

FINAL EXAM
Organic Chemistry
Chemistry 220a; 9 A.M., Friday, December 17, 2004

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 2 to 2-1/2 hours with an additional 1/2 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.

Question 2: Do 4 of 6.

Question 3: Do 6 of 8.

Question 4: Do 4 of 6.

REMEMBER: Neatness is to your advantage.

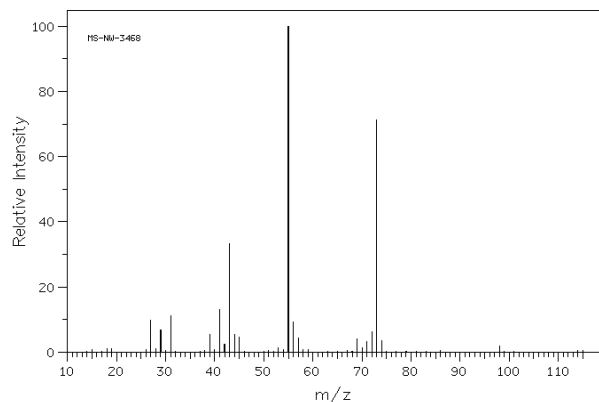
Have a GREAT winter break! See you next term for Chem 221b.

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|--|---|
| 1. Spectrometry/Structure I (30 pts) _____ | 5. Spectrometry/Structure II (30 pts) _____ |
| 2. Reactions I (32 pts) _____ | 6. Mechanisms (20 pts.) _____ |
| 3. Potpourri (48 pts) _____ | 7. Synthesis (29 pts.) _____ |
| 4. Reactions II (32 pts) _____ | 8. Radicals (29 pts.) _____ |
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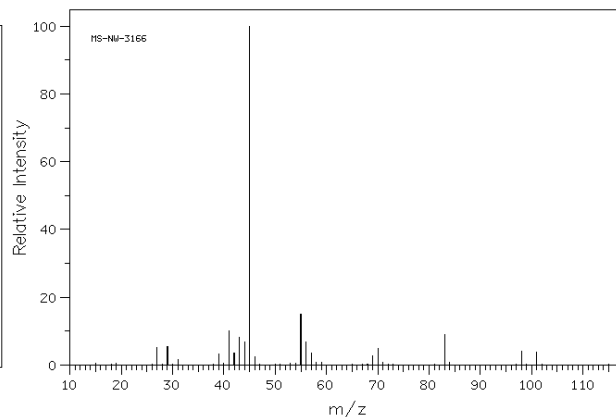
Total (250 pts)

1. (30 pts) **Spectrometry/Structure I:** A pair of students synthesize 2-, 3-, and 4-heptanol. Upon arriving at the lab the next morning, they discover that the labels have fallen off the bottles containing their samples. He wants to redo the syntheses but she suggests that they record the mass spectrum of each of the samples to determine their structures.

