

Chemistry 3B, Midterm 1

Thursday, October 20, 2005

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**).

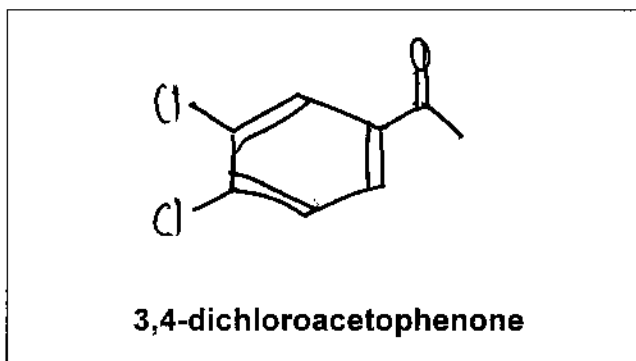
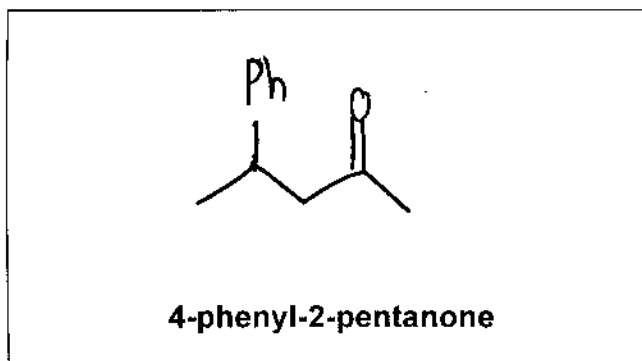
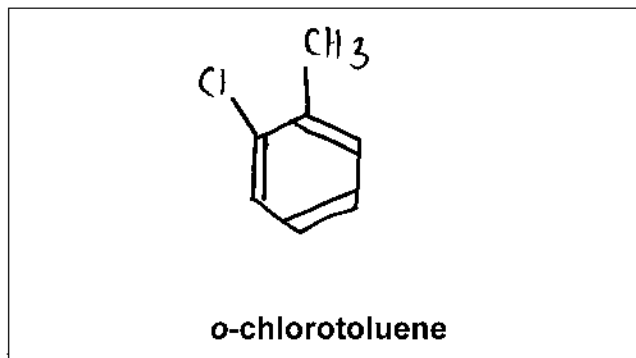
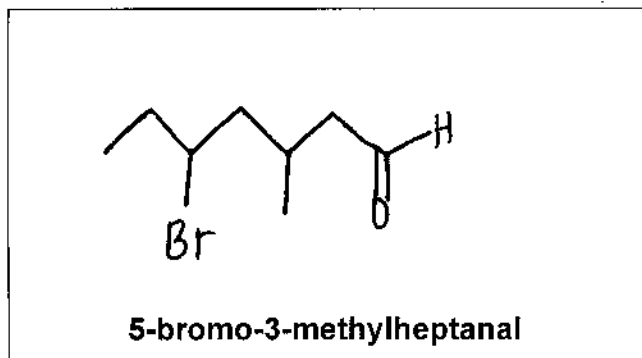
GOOD LUCK!

| | | |
|--------------|-------------------|-------|
| 1. | 12 points | _____ |
| 2. | 37 points | _____ |
| 3. | 60 points | _____ |
| 4. | 11 points | _____ |
| 5. | 15 points | _____ |
| 6. | 25 points | _____ |
| 7. | 25 points | _____ |
| 8. | 35 points | _____ |
| Total | 220 points | _____ |

MINI-PERIODIC TABLE

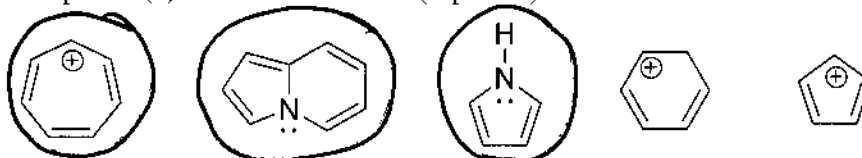
| | | | | | | | |
|-----------|-----------|------------|-----------|-----------|-----------|------------|-------------|
| I | II | III | IV | V | VI | VII | VIII |
| H | | | | | | | He |
| Li | Be | B | C | N | O | F | Ne |
| Na | Mg | Al | Si | P | S | Cl | Ar |
| K | Ca | Ga | Ge | As | Se | Br | Kr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

