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!

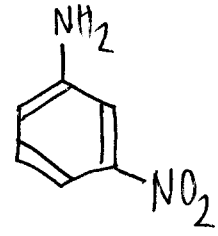
1.	8 points	_____
2.	30 points	_____
3.	50 points	_____
4.	17 points	_____
5.	10 points	_____
6.	20 points	_____
7.	20 points	_____
8.	25 points	_____
Total	**180 points**	_____

MINI-PERIODIC TABLE

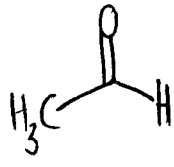
I	II	III	IV	V	VI	VII	VIII
H							**He**
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**

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

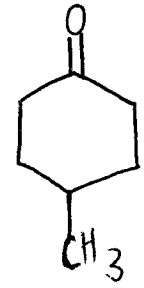
p-chlorophenol



3-nitroaniline



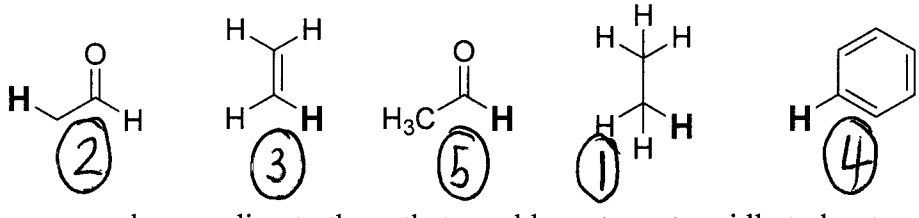
acetaldehyde



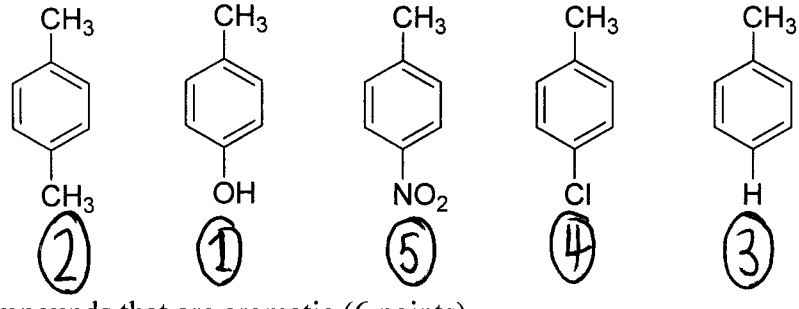
4-methylcyclohexanone

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

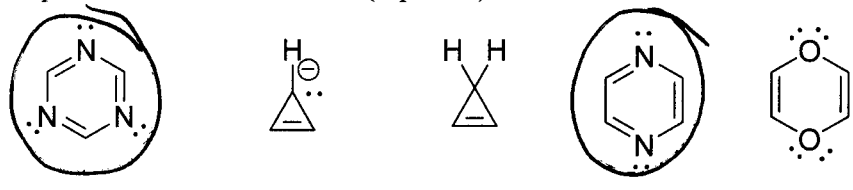
(a). Rank the **bold** hydrogens, that in an ^1H NMR spectra would be most shielded (**smallest** ppm) to most deshielded (**largest** ppm) [1 = most **shielded**, 5 = most **deshielded**] (6 points).



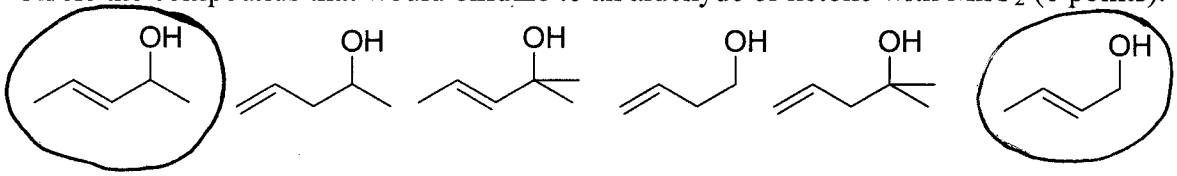
(b). Rank the compounds according to those that would react most rapidly to least rapidly with Cl_2, $FeCl_3$ [1 = **most**, 5 = **least**] (6 points).



