

CHEM 3311
Second Hour Exam
Summer 2005

Name (please print): _____

Key

Recitation T.A.: (circle one) Greg Matt Xin

Honor Code Statement

By printing your name above, you pledge that
"On my honor, as a University of Colorado at Boulder student,
I have neither given nor received unauthorized assistance on this exam."

| | | |
|------------|-------|-----|
| Question 1 | _____ | 10 |
| Question 2 | _____ | 14 |
| Question 3 | _____ | 15 |
| Question 4 | _____ | 9 |
| Question 5 | _____ | 16 |
| Question 6 | _____ | 13 |
| Question 7 | _____ | 11 |
| Question 8 | _____ | 4 |
| Question 9 | _____ | 8 |
| TOTAL | _____ | 100 |

General Instructions

This is a closed book exam. No notes and no molecular models may be used.

You have 2 hours to complete the exam.

Write your name on the top of each page.

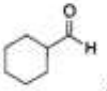

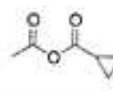
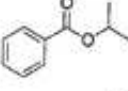


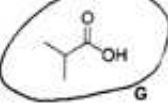
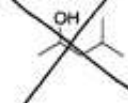
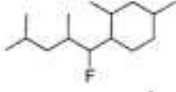

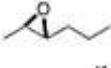
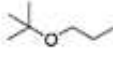
Use the back of pages for scratch paper.

Don't cheat!

There are 9 questions and 9 pages, including this cover sheet - be sure you have them all.

Good luck!

1a) In the column at the left, for each functional group name write the letter of the compound in the grid that contains the functional group (4 pts).

| | | | |
|----------------------|---|---|--|
| <u>D</u> ester |  |  |  |
| <u>B</u> ketone |  |  |  |
| <u>C</u> anhydride |  |  |  |
| <u>F</u> amine |  |  |  |
| <u>K</u> epoxide | | | |
| <u>L</u> ether | | | |
| <u>A</u> aldehyde | | | |
| <u>J</u> acid halide | | | |

Handwritten annotations: A circle around G, an 'X' through H, and a checkmark under D.

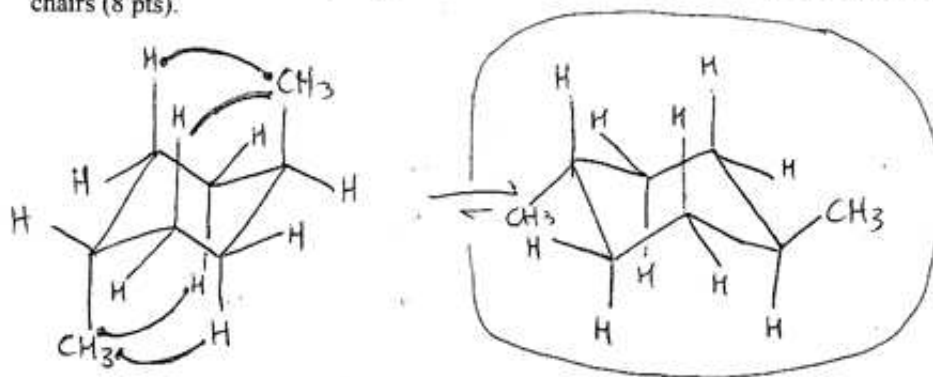
1b) In the grid in (1a), put a circle around the compound that has a pK_a around 4. (1 pt)

1c) In the grid in (1a), put an "X" through the compound whose acid strength is close to that of water. (1 pt)

2) Consider this bond-line structure:



2a) Draw both conformations of this molecule (*i.e.*, the chair and its ring-flipped conformer). Your chairs should be drawn carefully, using the technique presented in class and text. Include all hydrogens. Points will be deducted for improperly drawn chairs (8 pts).