1. Provide structures for the following chemical names (12 points)

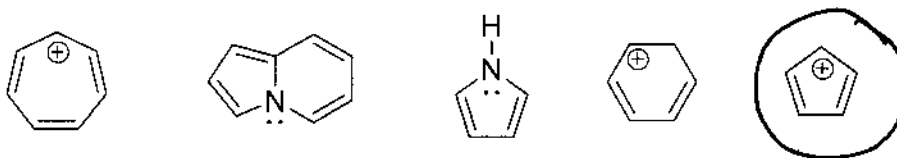


2. Answer the following questions. Every wrong answer cancels a correct answer (~~30~~ points). **37**

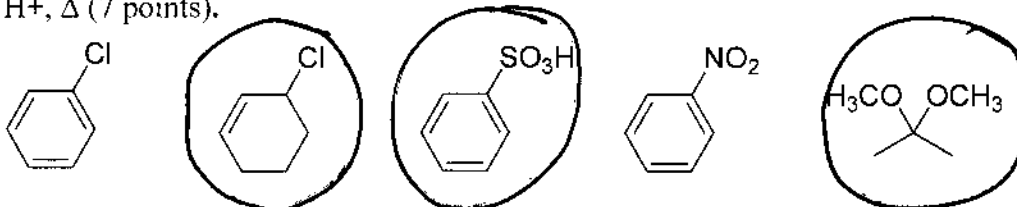
(a). **Circle** the compound(s) that are **aromatic** (8 points).



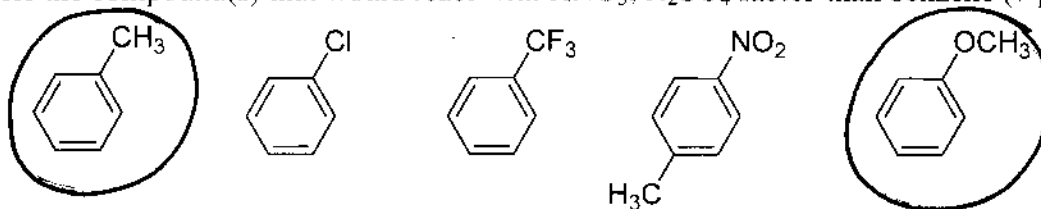
(b). **Circle** the compound(s) that are **antiaromatic** (8 points).



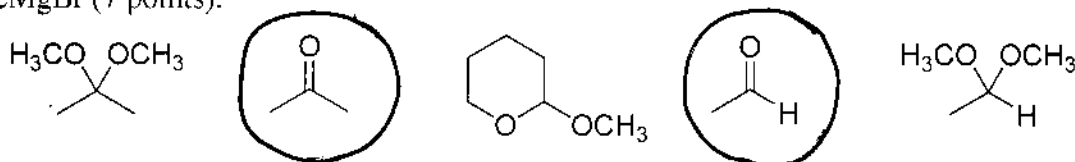
(c). **Circle** the compound(s) that would be converted to **different** compound(s) upon treatment with H_2O , H^+ , Δ (7 points).



