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)**.

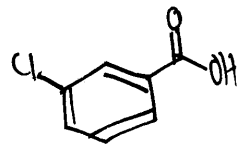
GOOD LUCK!

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

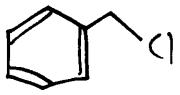
MINI-PERIODIC TABLE

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

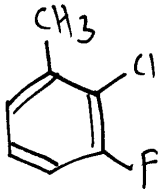
1. Provide structures for the following chemical names (8 points)



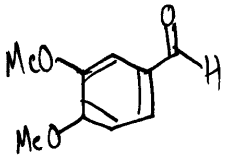
m-chlorobenzoic acid



benzyl chloride



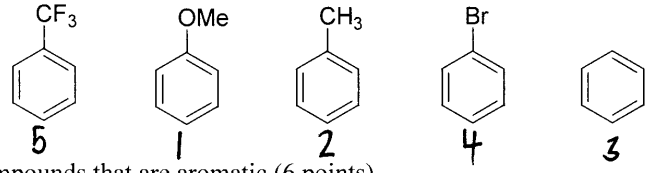
2-chloro-3-flourotoluene



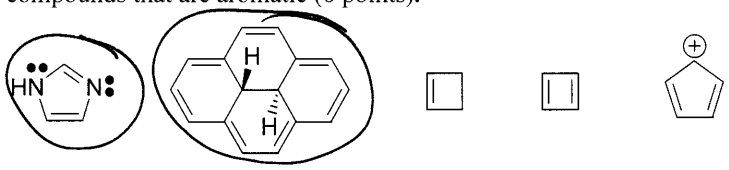
3,4-dimethoxybenzaldehyde

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

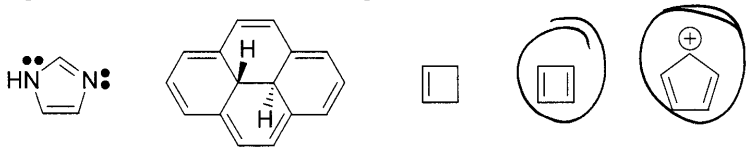
(a). Rank the compounds according to those that would react most rapidly with Br_2, $FeBr_3$ to those that would react the least rapidly [1 = **most** rapid, 5 = **least** rapid] (6 points).



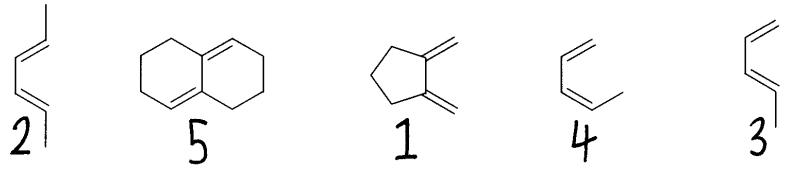
(b). Circle the compounds that are aromatic (6 points).



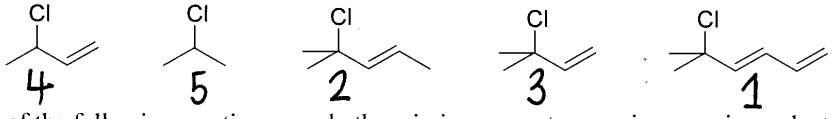
(c). Circle the compounds that are anti-aromatic (6 points).



(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).

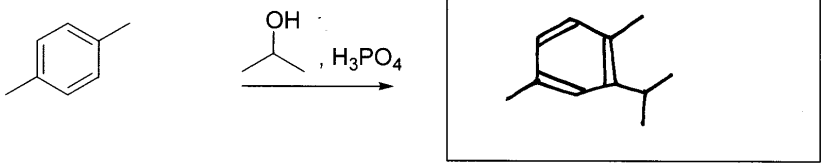


(e). Upon treatment with methanol, each of the following compounds produces methyl ether products with the rate-determining step being formation of a carbocation intermediate. Rank the compounds from 1 to 5 for rate of reaction [1 = **fastest** rate, 5 = **slowest** rate] (6 points).

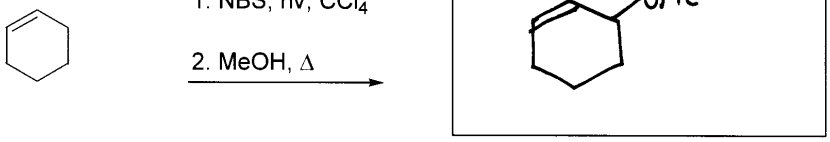


3. For each of the following reactions supply the missing reagents or major organic product in the space provided. If no reaction is expected indicate by N.R. (50 points total).

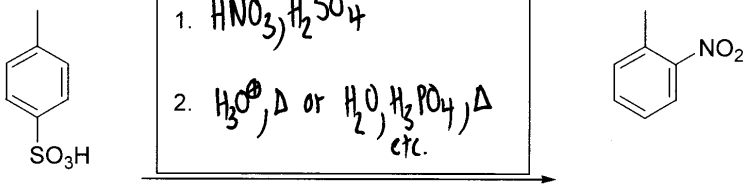
(a)



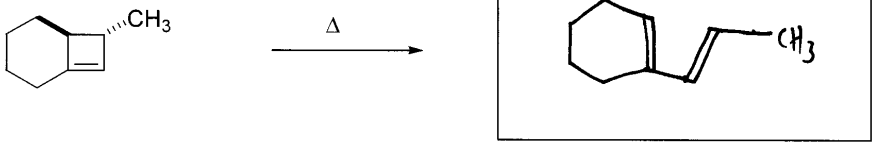
(b)

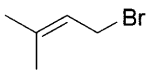


(c)



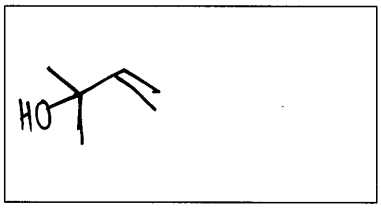
(d)