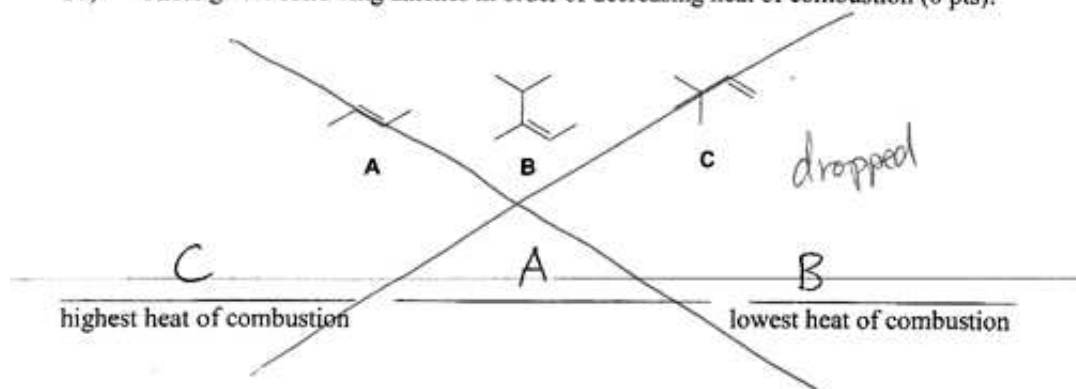
4 gauche butane
interactions
0.8 kcal/mole each
→ ≈ 3.2 kcal/mole

2b) Circle the more stable conformation of this molecule (1 pt) ✓

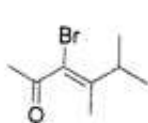
2c) In the less stable conformation, identify all structural features which contribute to raising its energy relative to the more stable isomer. "Identify" means to correctly name the structural feature(s) and to indicate where it is/they are in the molecule (4 pts). ✓

2d) Estimate the difference in energy in kcal/mol between the two conformations of the molecule you drew above (1 pt). ✓

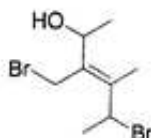
3a) Arrange the following alkenes in order of decreasing heat of combustion (6 pts).



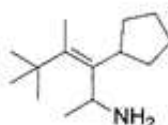
3b) Indicate whether each of the following alkenes should be designated "E" or "Z" according to Cahn-Ingold-Prelog priority rules (6 pts).



Z



Z



Z

3c) Which has a higher boiling point, pentane or pentanol (1 pt)? pentanol

3d) Explain *briefly* your answer to 3c. No more than 1 or 2 sentences is necessary (2 pts)

Stronger intermolecular forces (dipole-dipole, and specifically H bonding) in pentanol compared to pentane (an alkane with only induced dipole-induced dipole forces)

4) Provide short (one or two sentences) answers to each of the following questions.
(9 pts)

Why does the free radical halogenation of alkanes require light or heat?

To initiate the reaction by homolytically cleaving the X-X bond. Bond breaking is endothermic

What is the difference between a transition state and an intermediate?

Intermediate: All bonds are fully formed

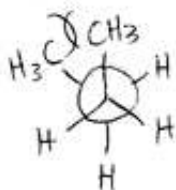
Transition state: Bonds are partially formed/broken

Define **one** of the following and give **one** example. Notice the use of **bold type** for the word **one**. (Hint: Define only one, not all three.)

Steric strain



Atoms or groups of atoms are too close to each other, leading to repulsion (vander Waals forces)



Torsional strain



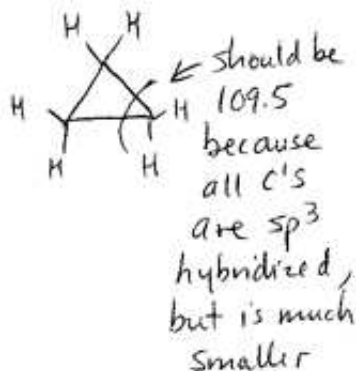
Bonding e⁻ in one bond too close to bonding e⁻ in another bond



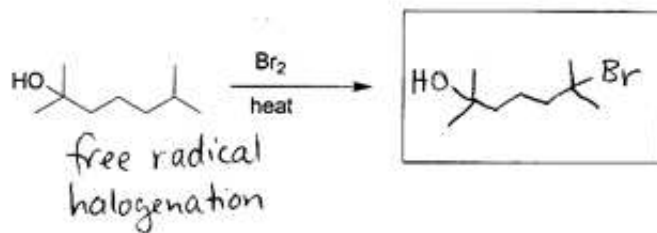
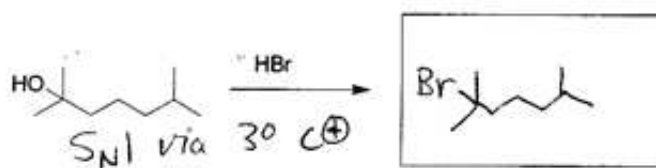
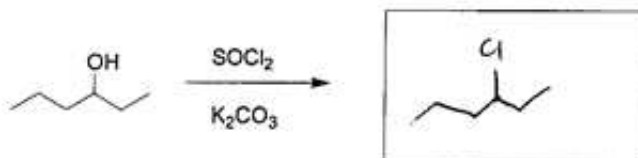
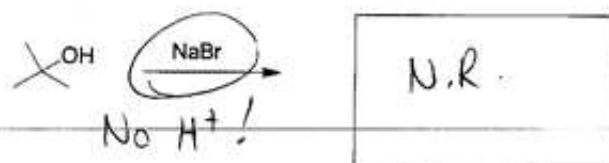
Angle strain



