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)**.

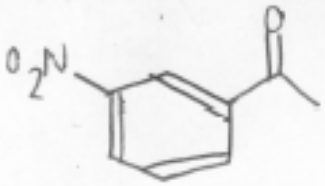
GOOD LUCK!

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**	_____

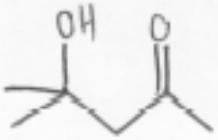
MINI-PERIODIC TABLE

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

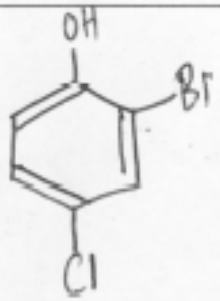
1. Provide structures for the following chemical names (8 points)



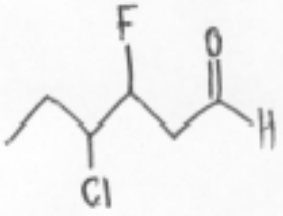
***m*-nitroacetophenone**



4-hydroxy-4-methyl-2-pentanone



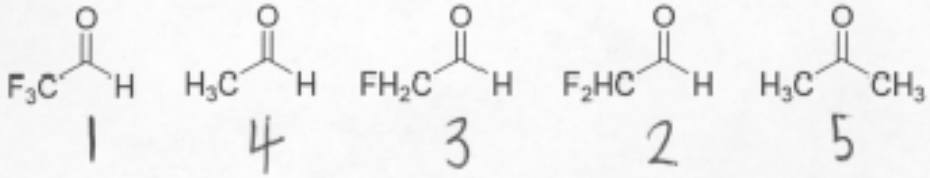
2-bromo-4-chlorophenol



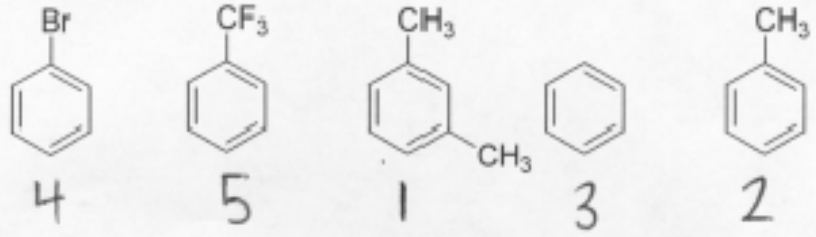
4-chloro-3-fluorohexanal

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

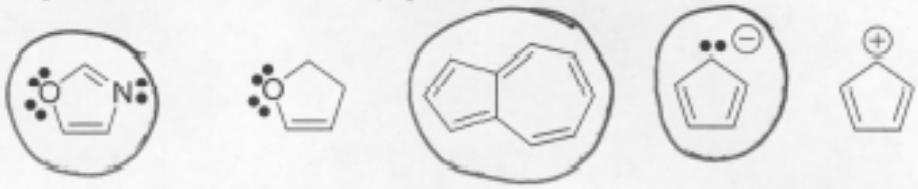
(a). Rank the compounds according to those that would most favor to least favor hydrate formation [1 = **most**, 5 = **least**] (6 points).



(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).

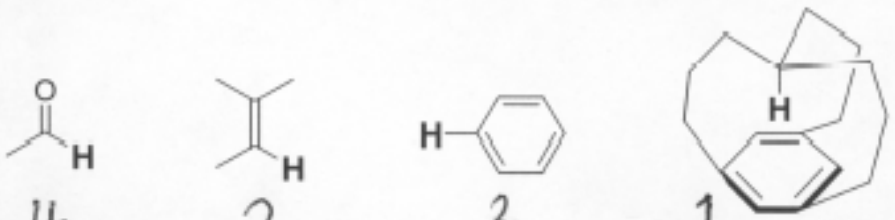


(c). Circle the compounds that are aromatic (6 points).