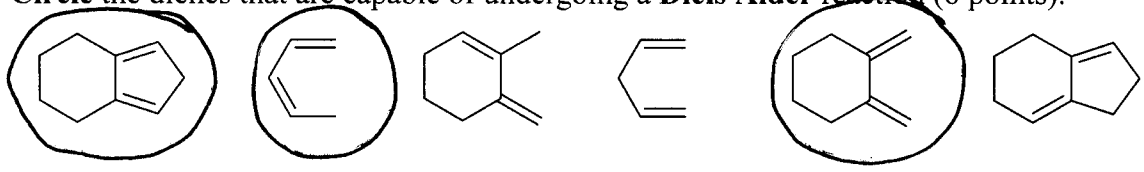
(c). **Circle** the compounds that are aromatic (6 points).



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

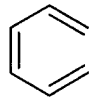


(e). **Circle** the dienes that are capable of undergoing a **Diels Alder** reaction (6 points).



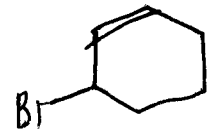
3. For each of the following reactions supply the missing reagents or major organic product in the space provided. If no reaction is expected indicate by N.R. (50 points total).

(a)

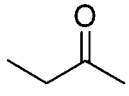


1. hν
2. HBr

→

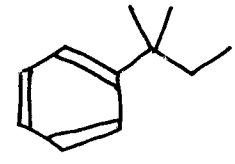


(b)

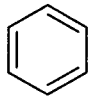


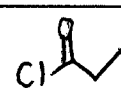
1. MeMgBr
2. aqueous workup
3. H_2SO_4, benzene (xs)

→

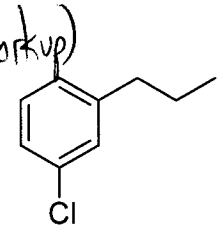


(c)

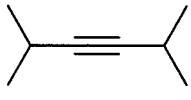


1.  , $AlCl_3$ (O.K to have aq. workup)
2. Cl_2, $FeCl_3$
3. H_2N-NH_2, $^{\ominus}OH$, Δ or Zn(Hg), HCl, Δ

→

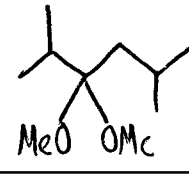


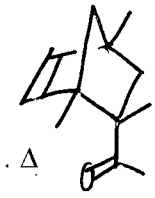
(d)



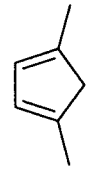
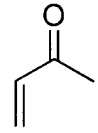
1. H_2O, H+, $HgSO_4$
2. MeOH, H+, sieves

→

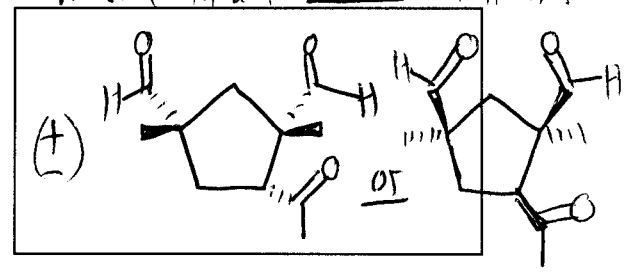


Via  (endo)

Note: could draw either enantiomer

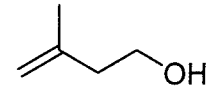
(e)  + 

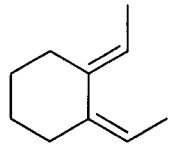
1. Δ
2. O_3
3. Zn, AcOH



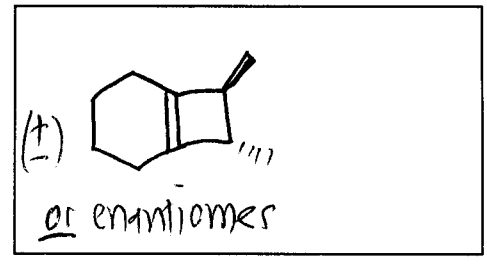
(f) 

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

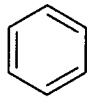


(g) 

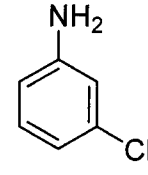
hν

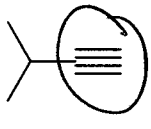


or enantiomers

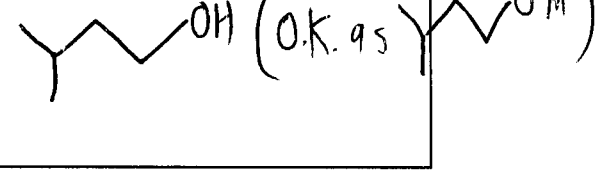
(h) 