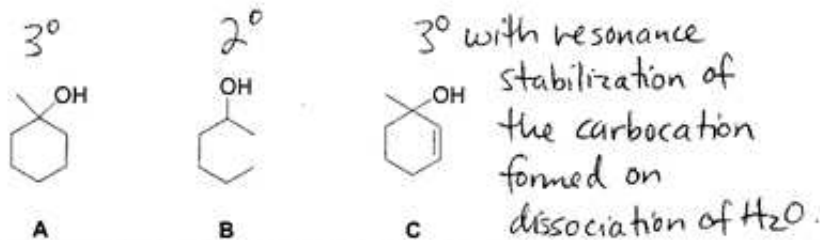
Bond Angles deviate from the ideal



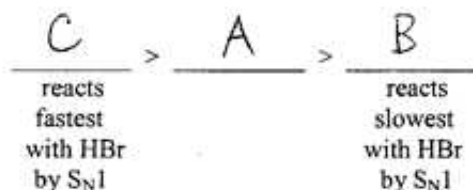
5. Predict the principal organic product following reaction. If no reaction occurs, write "N.R." (16 pts)



6) Assume each of the following alcohols reacts in an S_N1 fashion in the presence of HBr:

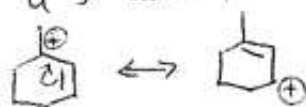


6a) Predict the relative reactivity of each of these alcohols in an S_N1 reaction mechanism with hydrogen bromide (3 pts).



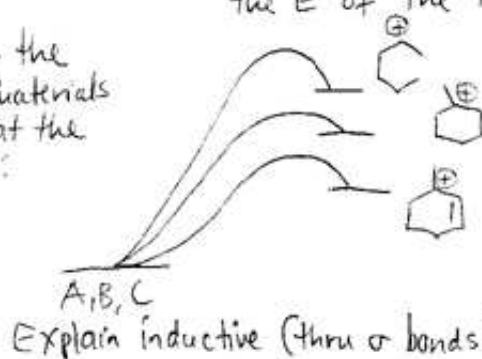
6b) Provide a concise explanation for your answer to 6a. Include a potential energy diagram showing the relative energies of any relevant transition states and intermediates and a brief discussion of the factors which stabilize each (10 pts)

A is a 3° alcohol and on protonation and dissociation of H_2O , a 3° carbocation is formed.
 B is a 2° alcohol and on protonation and dissociation of H_2O , a 2° carbocation is formed.
 C is a 3° alcohol. It forms a 3° carbocation with this structure:



Resonance stabilization can occur here that is not present in the 3° carbocation derived from A, thus lowering the E of the intermediate carbocation from C as well as the E of the transition state leading to it.

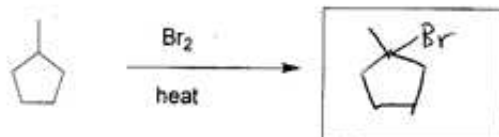
Assuming the starting materials are all at the same E:



All endothermic elementary steps.

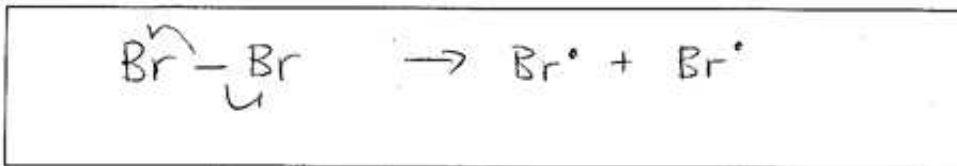
Comparing 2° and 3° carbocations, 3° has more stabilization from inductive effects and hyperconjugation than 2° (i.e., more alkyl groups).

