

FINAL EXAM
Organic Chemistry

Chemistry 220a; 2 P.M., Wednesday, December 14, 2005

NAME (print): _____

TA: _____ Section Day: _____ Section Time: _____

Take a few moments to look over the exam. Do problems first with which you are most comfortable. Important points and unknowns are in **bold** type. Do all **preliminary** work on the worksheets. The worksheets will **not** be graded. The exam is the length of two hour exams with an additional one hour for review. **STOP** writing when you are asked to do so. Put your name on the **cover sheet and subsequent pages** (except for Work Sheets) where indicated.

.REMEMBER: Neatness is to your advantage.

Have a GREAT winter break!

1. Spectrometry/Structure I (30 pts) _____ 5. The Standard State (25 pts) _____

2. Reactions I (32 pts; 4 of 6) _____ 6. Mechanisms (25 pts.) _____

3. Potpourri (48 pts; 6 of 8) _____ 7. Synthesis (25 pts.) _____

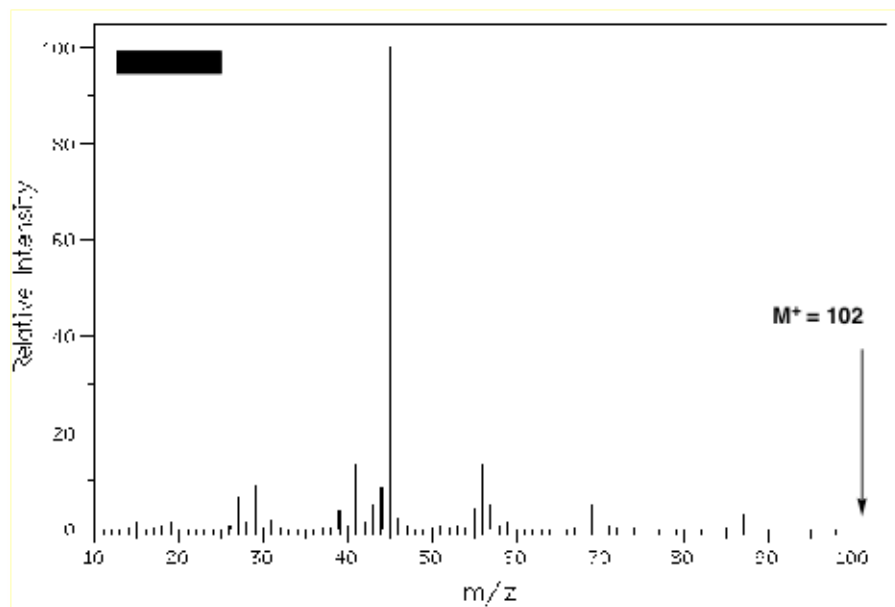
4. Reactions II (32 pts) _____ 8. P.M.H.S.W.W. (33 pts.) _____

Total (250 pts)

1. (30 pts) **Spectrometry/Structure:** Optically-active compound **A**, whose mass spectrum is shown below, is converted into ketone (*S*)-**B** with PCC or aqueous chromic acid. Compound **A** forms tosylate **C**, which upon treatment with aqueous KOH, produces achiral alkene **D** as the Zaitsev product. If tosylate **C** is exposed to LiBr in acetone (solvent), compound **E** is formed. When **E** is treated with aqueous KOH, achiral compound **F** is formed as the principal constitutional isomer. Hydrogenation of **D** or **F** produces the same alkane **G** but **D** liberates more heat (0.4 kcal/mol) than **F**. Warm permanganate oxidation of **D** or **F** affords **H** (C₄H₈O) and **I** (C₂H₄O₂). [Hint: Working backwards is useful.]

a) (25 pts) What are the structures **A-H**? Explain and illustrate. Do not forget absolute and relative stereochemistry where they apply. [The structures can be determined without the spectrum.]

b) (5 pts) Explain the source of the base peak in the spectrum, i. e., why is *m/z* 87 not the base peak.



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1. Continued

2. (4 x 8 pts = 32 pts) **Reactions I:** Provide the reagents (and conditions, if necessary) required to complete **4 of 6** of the following chemical transformations. If additional carbon atoms are necessary, select your own source. Several steps may be required. If you complete more than four questions, **cross out** the ones that you do not want graded.

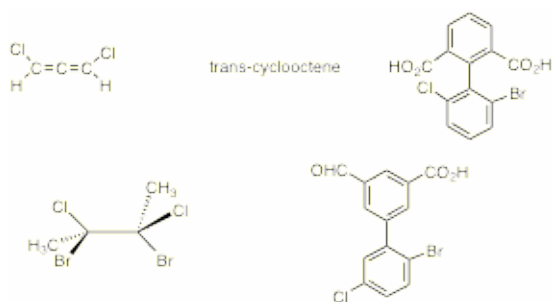


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3. (6 x 8 pts = 48 pts) **Potpourri:** Complete **6 of 8** of the following questions. If you complete more than six questions, **cross out** the ones that you do not want graded.