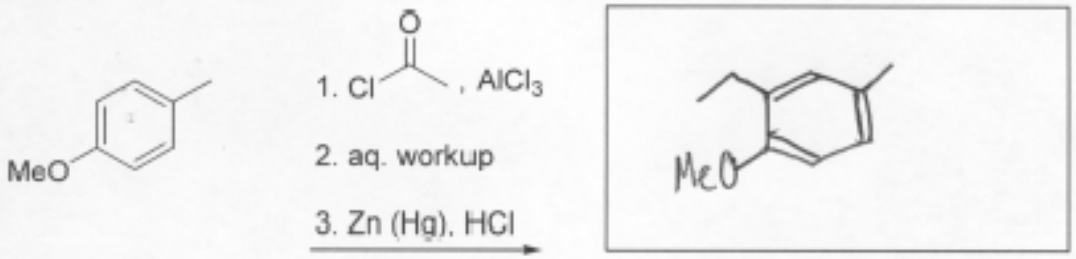
(d). **Circle** the compounds for which a thermal electrocyclic reaction would provide a **more** stable compound (6 points).

(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).

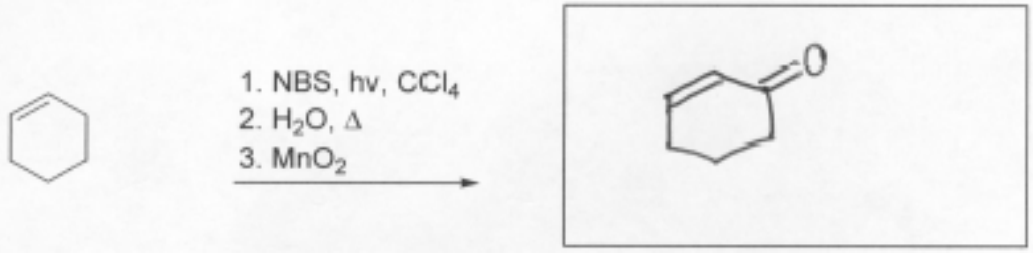


3. For each of the following reactions supply the missing reagents or major organic product in the space provided. If no reaction is expected indicate by N.R. (50 points total).

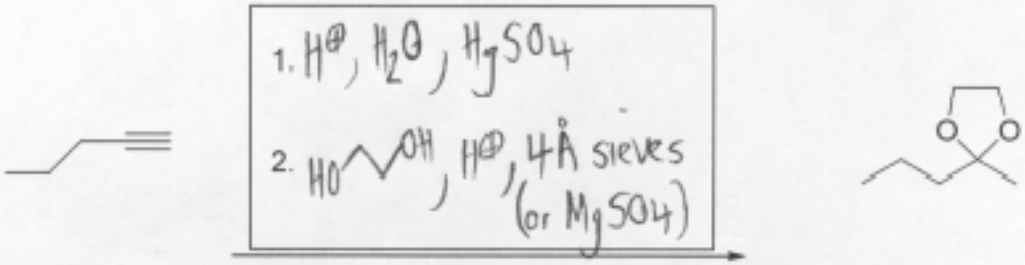
(a)



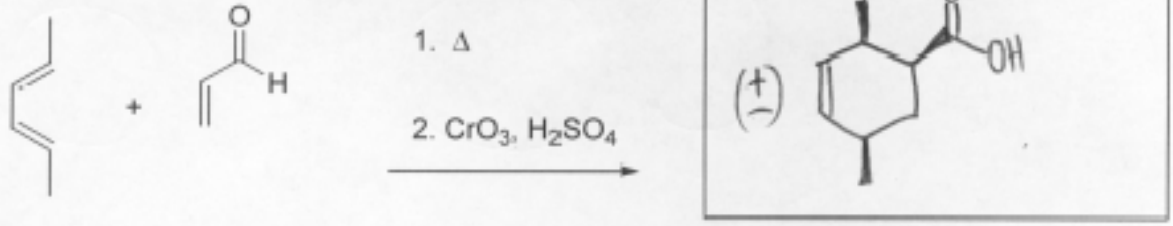
(b)

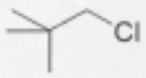


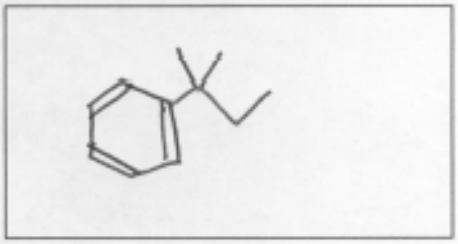
(c)



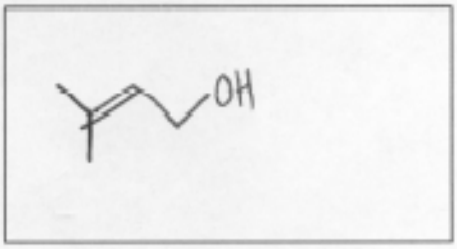
(d)