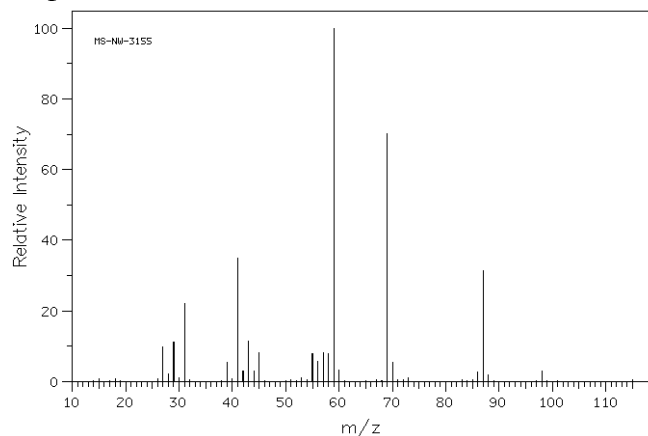
Heptanol A



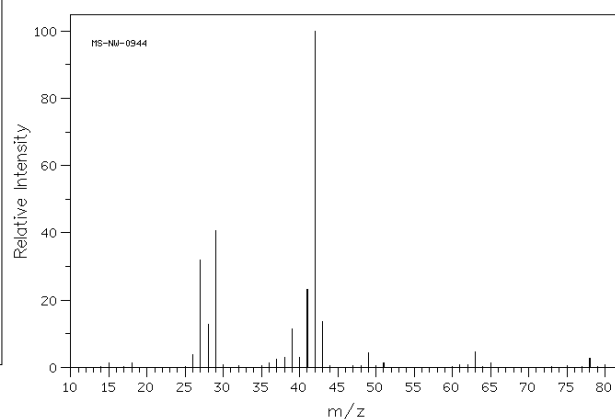
Heptanol B



Heptanol C



Alkyl Halide D

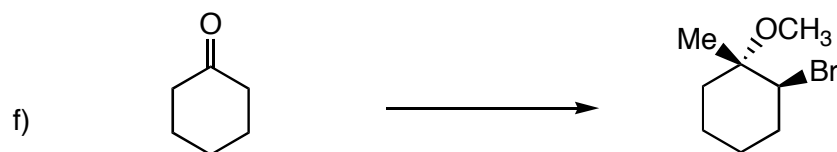
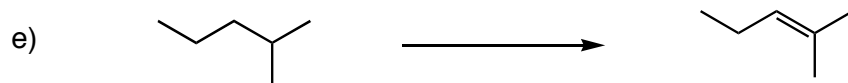
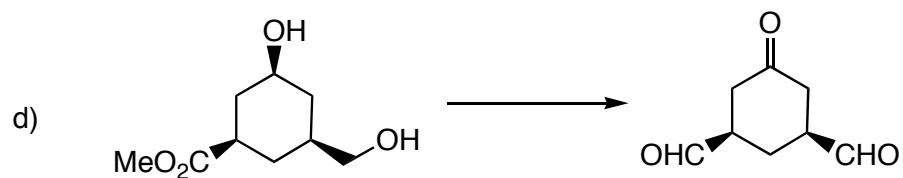
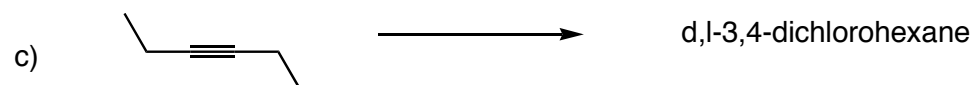
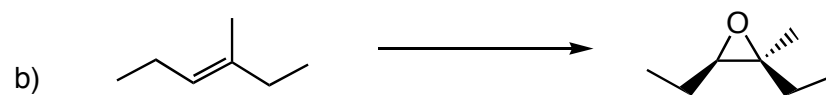
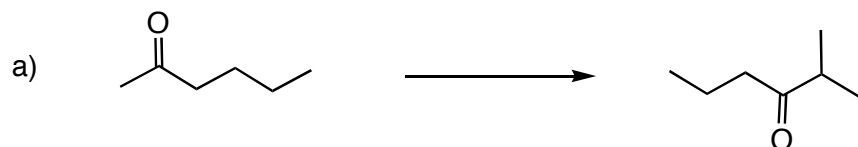


a) (18 pts) Assign structures to heptanols **A**, **B**, and **C**. **Show your reasoning.** [You do not have to account for all the peaks or even some of the more intense ones, only the ones that distinguish one structure from another.]

Continued on the next page...

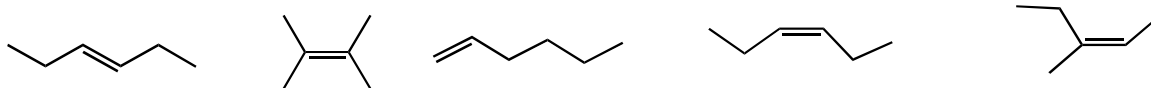
b) (12 pts) The students prepared one of the heptanols from alkyl halide **D** and n-butyraldehyde (butanal). Identify alkyl halide **D** (**show your reasoning**) and show how and which heptanol was prepared.

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. Several steps may be required. If you complete more than four questions, **cross out** the ones that you do not want graded.

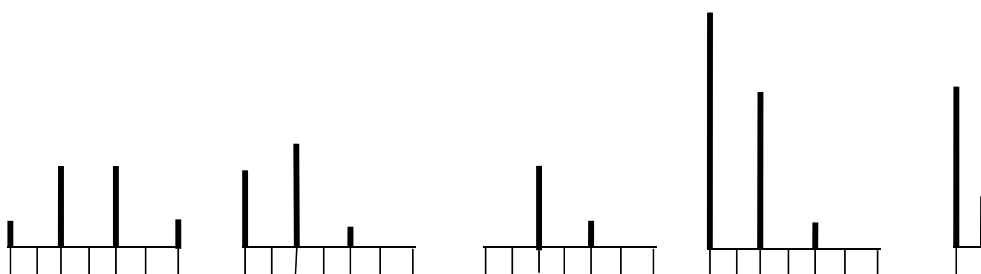


3. (6 x 8 pts = 48 pts) **Potpourri:** Complete **6 of 8** of the following questions. If you complete more than six questions, **cross out** the ones that you do not want graded.

a) **Circle** the compound with the greatest heat of combustion.



b) **Circle** the mass spectral pattern that most closely resembles the ion CHCl_2^+ . (Each hash mark is a mass unit.)



