appropriate molecular orbitals. Does the electron placement establish the molecule as aromatic or antiaromatic? **Briefly** explain (one sentence is all that is necessary) (5 points).

Antiaromatic. Two unpaired $e^{\ominus}$ are present

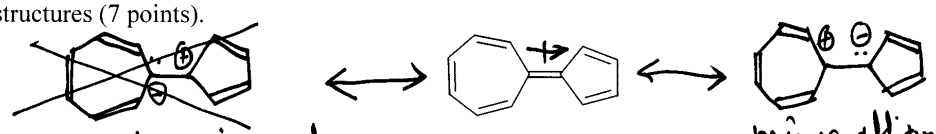
(c) Show an energy level diagram for the molecular orbitals of the cyclopentadienyl anion drawn below (10 points).



(d) Place the electrons in the appropriate molecular orbitals. Does the electron placement establish the molecule as aromatic or antiaromatic? **Briefly** explain (one sentence is all that is necessary) (5 points).

Aromatic. No unpaired e⊖

(e) The compound below has a rather large dipole moment. Indicate what you think that that dipole moment might be (with an arrow, NOT a number) and give a **brief** explanation. Hint: draw resonance structures (7 points).



Both tropylium anion and cyclopentadienyl cation are antiaromatic

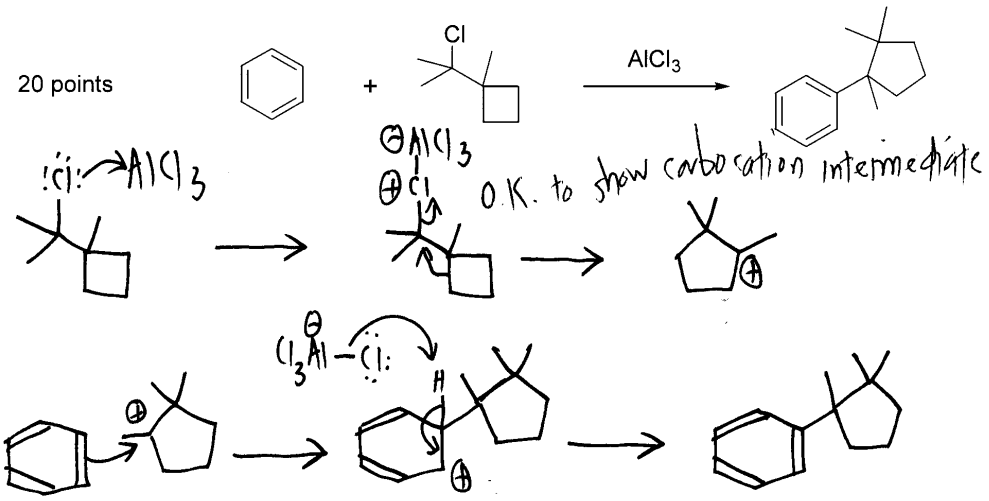
Resonance form not present

maj or. additional contributor

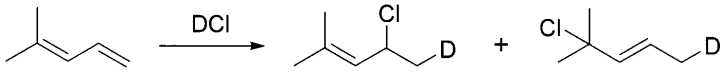
both tropylium cation and cyclopentadienyl anion are aromatic

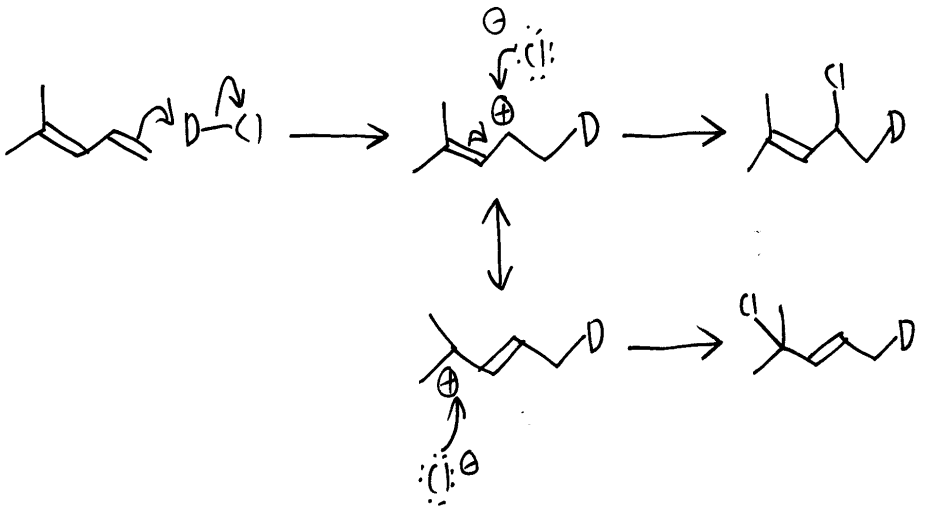
5. Provide detailed mechanisms for the following transformations (35 points).

(a) 20 points

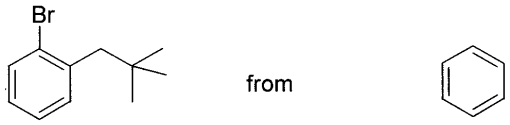


(b) 15 points

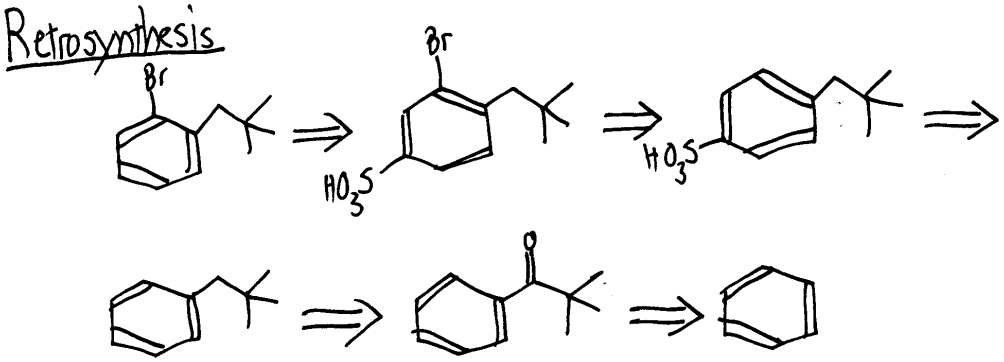




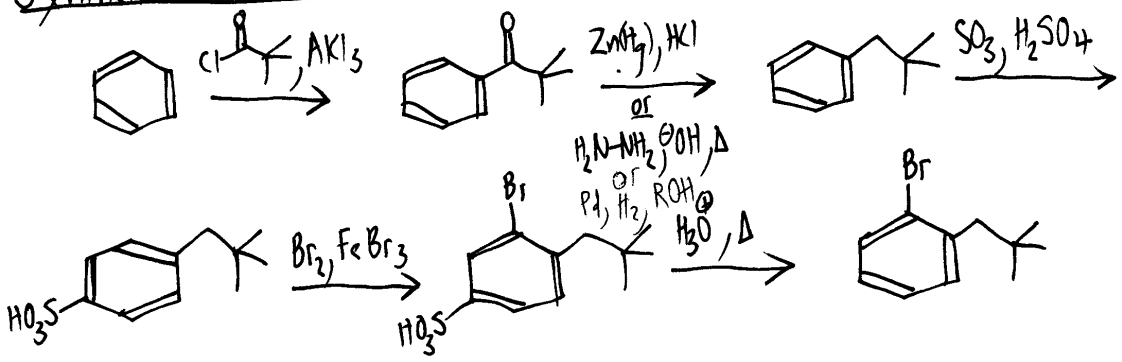
6. Provide the most efficient synthesis. You may employ any reagents of your choice (20 points).



Retrosynthesis



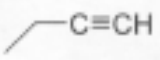
Synthetic direction



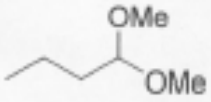
Chemistry 3B, Extra Practice Problems

2. For each of the following reactions supply the missing reagents or major organic product in the space provided. If no reaction is expected indicate by N.R.

