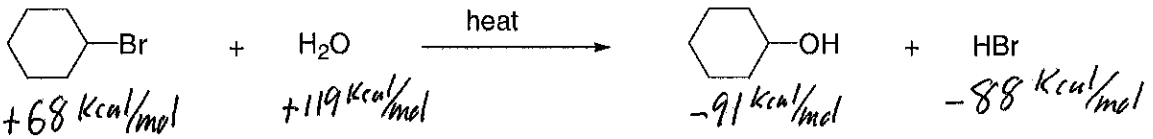
Spring 2012 Key

I. Theory

1. Provide an equation that shows the relationship between Gibb's free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). (3 points)

$\Delta G = \Delta H - T\Delta S$

2. Use the bond dissociation energy table on the last page to calculate the enthalpy of the reaction below in Kcal/mol. State whether the reaction is endothermic or exothermic. (4 points)

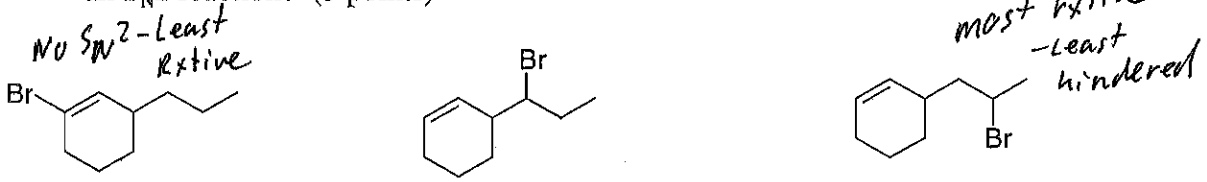


$+187 - 179 =$ +8 Kcal/mol, endotherm.

3. Provide a rate equation for the reaction above. (3 points)

S_N1 Rate = k_r[ⵔ-Br]

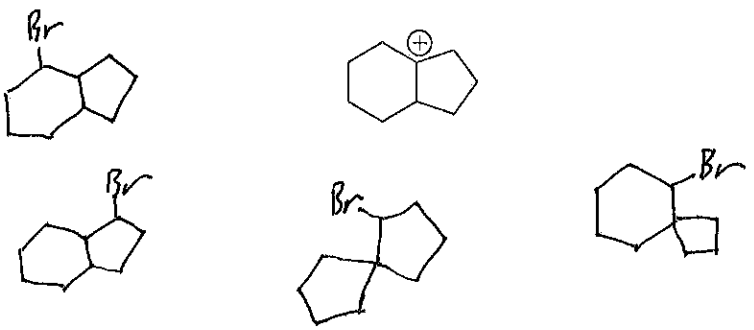
4. Which sequence ranks the following substrates in order of increasing reactivity in an S_N2 reaction? (3 points)



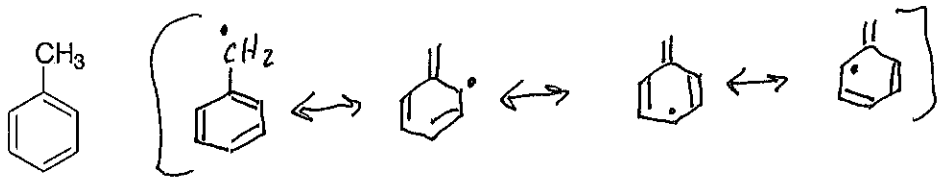
1 **2** **3**

a) 1<2<3 b) 2<3<1 c) 3<1<2 d) 3<2<1 e) 2<1<3 f) 1<3<2

5. Provide the structure of 4 constitutional isomers ($C_9H_{15}Br$) that undergo a structural rearrangement to produce the following carbocation. (8 points)

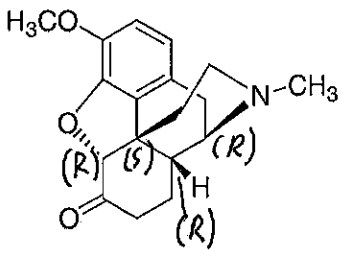


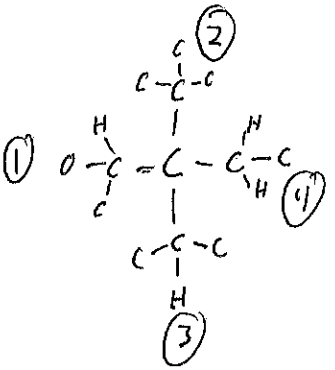
6. The benzylic carbon-hydrogen bond of toluene, shown below, has a low bond dissociation energy (85 kcal /mol) due to the stability of the intermediate resulting from homolytic bond dissociation. Draw a structure for this intermediate and all contributing resonance structures. (5 points)