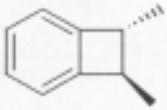
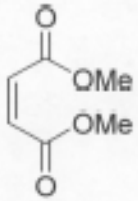


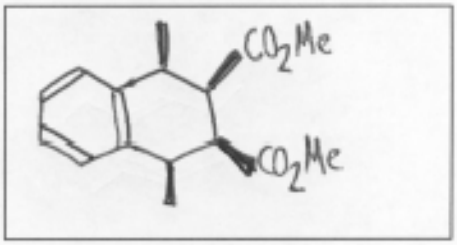
(e) 

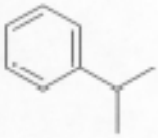
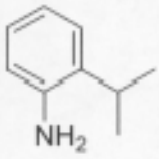
benzene (excess), $AlCl_3$ → 

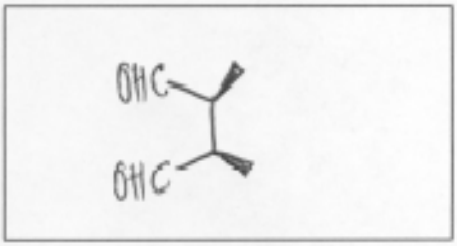
(f) 

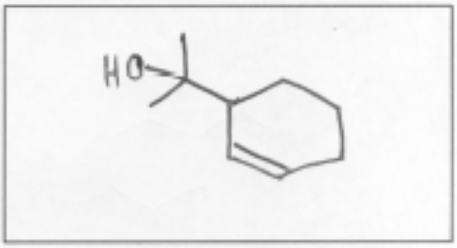
H_2O → (under thermodynamic control) 

(g)  + 

Δ → 

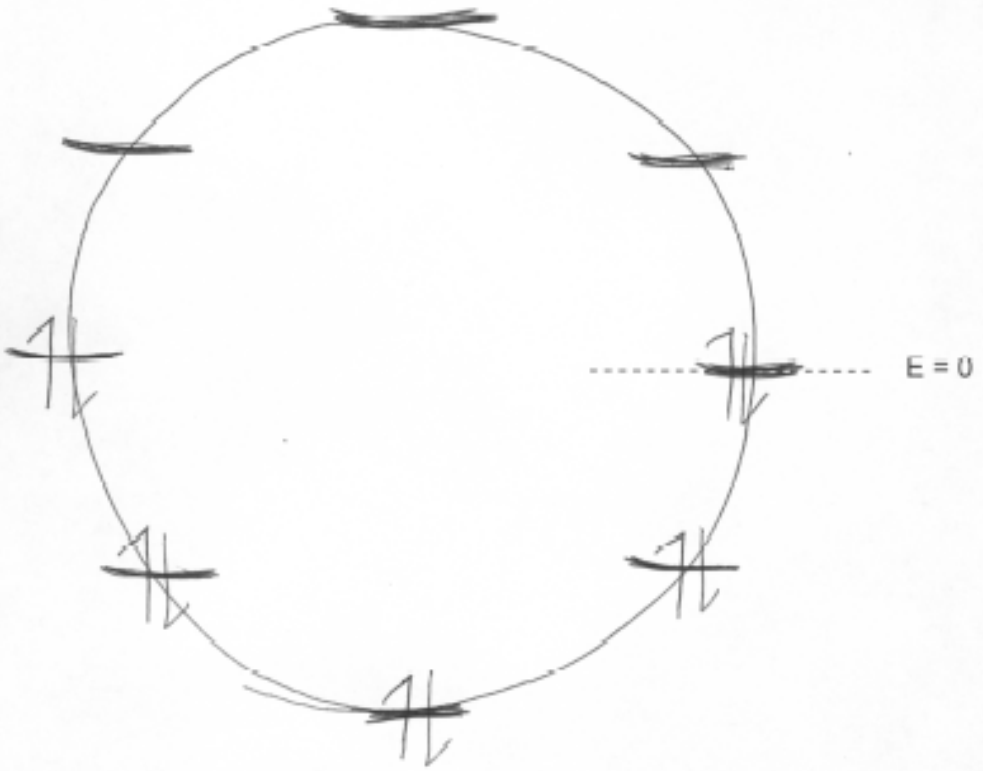
(h) 
1. SO_3, H_2SO_4
2. HNO_3, H_2SO_4
3. $HO^{\ominus}$, H_2O
4. $Zn(Hg)$, HCl or Fe, HCl
→ 

(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).



