FINAL EXAM

Organic Chemistry

Chemistry 220a; 2 P.M., Thursday, December 19, 2002

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 following tables are at the end of the exam: Periodic Table (page 19), BDEs (page 20), Common Isotopes (pg. 21). 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** where indicated.

For question 2, do 1 of 3 choices.
For question 3, do 3 of 4.
For question 4, do 5 of 6.
For question 5, do 4 of 6.
For question 8, do 4 of 5.
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REMEMBER: Neatness is to your advantage.

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

1. Structure/ Spectroscopy (30 pts) _____		5. Kinetics/ Thermodynamics (32 pts.) _____	
2. Mechanisms (30 pts) _____		6. Synthesis (30 pts.) _____	
3. Reactions (30 pts) _____		7. Structure II (36 pts.) _____	
4. Potpourri (30 pts) _____		8. Reactions (32 pts.) _____	

_____

Total (250 pts) _____

1. (30 pts; 5 x 6 pts) **Structure/Spectroscopy:** The alkyl halide **A**, whose mass spectrum (Fig. 1) is shown below, forms a Grignard reagent **B**. When an excess of **B** reacts with aldehyde **C**, compound **D** is formed. The infrared (Fig. 2) and mass (Fig. 3) spectra of **D** are shown below.

Fig. 1

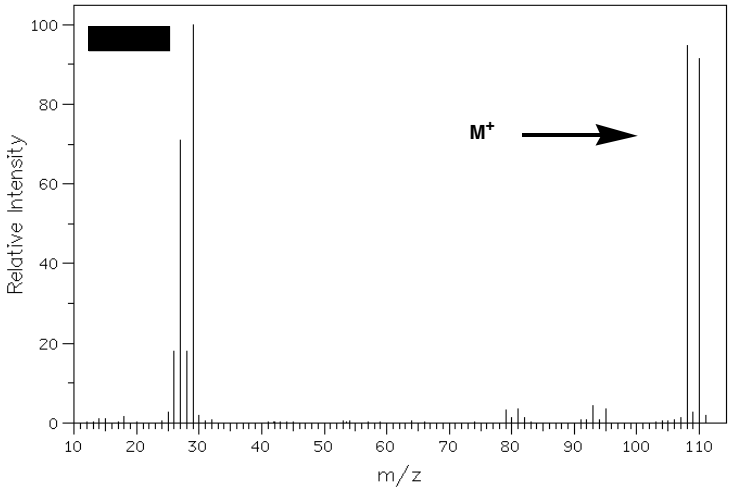


Fig. 2

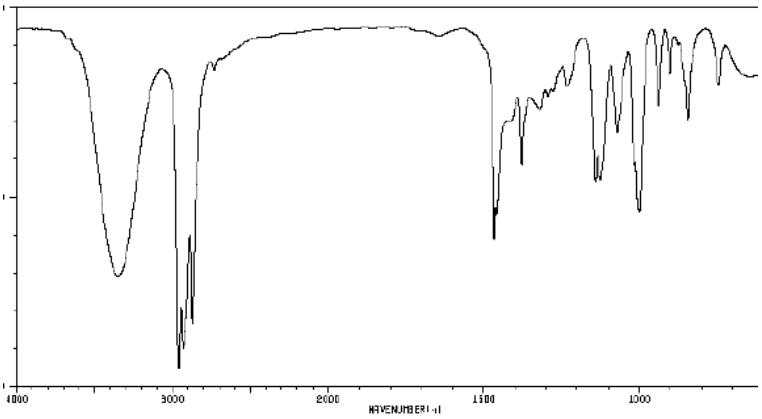
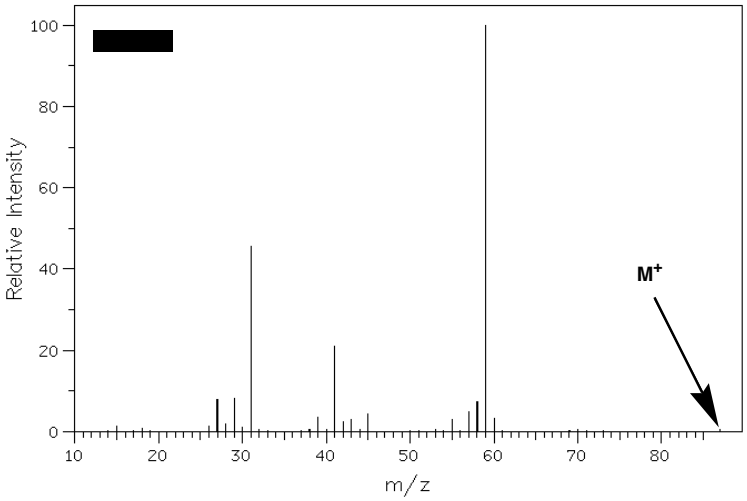


Fig. 3



a) Explain briefly how Fig. 1 reveals the structure of **A**?

