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) _____

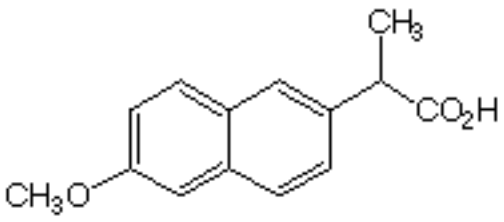
3. (20 pts) _____

4. (20 pts) _____

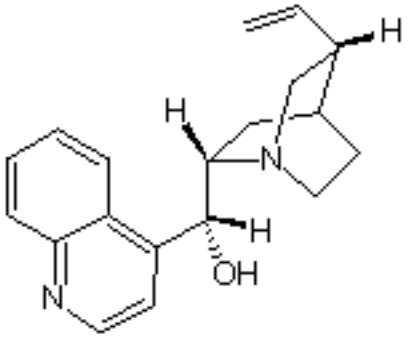
_____

Total (105 pts)

1. (8 x 5 pts = 40 pts) Naproxen **A** ($[\alpha]_D = +65^o$) 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.



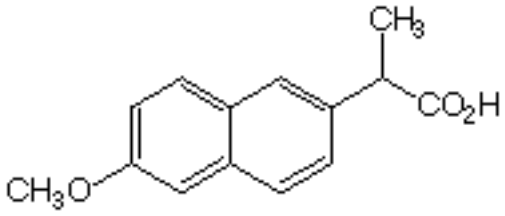
A (Naproxen)



B (Cinchonidine)

a) Is the phrase "(S)-(+)- enantiomer" redundant? Why or why not?

b) Draw the dextrorotatory enantiomer of Naproxen using the template below.

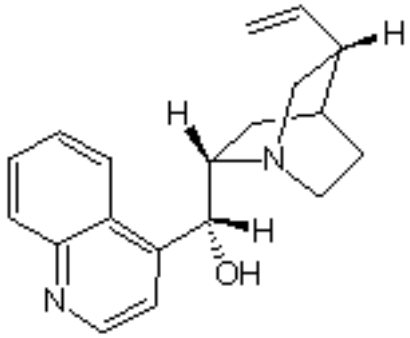


The original method for preparing (S)-(+)-Naproxen was to accomplish a large scale resolution of (±)-Naproxen with the naturally occurring base, cinchonidine **B** ($[\alpha]_D = -110^o$).

c) Describe briefly, in general terms, using the letters **A** (Naproxen) and **B** (Cinchonidine) and the signs of rotation, the principle behind the resolution.

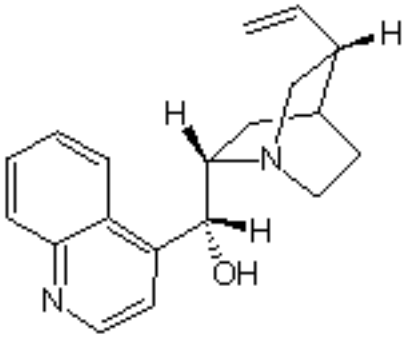
d) Which salt is more likely to be less soluble, seeing that cinchonidine got the job done?

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)