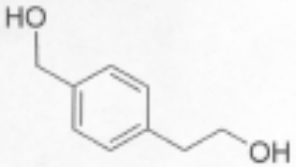
(a)



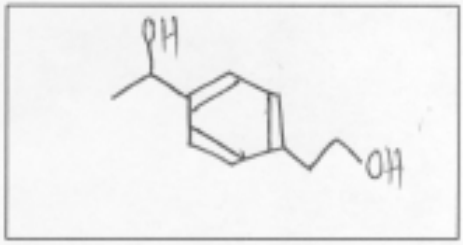
1. $(C_6H_5)_2BH$
2. $NaOH, H_2O_2$
3. $MeOH, H^{\oplus}$, 4Å sieves



(b)

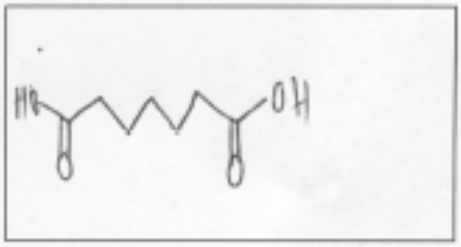


1. MnO_2
2. MeLi (xs)
3. aq. workup

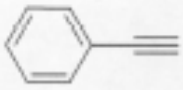


(c)

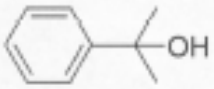
1. O_3
2. Zn, AcOH
3. CrO_3, H_2SO_4



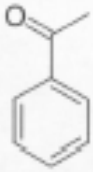
(d)



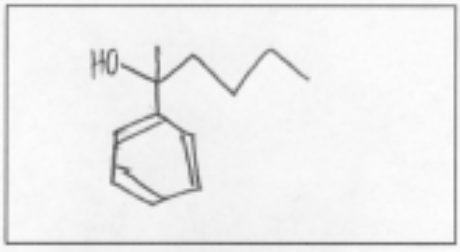
1. $H_2O, H^{\oplus}, H_2SO_4$
2. MeLi
3. aq. workup



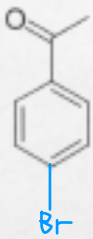
(e)



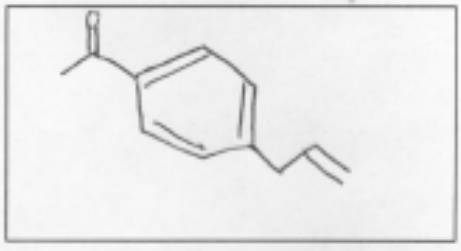
1. BuLi
2. aq. workup
3. PCC



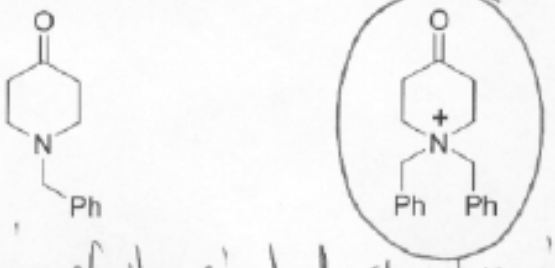
(f)



1. H+, MeOH, sieves
2. Mg, Et_2O
3. 
4. H^+, H_2O

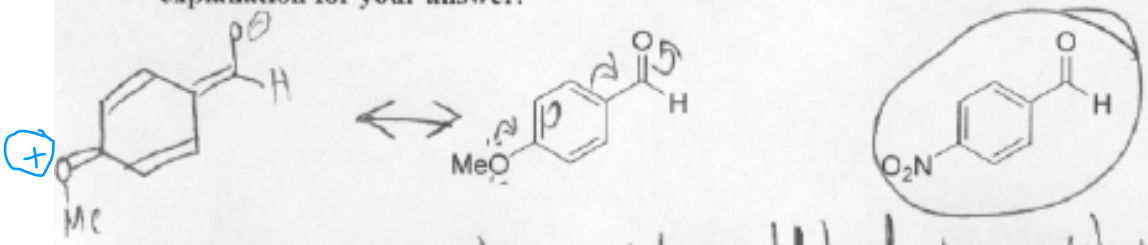


2 (a) The molecules drawn below are key building blocks in the synthesis of many psychoactive drugs. Circle the compound that would have the **largest** K_{eq} for hydrate formation. **Provide a brief explanation for your answer.**



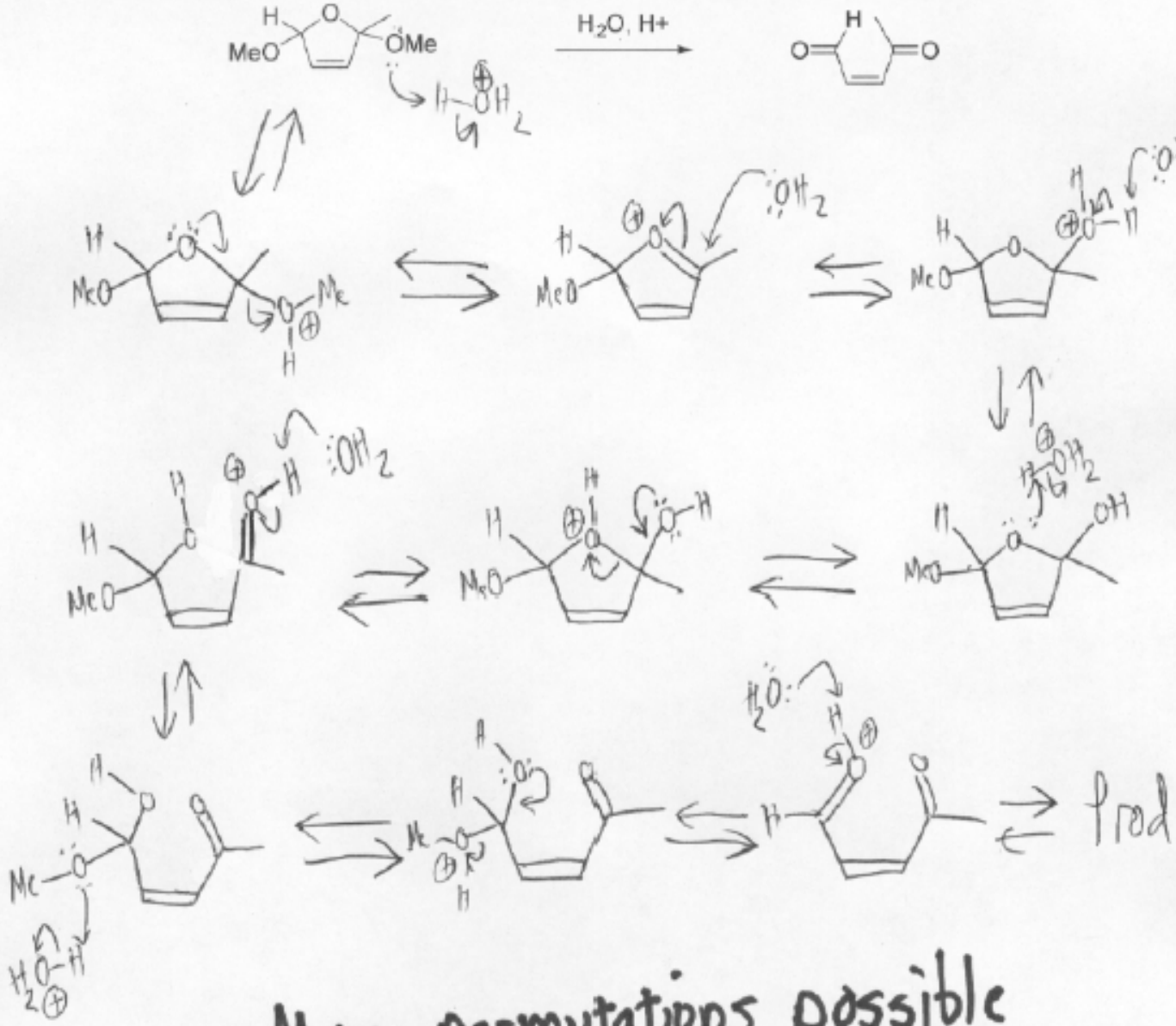
Resonance stabilization of the circled structure is minimized due to the inductive effect that results from the positively charged nitrogen.

(b) Circle compound below that would have the **largest** Keq for hydrate formation. **Provide a brief explanation for your answer.**



The 4-methoxy substituted benzaldehyde has much more resonance stabilization due to the resonance structure shown. In contrast resonance in the circled compound is minimized due to the $e^{\ominus}$ withdrawing nature of the NO_2 grp.

3. The following reaction is a key step in a commercial route to prostaglandin derivatives. Provide a mechanism.



Many permutations possible

Chemistry 3B, Midterm 1

Thursday, March 11, 2004

Student name: Answer Key

Student signature: _____

Write TA's full name (section number) or Lecture Only: _____

1. Please make sure that the exam has 9 pages including this one.
2. Please write your answers in the spaces provided.
3. Write clearly; illegible or ambiguous answers will be considered incorrect.
4. Only writing implements are allowed **(No Calculators)**.

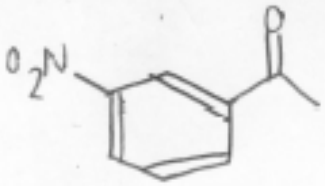
GOOD LUCK!

