

FINAL EXAM
Organic Chemistry

Chemistry 220a; 2 P.M., Wednesday, December 19, 2001

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 a **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 21), BDEs (page 22), Common Isotopes (pg. 23). 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 questions 2 and 4, you are to complete only one of the two choices that are offered for each.

For question 3, do 4 of 6. See directions on the exam.

For question 5, do 1 of 4.

For question 6, do 4 of 6.

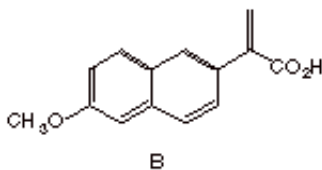
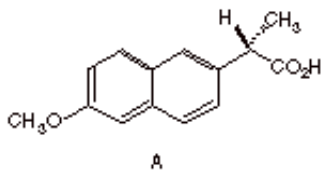
For question 8, do 5 of 6.

REMEMBER: Neatness is to your advantage. **Have a GREAT winter break! See you next term for Chem 221b.**

- | | |
|---|--|
| 1. Naproxen (36 pts) _____
Revisited | 5. Mechanism (20 pts.) _____ |
| 2. Structure (30 pts) _____ | 6. Kinetics/ (32 pts.) _____
Thermodynamics |
| 3. Potpourri (40 pts) _____ | 7. Radicals (32 pts.) _____ |
| 4. Synthesis (30 pts) _____ | 8. Reactions (30 pts.) _____ |

Total (250 pts) _____

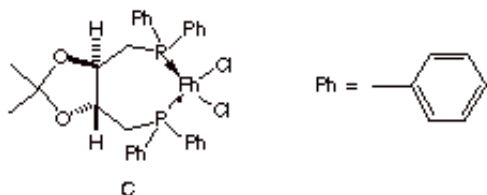
1. **Naproxen Revisited:** (6 x 6 pts. = 36 pts.) In exam 2, we considered the resolution of racemic Naproxen to isolate (*S*)-(+)-Naproxen (**A**). The current method for preparing (*S*)-(+)-Naproxen is by catalytic hydrogenation of carboxylic acid **B**.



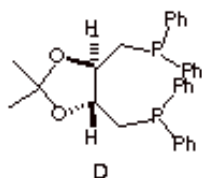
- a) Is **B** chiral or achiral? Why?

b) Will hydrogenation of **B** in the presence of a noble metal such as Pt form (*S*)-(+)-Naproxen efficiently (>75%)? Explain briefly.

c) The optically active rhodium catalyst **C**, Rh(DIOP)Cl₂, which was used in your text (pg. 219) to illustrate asymmetric hydrogenation [2001 Nobel Prize in Chemistry], might be an ideal catalyst to produce only a single enantiomer of Naproxen. **Briefly** illustrate and explain the principle of asymmetric hydrogenation in **general terms**. [Hint: Recall how you were to illustrate the resolution of Nap in exam 2.]



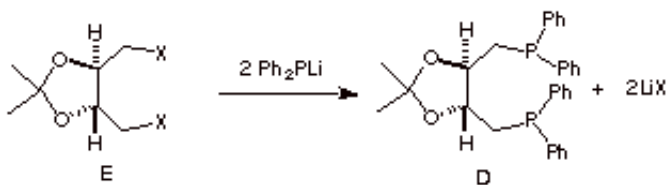
d) What are the configurations (R/S) of the stereocenters present in the ligand **D** used in the formation of catalyst **C**? Label them below.



e) The four carbon chain of the ligand **D** above is derived from one of the stereoisomers of tartaric acid. Which one is it? Draw it in a Fischer projection. [Hint: see below]



f) The tartaric acid is converted in three steps to compound **E** ($X = \text{a good leaving group}$). What type of mechanism is occurring in conversion **E** \rightarrow **D**?



g) Why is the asymmetric hydrogenation approach inherently more efficient than the resolution strategy? Be **brief**.