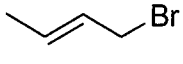
1. HNO_3, H_2SO_4
2. Cl_2, $FeCl_3$
3. Fe, HCl or other redn methods



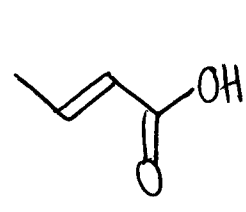
(i) 

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

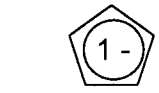


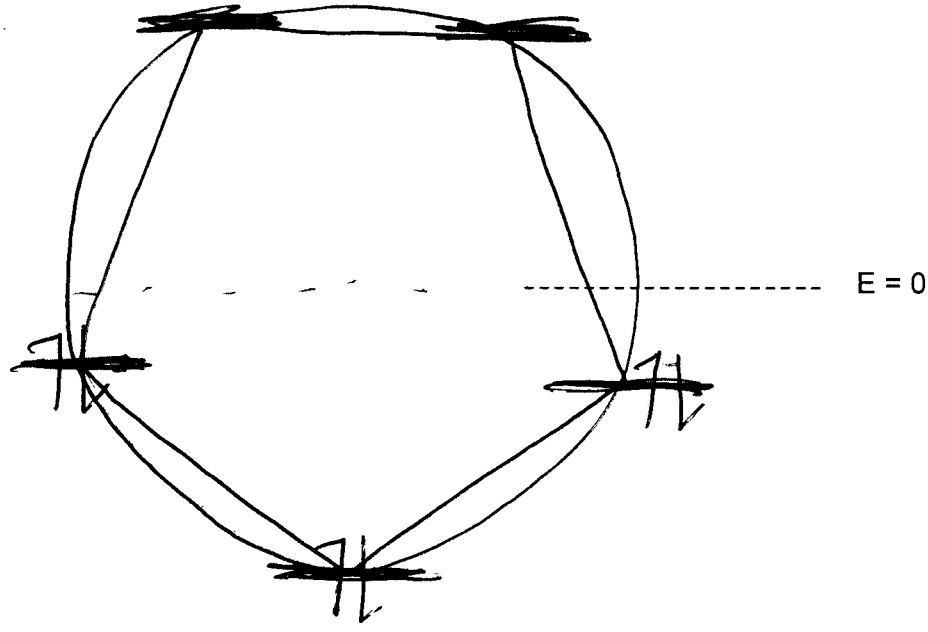
(j) 

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).

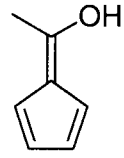




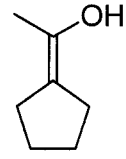
(b) Place the electrons for the **anion** in the appropriate molecular orbitals. Does the electron placement establish the molecule as aromatic or antiaromatic? **Briefly** explain (one sentence is all that is necessary) (5 points).

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).

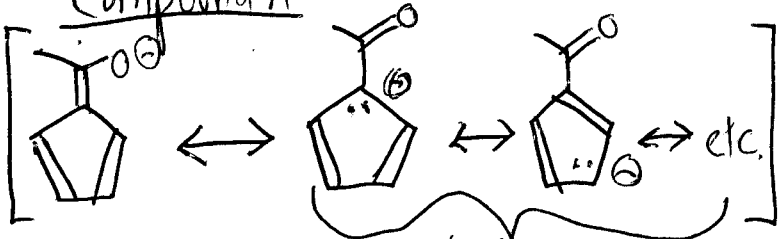


Compound A



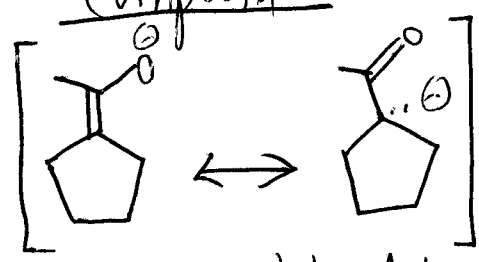
Compound B

Compound A



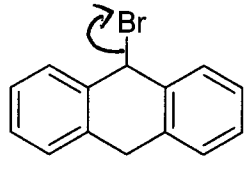
aromatic ($6e^{\ominus}$) π-system stabilized

Compound B

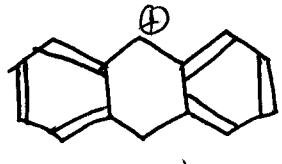


resonance stabilized but not with aromatic system

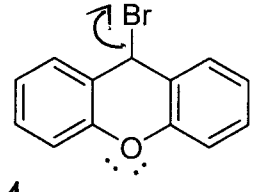
5. **Circle** the compound below that upon heating in water **more** rapidly undergoes an S_N1 reaction to give an alcohol. Briefly explain why the compound you circled undergoes the more rapid S_N1 reaction (10 points).