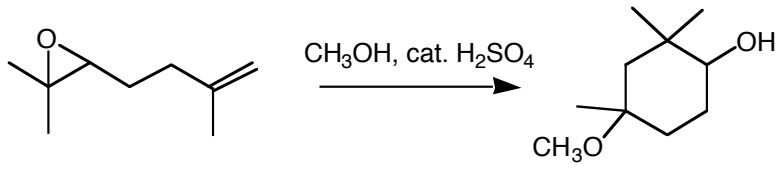
b) What is the significance of the absorption at ~3300 cm^{-1} in Fig. 2?

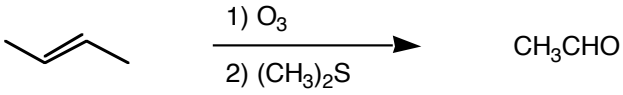
c) What is the molecular weight of **D**? Assume z=1 for m/z.

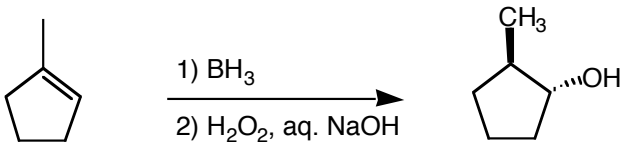
d) What is the structure of **D**?

e) What is the structure of the ion that represents the base peak in Fig. 3?

2. (30 pts) **Mechanism:** Provide a mechanism (curved arrow formalism) for **one** the following three reactions.

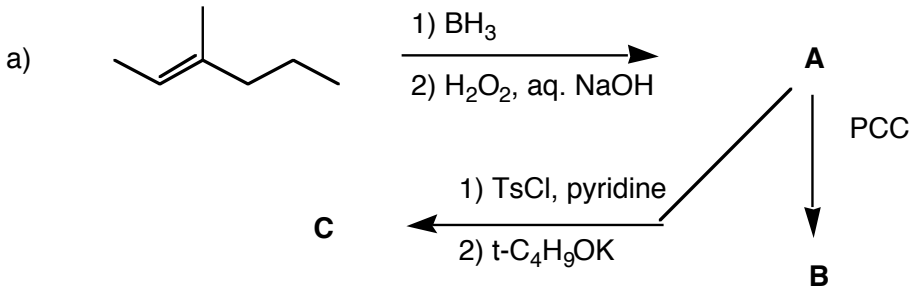
a) 

b) 

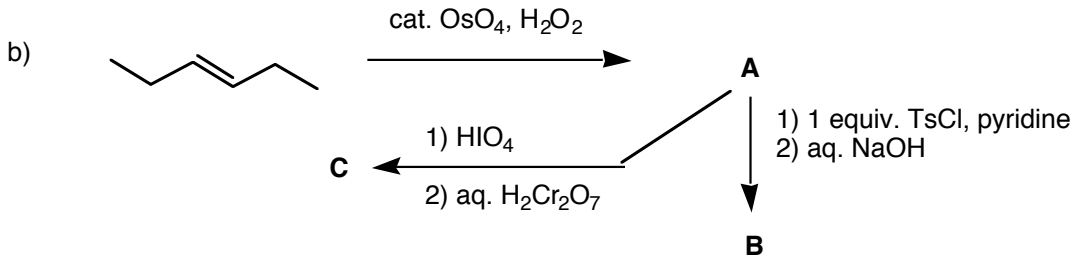
c) 

3. (30 pts; 3 x 10 pts) **Reactions:** Provide the structures in **three** of the following **four** problems. **Pay attention to stereochemistry.** If you do four problems, **cross out** the one you do not want graded.

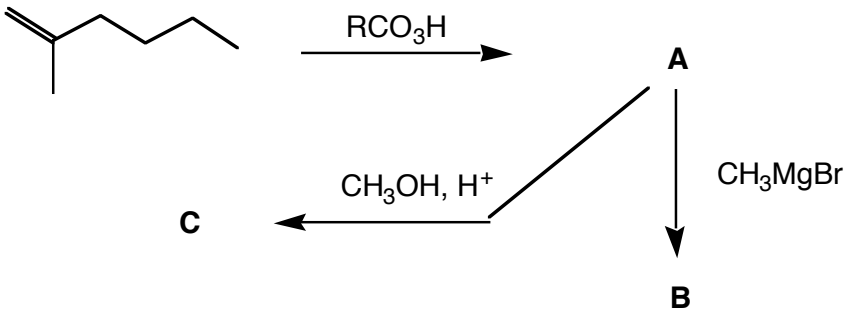
a)