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-heptane. Show work.

d) Given that the relative rates in free radical chlorination are: $1^0 = 1$; $2^0 = 4.5$; $3^0 = 5.5$, provide the structure and percent of the major free radical monochlorination product of 2,4-dimethylpentane. Show work.

e) Complete **each** of the following true or false questions.

- i) All meso compounds have an associated d,l-pair. T ____ F ____
- ii) All d,l compounds have an associated meso compound. T ____ F ____
- iii) All conformations of meso compounds are achiral. T ____ F ____
- iv) All achiral compounds are meso. T ____ F ____

f) **Circle** the third compound in order of pKa.

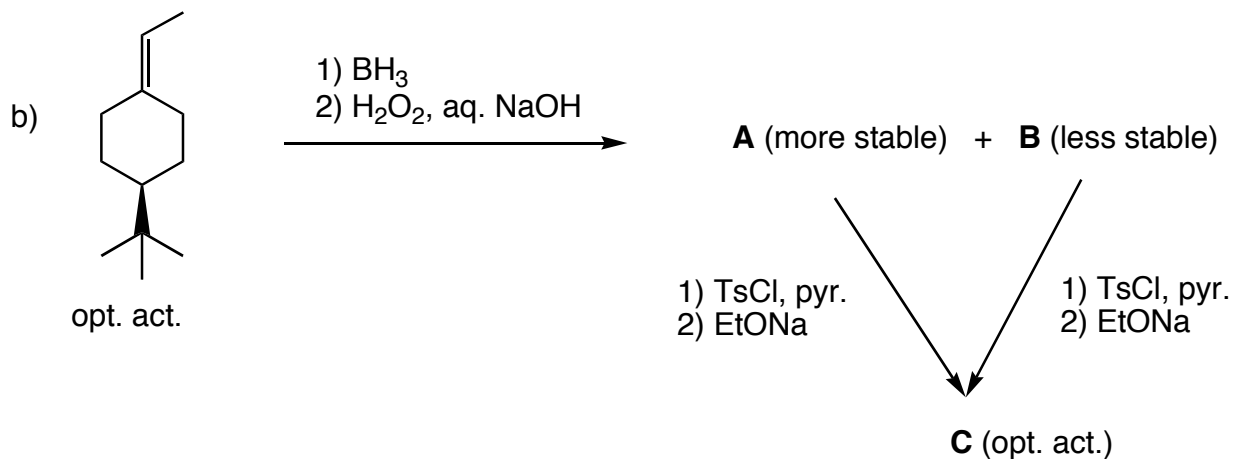
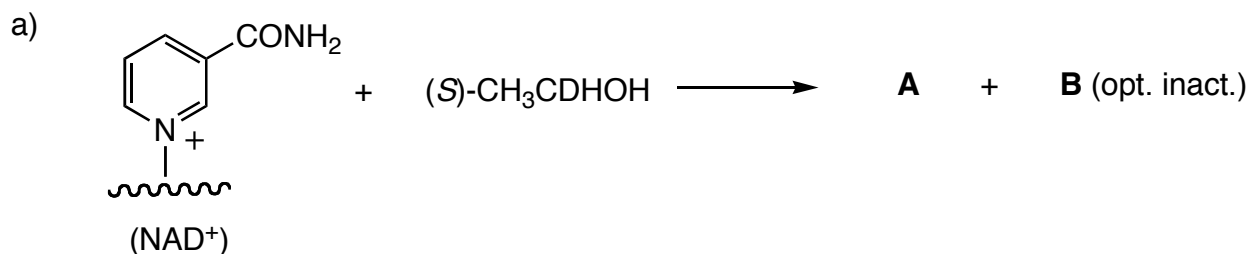
acetic acid phenol β -chloroethanol propyne ammonia

g) **Circle** the compounds that contain atoms with sp² hybridization.