1.	8 points	_____
2.	30 points	_____
3.	50 points	_____
4.	20 points	_____
5.	12 points	_____
6.	20 points	_____
7.	15 points	_____
8.	25 points	_____
Total	**180 points**	_____

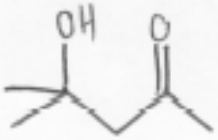
MINI-PERIODIC TABLE

I	II	III	IV	V	VI	VII	VIII
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr

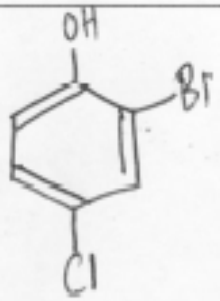
1. Provide structures for the following chemical names (8 points)



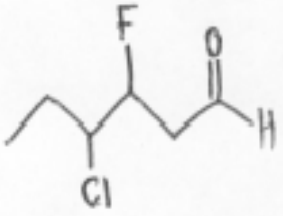
***m*-nitroacetophenone**



4-hydroxy-4-methyl-2-pentanone



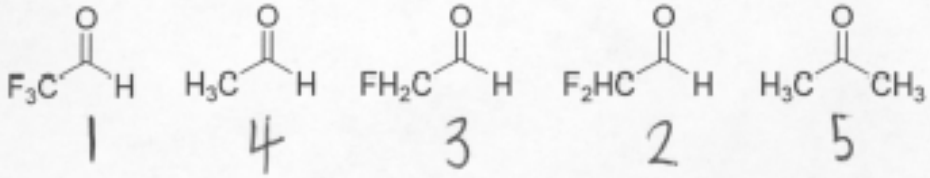
2-bromo-4-chlorophenol



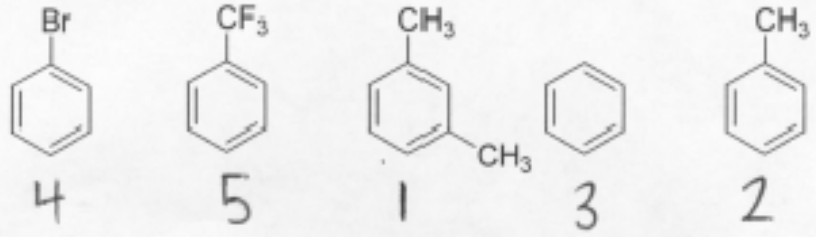
4-chloro-3-fluorohexanal

2. Answer the following questions. Every wrong answer cancels a correct answer (30 points).

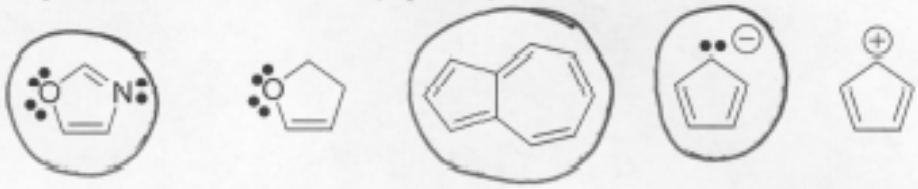
(a). Rank the compounds according to those that would most favor to least favor hydrate formation [1 = **most**, 5 = **least**] (6 points).



(b). Rank the compounds according to those that would react most rapidly to least rapidly with HNO_3, H_2SO_4 [1 = **most**, 5 = **least**] (6 points).

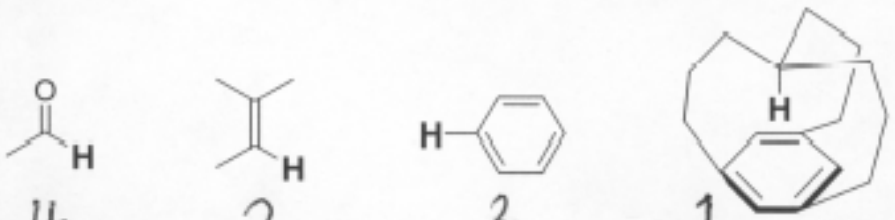


(c). Circle the compounds that are aromatic (6 points).



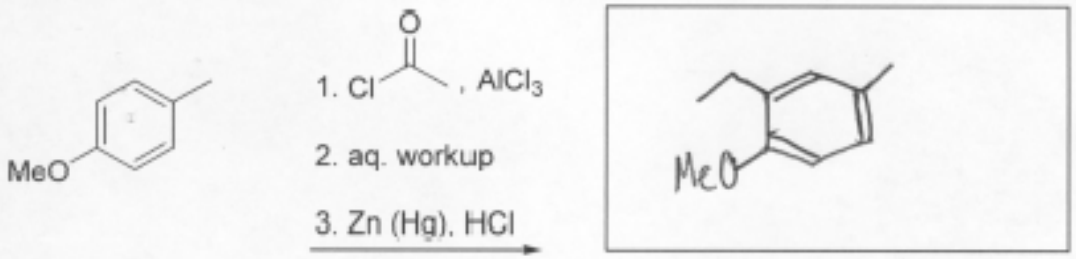
(d). **Circle** the compounds for which a thermal electrocyclic reaction would provide a **more** stable compound (6 points).

(e). Rank the **bold** hydrogens, that in an ^1H NMR spectra, would be most shielded (smallest ppm) to most deshielded (largest ppm [1 = most **shielded**, 5 = most **deshielded**] (6 points).

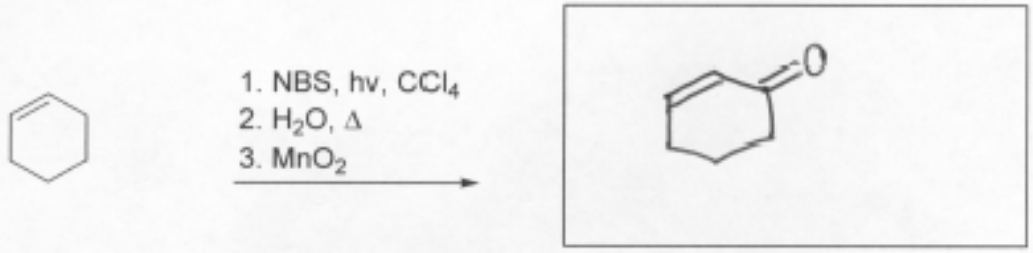


3. For each of the following reactions supply the missing reagents or major organic product in the space provided. If no reaction is expected indicate by N.R. (50 points total).

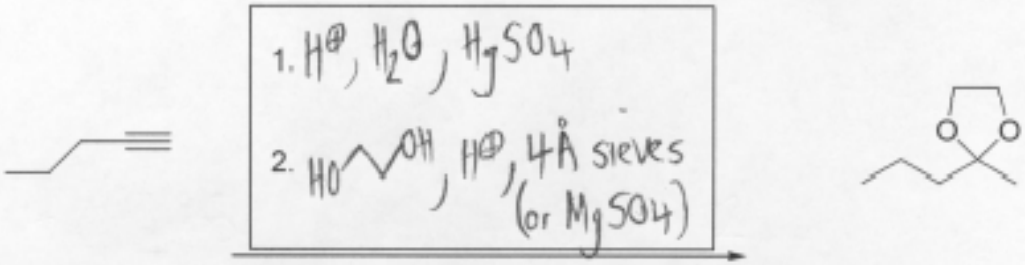
(a)



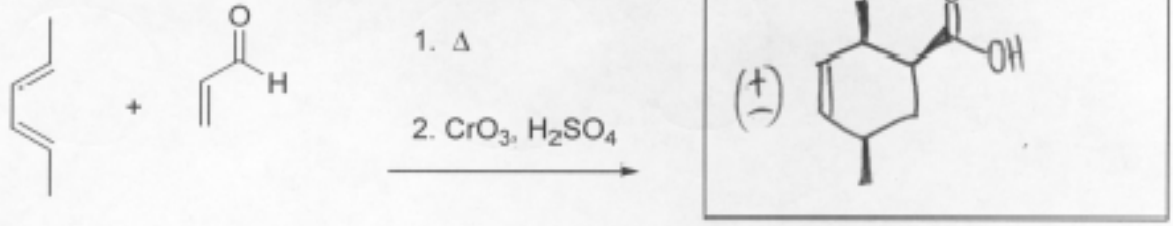
(b)

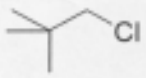


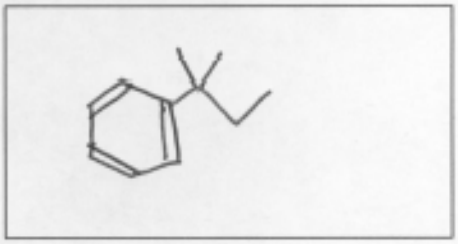
(c)



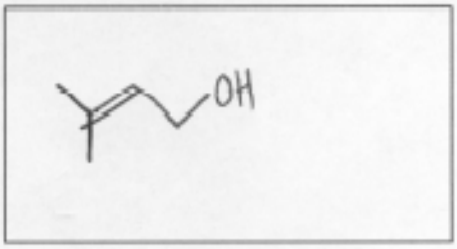
(d)

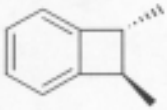
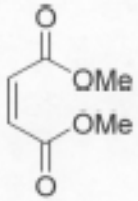


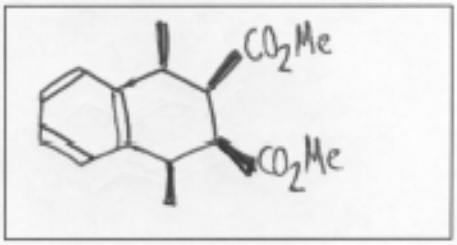
(e) 

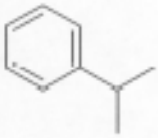
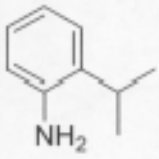
benzene (excess), $AlCl_3$ → 