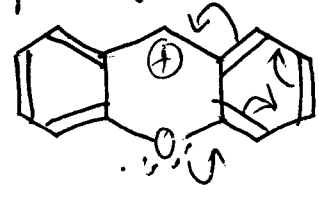
step 1 of S_N1 rxn

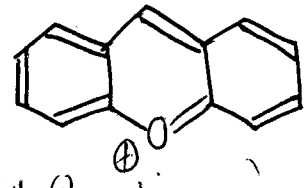


resonance stabilized cation



step 1

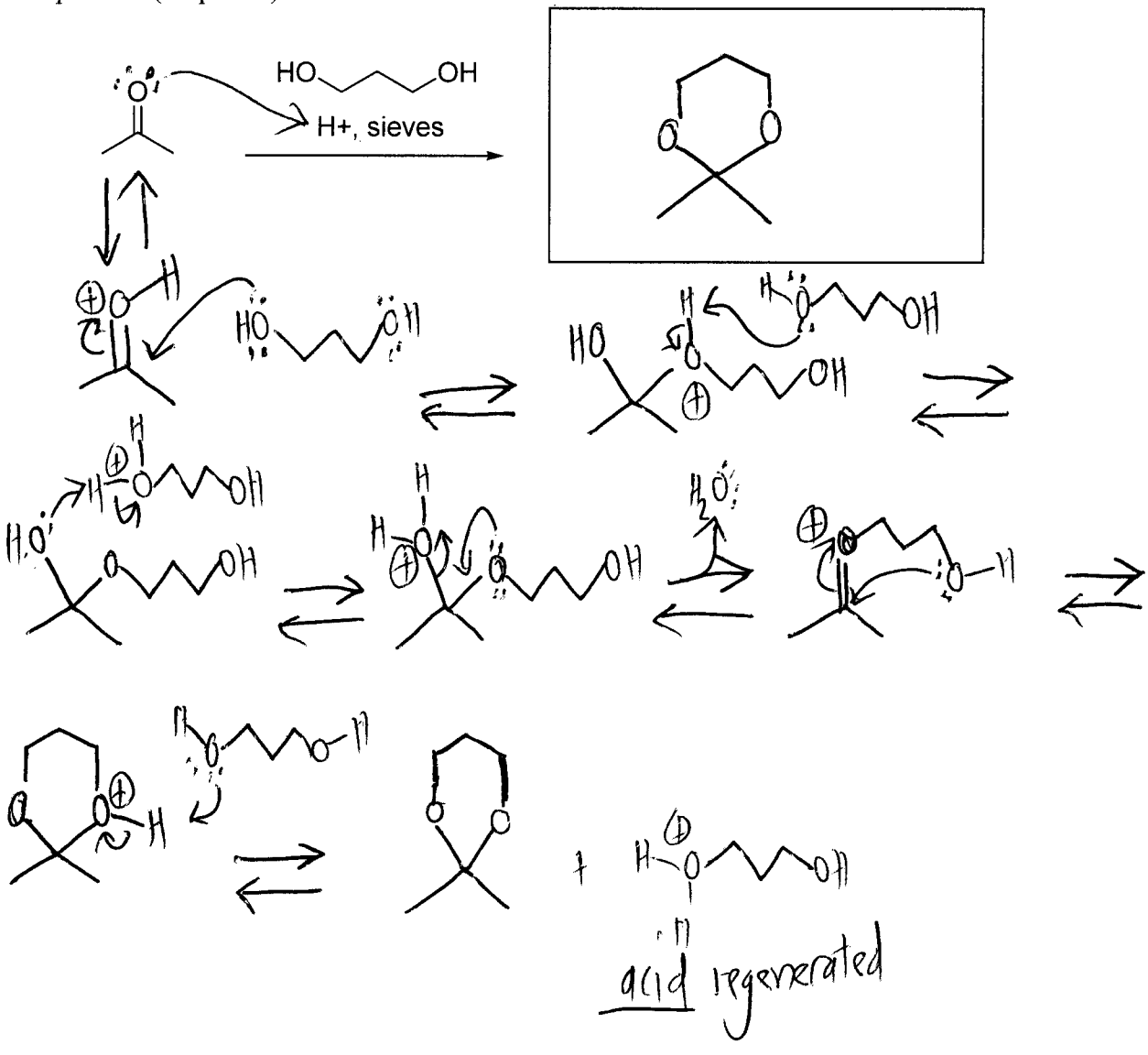




$14e^{\ominus}$ cyclic conjugated π-system

cation is aromatic so forms more easily

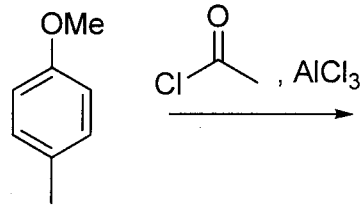