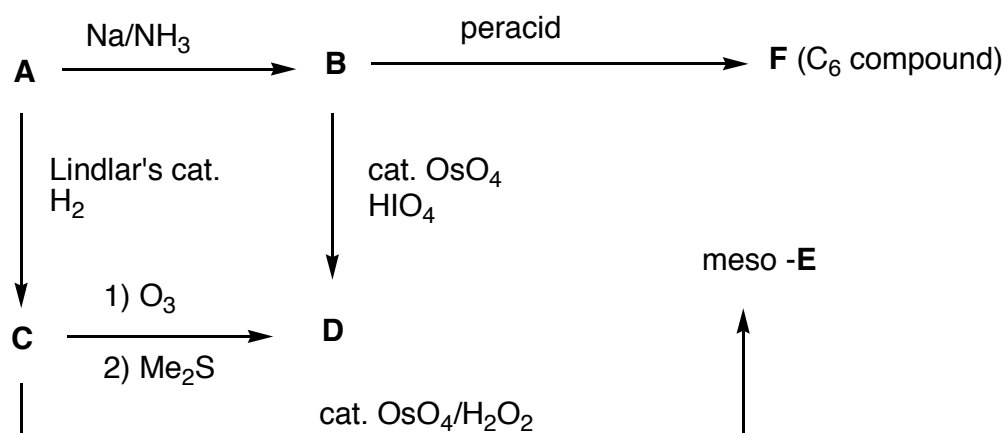
vinylacetylene(C₄H₄) BEt₃ acetone dimethyl sulfoxide cholesterol

h) The optical rotations of the enantiomers of limonene have been reported as $[\alpha]_D = +125^\circ$ and $[\alpha]_D = -100^\circ$. Assuming only one of the enantiomers is pure and other one is contaminated with its enantiomer, determine the enantiomeric excess of the impure sample. **Show work.**

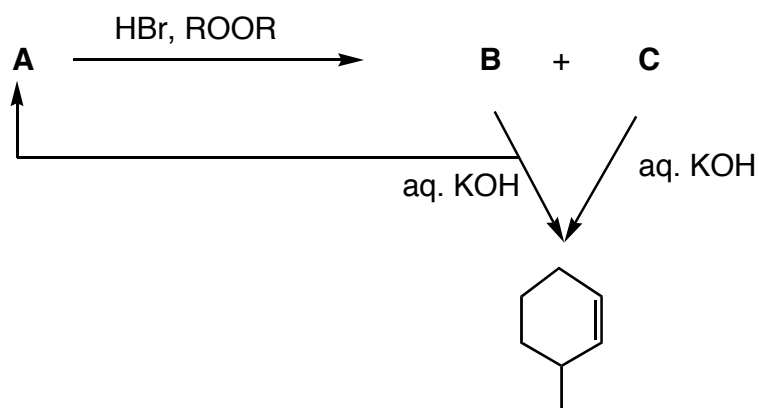
4. (4 x 8 pts = 32 pts) **Reactions II:** Complete **4 of 6** of the following questions, **but you must do either 4a or 4f**. If you complete more than four questions, **cross out** the one that you do not want graded.

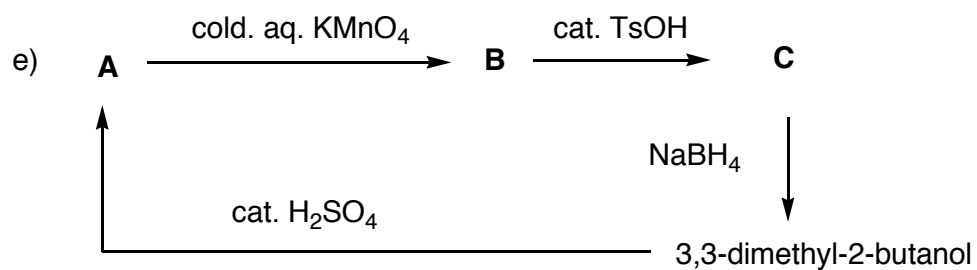


c)

