

## EXAM 2

CHEMISTRY 220a

Friday, October 19, 2001

NAME (print): \_\_\_\_\_

TA: \_\_\_\_\_ Section Day: \_\_\_\_\_ Section Time: \_\_\_\_\_

Take a few moments to look over the exam. Answer each question on the exam paper.

Important clues and structures are in **bold**.

Do all **preliminary** drawing or computations on the work sheets at the end of the exam. The work sheets will not be graded. There is a Periodic Table on page 11 of the exam.

The exam is 55 minutes.

STOP writing and hand in your exam when you are asked to do so.

**REMEMBER:** Neatness is to your advantage.

1. (40 pts) \_\_\_\_\_

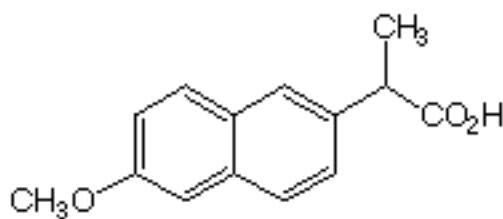
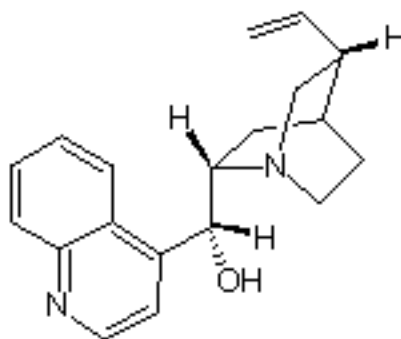
2. (25 pts) \_\_\_\_\_

3. (20 pts) \_\_\_\_\_

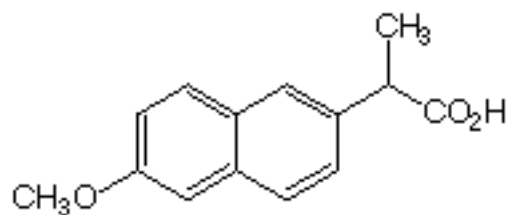
4. (20 pts) \_\_\_\_\_

\_\_\_\_\_  
Total (105 pts)

1. (8 x 5 pts = 40 pts) Naproxen **A** ( $[\alpha]_D = +65^\circ$ ) is an analgesic that is sold by prescription. Its sodium salt is the active ingredient in the over-the-counter product, Alleve. It is the (S)-(+)-enantiomer of Naproxen that is active and it is sold as such.

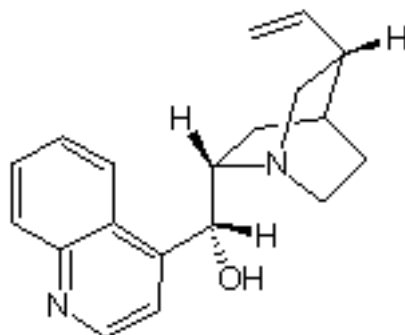
**A** (Naproxen)**B** (Cinchonidine)

- a) Is the phrase "(S)-(+)- enantiomer" redundant? Why or why not?
- b) Draw the dextrorotatory enantiomer of Naproxen using the template below.

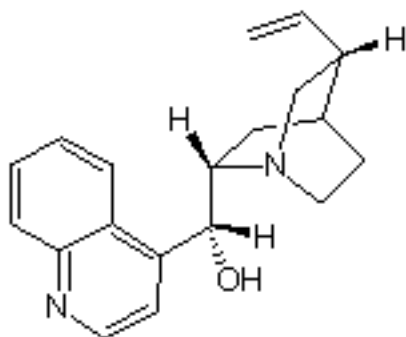


The original method for preparing (S)-(+)-Naproxen was to accomplish a large scale resolution of (±)-Naproxen with the naturally occurring base, cinchonidine **B** ( $[\alpha]_D = -110^\circ$ ).

- c) Describe briefly, in general terms, using the letters **A** (Naproxen) and **B** (Cinchonidine) and the signs of rotation, the principle behind the resolution.
- d) Which salt is more likely to be less soluble, seeing that cinchonidine got the job done?
- e) Circle the chiral centers in cinchonidine.

**B** (Cinchonidine)

e) Label **half** [your choice] of the chiral centers with their R/S configurations. Use the structure below.

**B** (Cinchonidine)

f) On a bad day, the rotation of a sample of Naproxen obtained by resolution was

+39°. What percentage of each enantiomer was present and what was the enantiomeric excess of the sample? Show work.

g) Why is resolution generally a relatively expensive way of preparing pure (S)-(+)-Naproxen? Be brief [Hint: Think about the % yield of the reaction.]

