EXAM 2

CHEMISTRY 220a

Friday, October 16, 2009

NAME (print): ____

TA:_________________ Sect. Day:_________________ Sect. Time:_____________

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

No calculators. You may use molecular models. 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.

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. (20 pts) Thermochemistry ______

2. (20 pts) Optical Activity ______

3. (20 pts) Stereochemistry ______

4. (20 pts) Reactions 1 (Do 3 of 4) ______

5. (20 pts) Reactions 2 (Do 3 of 4) ______

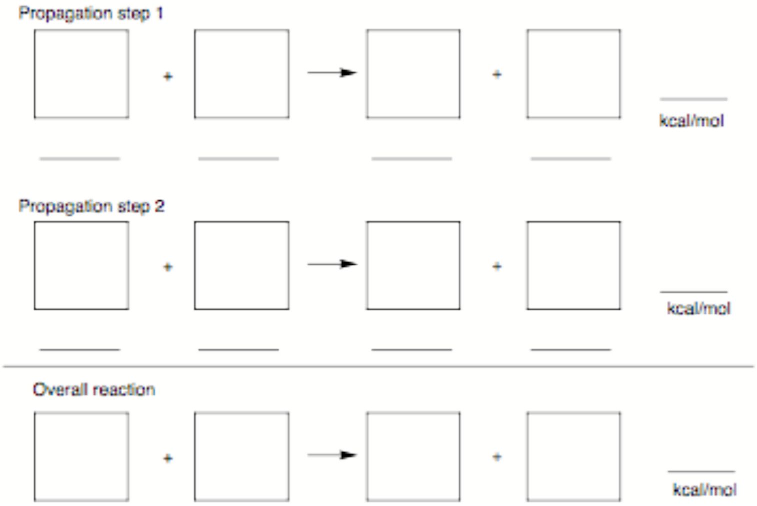
____

Total (100 pts)

1) **Thermochemistry:** (20 pts.) Problem 1 in the alkane module of ORGO (a reading assignment on

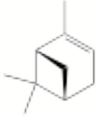
PS3) dealt with the free radical chlorination of 2,2-dimethylpropane (neopentane) to form 1-chloro-2,2-dimethylpropane.

a) (8 pts.) Provide the two propagation steps and the overall reaction for this process. **Place the reactants and products in the appropriate boxes.**



b) (6 pts.) Determine the heat of reaction for each of the propagation steps and for the overall reaction given the typical BDE's in the BDE Table (page 8). Place the values on the appropriate lines **under the boxes and at end** of each reaction. **Show any calculations below.**

c) (6 pts.) Using Hess's Law and the overall reaction, determine the heat of formation of 1-chloro-2,2-dimethylpropane given: DH_f^o (neopentane) = -40 kcal/mol; DH_f^o (HCl) = -22 kcal/mol. **Show work below**.

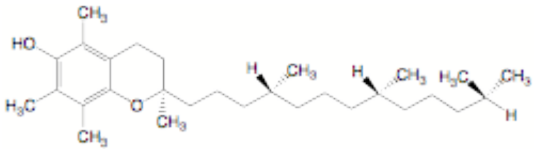
2) **Optical Activity:** (20 pts.) a-Pinene (**1**) isolated from European pines is principally levorotatory, whereas North American pines afford mainly the dextrorotatory enantiomer.	 1

a) (8 pts.) An 80/20 mixture of a-pinene from European sources shows $[a] = -30^o$. What is the rotation of the pure, major enantiomer of European a-pinene? **Show work.**

b) (8 pts.) Using the results of **1a**, what is the percentage composition of a sample of a-pinene of North American origin that displays [a] = +40°? **Show work**.

c) (4 pts.) Is a-pinene (**1**) dextro- or levorotatory? **Explain briefly**.

3) **Stereochemistry:** (20 pts.) The fat-soluble, optically-active anti-oxidant vitamin E (a-tocopherol) is shown below.



a) (8 pts.) How many stereoisomers of vitamin E are there (including the one shown. **Explain briefly**.

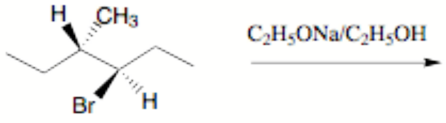
b) (8 pts.) Provide the R/S-configuration for each of the carbons that require them. [**Enter your**

configurations on the structure.]

c) (4 pts.) *Nature Made* sells vitamin E (d,l-a-tocopherol) and vitamin E natural (d- a -tocopherol). What might be the sources of these two a –tocopherols?