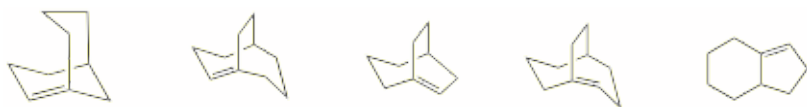
a) **Circle** the racemic compounds that are capable of resolution.



b) **Describe fully** (name, structure, etc.) the major monobromide derived from the free radical bromination of (*S*)-1-chloro-2-methylbutane. Briefly explain your answer.

c) For n-octane at 25°C: $\Delta H_f^0 = -49.8 \text{ kcal/mol}$; $\Delta H_{(\text{combustion})}^0 = -1,317 \text{ kcal/mol}$. Estimate the heats of formation and combustion for n-hexane. Show work.

d) **Circle** the compounds that are in violation of Bredt's Rule.



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e) **Circle** the reactions that are stereospecific with the (*E*)- and (*Z*)-2-butenes.

bromination epoxidation osmylation hydroboration
permanganate dihydroxylation

f) **Circle** the compounds that are readily deprotonated by aqueous KOH.

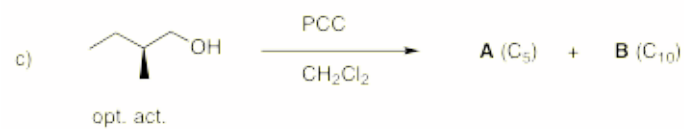
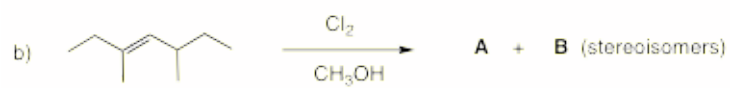
acetic acid phenol methanethiol butyne ammonia

g) **Circle** the compounds that contain atoms with sp hybridization.

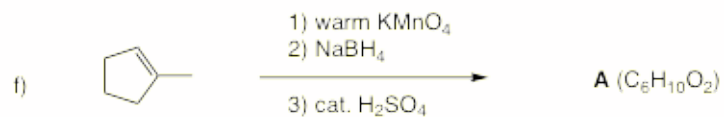
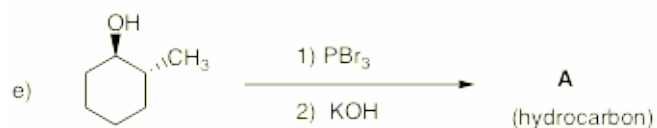
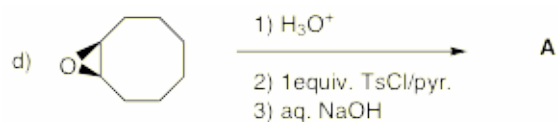
Vinylacetylene-(C₄H₄) BEt₃ acetone CO₂ allene

h) What is the percentage of the minor enantiomer when a mixture of enantiomers has an optical purity of 40%. **Show work.**

4. (4 x 8 pts = 32 pts) **Reactions II:** Complete **4 of 6** of the following questions. If you complete more than four questions, **cross out** the ones that you do not want graded.



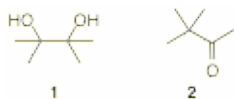
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5. (25 pts) **Standard State:** Draw a Standard State Diagram that illustrates the heat of formation of a methyl radical and the heat of combustion of methane. In addition, calculate these two quantities from the data provided. The diagram need not be to scale. **Show work.** DH_f° (methane) = -17.4 kcal/mol; $\text{DH}_{\text{combustion}}^\circ$ (graphite) = -94.0 kcal/mol; $\text{DH}_{\text{combustion}}^\circ$ (H_2) = -68.3 kcal/mol; BDE (H_2) = 104 kcal/mol; BDE (methane) = 104 kcal/mol.

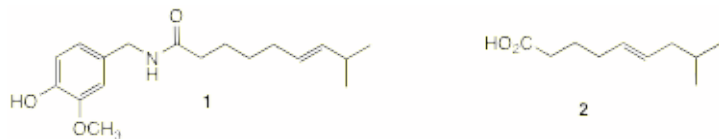
Standard State

6. (25 pts) **Mechanism:** One of the reactions of diols that I neglected to discuss is the pinacol rearrangement. The prototypical rearrangement is the conversion of 2,3-dimethylbutane-2,3-diol (“pinacol”, **1**) into 3,3-dimethyl-2-butanone (“pinacolone”, **2**).