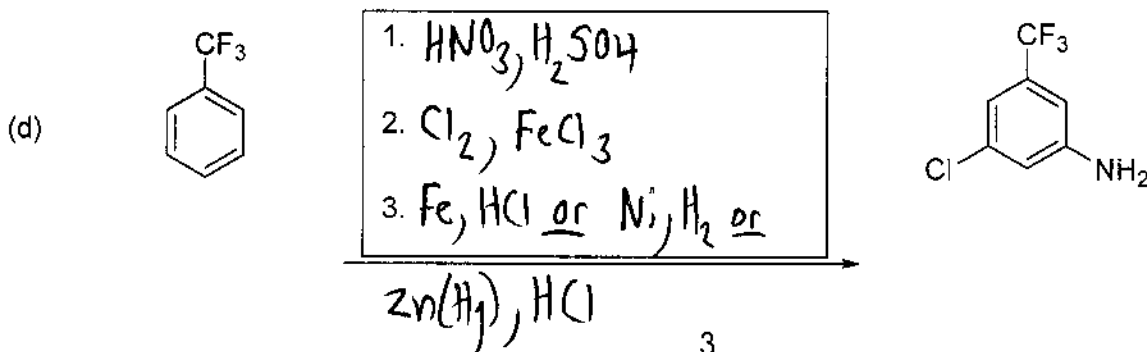
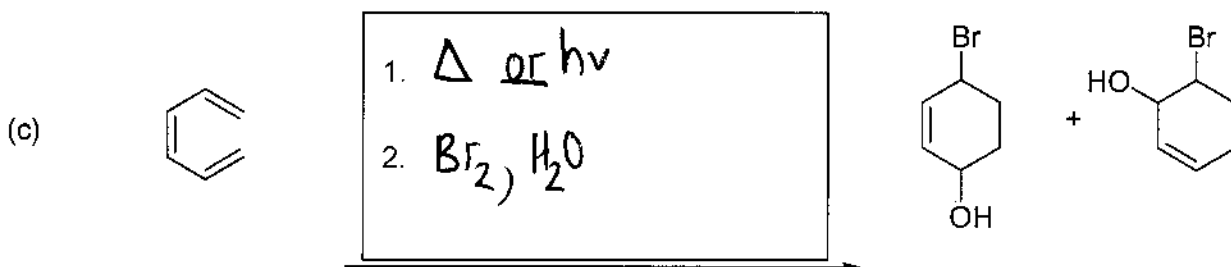
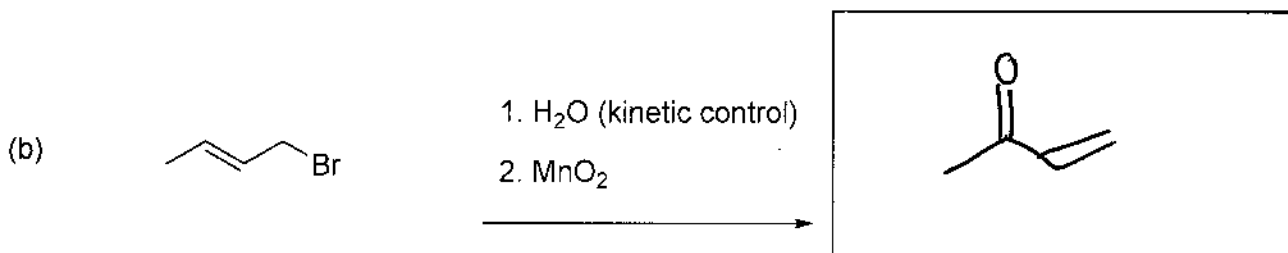
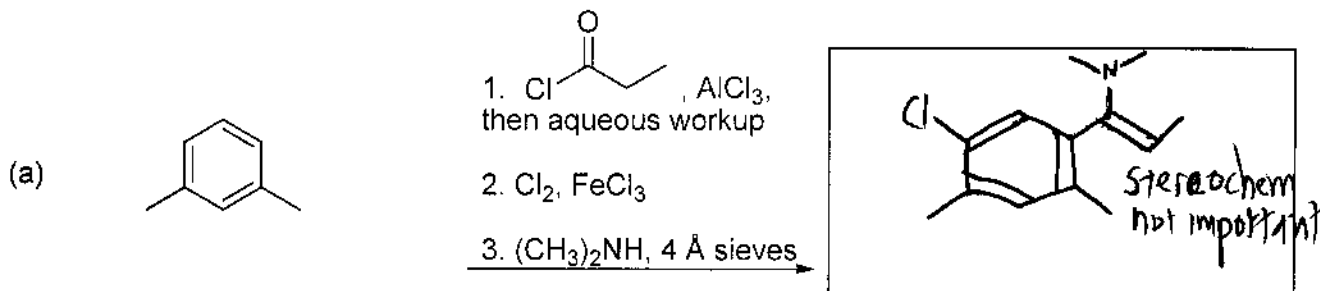
(d). Circle the compound(s) that would react with HNO_3 , H_2SO_4 **faster** than benzene (7 points).