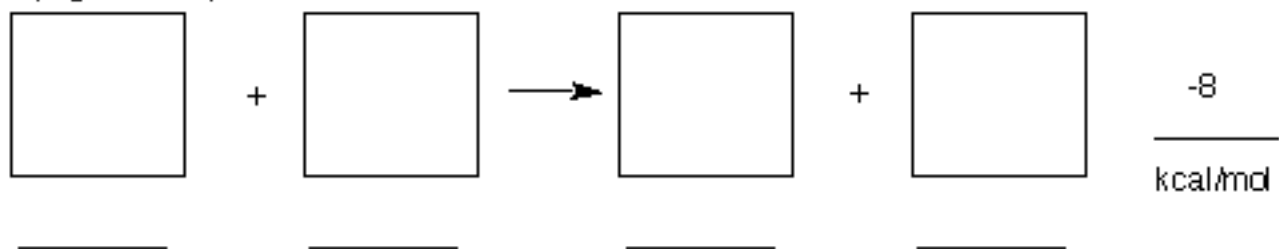
2. (25 pts) Consider the free radical chlorination of cyclopentane.

a) ( 4 pts.) What is the initiation step?

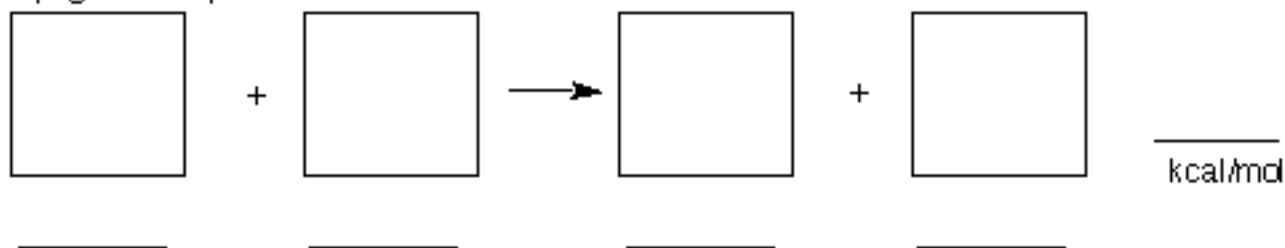
b) ( 7 pts.) Provide the two propagation steps and the overall reaction for this process.

Place the reactants and products in the appropriate boxes. **Cyclopentane goes in the first box.**

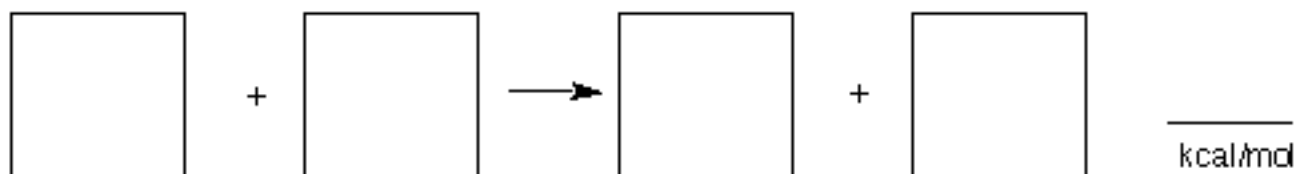
Propagation step 1



Propagation step 2



Overall reaction



c) ( 7 pts.) Determine the bond dissociation energy ( $DH^{\circ}$ ) of a C-H bond in cyclopentane using the data on the [last page \(pg. 12\)](#) of the exam. Place the data on the lines **under the appropriate boxes and at the end of each reaction that requires a value. Show any calculations below.**

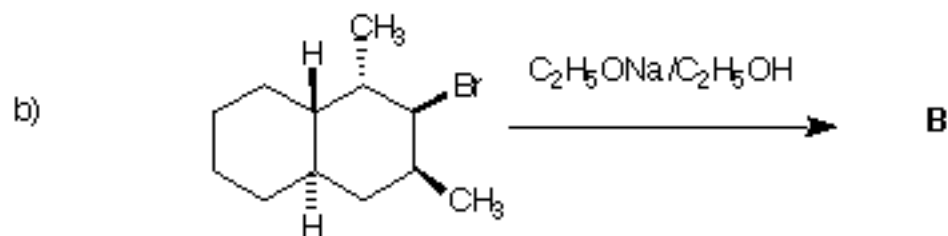
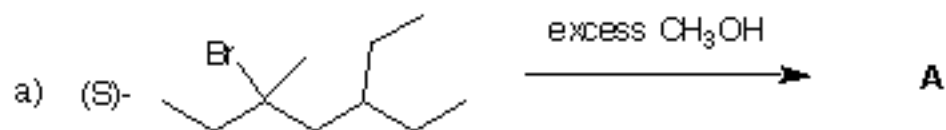
d) ( 7 pts.) Using Hess's Law [ $\Delta H^{\circ}(\text{rxn}) = \Delta H^{\circ}(\text{products}) - \Delta H^{\circ}(\text{reactants})$ ] and the

heat of the overall reaction, determine the **heat of formation** of chlorocyclopentane