6. Provide the product of the below transformation. Provide a detailed mechanism for the formation of the product (20 points).

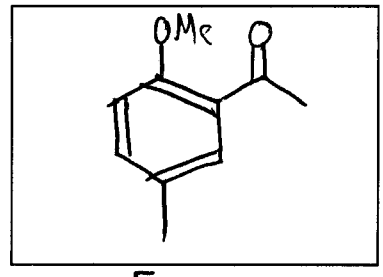


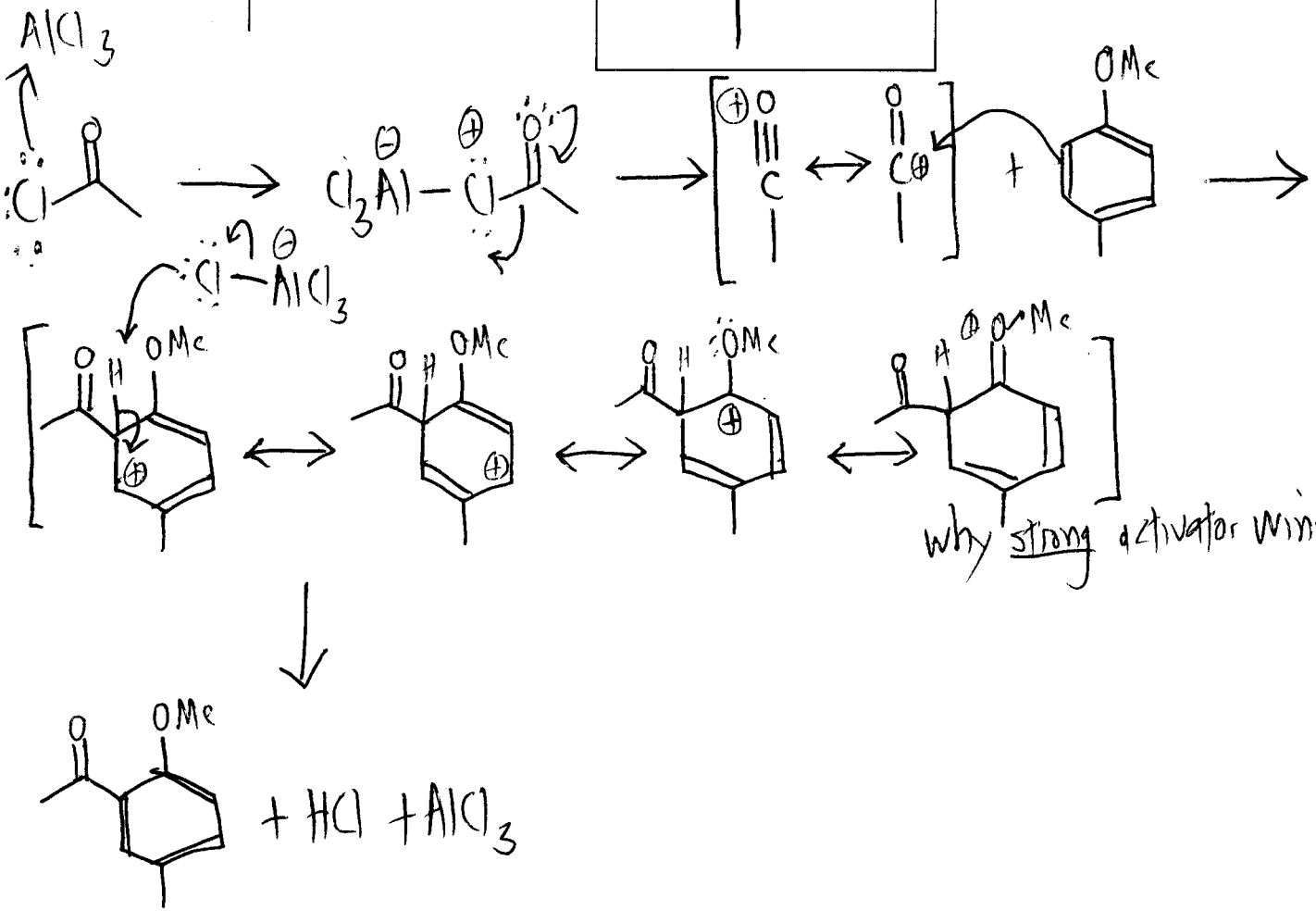
Notes:

- 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).