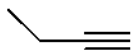
(e). Circle the compound(s) that would be converted to **different** compound(s) upon treatment with MeMgBr (7 points).



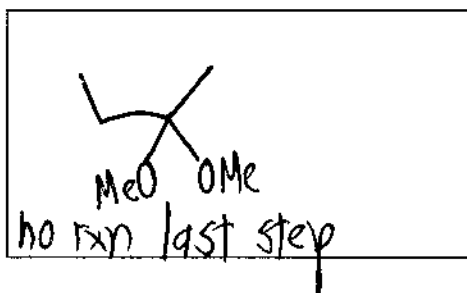
3. For each of the following reactions supply the missing reagents or major organic product in the space provided. If no reaction is expected indicate by N.R. (60 points total).



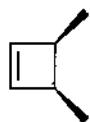
(e)



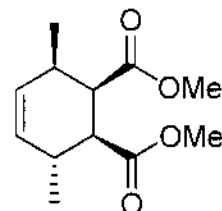
1. $\text{H}_2\text{O}, \text{H}^+, \text{HgSO}_4$
2. MeOH, H^+ 4 Å sieves
3. PhMgBr



(f)



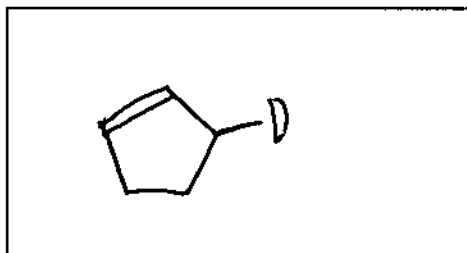
1. Δ
- 2.



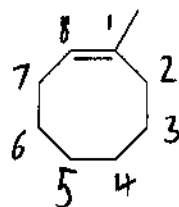
(g)



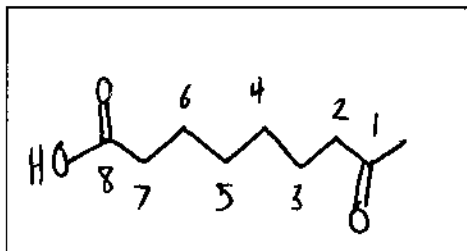
1. $h\nu, \text{NBS}, \text{CCl}_4$
2. Mg
3. D_2O



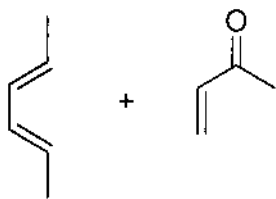
(h)



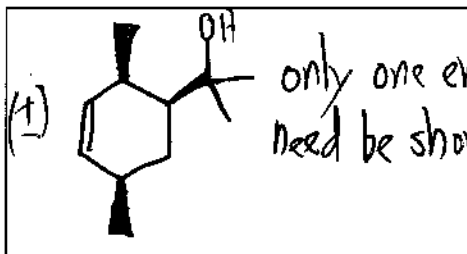
1. O_3
2. Zn, AcOH
3. $\text{CrO}_3, \text{H}_2\text{O}$



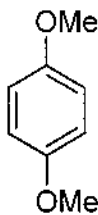
(i)



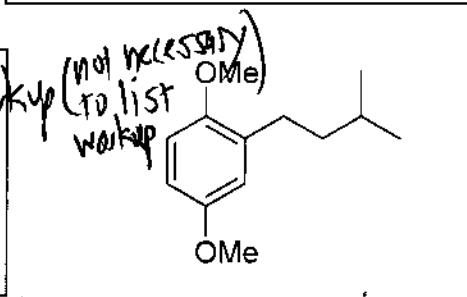
1. Δ
2. MeLi
3. aqueous workup



(j)