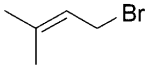


(e) 

H_2O

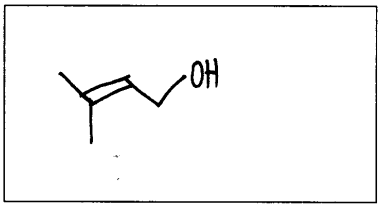
(under kinetic control, i.e., low temp)

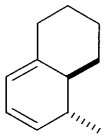


(f) 

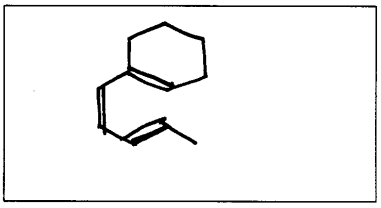
H_2O

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

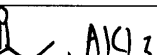


(g) 

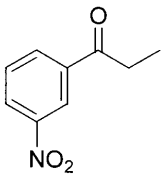
hv

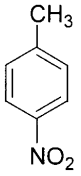


(h) 

1. 

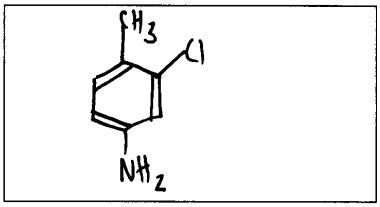
2. HNO_3, H_2SO_4

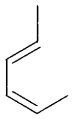


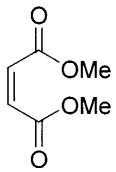
(i) 

1. Cl_2, $FeCl_3$

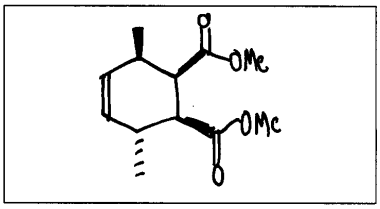
2. Fe, HCl



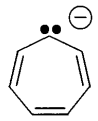
(j) 

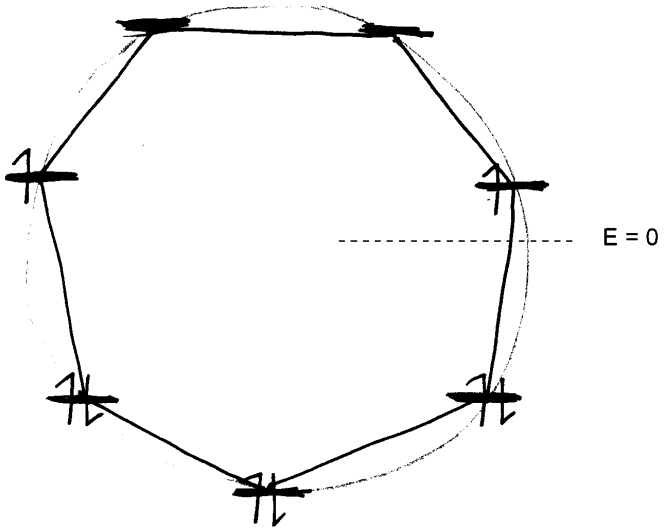
+ 

Δ



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

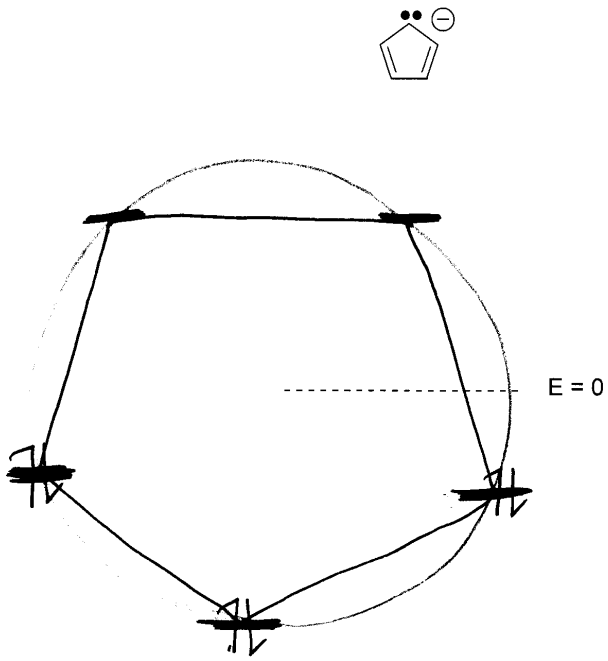




(b) Place the electrons in the appropriate molecular orbitals. Does the electron placement establish the molecule as aromatic or antiaromatic? **Briefly** explain (one sentence is all that is necessary) (5 points).

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

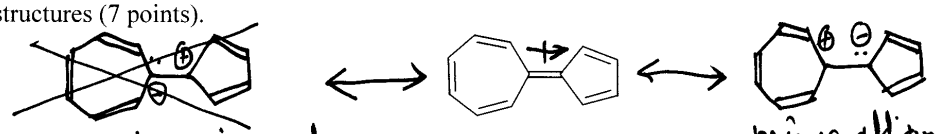
(c) Show an energy level diagram for the molecular orbitals of the cyclopentadienyl anion drawn below (10 points).