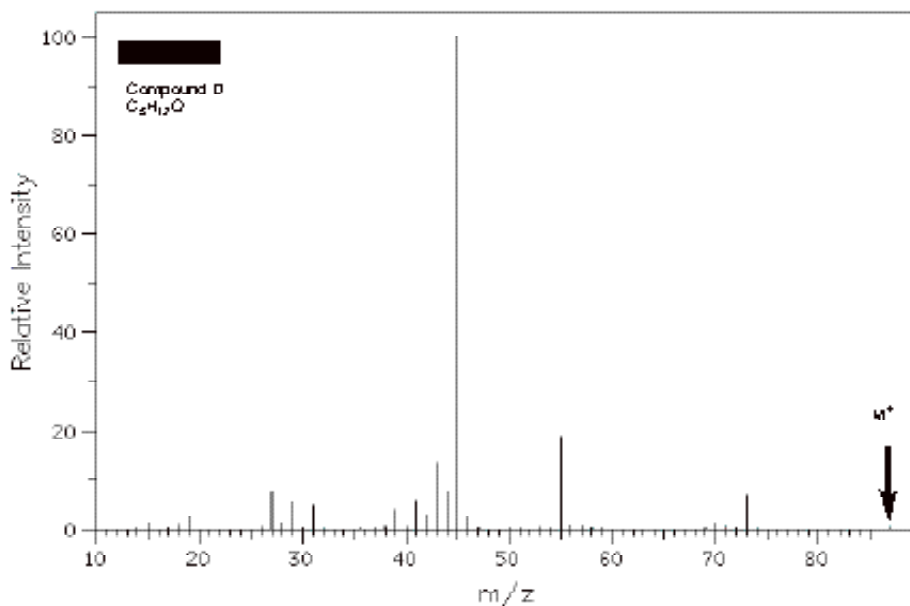
Do only 2a or 2b, not both of them!

2a. **Structure:** (30 pts.) Alkene **A**, $\text{C}_{10}\text{H}_{20}$, reacts with $\text{OsO}_4/\text{H}_2\text{O}_2$, to give (\pm)-diol **B**. This substance reacts with periodic acid to produce **single** compound **C**, $\text{C}_5\text{H}_{10}\text{O}$. Compound **C** can be synthesized from 1-pentyne in a single chemical reaction. Compound **C** is **inert** toward aqueous chromic acid but it reacts with $\text{NaBH}_4/\text{H}_2\text{O}$ or $\text{LiAlH}_4/\text{ether}$ to form **D**, $\text{C}_5\text{H}_{12}\text{O}$.

Place an "X" here if you want 2a graded. _____

i) (25 pts.) What are the structures of **A - D**? **Briefly** justify your answers.

ii) (5 pts.) The mass spectrum of **D** is shown below.



What is the value of m/z for the base peak?

What is the value of m/z for the molecular ion?

Do only 2a or 2b, not both of them!

2b. **Structure:** (30 pts.) Ester **A**, $C_6H_{12}O_2$, reacts with **two equivalents** of $RMgX$ (compound **B**) to provide alcohol **C** ($C_4H_{10}O$) and alcohol **D** ($C_8H_{18}O$). Alcohol **C** is converted into **E** (C_4H_8O) by either PCC/ CH_2Cl_2 or aqueous chromic acid. Treatment of alcohol **D** with H_2SO_4 leads to compounds (*E*)-**F**, (*Z*)-**G**, and **H**, all three of which have the formula C_8H_{16} . Compound **H** is the least abundant of the three. The reaction of compound **H** with O_3 and then $(CH_3)_2S$ permits the ready isolation of 4-heptanone. What are the structures of **A-H**? **Briefly** justify your answer.

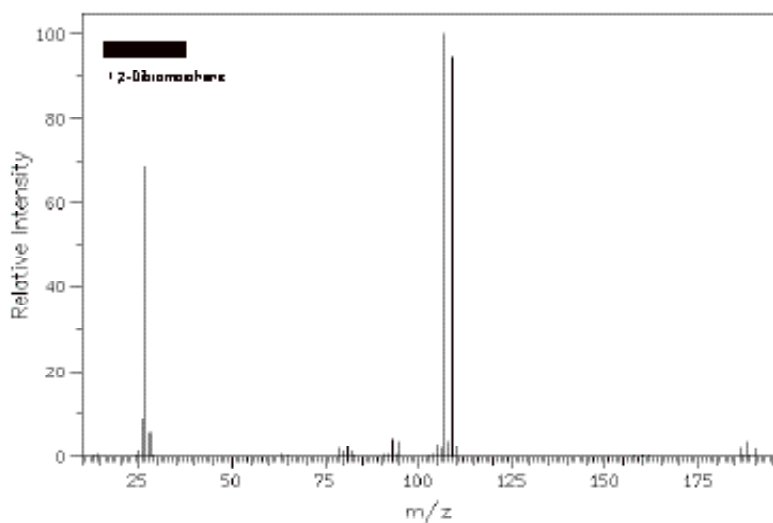
Place an "X" here if you want 2b graded. _____

Do 3a and 3b and two of the remaining four questions (3c-f).