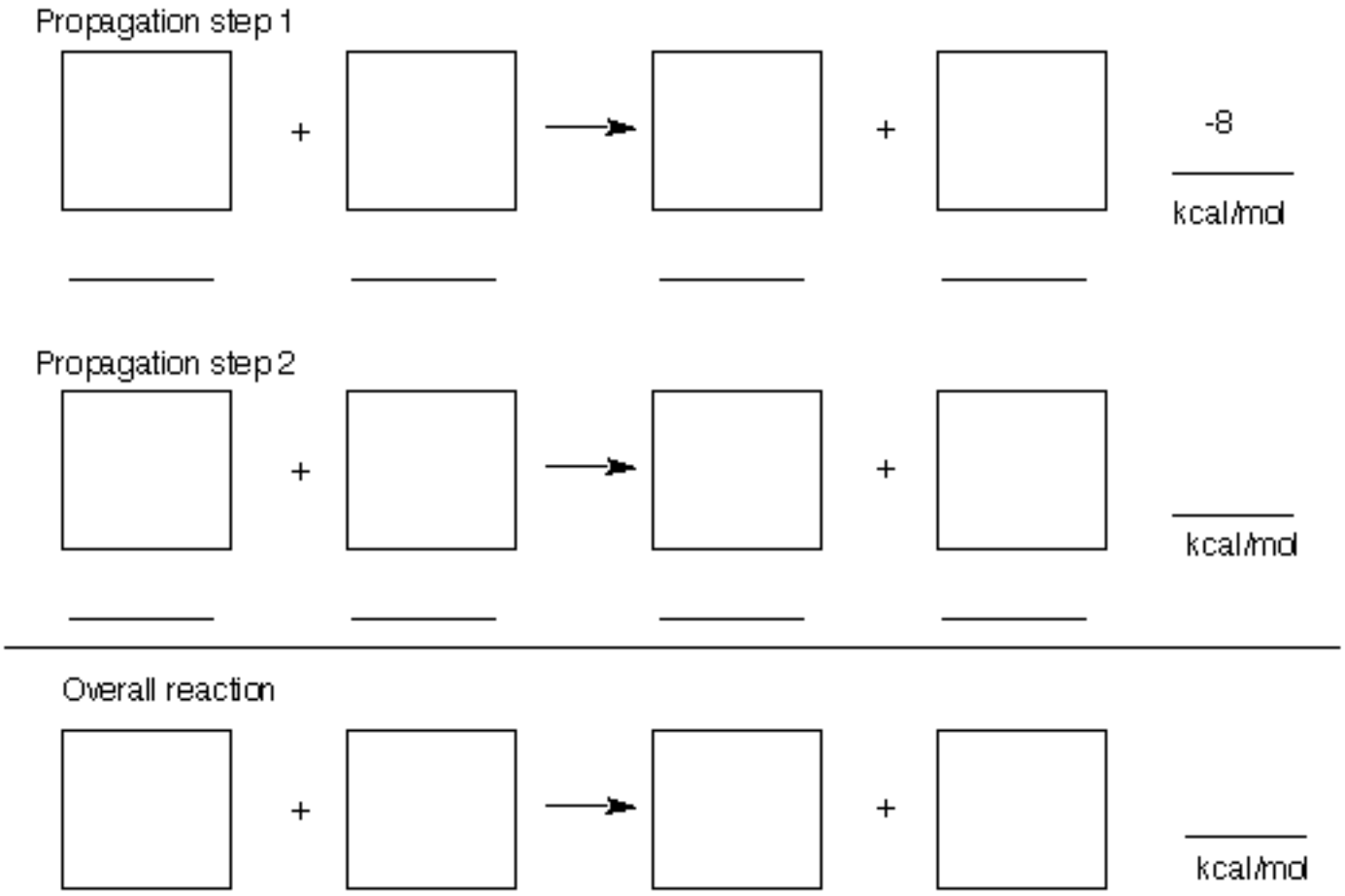
f) On a bad day, the rotation of a sample of Naproxen obtained by resolution was $+39^{o}$. What percentage of each enantiomer was present and what was the enantiomeric excess of the sample? Show work.

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.**



c) (7 pts.) Determine the bond dissociation energy (DH^o) 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.**

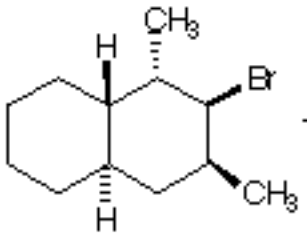
d) (7 pts.) Using Hess's Law [ΔH^o (rxn) = ΔH^o (products) - ΔH^o (reactants)] and the

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

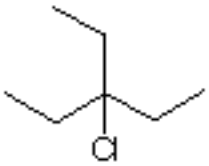
given: ΔH_f^o (cyclopentane) = -18 kcal/mol; ΔH_f^o (HCl) = -22 kcal/mol. **Show work.**

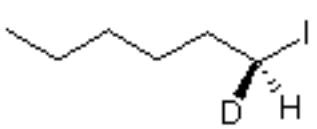
3. (4 x 5 pts. = 20 pts.) Provide the **major product** expected in each of the following reactions and the **mechanism** of formation: S_N2, E2, S_N1, or E1. **Pay attention to stereochemistry and optical activity.**