(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

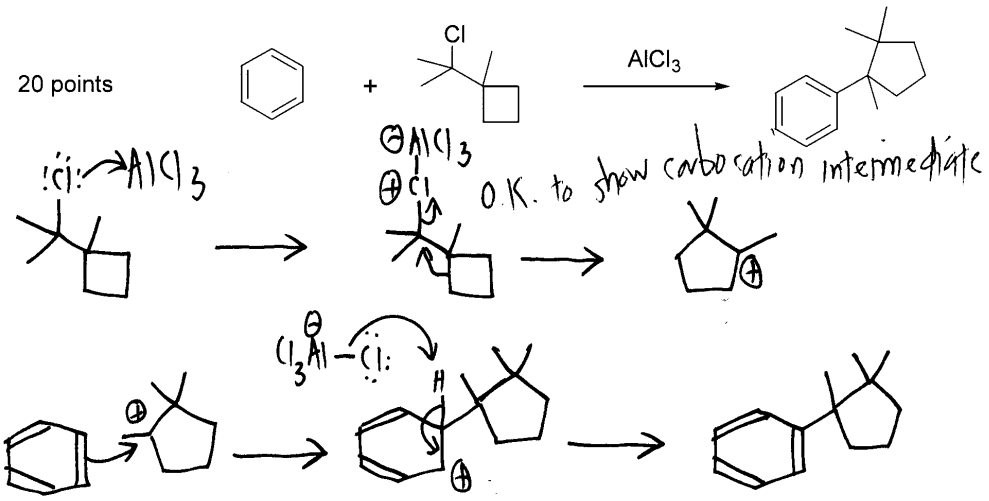
Resonance form not present

maj or. additional contributor

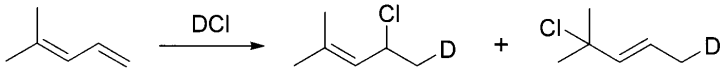
both tropylium cation and cyclopentadienyl anion are aromatic

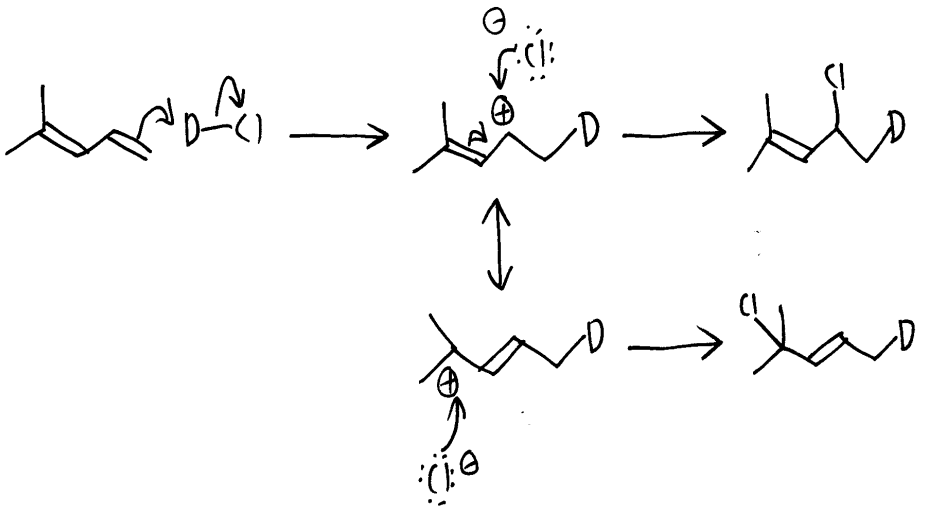
5. Provide detailed mechanisms for the following transformations (35 points).

(a) 20 points

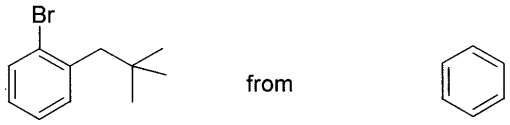


(b) 15 points

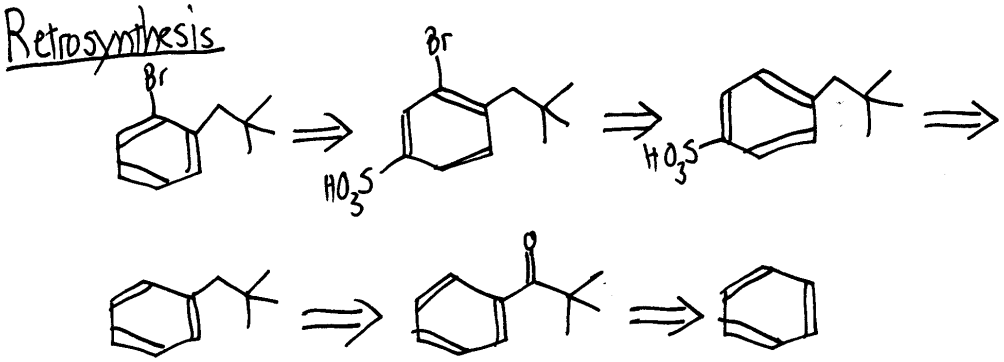




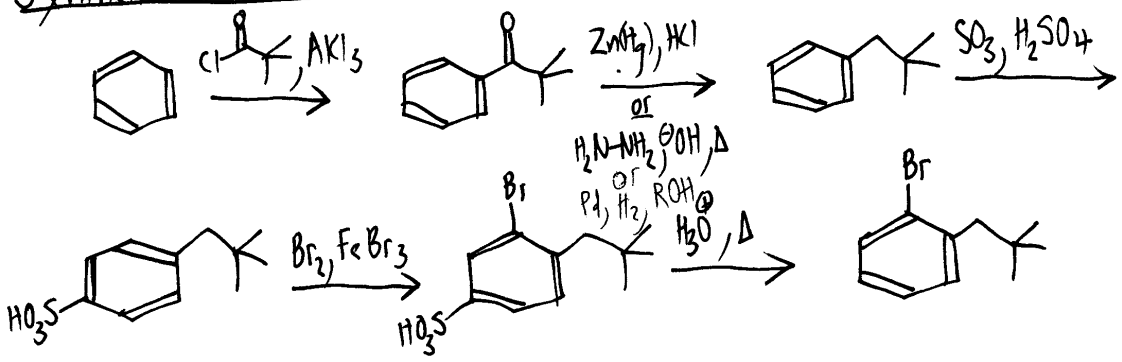
6. Provide the most efficient synthesis. You may employ any reagents of your choice (20 points).