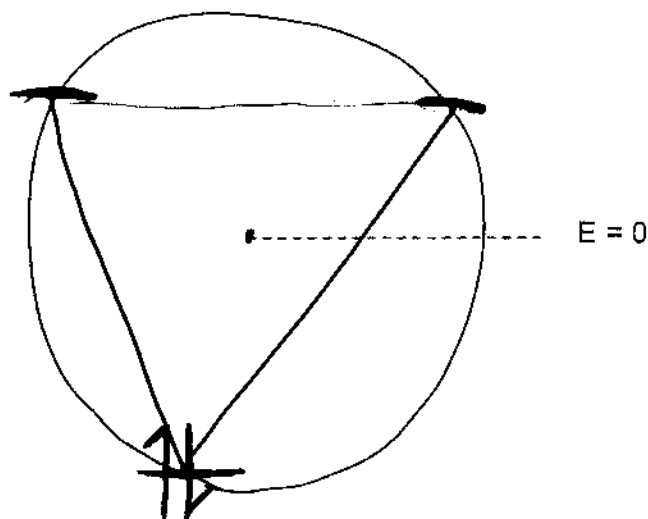


1. $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Cl}, \text{AlCl}_3$ then aq workup
2. $\text{Zn}(\text{Hg}), \text{HCl}, \Delta$ or $\text{H}_2\text{N}-\text{NH}_2, \text{EtOH}, \Delta$



~~4~~ ~~2~~ points total:

(a) Show an **energy level diagram** for the cyclopropenyl cation shown below (6 points).

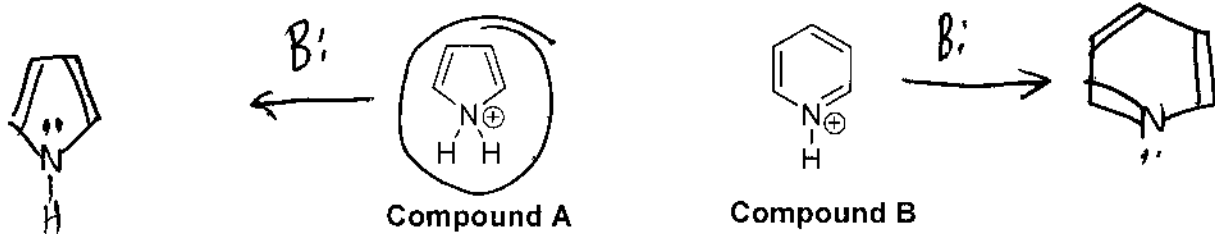


(b) Place the electrons for the **cation** in the appropriate molecular orbitals. Does the electron placement establish the molecule as aromatic or antiaromatic? **Briefly** explain (one sentence is all that is necessary) (5 points).

aromatic because the bonding orbital is filled, i.e., has paired e^-

5.

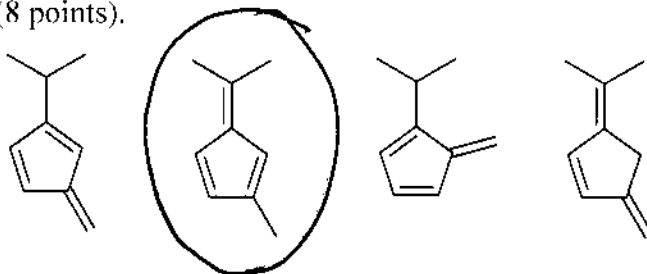
(a) Circle the more acidic compound. Briefly explain why it is more acidic (7 points).