II. Stereochemistry

1. Hydrocodone is a powerful pain reliever and when combined with the acetaminophen make up the #1 best selling prescription medication in the U.S.. Assign each chiral center as having R or S configuration. (8 points)



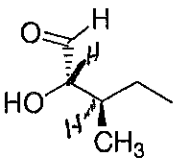


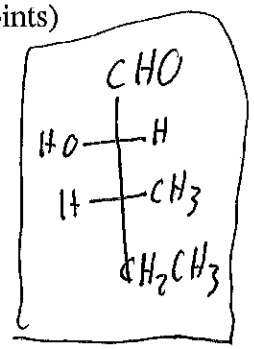
2. How does relative stereochemistry differ from absolute stereochemistry? (2 points)

Relative stereochem. is a comparison between 2 chiral centers. Absolute ster. provide exact configuration & stands alone.

3. Compounds that rotate plane polarized light are said to be optically active. (2 points)

4. Translate the following structure to a Fischer projection **and** then draw its enantiomer in its most stable Newman projection siting down the C2-C3 bond. (10 points)





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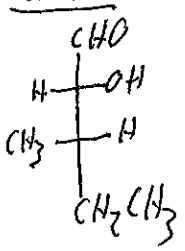
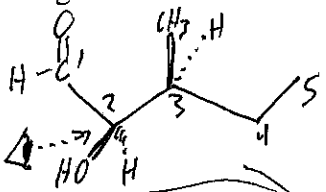
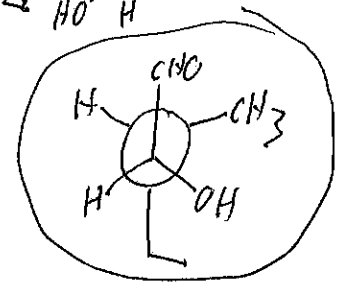
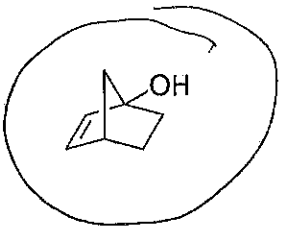
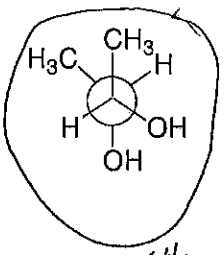


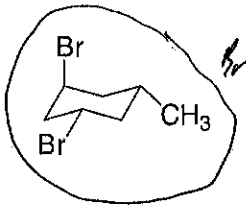


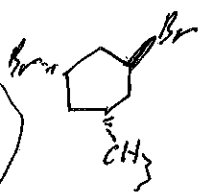


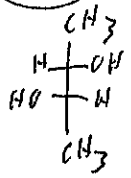
5. Circle all chiral structures below. Indicate any meso structures. (6 points)











6. A reaction produced a nonracemic mixture of two enantiomeric compounds, A and A'. The chiral mixture had a specific rotation of +25°. It was found that pure enantiomer A, had an specific rotation of -65°. Calculate the optical purity of this mixture and then state the percent abundance of each enantiomer in the reaction mixture. Show all of your work for full credit. (4 points)

$[\alpha_D]_{mix} = +25^\circ$

$[\alpha_D]_A = -65^\circ$

$[\alpha_D]_{A'} = +65^\circ$

optic. purity $= \left|\frac{[\alpha_D]_{mix}}{[\alpha_D]_{pure}}\right| \times 100\% = \left|\frac{25^\circ}{-65^\circ}\right| \times 100\% = 38.5\%$

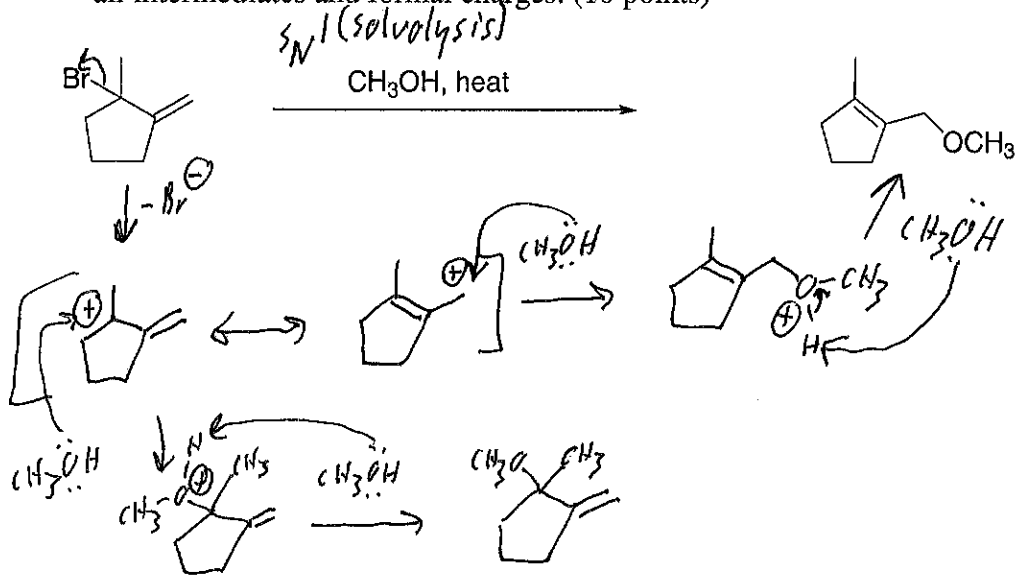
$100\% - 38.5\% = 61.5\%$ $\quad 61.5\% / 2 = 30.75\%$