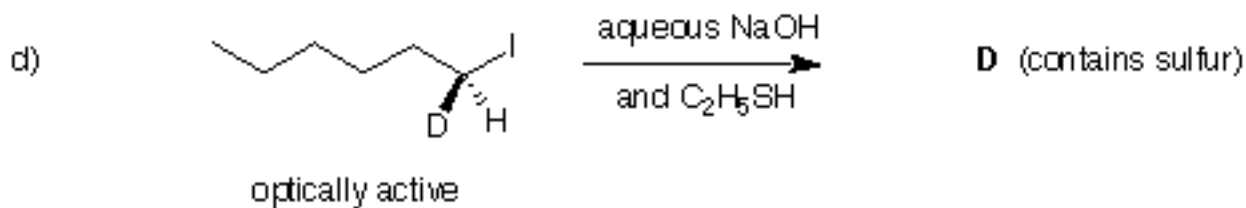
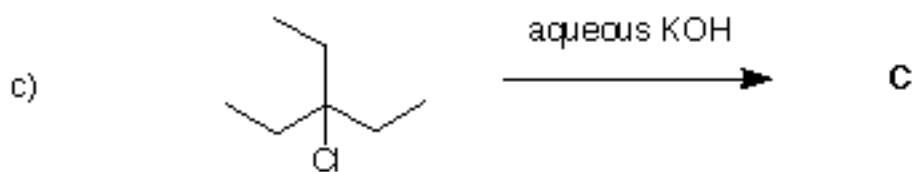
given:  $\Delta H_f^\circ$  (cyclopentane) = -18 kcal/mol;  $\Delta H_f^\circ$  (HCl) = -22 kcal/mol. **Show**

**work.**

3. (4 x 5 pts. = 20 pts.) Provide the **major product** expected in each of the following reactions and the **mechanism** of formation:  $S_N2$ , E2,  $S_N1$ , or E1. **Pay attention to stereochemistry and optical activity.**

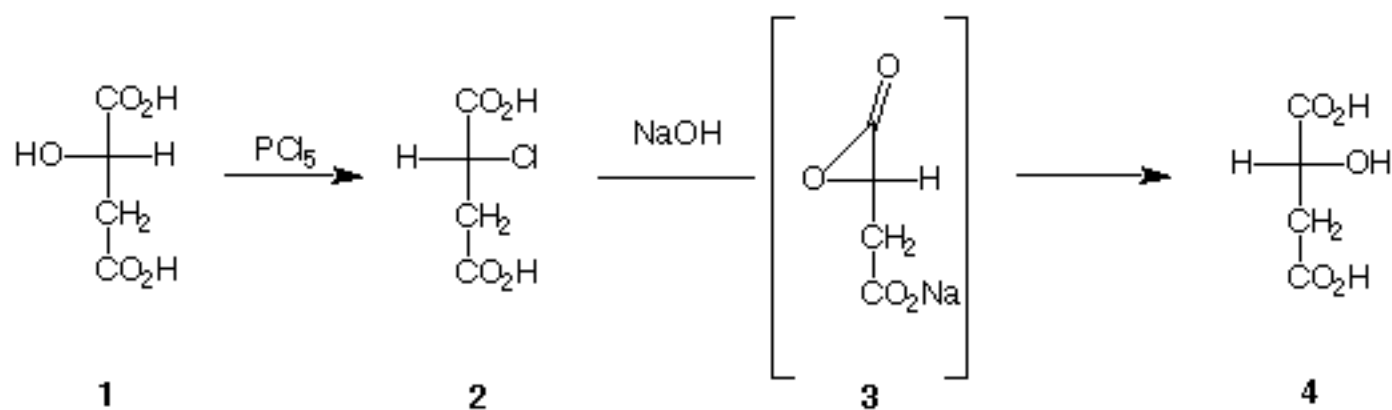


[Hint: remember what is true about trans-decalin and the hydrogen atoms that are shown]