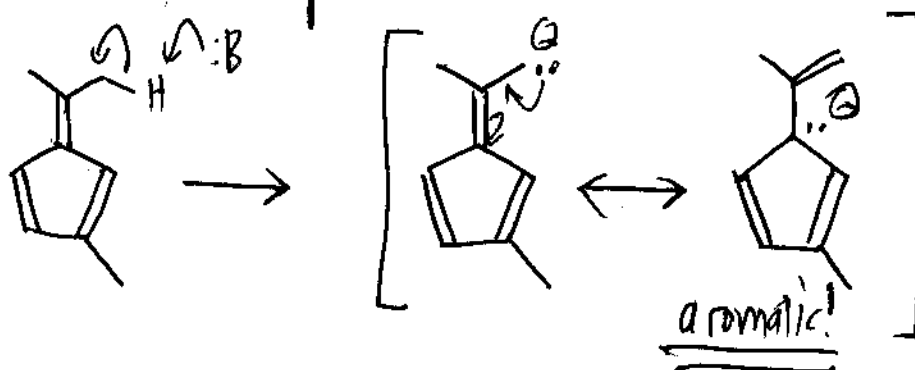
The conjugate base of compd A is aromatic while compd A is not aromatic. This provides considerable driving force for deprotonation.

Both compound B and its conjugate base are aromatic so aromaticity is not relevant to acidity.

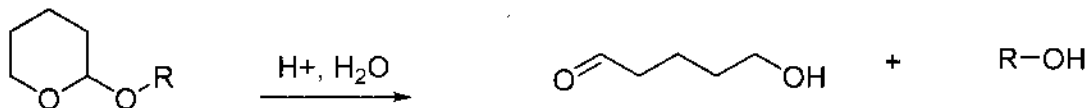
(b) Circle the hydrocarbon that is much more acidic than the others. Briefly explain why the compound you circled is more acidic (8 points).