Retrosynthesis



Synthetic direction



Chemistry 3B, Practice Midterm 1

Tuesday, October 1, 2002

Student name: Answer Key

Student signature: _____

Write TA's name or Lecture Only: _____

1. 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)**.

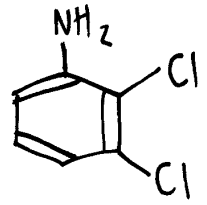
GOOD LUCK!

1.	10 points	_____
2.	30 points	_____
3.	55 points	_____
4.	30 points	_____
5.	35 points	_____
6.	20 points	_____
Total	**180 points**	_____

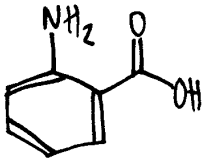
MINI-PERIODIC TABLE

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 (10 points)

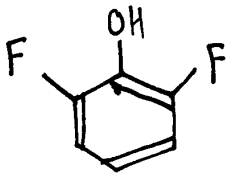


2,3-dichloroaniline

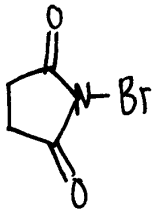


***o*-aminobenzoic acid**

2-phenylethanol



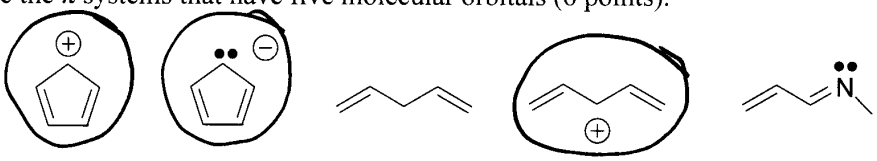
2,5-difluorophenol



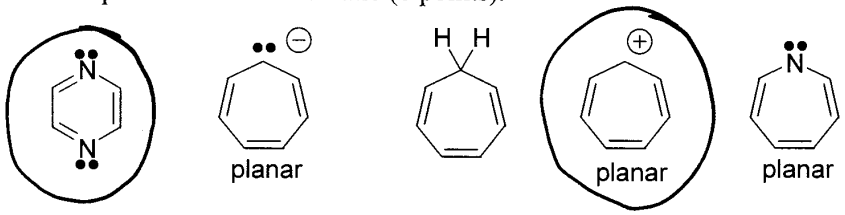
N-bromosuccinimide (NBS)

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

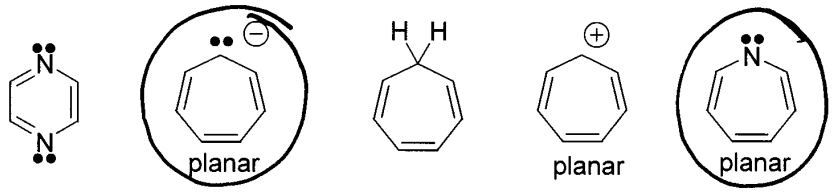
(a). Circle the π systems that have five molecular orbitals (6 points).



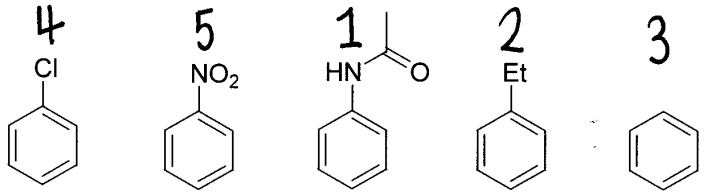
(b). Circle the compounds that are aromatic (6 points).



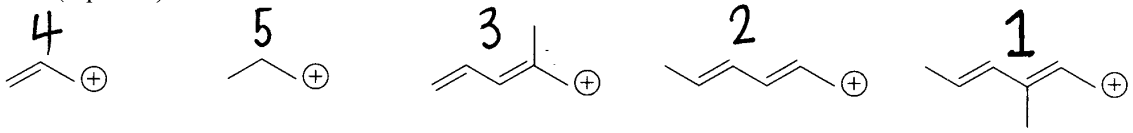
(c). Circle the compounds that are anti-aromatic (6 points).



(d). 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).

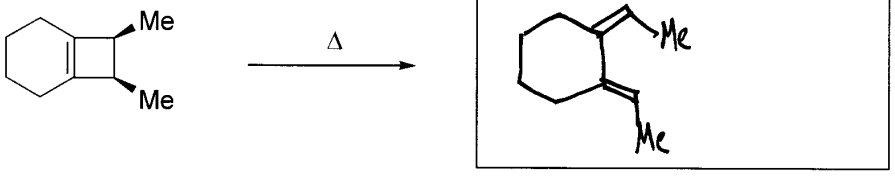


(e). Rank the following cations from most stable to least stable [1 = **most** stable, 5 = **least** stable] (6 points).



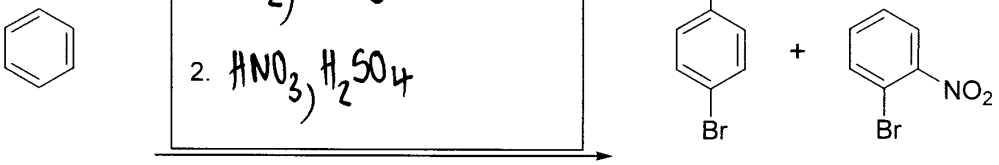
2. For each of the following reactions supply the missing reagents or major organic product in the space provided. If no reaction is expected indicate by N.R. (50 points total).