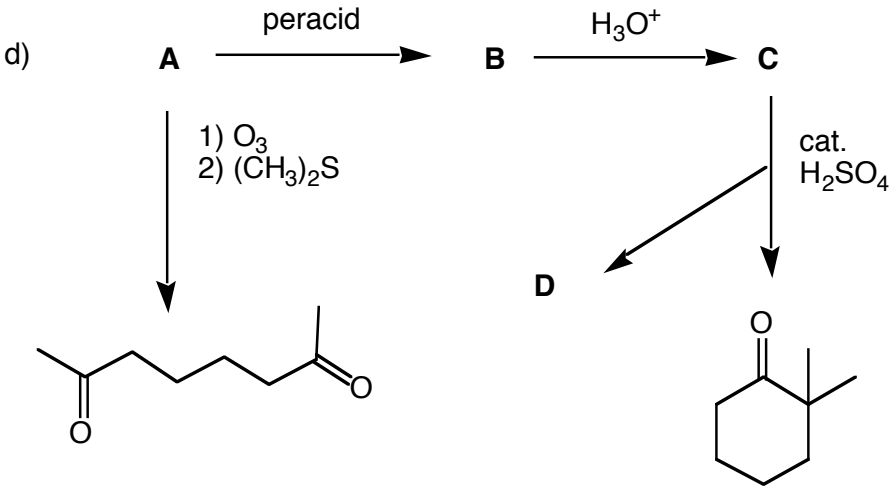
b)



c)

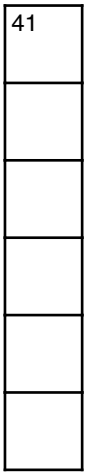


d)



4. (30 pts; 5 x 6 pts) **Potpourri:** Complete **five** of the following **six** problems. If you do six problems, **cross out** the one you do not want graded..

a) N. Y. Times Crossword Puzzle, 41 Down. Clue: C_4H_8. (Monday, December 2, 2002)



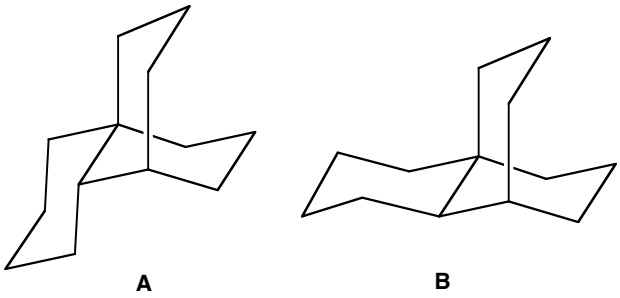
b) The mass spectrum of chloroform, $CHCl_3$, is expected to have molecular ions at M^+ = 118, 120, 122, and 124. The ions at 118 and 120 are expected to be equal in intensity even though the abundance of ^{35}Cl: ^{37}C is 3:1. Show work.

c) The structure of the optically inactive, racemic dibromide derived from the free radical bromination of (R)-1-bromo-2-methylpentane. Why is it optically inactive and racemic?

d) The structure and name of the cyclohexane, C_8H_{16}, whose two chair conformations are achiral and equal in energy.

e) A mixture of enantiomers (20% enantiomeric excess) has a rotation $[\alpha] = -24^{o}$. What is the rotation of the dextrorotatory enantiomer? Show work.

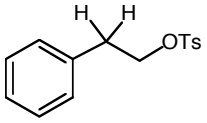
f) The relationship between structures **A** and **B**.

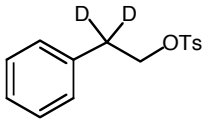


5. (32 pts; 4 x 8 pts) **Kinetics/Thermodynamics:** Complete **four** of the following **six** problems. If you do five or six problems, **cross out** the one you do not want graded.

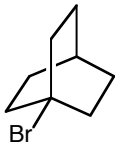
a) Of cis- and trans-2-butene, the one with the greater heat of combustion. Explain briefly.

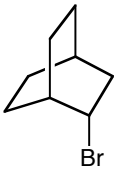
b) The tosylate that undergoes E2 elimination faster in the presence of C_2H_5OH/C_2H_5ONa. Explain briefly.





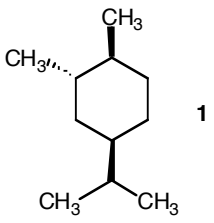
c) The compound more likely to react via S_N2 substitution. Explain.





d) A nearly equal mixture of two monochloro compounds is anticipated in the free radical chlorination of 2,3-dimethylbutane. Explain and illustrate briefly. [relative rates: $1^o = 1$; $2^o = 4.5$; $3^o = 5.5$]

e) The difference in energy between the two chair conformations of cyclohexane **1** is 0.6 kcal/mol. Illustrate and show work. [Axial vs. equatorial for monosubstituted cyclohexanes: i-C_3H_7 = 2.1 kcal/mol; C_2H_5 = 1.9 kcal/mol; CH_3 = 1.8 kcal/mol; gauche butane = 0.9 kcal/mol]



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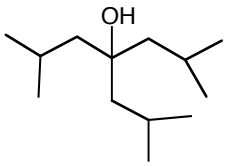
f) The heat of reaction in the monochlorination of cyclohexane. Show work.