a) (S)-  excess CH_3OH → **A**

b)  C_2H_5ONa/C_2H_5OH → **B**

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

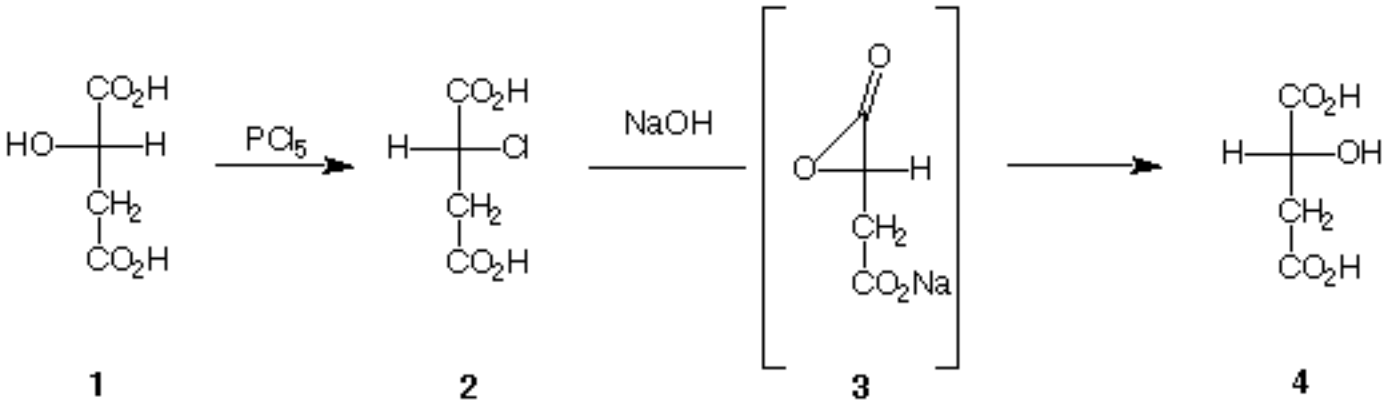
c)  aqueous KOH → **C**

d)  aqueous NaOH and C_2H_5SH → **D** (contains sulfur)

optically active

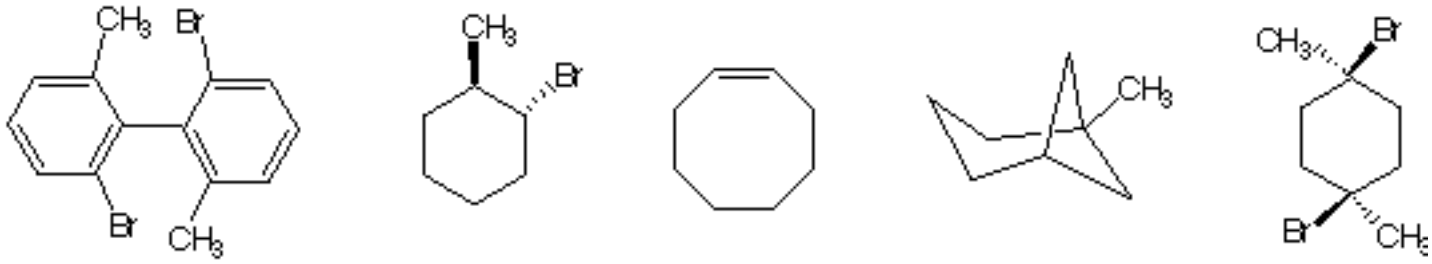
4. (4 x 5 pts. = 20 pts.) Circle the **best** answer(s) in each of the following questions.

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



1 **2** **3** **4**

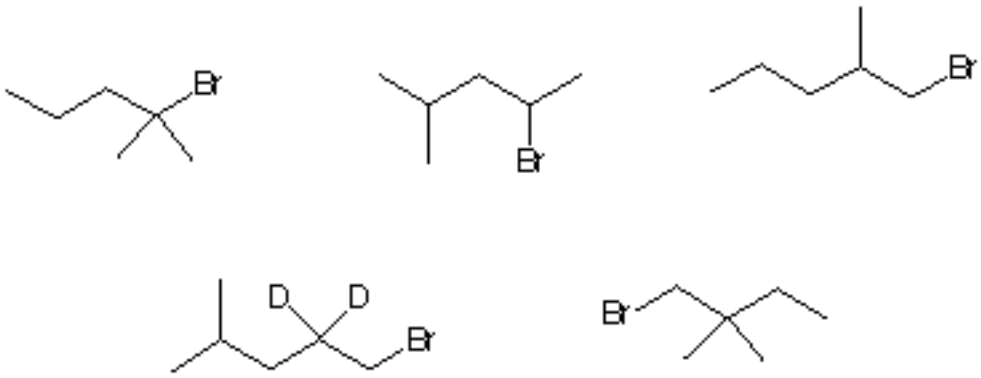
b) Which of the following compounds are capable of existing as enantiomers?



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

g/mL	cm^{-1}	degrees	dm	cm

d) The alkyl bromide that undergoes S_N2 reaction the fastest



Bond Dissociation Energies (kcal/mol)

(X-Y -----> X · + Y ·)

C-H Bonds

CH_3-H	CH_3CH_2-H	$(CH_3)_2CH$-H	$(CH_3)_3C$-H	CH_2=$CHCH_2$-H	$PhCH_2$-H	CH_2=CH-H

C-C Bonds

CH_3-CH_3	CH_3CH_2-CH_3	$(CH_3)_2CH$-CH_3	CH_3CH_2-CH_2CH_3	$(CH_3)_3C$-CH_3
88	85	84	82	81

C-Cl Bonds

CH_3-Cl	CH_3CH_2-Cl	$(CH_3)_2CH$-Cl	$(CH_3)_3C$-Cl
84	81	80	79

C-Br Bonds

CH_3-Br	CH_3CH_2-Br	$(CH_3)_2CH$-Br	$(CH_3)_3C$-Br
70	68	68	65

C-I Bonds

CH_3-I	CH_3CH_2-I	$(CH_3)_2CH$-I	$(CH_3)_3C$-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