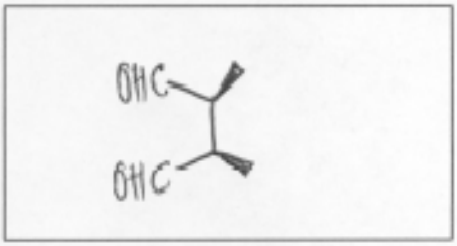
(f) 

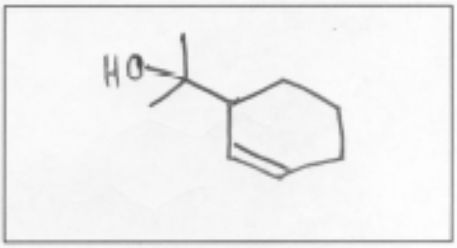
H_2O → (under thermodynamic control) 

(g)  + 

Δ → 

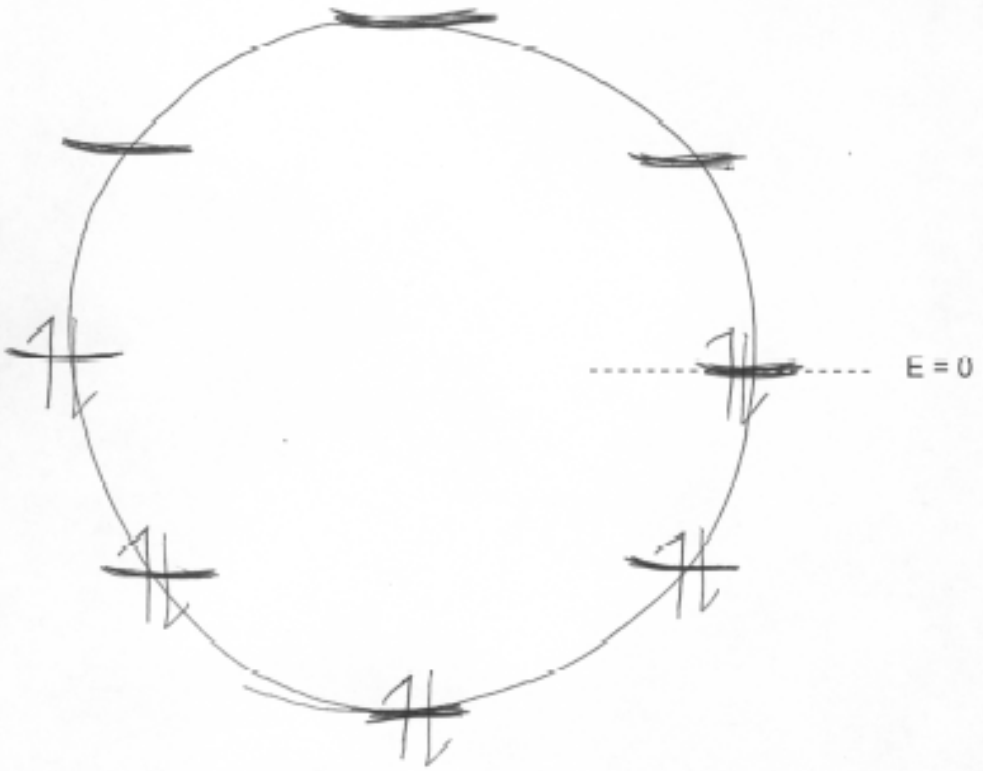
(h) 
1. SO_3, H_2SO_4
2. HNO_3, H_2SO_4
3. $HO^{\ominus}$, H_2O
4. $Zn(Hg)$, HCl or Fe, HCl
→ 

(i) 
1. hν
2. O_3
3. Zn, AcOH
→ 

(j) 
1. HBr
2. Mg, Et_2O
3. acetone
4. aq workup
→ 

4. 20 points total.

(a) Show an energy level diagram for the cyclooctatetraenyl **dianion** (formed from cyclooctatetraene and potassium metal as shown below) (10 points).



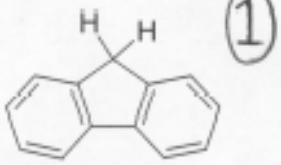
(b) Place the electrons for the **dianion** in the appropriate molecular orbitals. Does the electron placement establish the molecule as aromatic or antiaromatic? **Briefly** explain (one sentence is all that is necessary) (5 points).

Aromatic. The compound has 4n+2 electrons, which are placed in filled bonding and nonbonding M.O.s.

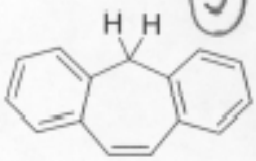
(c) Cyclooctatetraene and cyclooctatetraene dianion have very different conformations. Specifically, one is planar and the other is not. Which of the two compounds is planar? **Briefly** explain (5 points).

The dianion is planar because this is necessary for achieving aromatic stabilization. The neutral compound is nonplanar because planarity would result in an antiaromatic system.

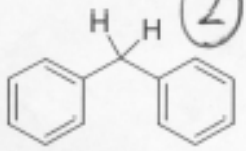
5. Rank the compounds listed below from most acidic to least acidic [1 = **most** acidic, 3 = **least** acidic]. Briefly explain your ranking (12 points).