6. (30 pts) **Synthesis:** A student wishes to study the effect of hindered bases on E2 elimination reactions. To this end, she requires the alcohol **1**. Because alcohol **1** is not available commercially, she designs and executes a synthesis of **1** using only isobutylene (2-methyl-1-propene) and formaldehyde as her only sources of carbon that find their way into **1**. All reagents and solvents were available to her, and to you, as you reconstruct the synthetic plan that she may have used.



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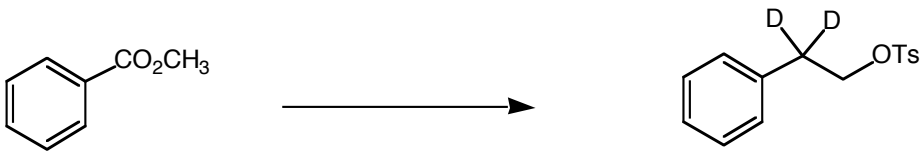
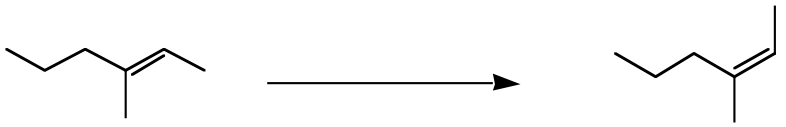
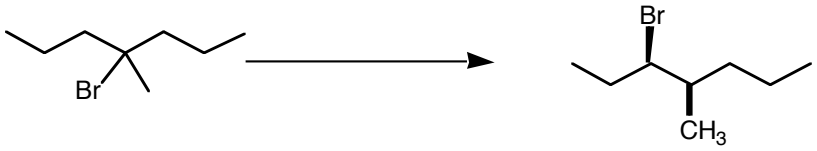
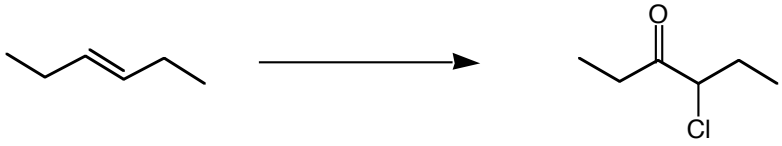
7. (36 pts) **Structure II**: Compound **A**, $C_7H_{14}O$, which has an infrared absorption at 1710 cm^{-1}, reacts with methyl magnesium bromide to produce **B**, $C_8H_{18}O$. Compound **B** does not react with Cr (VI) reagents but it readily reacts with H_2SO_4 to form several compounds having the formula C_8H_{16}. One of these compounds **C**, gives **D** and **E** upon ozonolysis and dimethylsulfide reduction. Both **D** and **E** have the formula C_4H_8O, but **D** is oxidized to **F** ($C_4H_8O_2$) with chromic acid while **E** is inert to these conditions. **F** is not n-butyric acid. Compound **C** is measurably less exothermic than its geometrical isomer **G** upon catalytic hydrogenation. [Hint: What are **D** and **E**? The infrared absorption is not essential but it is helpful.]

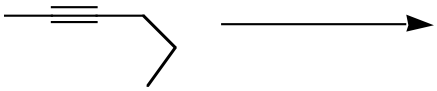
8. (32 pts; 4 x 8 pts) **Reactions II:** Do **four** of the following **five** problems by efficient pathways. If you do five, **cross out** the one you do not want graded.

a) 

b) 

c) 

d) 

e)  2-hexanone

Work Sheets

Work Sheets

Work Sheets

Work Sheets

Periodic Table

Bond Dissociation Energies

Natural Abundance of Common Isotopes

Hydrogen	$^{1}H = 99.985\%$	$^{2}H = 0.015\%$
Carbon	$^{12}C = 98.90\%$	$^{13}C = 1.10\%$
Nitrogen	$^{14}N = 99.63\%$	$^{15}N = 0.37\%$
Sulfur	$^{32}S = 95.02\%$	$^{33}S = 0.75\%$
	$^{34}S = 4.21\%$	$^{36}S = 0.02\%$
Chlorine	$^{35}Cl = 75.77\%$	$^{37}Cl = 24.23\%$
Bromine	$^{79}Br = 50.69\%$	$^{81}Br = 49.31\%$