69.25% + 30.75%

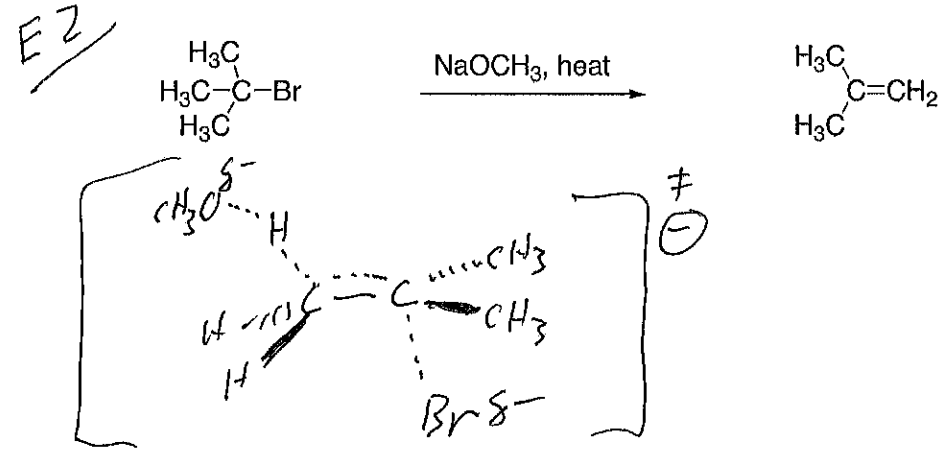
A' A

III. Mechanisms

1. Provide an arrow pushing mechanism that accounts for the ~~two products~~ product shown. Include all intermediates and formal charges. (10 points)

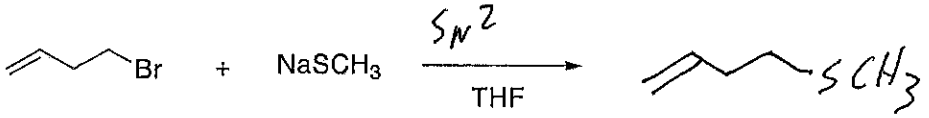


2. Provide a structure for the transition state of the following reaction. (4 points)

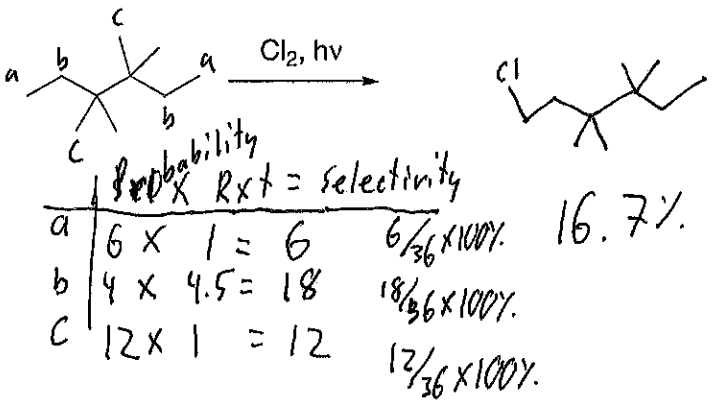


IV. Reactions

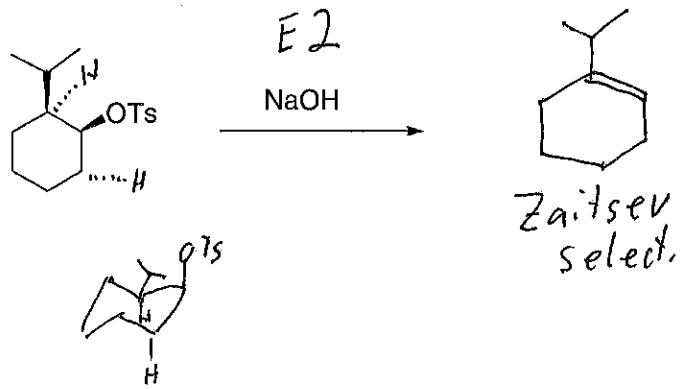
1. Predict the product of the following reaction. (3 points)