1



3

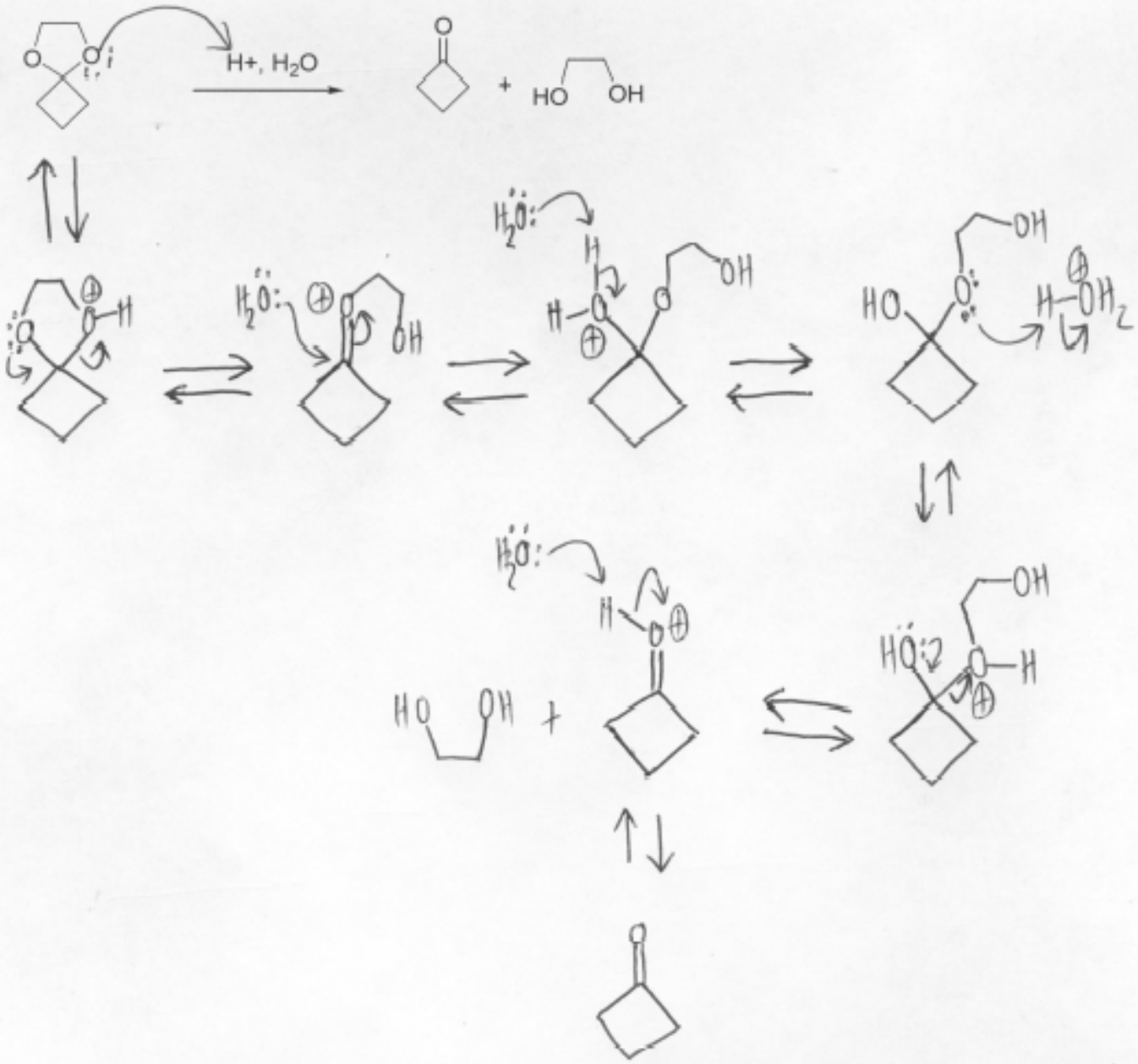


2

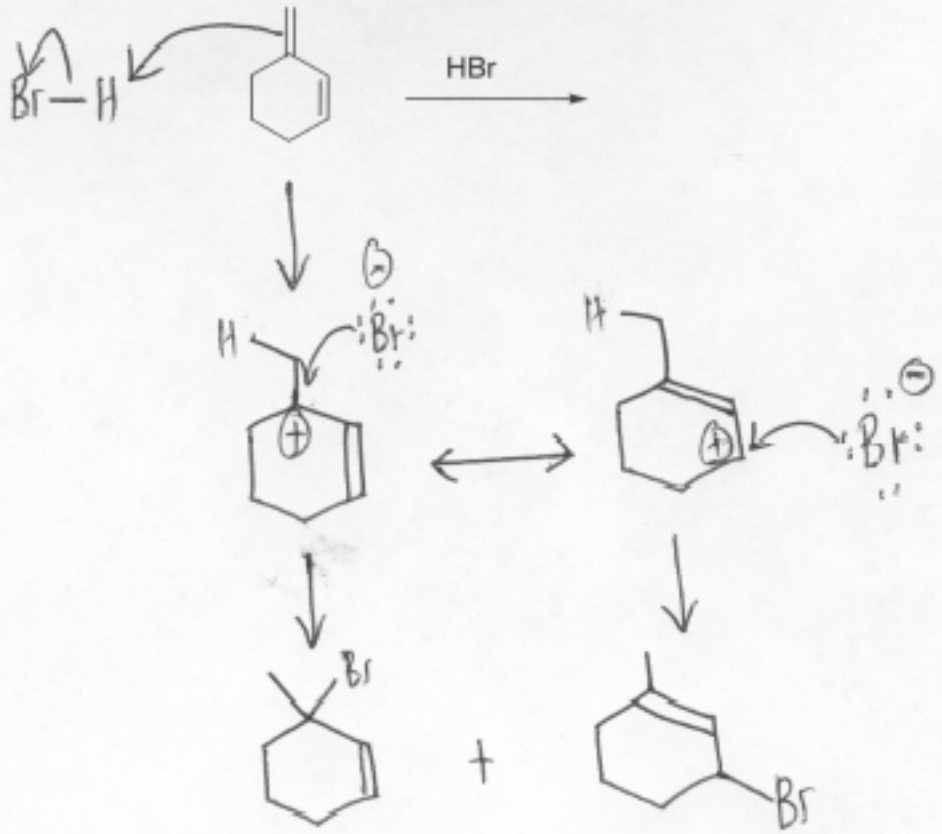
Note that the highly acidic nature of one these compounds is the basis of the most popular protecting group for the chemical synthesis of peptides and proteins.

The anion for compound (1) has $14e^{\ominus}$ and is aromatic and consequently is most stable. The anion for (3) has $16e^{\ominus}$ and is antiaromatic and is consequently least stable.

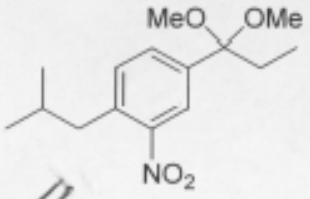
6. The cyclic acetal derived from ethylene glycol is extensively used as a protecting group. Provide a mechanism for its hydrolysis shown below (20 points).



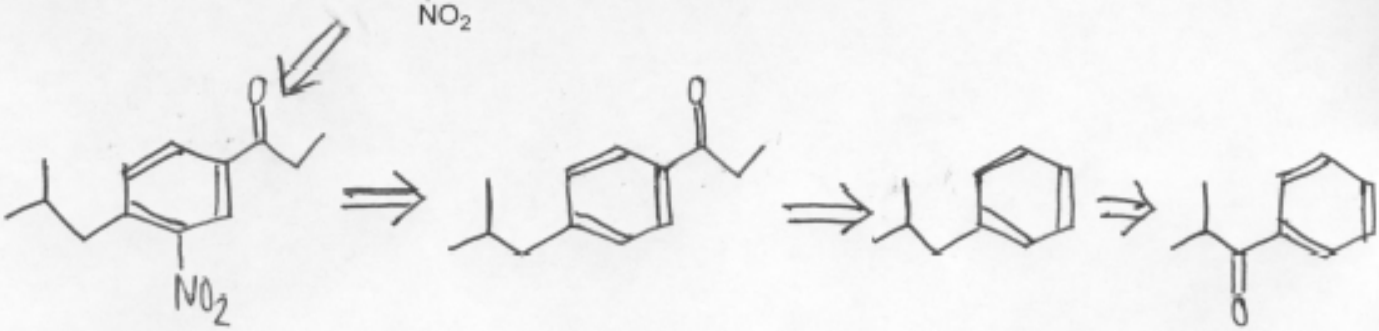
7. Draw the **two** major products of the below reaction. Provide the mechanism by which these products are obtained (15 points).



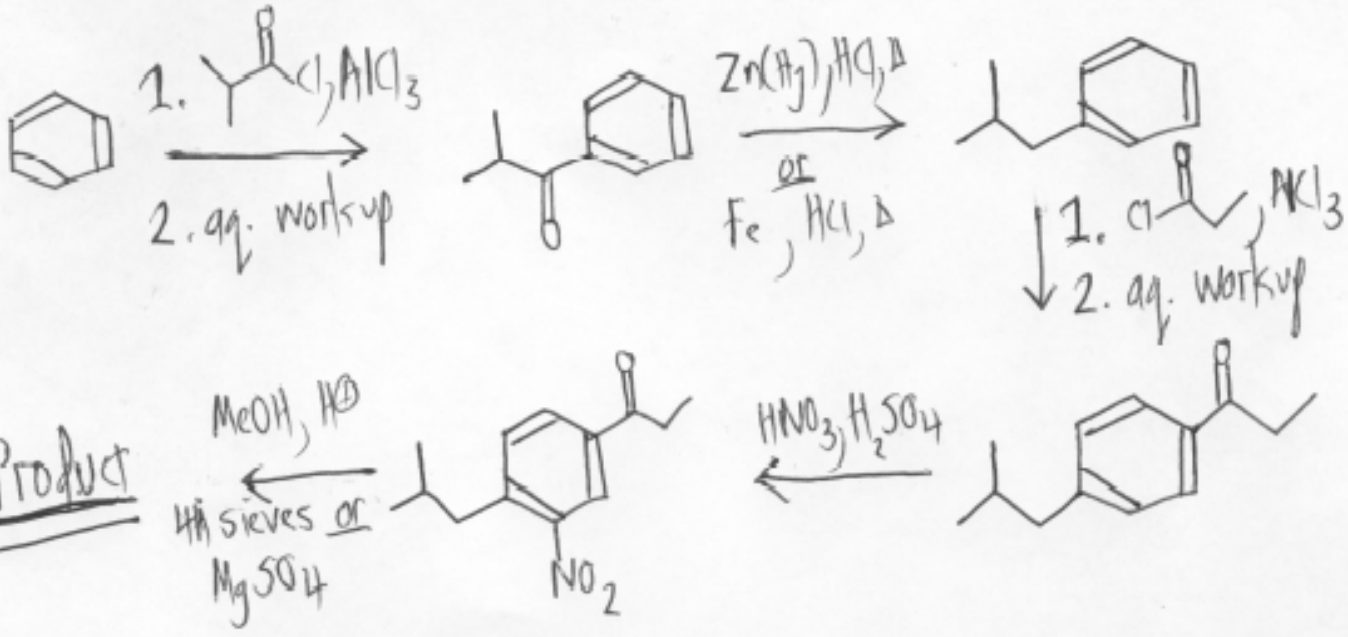
8. Provide the most efficient synthesis. You may employ any reagents of your choice. Points will be assigned according to steps listed in the forward synthesis direction (25 points).



from



Syn. direction:



Product

Points not taken off when intermediates not drawn. For future exams will require that intermediates be drawn.

Chemistry 3B, Midterm 1

Wednesday, October 20, 2004

Student name: Answer Key

Student signature: _____

Write TA's full name (section number) or Lecture Only: _____

1. Please make sure that the exam has 9 pages including this one.
2. Please write your answers in the spaces provided.
3. Write clearly; illegible or ambiguous answers will be considered incorrect.
4. Only writing implements are allowed **(No Calculators)**.

GOOD LUCK!