only the circled compound can be deprotonated to give an aromatic compound

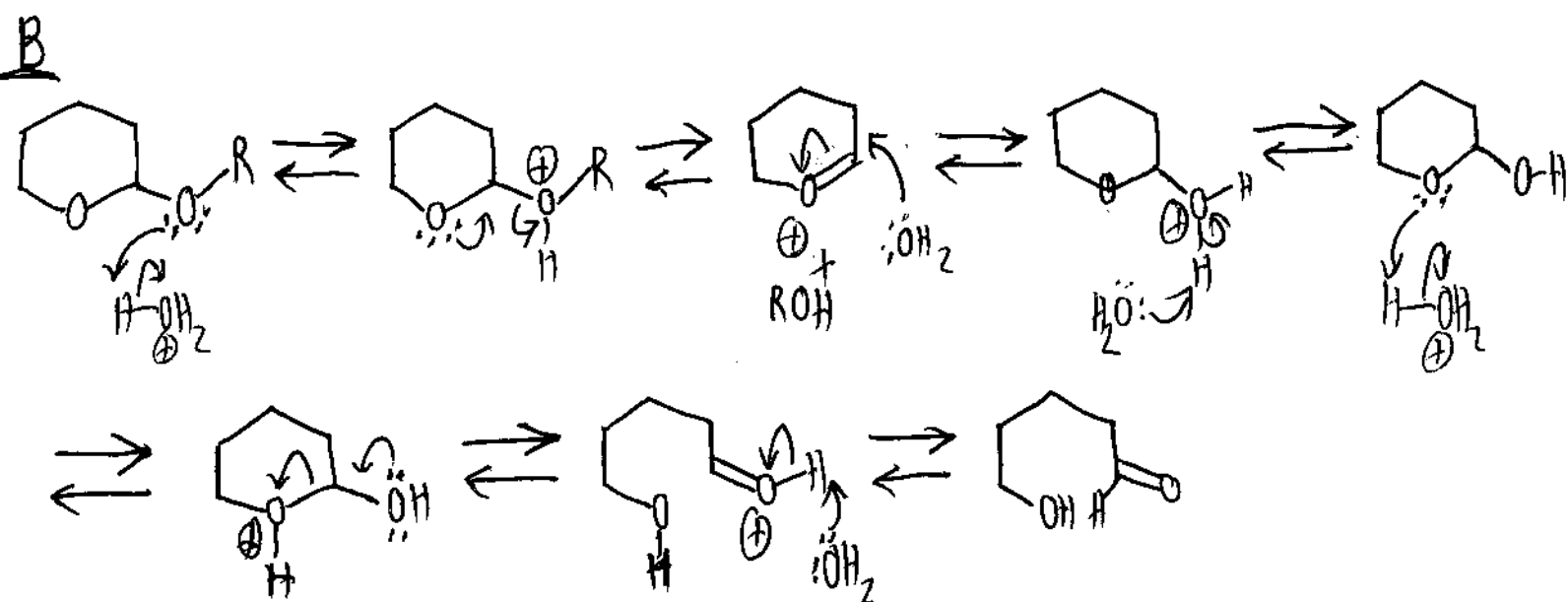
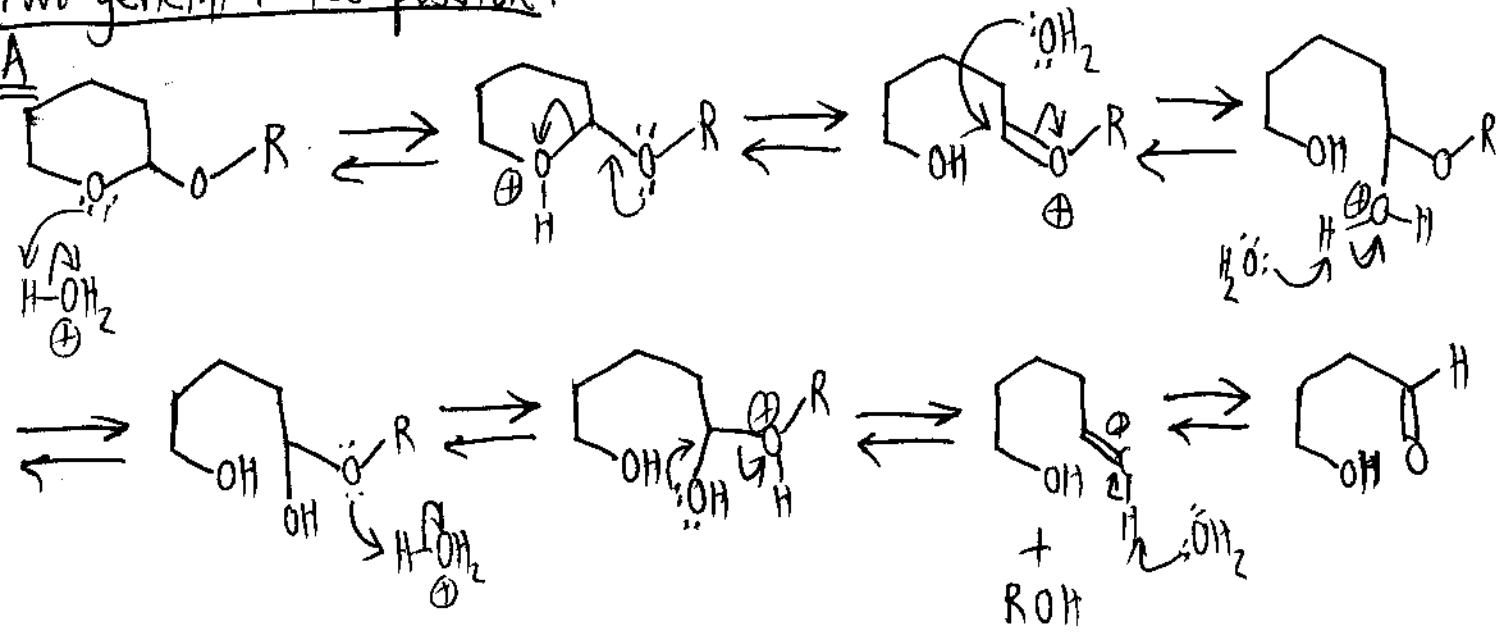