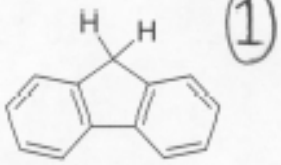
(b) Place the electrons for the **dianion** in the appropriate molecular orbitals. Does the electron placement establish the molecule as aromatic or antiaromatic? **Briefly** explain (one sentence is all that is necessary) (5 points).

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

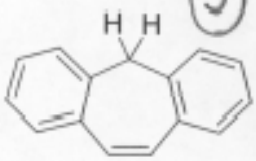
(c) Cyclooctatetraene and cyclooctatetraene dianion have very different conformations. Specifically, one is planar and the other is not. Which of the two compounds is planar? **Briefly** explain (5 points).

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.

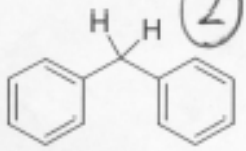
5. Rank the compounds listed below from most acidic to least acidic [1 = **most** acidic, 3 = **least** acidic]. Briefly explain your ranking (12 points).



1



3

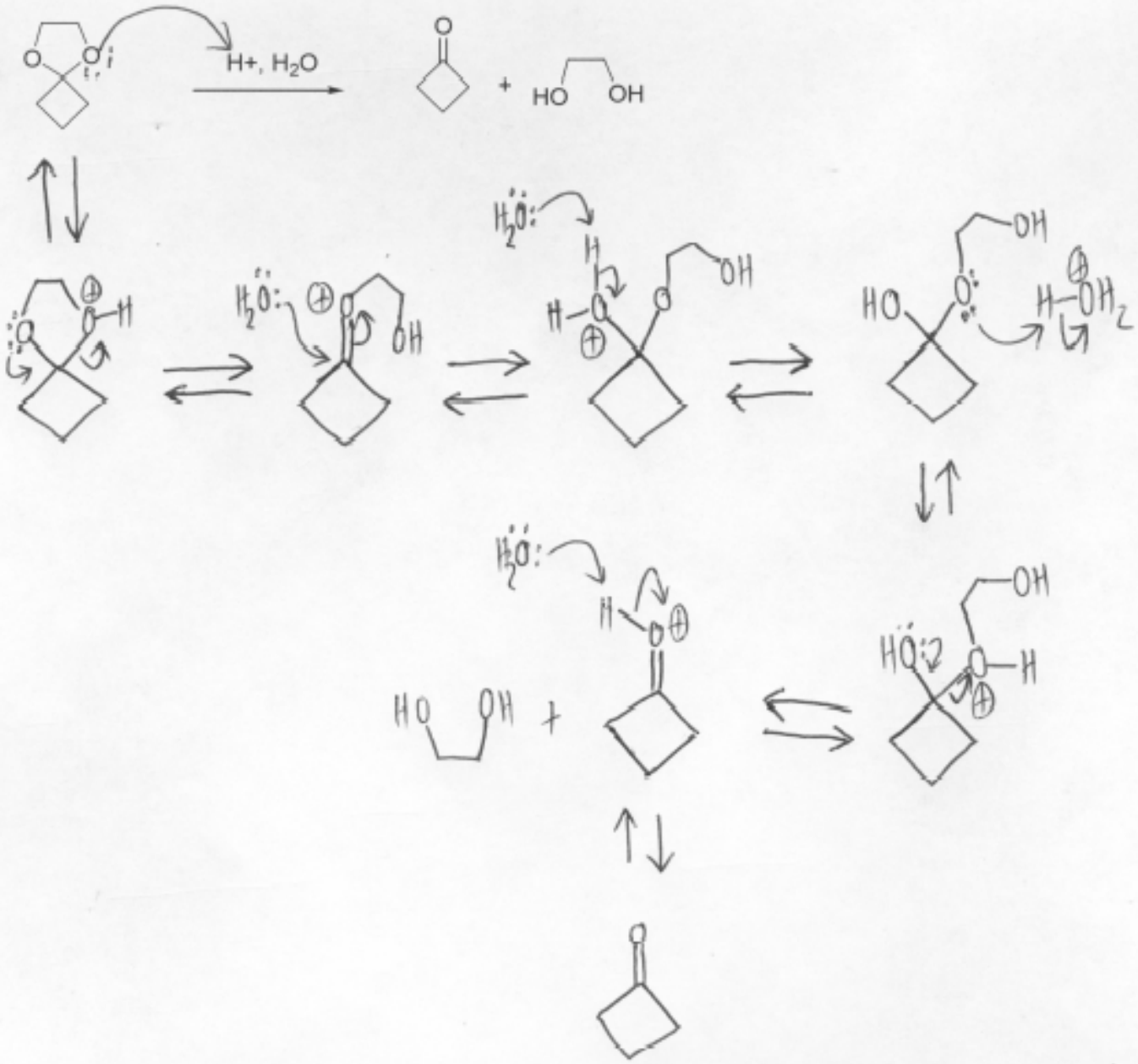


2

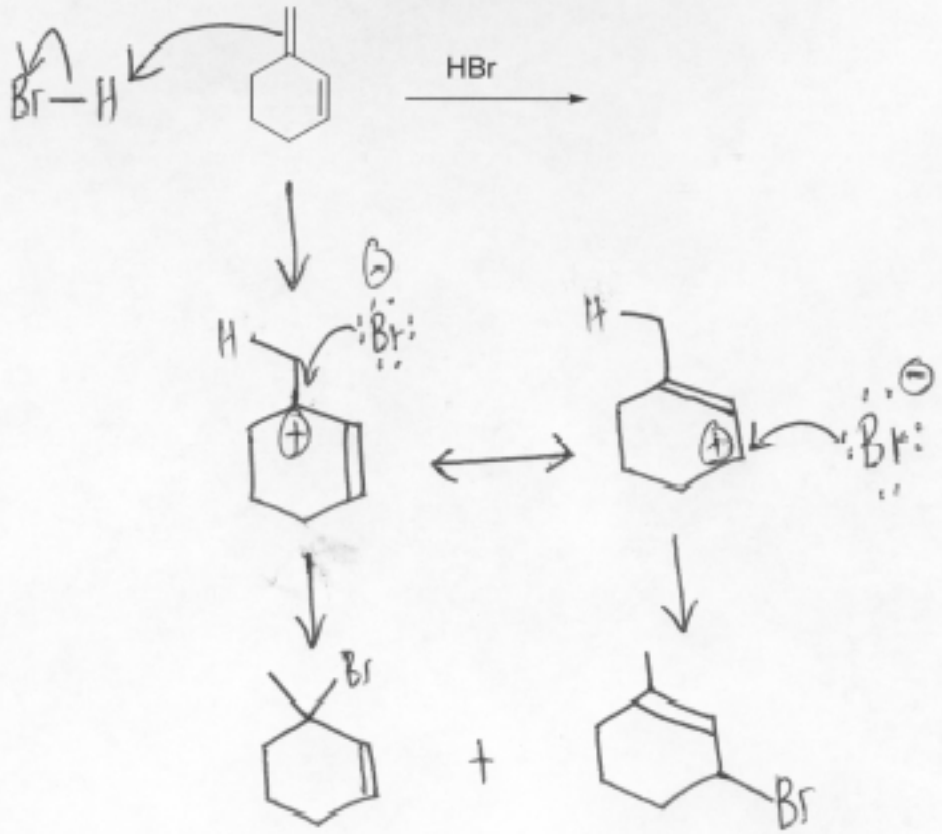
Note that the highly acidic nature of one these compounds is the basis of the most popular protecting group for the chemical synthesis of peptides and proteins.

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.

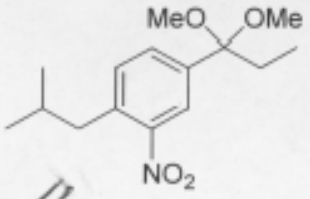
6. The cyclic acetal derived from ethylene glycol is extensively used as a protecting group. Provide a mechanism for its hydrolysis shown below (20 points).