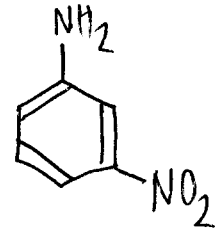
1.	8 points	_____
2.	30 points	_____
3.	50 points	_____
4.	17 points	_____
5.	10 points	_____
6.	20 points	_____
7.	20 points	_____
8.	25 points	_____
Total	**180 points**	_____

MINI-PERIODIC TABLE

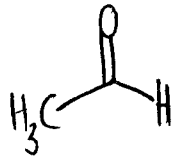
I	II	III	IV	V	VI	VII	VIII
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr

1. Provide structures for the following chemical names (8 points)

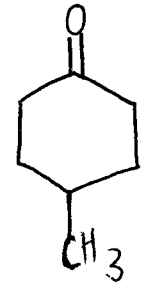
p-chlorophenol



3-nitroaniline



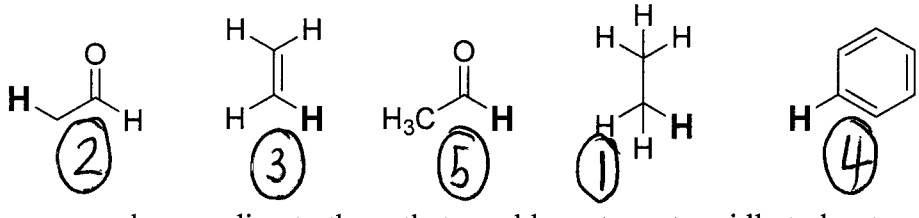
acetaldehyde



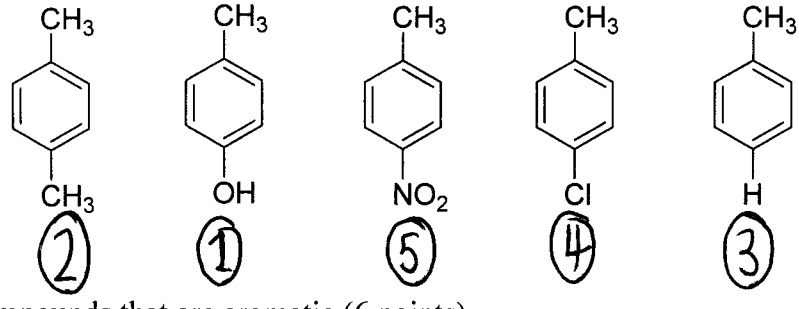
4-methylcyclohexanone

2. Answer the following questions. Every wrong answer cancels a correct answer (30 points).

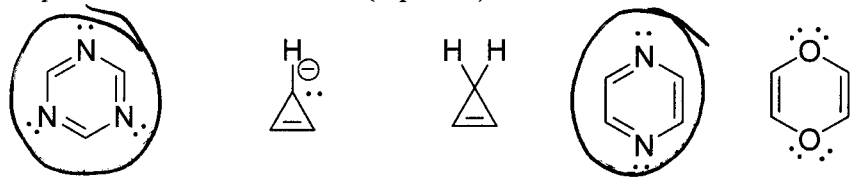
(a). Rank the **bold** hydrogens, that in an ^1H NMR spectra would be most shielded (**smallest** ppm) to most deshielded (**largest** ppm) [1 = most **shielded**, 5 = most **deshielded**] (6 points).



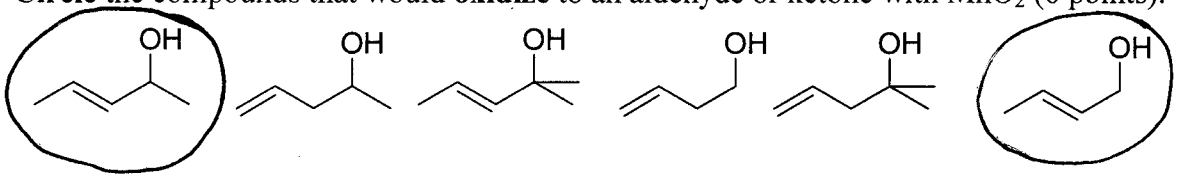
(b). Rank the compounds according to those that would react most rapidly to least rapidly with Cl_2, $FeCl_3$ [1 = **most**, 5 = **least**] (6 points).



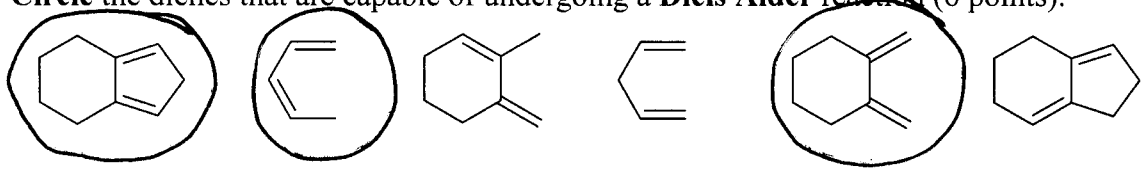
(c). **Circle** the compounds that are aromatic (6 points).



(d). **Circle** the compounds that would **oxidize** to an aldehyde or ketone with MnO_2 (6 points).

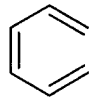


(e). **Circle** the dienes that are capable of undergoing a **Diels Alder** reaction (6 points).



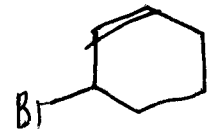
3. For each of the following reactions supply the missing reagents or major organic product in the space provided. If no reaction is expected indicate by N.R. (50 points total).

(a)

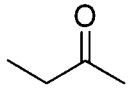


1. hν
2. HBr

→

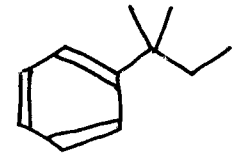


(b)

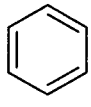


1. MeMgBr
2. aqueous workup
3. H_2SO_4, benzene (xs)

→

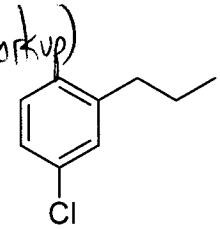


(c)

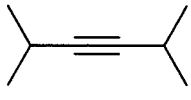


1.  $AlCl_3$ (O.K to have aq. workup)
2. Cl_2, $FeCl_3$
3. H_2N-NH_2, $^{\ominus}OH$, Δ or Zn(Hg), HCl, Δ

→

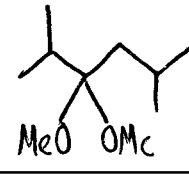


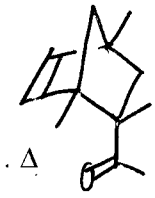
(d)



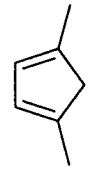
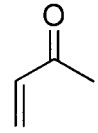
1. H_2O, H+, $HgSO_4$
2. MeOH, H+, sieves

→

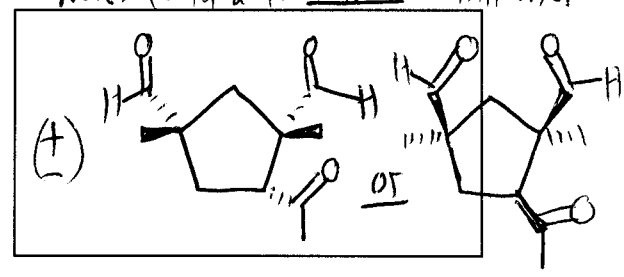


Via  (endo)

Note: could draw either enantiomer

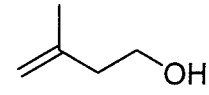
(e)  + 

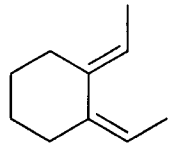
1. Δ
2. O_3
3. Zn, AcOH



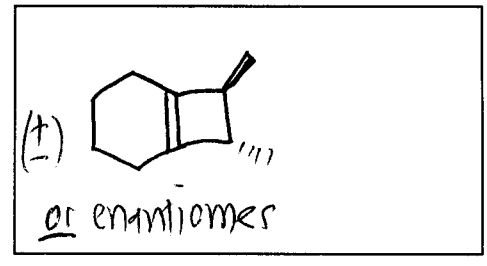
(f) 

1. NBS, CCl_4, hv
2. Mg, Et_2O
3. $H_2C{=}O$
4. aqueous workup

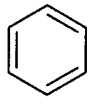


(g) 

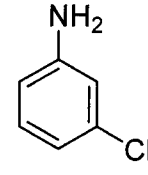
hν

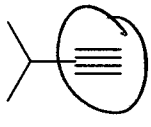


or enantiomers

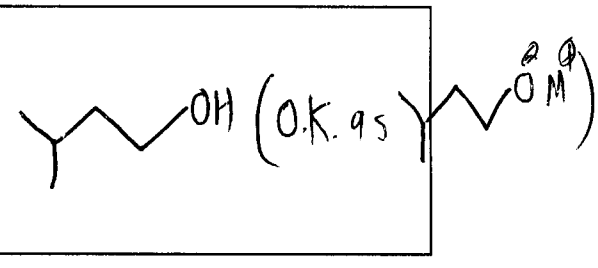
(h) 

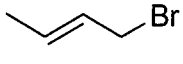
1. HNO_3, H_2SO_4
2. Cl_2, $FeCl_3$
3. Fe, HCl or other redn methods



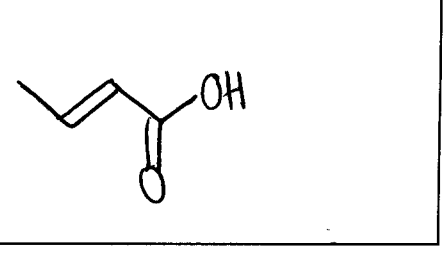
(i) 