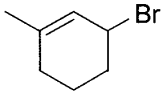
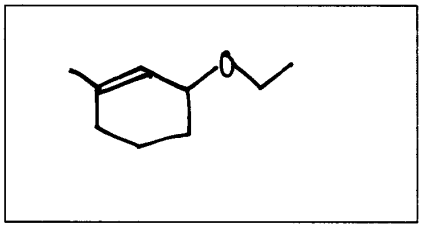
(a)

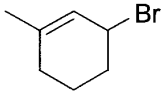
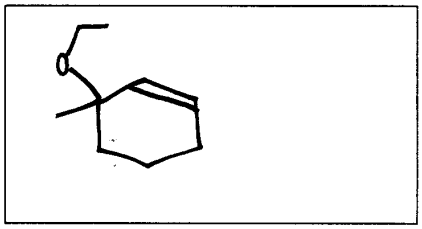


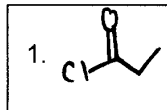
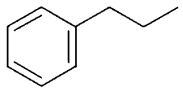
(b)

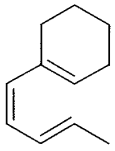
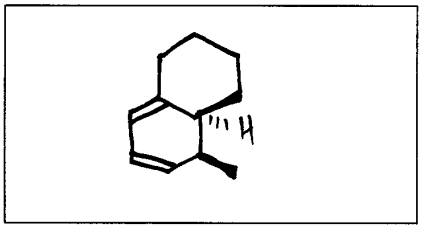
(c)

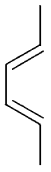
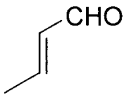
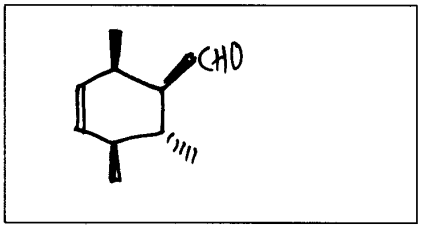


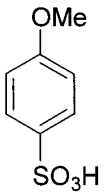
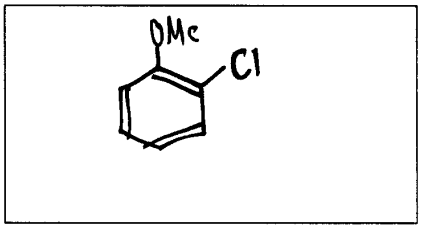
(d)  CH_3CH_2OH (under thermodynamic, control, i.e., high temp) 

(e)  CH_3CH_2OH (under kinetic control, i.e., low temp) 

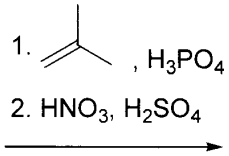
(f)  1.  2. $Zn(Hg)$, HCl or H_2N-NH_2, $\ominus OH$, Δ 

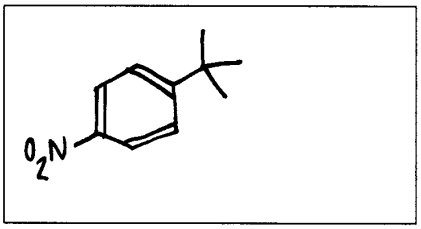
(g)  Δ 

(h)  +  Δ 

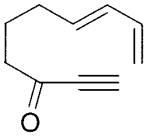
(i)  1. Cl_2, $FeCl_3$ 2. H_3O+, Δ 

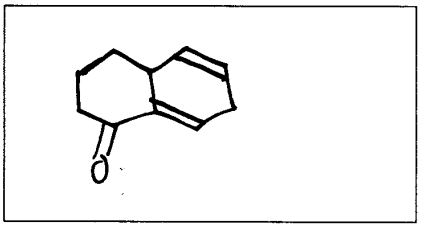
(j)



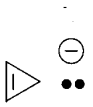


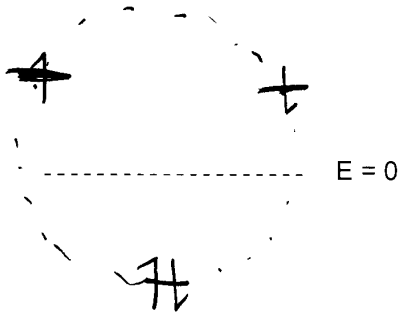
(k)





3. 30 points total.
(a) Show an energy level diagram for the molecular orbitals of the cyclopropenyl anion drawn below (10 points).

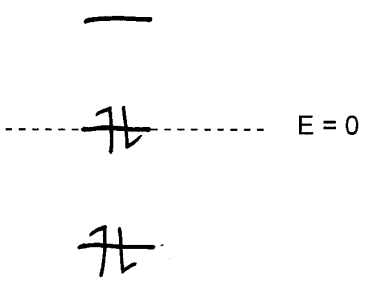




(b) Place the electrons in the appropriate molecular orbitals. Does the electron placement establish that the molecule as aromatic or antiaromatic. **Briefly** explain your answer (5 points).

AntiAromatic. The cmpd has unpaired electrons in antibonding orbitals.

(c) Show the energy level diagram for the molecular orbitals for **allyl anion** (10 points).