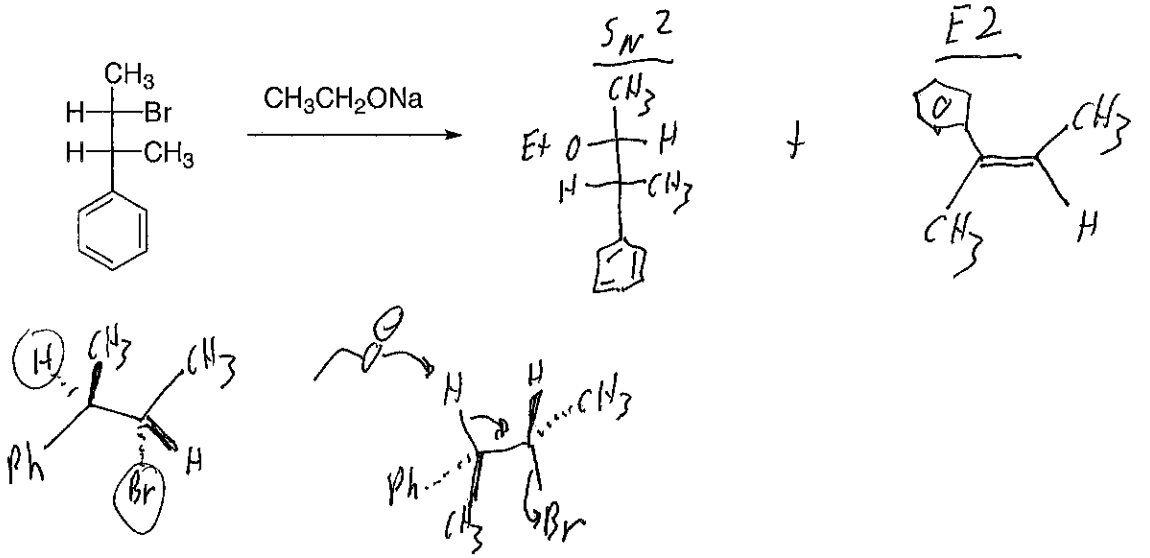
2. Draw the monochlorination products resulting from the following reaction. Use the relative reactivity of each type of hydrogen to determine the percent abundance of each product. (8 points)



3. Provide the major elimination product of the following reaction. Include all relevant stereochemistry. (3 points)

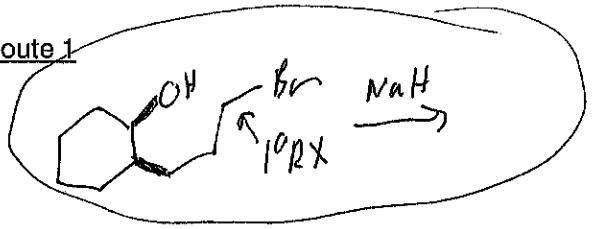


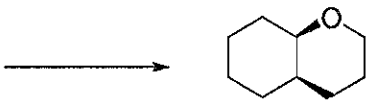
4. Provide a Fischer projection for the major substitution product and draw the major elimination product in a line-angle structure. (6 points)



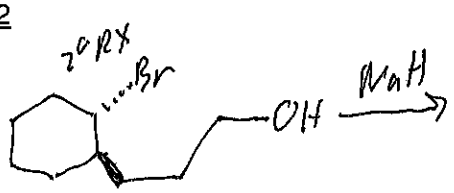
5. Provide the starting materials for two possible intramolecular S_N2 reactions that produce the following product. Circle the better of the two routes. (8 points)

Route 1





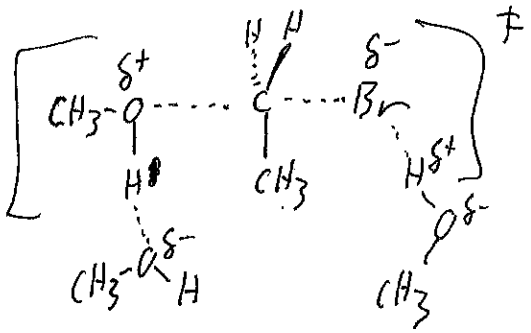
Route 2



V. **Extra Credit** (5 points)

1. Using the reaction below, show how a polar protic solvent is able to stabilize the transition state of this reaction.

$$CH_3CH_2Br \xrightarrow{CH_3OH} CH_3CH_2OCH_3$$



You received _____ points out of 100 points possible. To check your overall performance in lecture see http://vista.weber.edu/.