1. Cy_2BH
2. H_2O_2, NaOH
3. $NaBH_4$

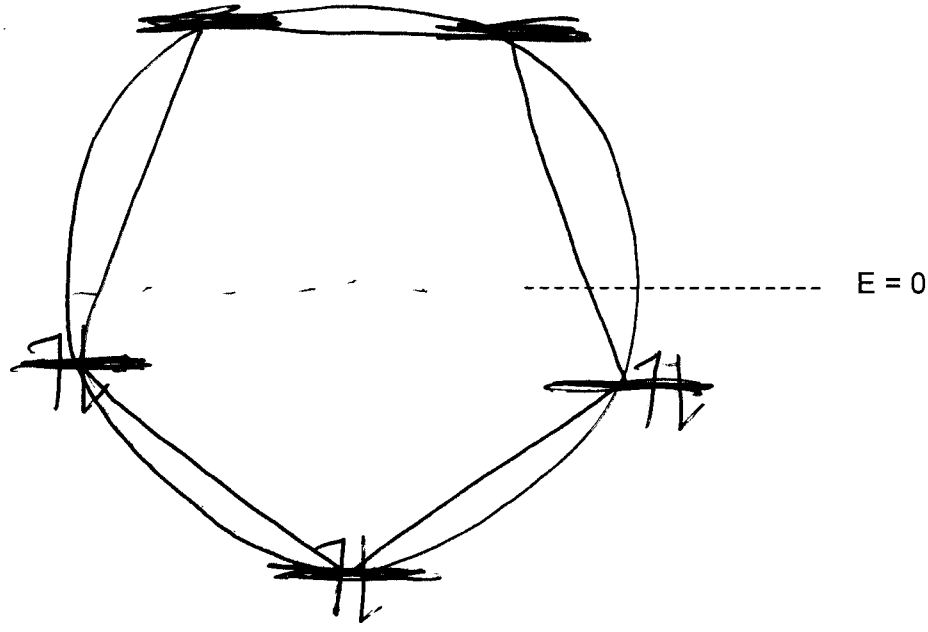


(j) 

1. H_2O (under thermodynamic control)
2. PCC, H_2O



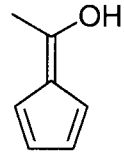
4. 22 points total.
(a) Show an energy level diagram for the cyclopentadienyl anion shown below (5 points).



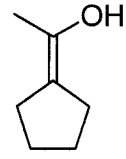
(b) Place the electrons for the **anion** in the appropriate molecular orbitals. Does the electron placement establish the molecule as aromatic or antiaromatic? **Briefly** explain (one sentence is all that is necessary) (5 points).

all $e^{\ominus}$ are in bonding orbitals and none are unpaired so aromatic

(c) Compound A is greater than ten orders of magnitude **more** acidic than Compound B. Explain why compound A is so much more acidic [**hint**: draw the resonance contributors of the conjugate bases of compounds A and B] (7 points).

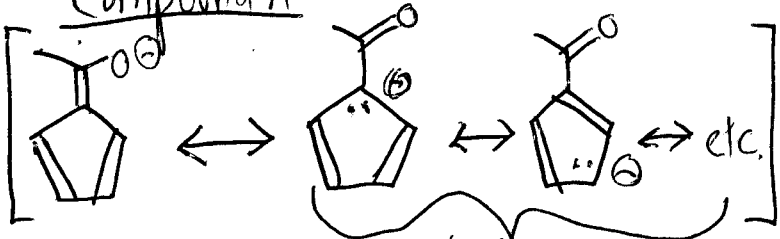


Compound A



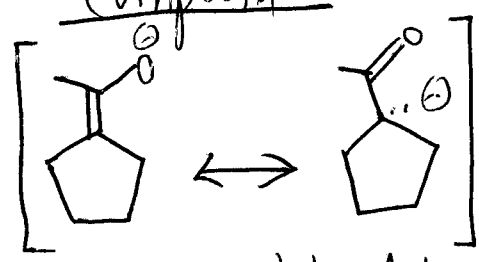
Compound B

Compound A



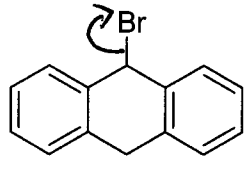
aromatic ($6e^{\ominus}$) π-system stabilized

Compound B

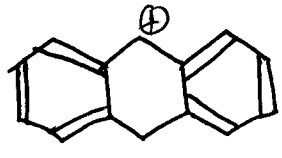


resonance stabilized but not with aromatic system

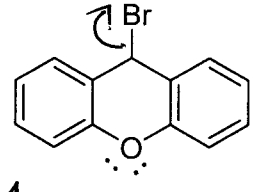
5. **Circle** the compound below that upon heating in water **more** rapidly undergoes an S_N1 reaction to give an alcohol. Briefly explain why the compound you circled undergoes the more rapid S_N1 reaction (10 points).



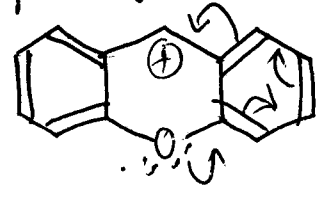
step 1 of S_N1 rxn

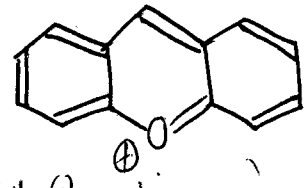


resonance stabilized cation



step 1

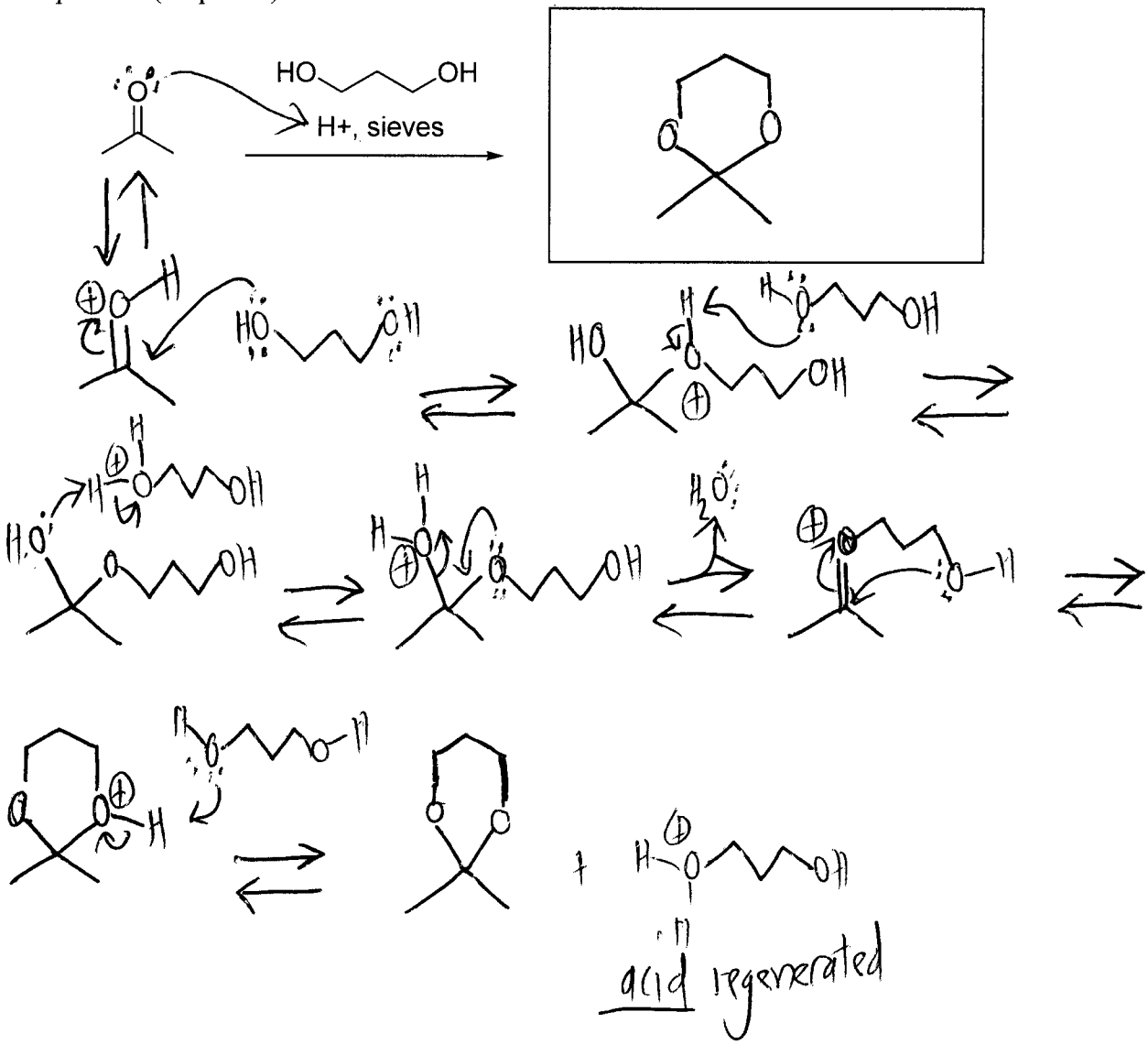




$14e^{\ominus}$ cyclic conjugated π-system

cation is aromatic so forms more easily

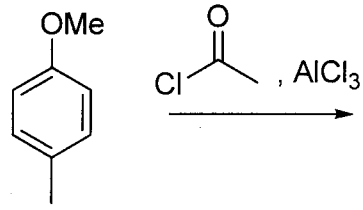
6. Provide the product of the below transformation. Provide a detailed mechanism for the formation of the product (20 points).