6. Provide a mechanism for the hydrolysis of the tetrahydropyranyl group (25 points).



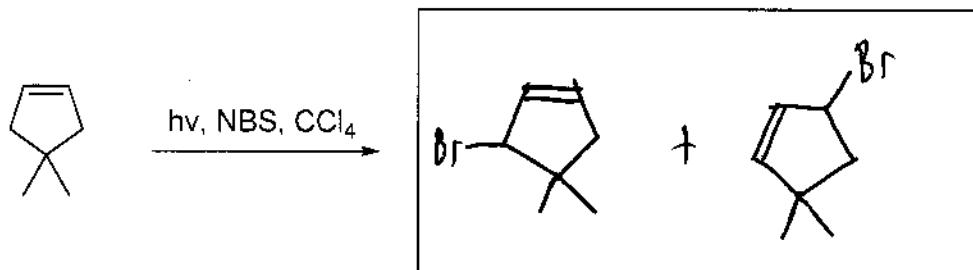
Note: the tetrahydropyranyl group is commonly used to protect alcohols, and is cleaved by acidic conditions.

Two general routes possible:

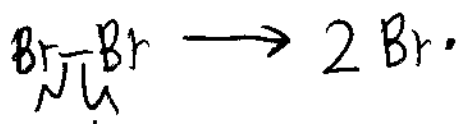


7. (a) Provide the **product(s)** of the reaction listed below (5 points).

(b) Provide the **mechanism** by which the reaction product(s) are formed. **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).

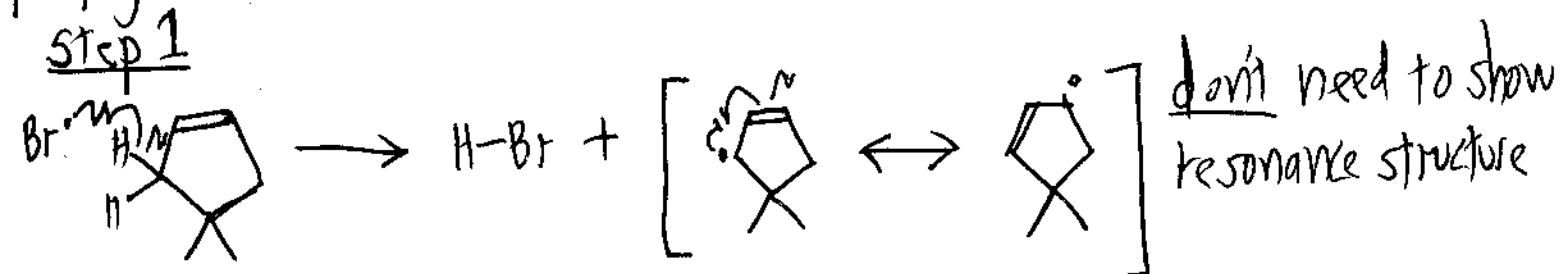


initiation

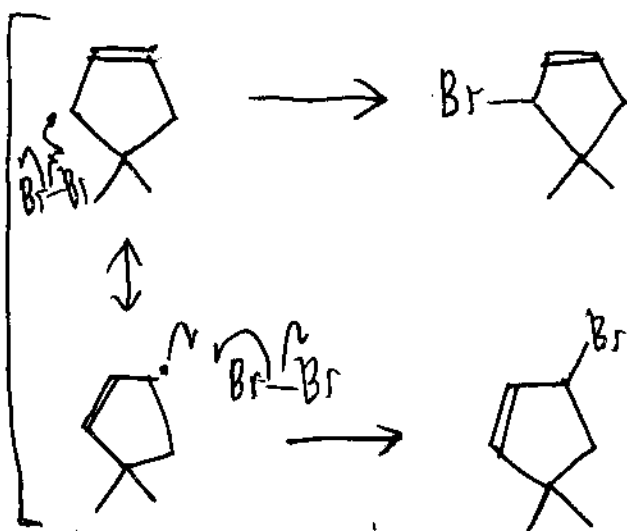


propagation

Step 1



Step 2



termination - radical recomb. (don't need to show)

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 (35 points).