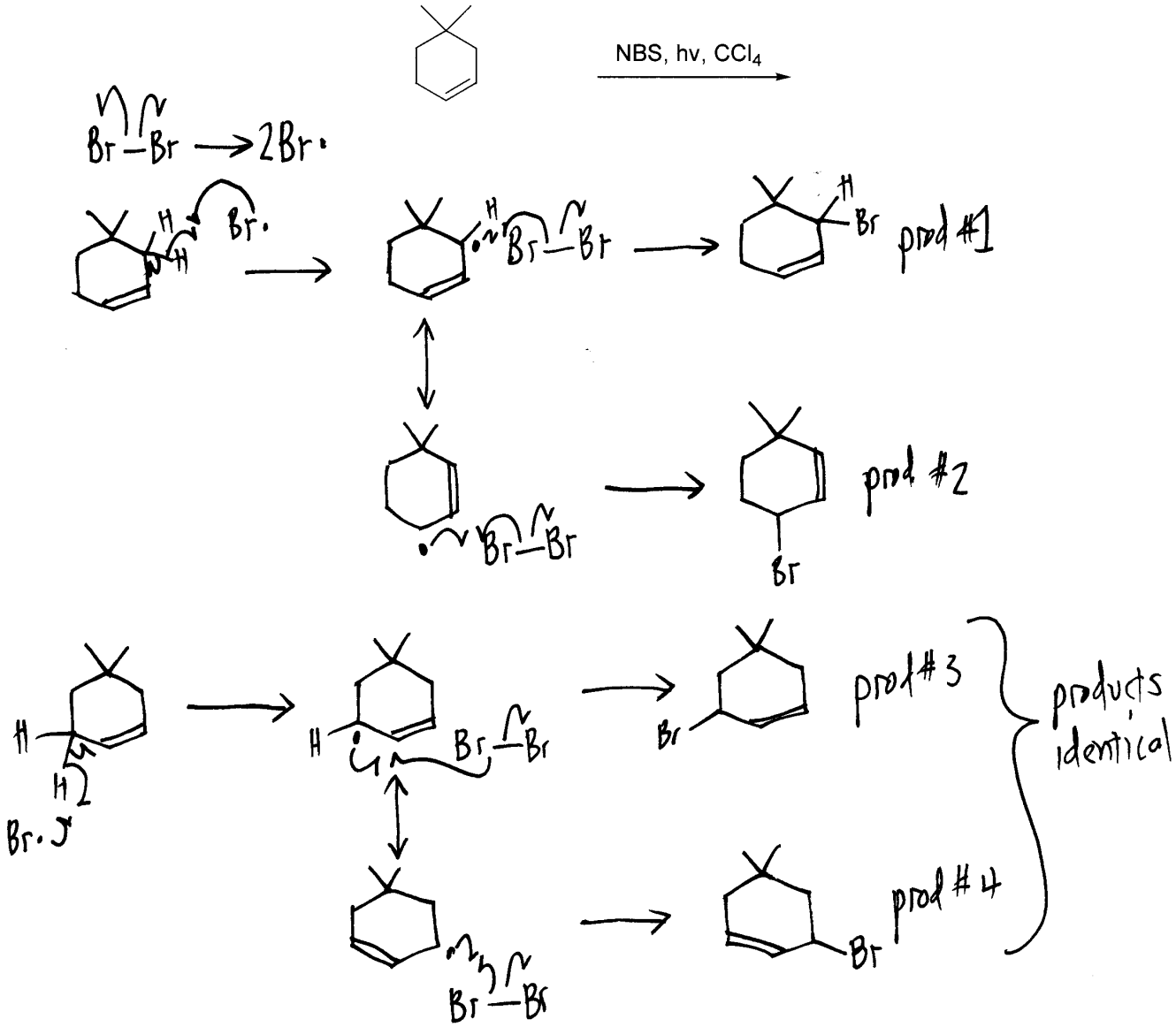
(d) Place the electrons in the appropriate molecular orbitals. Is allyl anion more stable or less stable than cyclopropenyl anion? **Briefly** explain your answer (5 points).

More stable. Allyl anion has no unpaired $e^{\ominus}$ while the cyclopropenyl anion has two. Allyl anion has $2e^{\ominus}$ in nonbonding orbital, but " " has $2e^{\ominus}$ in antibonding orbital.

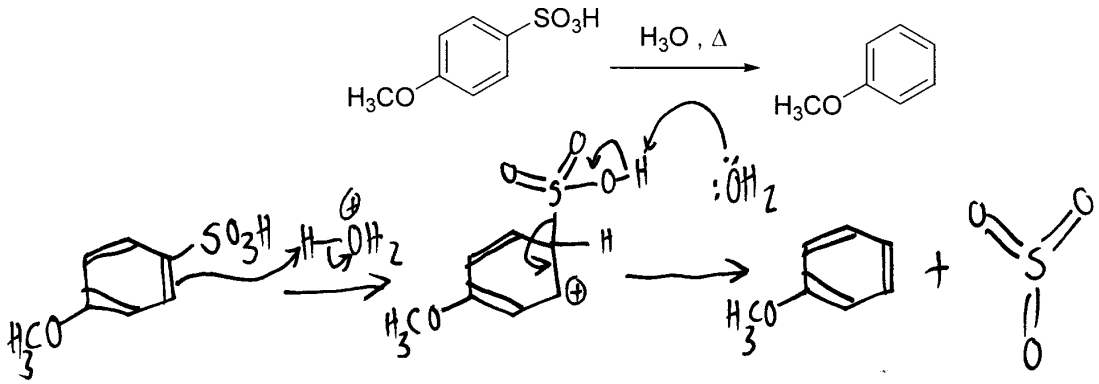
4. Provide a detailed mechanism for the following transformations (35 points).

(a) Provide all of the monobromination products for this transformation.

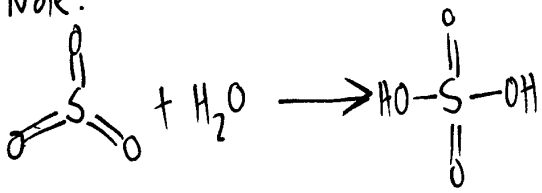
Note: Because NBS is solely used to generate low concentrations of Br_2 you may simply use Br_2 in your reaction mechanism (20 points).



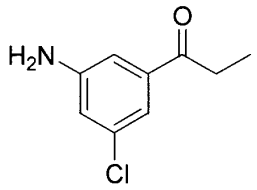
(b) (15 points).