7a) What is the major product of the following reaction? (1 pt)

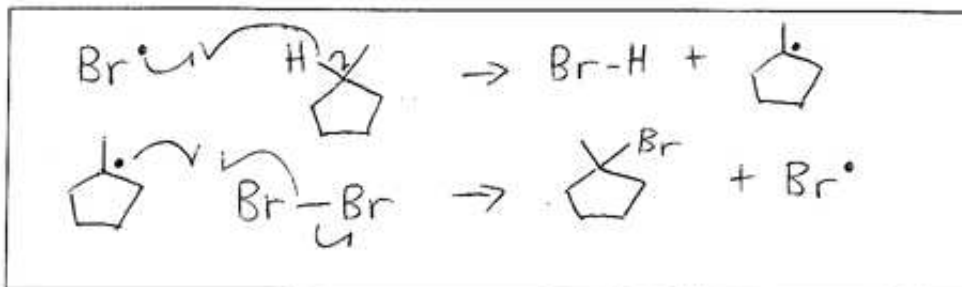


7b) Draw a mechanism for the formation of this product. Include the initiation step, all chain propagation steps, and all possible termination steps. (10 pts)

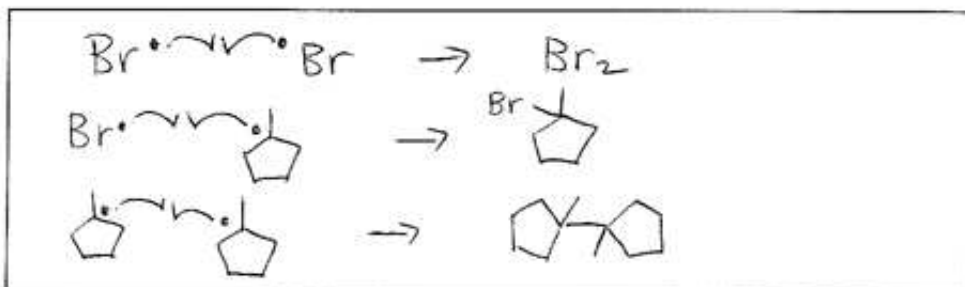
Initiation step:



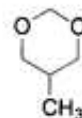
Chain propagation steps:



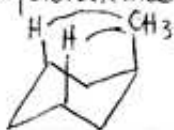
Termination steps:



8) The compound shown at right exhibits less of a preference for having its methyl group equatorial than methylcyclohexane. Suggest a concise explanation for this observation, using drawings to indicate any structural features that support your reasoning. (4 pts)



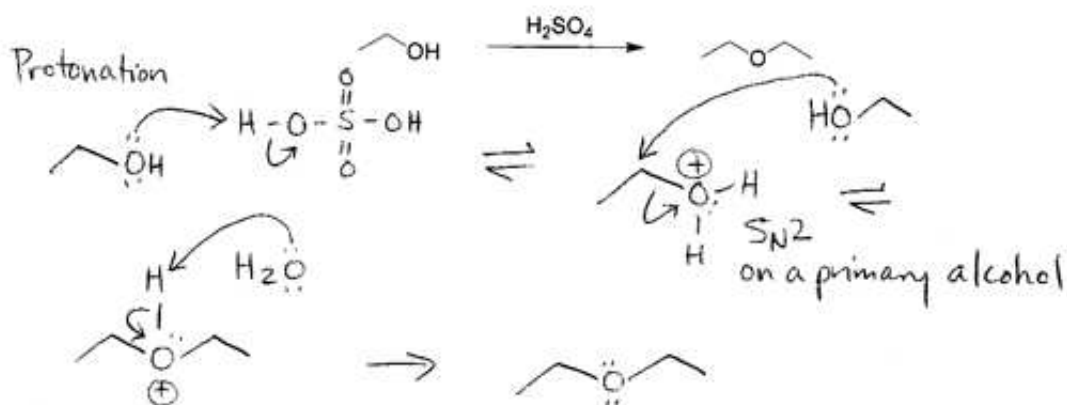
In methylcyclohexane there are 2 gauche butane interactions:



In the other compound (shown above) there are lone pairs at the axial positions. The lone pairs are more polarizable and can distort to minimize 1,3 diaxial interactions



9) Using appropriate curved arrow notation, propose a reasonable mechanism for the following transformation. Show all intermediates and include all non-zero formal charges and lone pairs of electrons. (8 pts)



Mop up the proton with the weak base, H_2O .