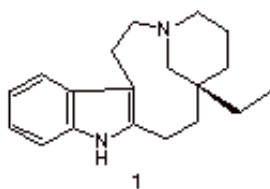
3. **Potpourri:** (4 x 10 pts. = 40 pts.) If you manage to do 5 or 6 problems, **cross out** the one(s) of 3c-f that you do not want graded.

a) Three compounds, **A**, **B**, and **C**, have the formula C_5H_{10} and all three of them afford 2-methylbutane upon catalytic hydrogenation. The three compounds have the following heats of formation (kcal/mol): **A**, -6.8; **B**, -8.4; **C**, -9.9. What are the structures of **A**, **B**, and **C**. Illustrate and explain **briefly**.

b) 1,2-Dibromoethane has three peaks for its molecular ion(s) of relative intensity 1:2:1. What are the masses of these 3 peaks and why are their relative intensities what they are?
(Common Isotopes, pg. 23)



c) The indole alkaloid quebrachamine (**1**) has a specific rotation $[\alpha]_D = -110^\circ$. An attempted resolution of (\pm)-**1** led to a sample that had $[\alpha]_D = -33^\circ$. What percentage of the **dextrorotatory** enantiomer was present? Show work.



d) The peracid epoxidation of (*E*)-2-butene (zero inversions) is the operational equivalent of what two inversion process? Illustrate and explain **briefly**.

e) What is one property that the compounds acetylene, hydrogen cyanide, and BeCl_2 share in common? Explain **briefly**.

f) Arrange (left to right) the following carbocations in increasing order of stability: $(\text{CH}_3)_3\text{C}^+$ (t-butyl cation), $(\text{CH}_3)_2\text{CH}^+$ (2-propyl cation), and $\text{CH}_3\text{OC}(\text{CH}_3)_2$ (2-methoxy-2-propyl cation). Explain **briefly**.

Do only 4a or 4b, not both of them!

4a. **Synthesis:** (30 pts.) A chemist requires a sample of 2,5-dimethyl-2-hexanol (**1**, $\text{C}_8\text{H}_{18}\text{O}$). She recognizes an element of symmetry ($\text{C}_4 + \text{C}_4$) in the hydrocarbon structure of the alcohol. She designs and executes a synthesis of **1** from acetone and methanol. She has all reagents and solvents available to her as do you. How would you complete the synthesis of this alcohol under the restrictions indicated?

Place an "X" here if you want 4a graded. _____

Do only 4a or 4b, not both of them!

4b. **Synthesis:** (30 pts.) A chemist isolates an optically active compound from nature which he believes to be (Z)-3-methyl-4-heptene-3-ol (**1**, C₈H₁₆O). He synthesizes **1** from 2-butyne as his only source of carbon. All reagents and solvents are available to you as they were to him. Reconstruct his synthesis.

Place an "X" here if you want 4b graded. _____

Is the synthetic alcohol optically active? **Justify**.

5. **Mechanism:** (20 pts.) Provide the mechanism of **one, and only one**, of the following reactions. Use the curved arrow formalism.

The Na/NH₃ reduction of 2-butyne

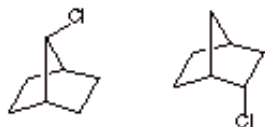
The ozonolysis/dimethyl sulfide reduction of (E)-2-butene

The hydroboration/oxidation of (E)-3-methyl-2-pentene

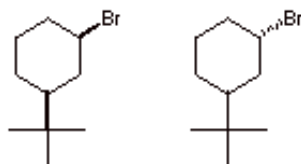
The reaction of HBr in the presence of a peroxide with 2-methyl-2-butene

6. **Kinetics/Thermodynamics:** (4 x 8 pts. = 32 pts.) Do 4, and **only 4**, of the following 6 problems. If you manage to do 5 or 6 problems, **cross out** the one(s) that you do not want graded. If structures are shown, **circle** the correct answer and provide a few words of justification. If no structure is shown, give a **brief** explanation.