Note:

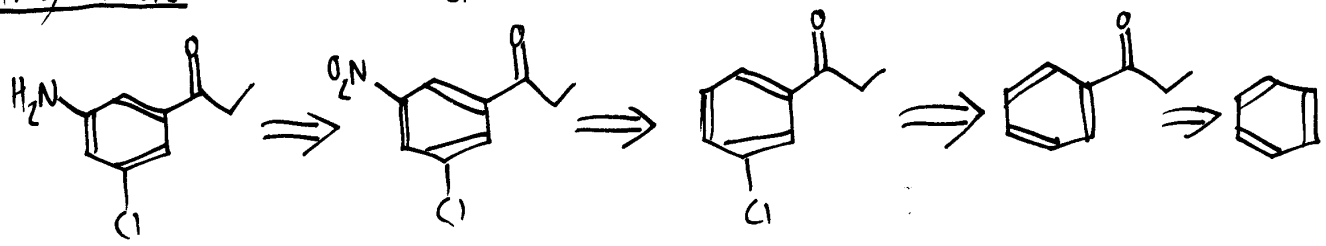


5. Provide the most efficient synthesis. You may employ any reagents of your choice (20 points).

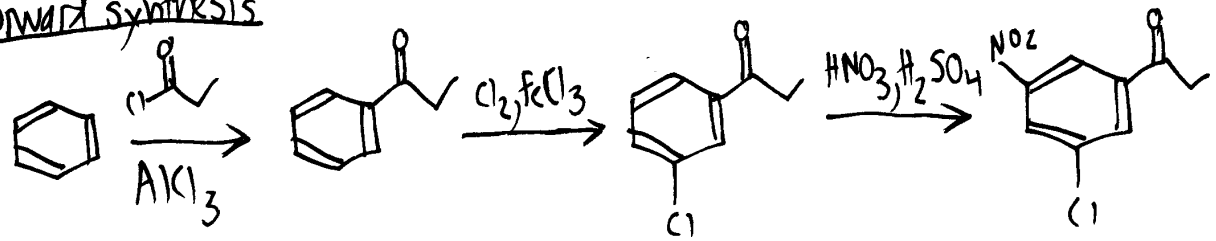


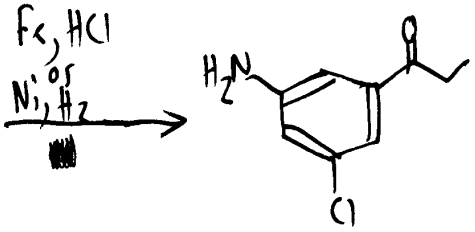
from 

Retrosynthesis



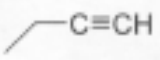
Forward synthesis

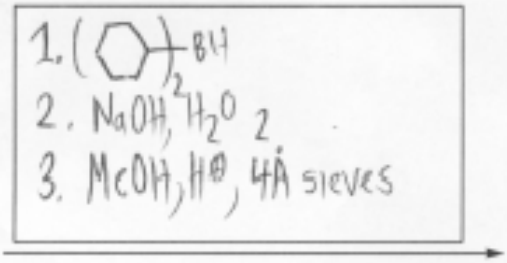


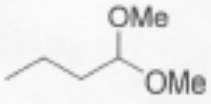


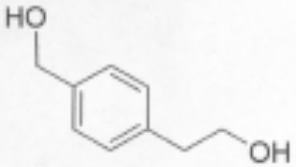
Chemistry 3B, Extra Practice Problems

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.

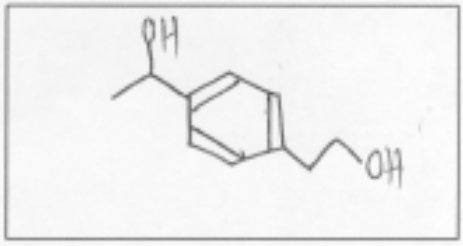
(a) 





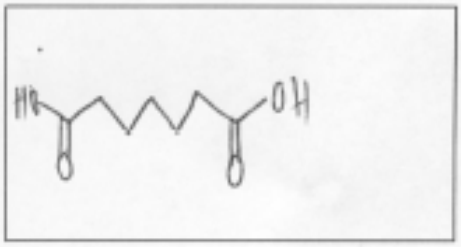
(b) 

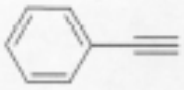
1. MnO_2
2. MeLi (xs)
3. aq. workup

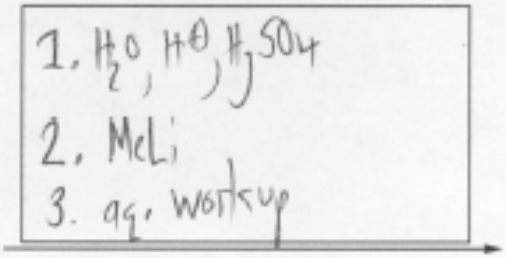


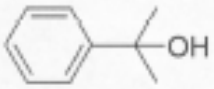
(c) 

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



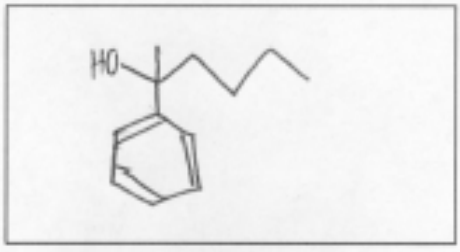
(d) 

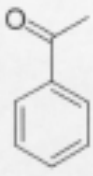




(e) 