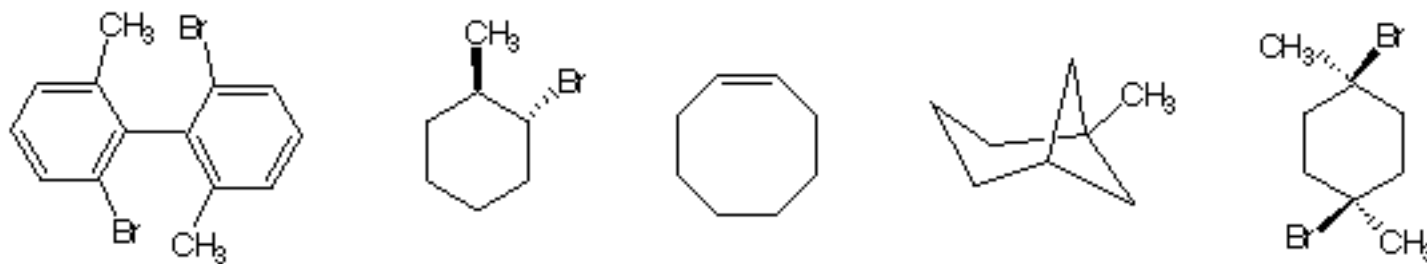


4. (4 x 5 pts. = 20 pts.) Circle the **best** answer(s) in each of the following questions.

a) Which of the compounds (1-4) in the Walden cycle are of the (S)-configuration?



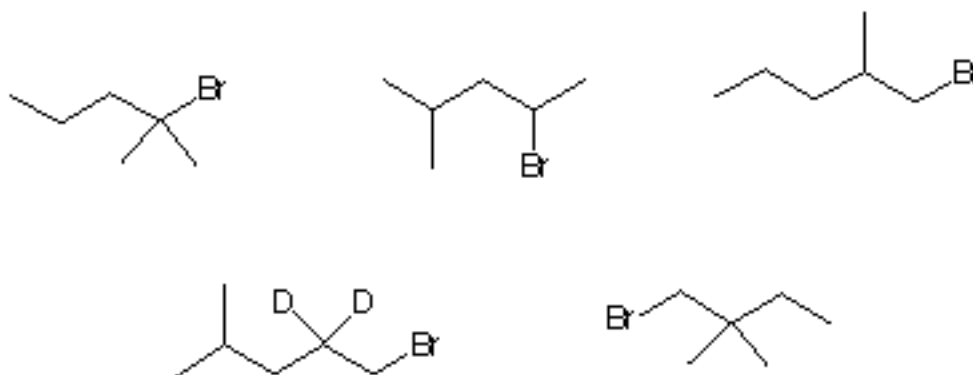
b) Which of the following compounds are capable of existing as enantiomers?



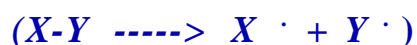
c) In calculating  $[\alpha]_D = \alpha_{\text{obs}} / c \cdot l$ , the value of "l" is measured in

g/mL	$\text{cm}^{-1}$	degrees	dm	cm
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d) The alkyl bromide that undergoes  $\text{S}_{\text{N}}2$  reaction the fastest



## Bond Dissociation Energies (kcal/mol)



### C-H Bonds

$\text{CH}_3\text{-H}$	$\text{CH}_3\text{CH}_2\text{-H}$	$(\text{CH}_3)_2\text{CH-H}$	$(\text{CH}_3)_3\text{C-H}$	$\text{CH}_2=\text{CHCH}_2\text{-H}$	$\text{PhCH}_2\text{-H}$	$\text{CH}_2=\text{CH-H}$

### C-C Bonds

$\text{CH}_3\text{-CH}_3$	$\text{CH}_3\text{CH}_2\text{-CH}_3$	$(\text{CH}_3)_2\text{CH-CH}_3$	$\text{CH}_3\text{CH}_2\text{-CH}_2\text{CH}_3$	$(\text{CH}_3)_3\text{C-CH}_3$
88	85	84	82	81

### C-Cl Bonds

$\text{CH}_3\text{-Cl}$	$\text{CH}_3\text{CH}_2\text{-Cl}$	$(\text{CH}_3)_2\text{CH-Cl}$	$(\text{CH}_3)_3\text{C-Cl}$
84	81	80	79

### C-Br Bonds

$\text{CH}_3\text{-Br}$	$\text{CH}_3\text{CH}_2\text{-Br}$	$(\text{CH}_3)_2\text{CH-Br}$	$(\text{CH}_3)_3\text{C-Br}$
70	68	68	65

### C-I Bonds

$\text{CH}_3\text{-I}$	$\text{CH}_3\text{CH}_2\text{-I}$	$(\text{CH}_3)_2\text{CH-I}$	$(\text{CH}_3)_3\text{C-I}$
56	53	53	50



**H-X and X-X Bonds**

H-Cl	H-Br	H-I	H-H	Cl-Cl	Br-Br	I-I
103	88	71	104	58	46	36