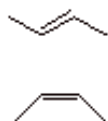
a) The compound with the lower rate for E2 elimination. **Justify.**



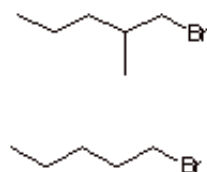
b) The compound with the greater rate of E2 elimination. **Justify.**



c) Of (Z)-2-butene and (E)-butene, the one with the greater heat of hydrogenation. **Illustrate and justify.**



d) The compound that gives the higher ratio (SN2/E2) of SN2 to E2 product when reacted with KOH. **Justify.**

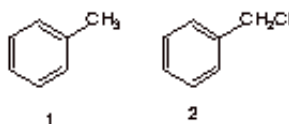


e) The heat of hydrogenation of ethylene to ethane is -32.9 kcal/mol and the heat of hydrogenation of acetylene to ethane is -74.5 kcal/mol.

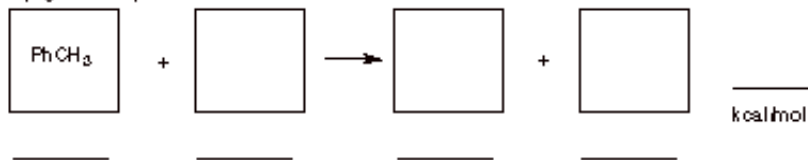
What is $\Delta H_{\text{f}}^{\circ}$ for ethylene given that $\Delta H_{\text{f}}^{\circ}$ for acetylene is +54.3 kcal/mol.

f) The C-H bond in acetylene is stronger than the C-H bond of ethane yet the C-H bond in acetylene is ~25 orders of magnitude more acidic than that in ethane. Explain **briefly**.

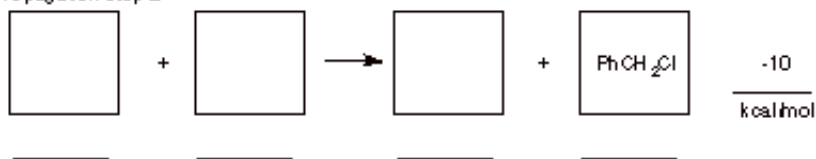
7. **Radicals:** (32 pts.) Benzylic C-H bonds, like allylic C-H bonds, have low bond dissociation energies relative to alkane C-H bonds (see page 22, BDEs). The free radical chlorination of toluene (PhCH_3 , **1**) gives benzyl chloride (PhCH_2Cl , **2**). The second propagation step has $\Delta H_{\text{o}} = -10$ kcal/mol.



Propagation step 1



Propagation step 2



Overall reaction

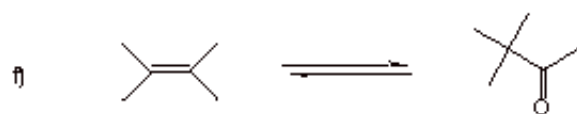
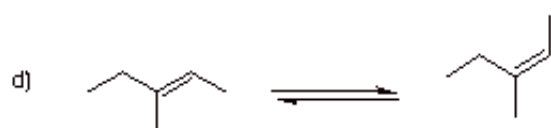


a) (12 pts.) Write the propagation steps for this reaction. Place the structures in the boxes and the BDEs on the appropriate lines. Determine the heat of reaction for the 1st propagation step. Put your answer on the appropriate line.

b) (8 pts.) Determine the overall heat of the reaction. Place your answer in the designated place.

c) (12 pts.) Given the following values for $\Delta H_{\text{f}}^{\circ}$ (kcal/mol): $\text{PhCH}_3 = +12$; $\text{HCl} = -22$, determine the heat of formation ($\Delta H_{\text{f}}^{\circ}$) of PhCH_2Cl .

8. **Reactions:** (5 x 6 pts. = 30 pts.) Do 5, and **only 5**, of the following 6 problems. If you manage to do 6 problems, **cross out** the one that you **do not** want graded. Provide the reagent(s) for the forward reaction (above the arrows) and for the reverse reaction (below arrows). Each reaction requires one or two steps. [Note: The arrows do not indicate equilibria.]



Work Sheets
Work Sheets
Work Sheets
Work Sheets

Periodic Table

Bond Dissociation Energies

Natural Abundance of Common Isotopes

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