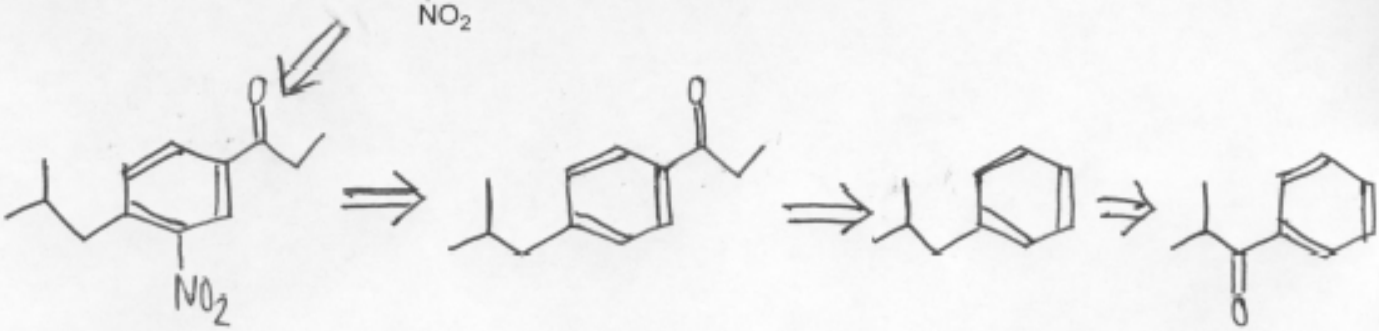
7. Draw the **two** major products of the below reaction. Provide the mechanism by which these products are obtained (15 points).



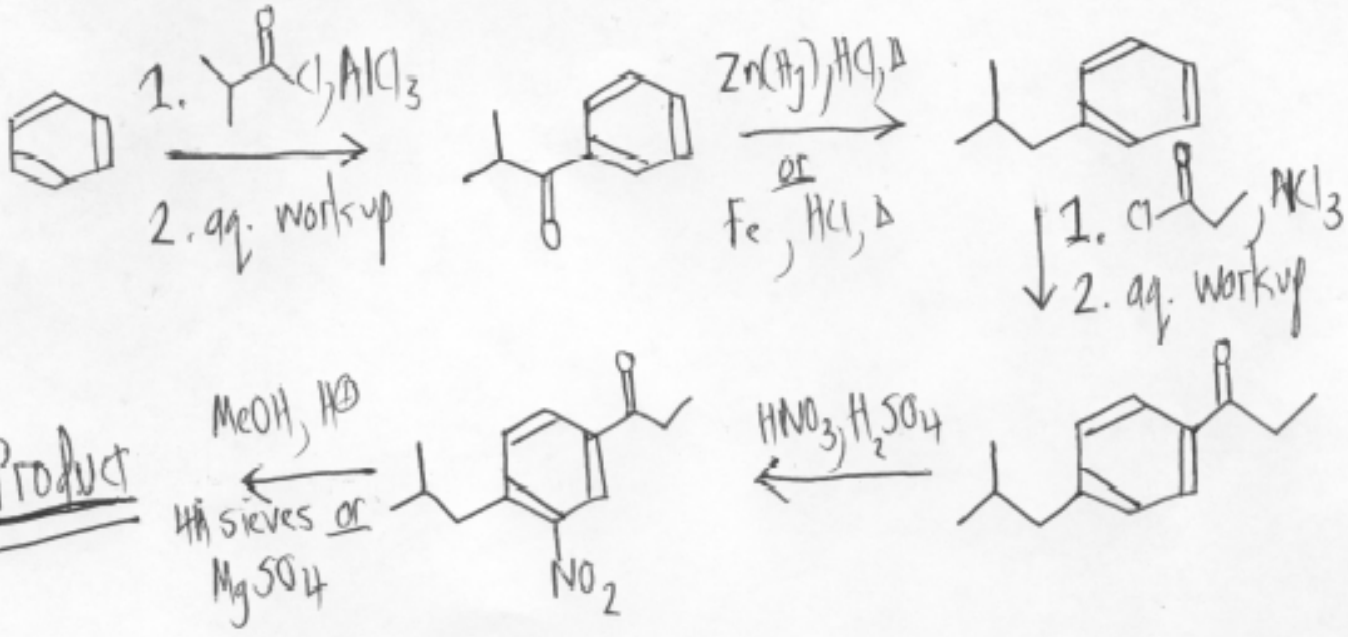
8. Provide the most efficient synthesis. You may employ any reagents of your choice. Points will be assigned according to steps listed in the forward synthesis direction (25 points).



from



Syn. direction:



Product

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