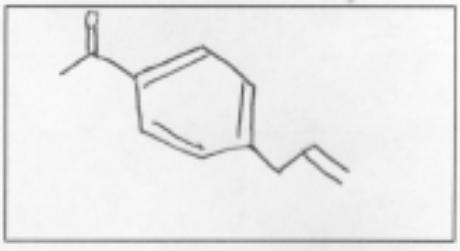
1. BuLi
2. aq. workup
3. PCC



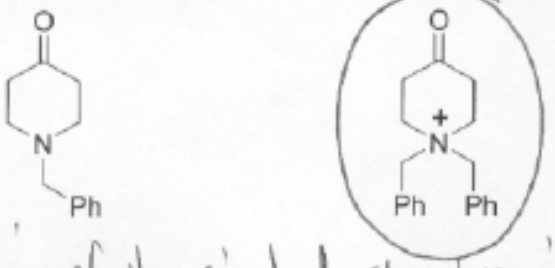
(f) 

1. H+, MeOH, sieves
2. Mg, Et_2O
3. 

4. H+, H_2O

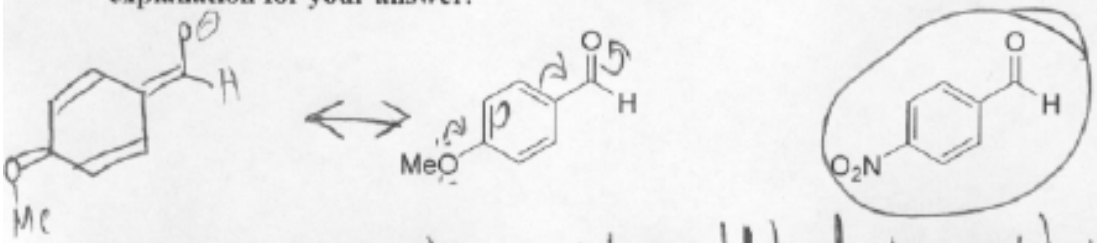


2 (a) The molecules drawn below are key building blocks in the synthesis of many psychoactive drugs. Circle the compound that would have the **largest** K_{eq} for hydrate formation. **Provide a brief explanation for your answer.**



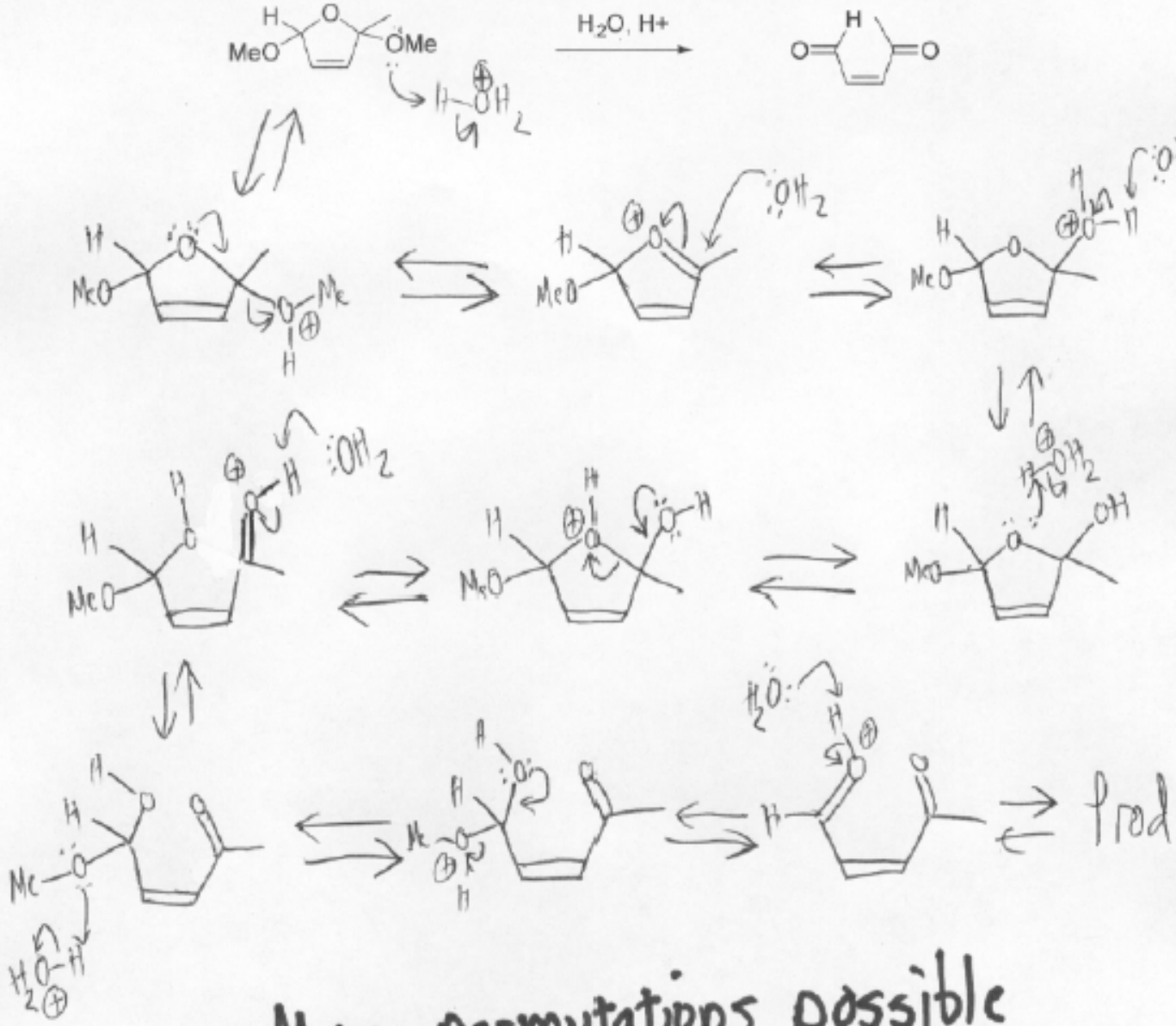
Resonance stabilization of the circled structure is minimized due to the inductive effect that results from the positively charged nitrogen.

(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