- a) What is the electron change in the reaction **1** \rightarrow **2**?
- b) Provide a mechanism (curved arrow formalism) using the reagent that catalyzes this reaction.
- c) Provide the three individual steps and reagents for the reverse reaction,---namely the conversion of **2** \rightarrow **1**.
- d) The answer to a) must be the same as the total electron change in c). Illustrate and explain briefly.

7. (25 pts) **Synthesis:** Capsaicin (**1**) is the “hot” in hot chili peppers. This compound has found use in pain management in medicine. To study the effect of double bond location in **1**, acid **2** is required to synthesize a double bond analog of **1**. A student designs a synthesis of **2** from acetylene, isobutylene, and 4-bromo-1-butanol. Her plan is to use acetylene chemistry. She also recognizes that isobutylene will not only be incorporated into carboxylic acid **2** but it will also serve as a protecting group in her planned synthesis. She has all reagents available to her. Show what she has in mind.



8. (33 pts.; 4 x 8 potions; 1 pt. re: gate) **P.M.H.S.W.W.** “Known for tormenting students with laborious homework assignments while cooking up sinister potions in class, Snape seems like a textbook Orgo professor.”

"Snape's Yale analogue is most definitely Professor Frederick Ziegler," Mark Fisher '07 said. "Infamous for his tacit encouragement of competition among his more elite students, so I hear, he seems the most likely candidate to have invented high-level, malicious organic chemistry reactions in the margins of his college text book." YDN, 11/18/05.

Alas, my alter ego has been revealed (**P**otions **M**aster of the **H**ogwarts **S**chool of **W**itchcraft and **W**izardry). I leave you budding wizards of Slytherin House, Gryffindor (particularly you, Potter!), Sillimania, and Branfordium (quod alii loci [*sic*]) to **provide the correct “potions” for the alchemical transformations on the next page.** [Note: The original potions were provided by three horrid hags, close associates of the soon to be Thane of Cawdor.]

"Eye of newt, and toe of frog,
Wool of bat, and tongue of
dog,
Adder's fork, and blind-
worm's sting,
Lizard's leg, and howlet's
wing,--
For a charm of powerful
trouble,
Like a hell-broth boil and
bubble."

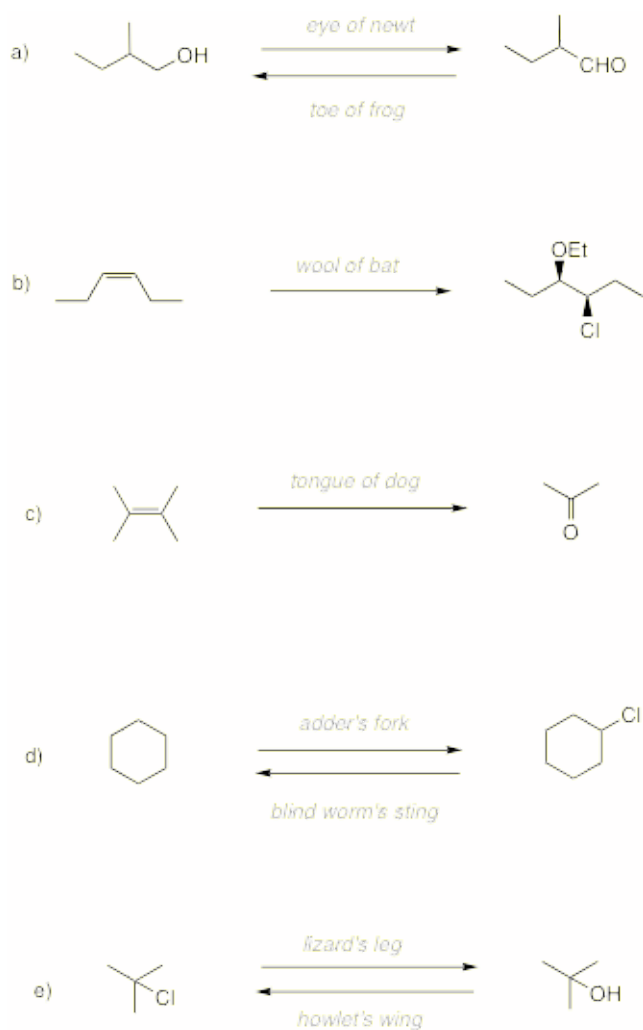


H. P. aka E. Z.

--From *Macbeth* (IV, i, 14-15)

(What? No wolfsbane!)

persevero...



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8. Continued ...(1 pt.) State something knowledgeable about the chirality of the tetrahedra on the CRB gate.

Work Sheets
Work Sheets
Work Sheets

Work Sheets