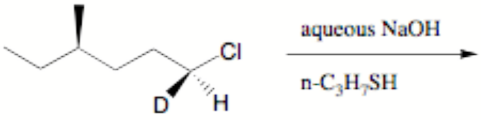
4) **Reactions 1:** (20 pts.; equal weight) Provide the product in **3 of 4** of the following reactions. **If you do more than three, cross out the one that you do not want graded. Pay attention to stereochemistry!**

a)



A (major Saytzeff product)

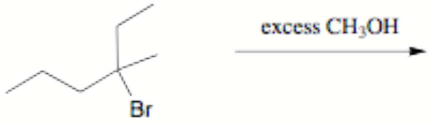
b)



optically active

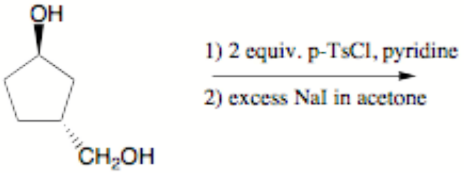
A (optically active; define R/S-centers)

c) (R)-



A (configuration)

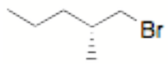
d)

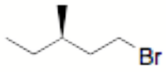


A (diiodide)

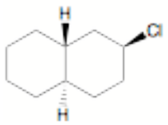
5. **Reactions 2:** (20 pts.; equal weight) Complete **3 of 4** of the following problems. **If you do more than three, cross out the one that you do not want graded.**

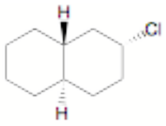
a) Of the two optically-active bromides shown below, **circle** the one that will have the higher S_N2/E2 ratio when treated with sodium methoxide in methanol. Give a brief rationale.





b) **Circle** the choride that will undergo E2 elimination at a faster rate. Give a brief rationale.





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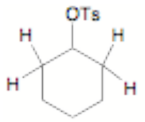
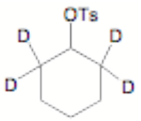
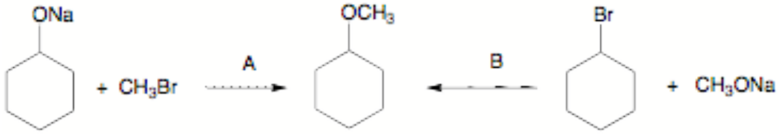
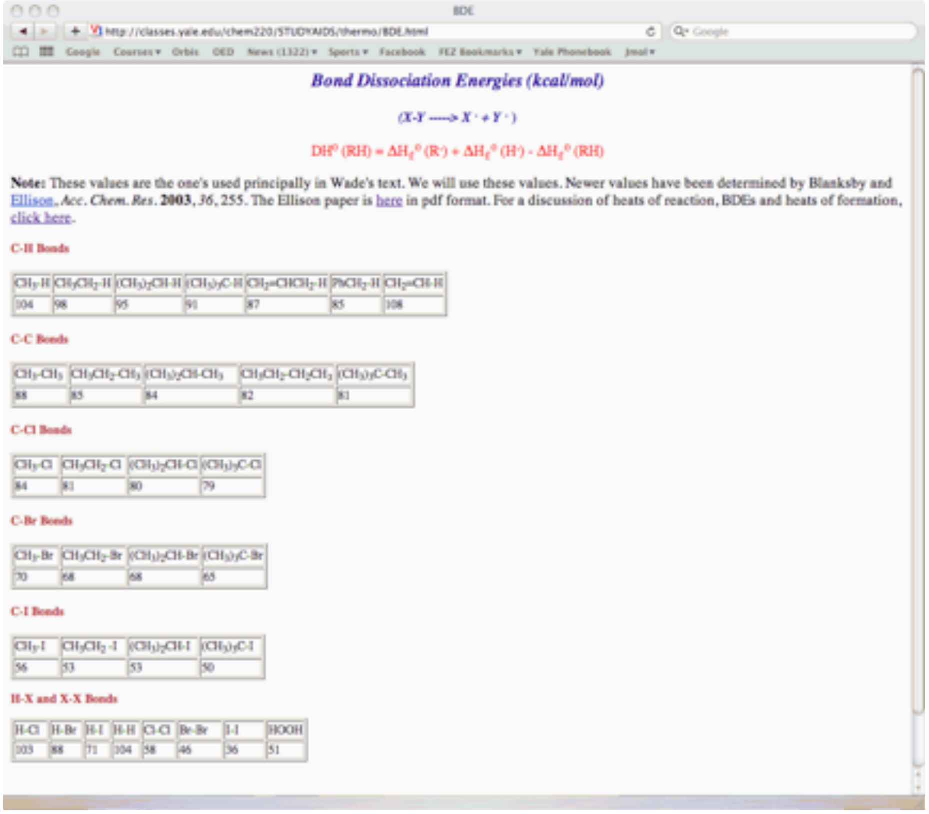
c) **Circle** the tosylate that will undergo E2 elimination slower with aqueous KOH. Give a brief rationale.





d) Is path A or B the more efficient way to prepare cyclohexylmethyl ether? Give a brief rationale.





Bond Dissociation Energies (kcal/mol)

(X-Y ----> X · + Y ·)

DH° (RH) = $\Delta H_f°$ (R·) + $\Delta H_f°$ (H·) - $\Delta H_f°$ (RH)

Note: These values are the one's used principally in Wade's text. We will use these values. Newer values have been determined by Blanksby and Ellison, *Acc. Chem. Res.* **2003**, *36*, 255. The Ellison paper is here in pdf format. For a discussion of heats of reaction, BDEs and heats of formation, click here.

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
104	98	95	91	87	85	108

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	HOOH
103	88	71	104	58	46	36	51

Work Sheets
Work Sheets
Work Sheets