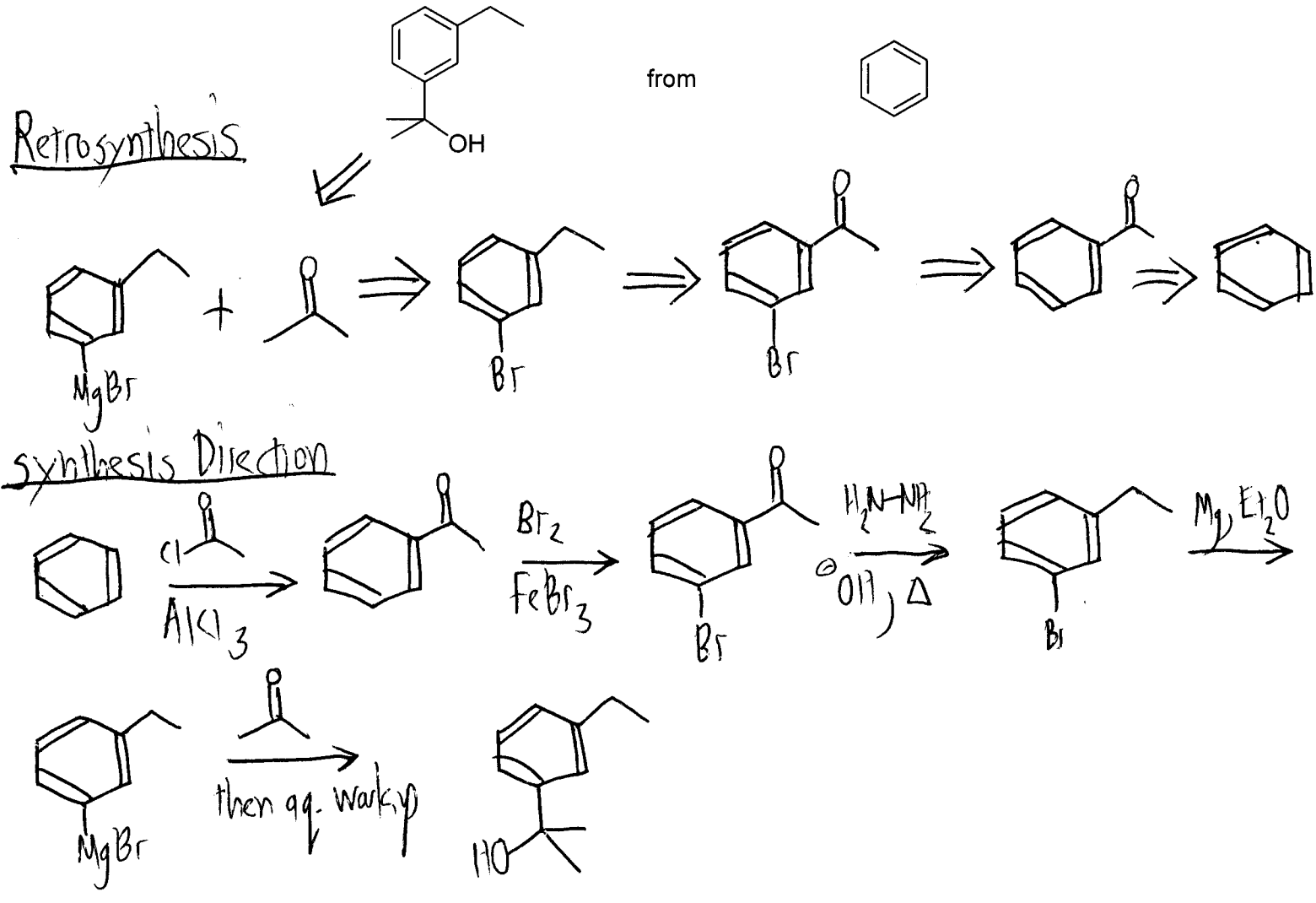




Notes:

- 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