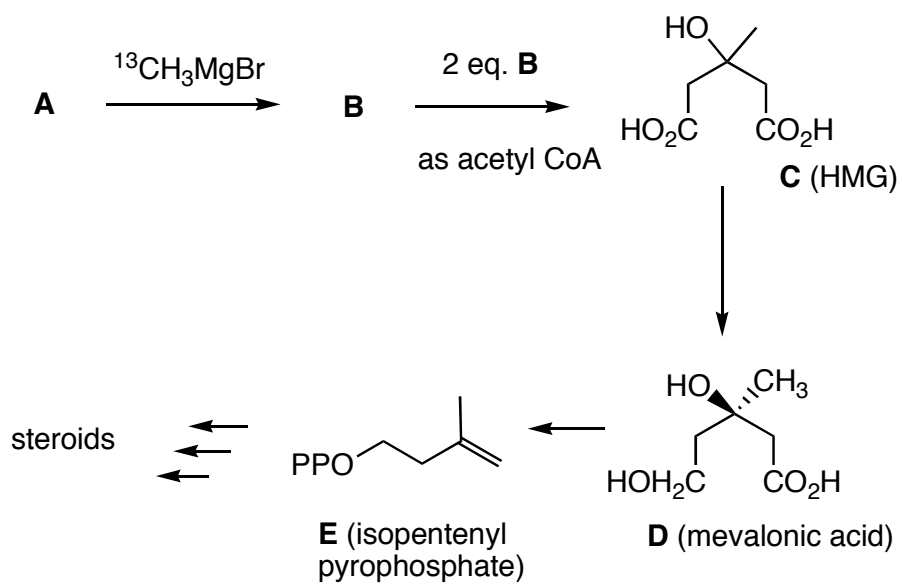


d)

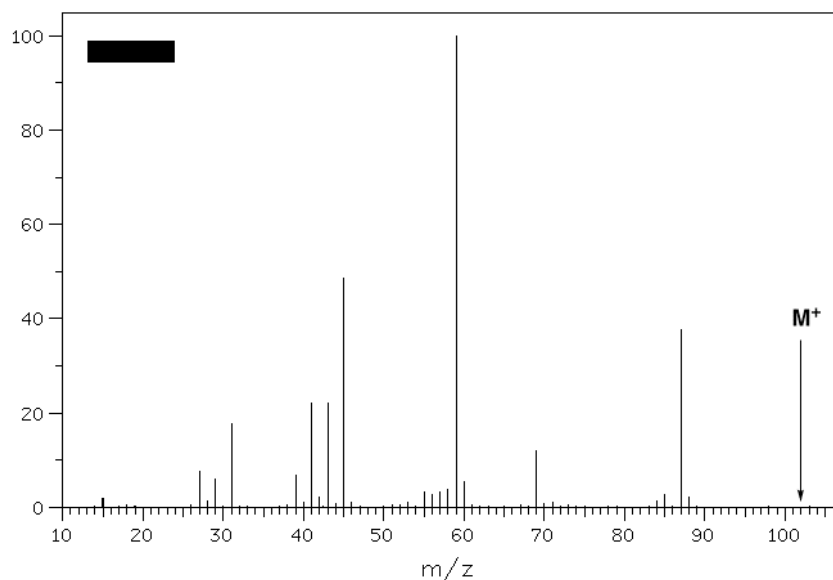




- f) What are the structures of **A** and **B**? **Circle** the labeled atoms in **B-E**. [Note: the carbon in the Grignard reagent is labeled with carbon-13.]



5. (30 pts) **Spectrometry/Structure II:** Compound **A**, whose mass spectrum is shown, is inert to PCC and hydrogenation. Compound **A** is readily converted into compounds **B** (minor) and **C** (major) upon exposure to H_2SO_4 . Ozonolysis and dimethyl sulfide reduction of **B** affords compound **D** ($\text{C}_5\text{H}_{10}\text{O}$), which is inert to Jones reagent, and compound **E**. Treatment of **C** with cat. $\text{OsO}_4/\text{HIO}_4$ gives rise to compounds **F** and **G**, both of which have the same molecular formula. Compound **F** is inert to cold aq. KMnO_4 , but compound **G** reacts with cold aq. KMnO_4 to form **H**. What are the structures **A-H**? Explain and illustrate.



6. (20 pts) **Mechanisms:** Provide a mechanism (curved arrow formalism) for one, **and only one**, of the following reactions.

- a) Hydroboration and oxidation of (*E*)-3-methyl-2-pentene.
- b) Ozonolysis and reduction of (*E*)-3-methyl-2-pentene.
- c) The formation of pinacolone (3,3-dimethyl-2-butanone) from pinacol.

7. (29 pts) **Synthesis:** Design a synthesis of 3-ethyl-2-methyl-3-hexanol from propene as the exclusive source of carbon. All reagents are available.

8. (29 pts) **Radicals:** Determine the heat of formation of chlorocyclohexane given the bond dissociation energies on page 14 and the following heats of formation (kcal/mol): n-hexane, -40.0; cyclohexane, -29.5; HCl, -22.1. Show work.

Name: _____

Work Sheets

Work Sheets

Work Sheets

Work Sheets

Work Sheets