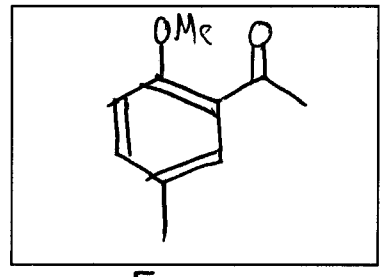


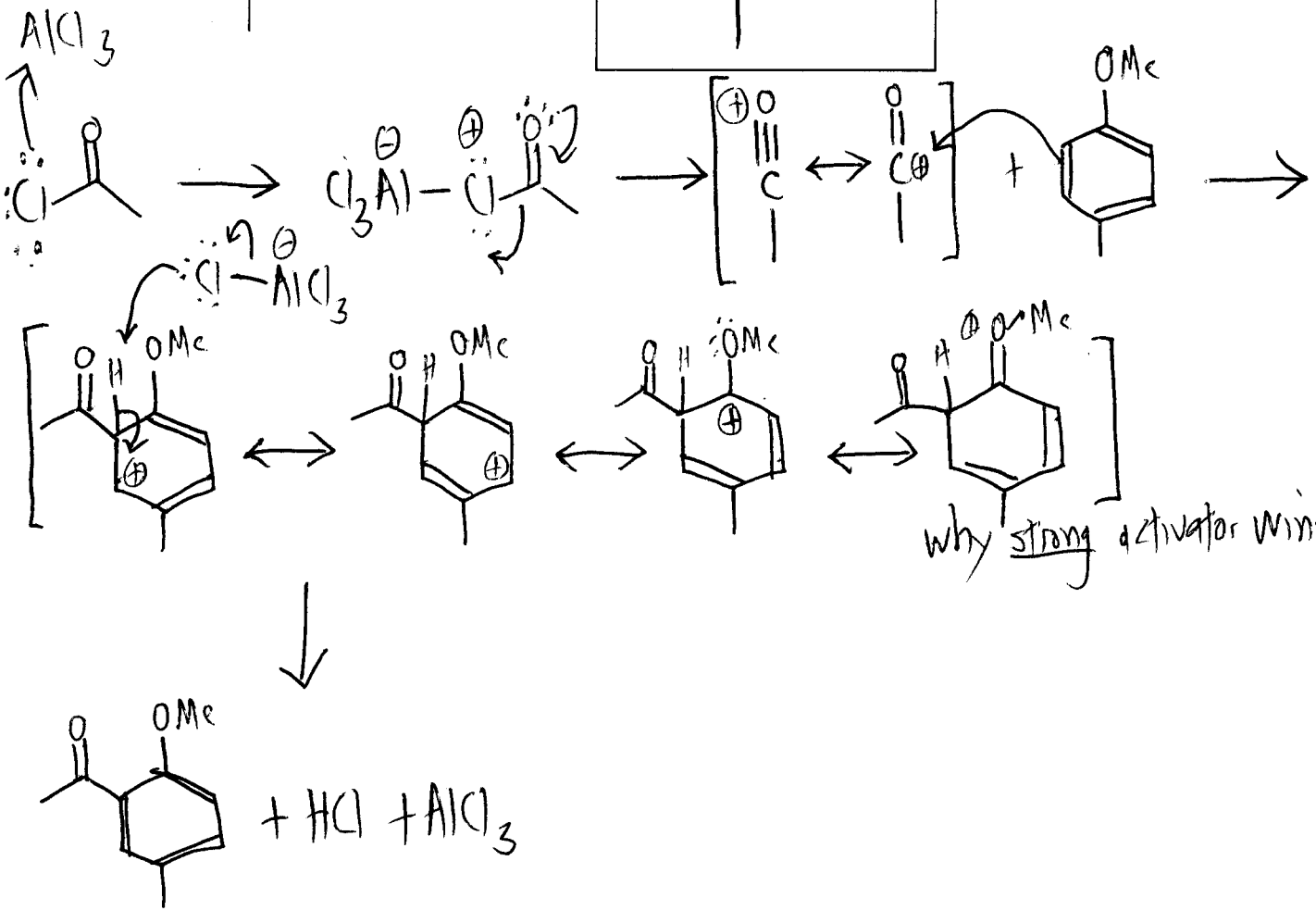
Notes:

- Irreversible step: H_2O + sieves → sieves·H_2O adduct (don't need to show)
- O.K. to use B: and B–H

7. Provide the product of the reaction listed below. Provide the mechanism by which the reaction product is formed (20 points).



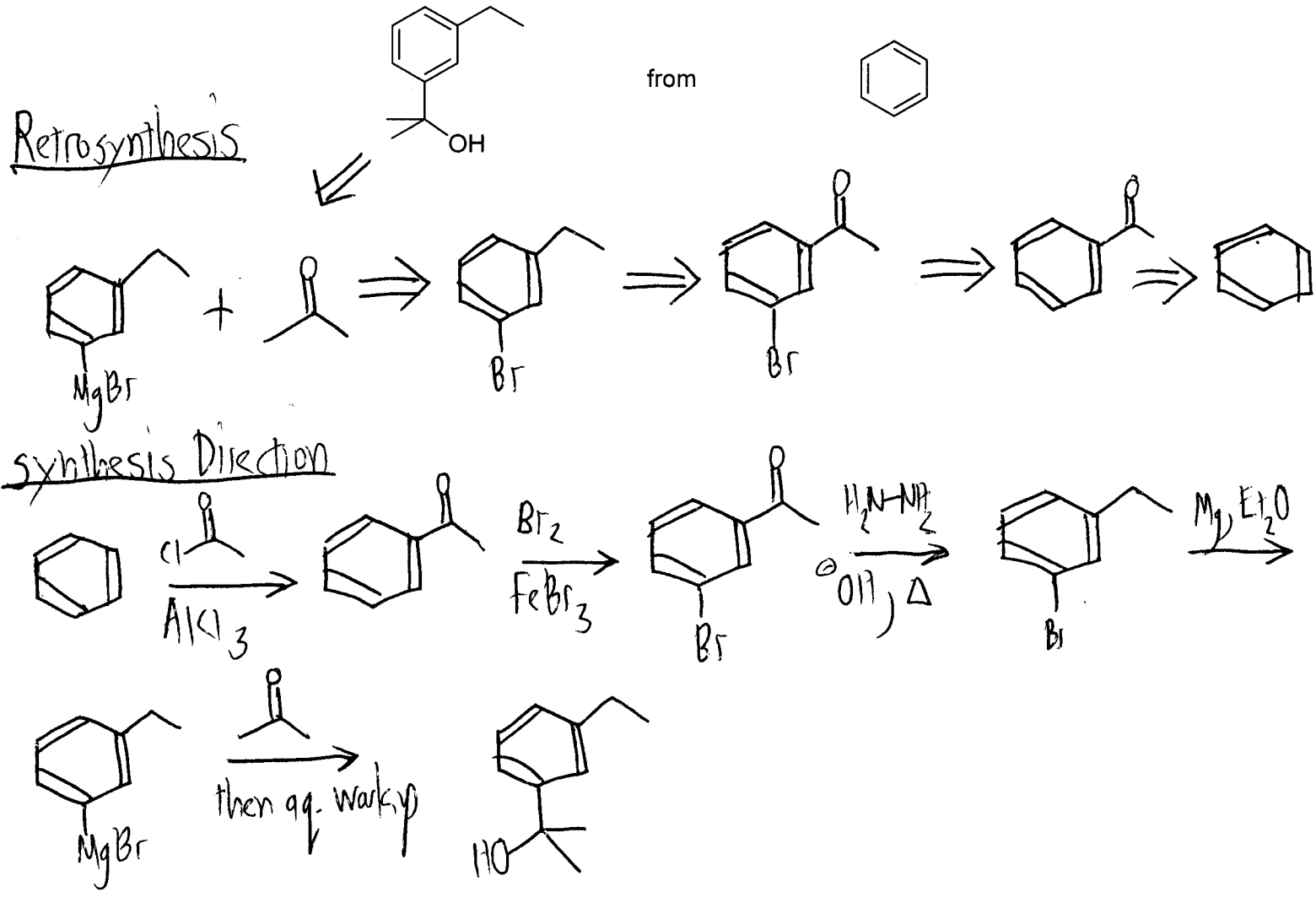




Notes:

- O.K. to show carbonyl · $AlCl_3$ adduct
- not necessary to show all cyclopentadienyl cation resonance contributors

8. Provide the most efficient synthesis. You may employ any reagents of your choice. Points will be assigned according to steps listed in the forward synthesis direction (25 points).



Note: For all future exams, the products of each reaction should be drawn as listed above