Printed Name:_____

CHEM 3311-100, Fall 2013
Professor Walba
Third Hour Exam
November 19, 2013

scores:

1)

2)

3)

4)

5)

_____

CU Honor Code Pledge: On my honor, as a University of Colorado at Boulder Student, I have neither given nor received unauthorized assistance.

Signature: _____

Recitation TA Name: _____

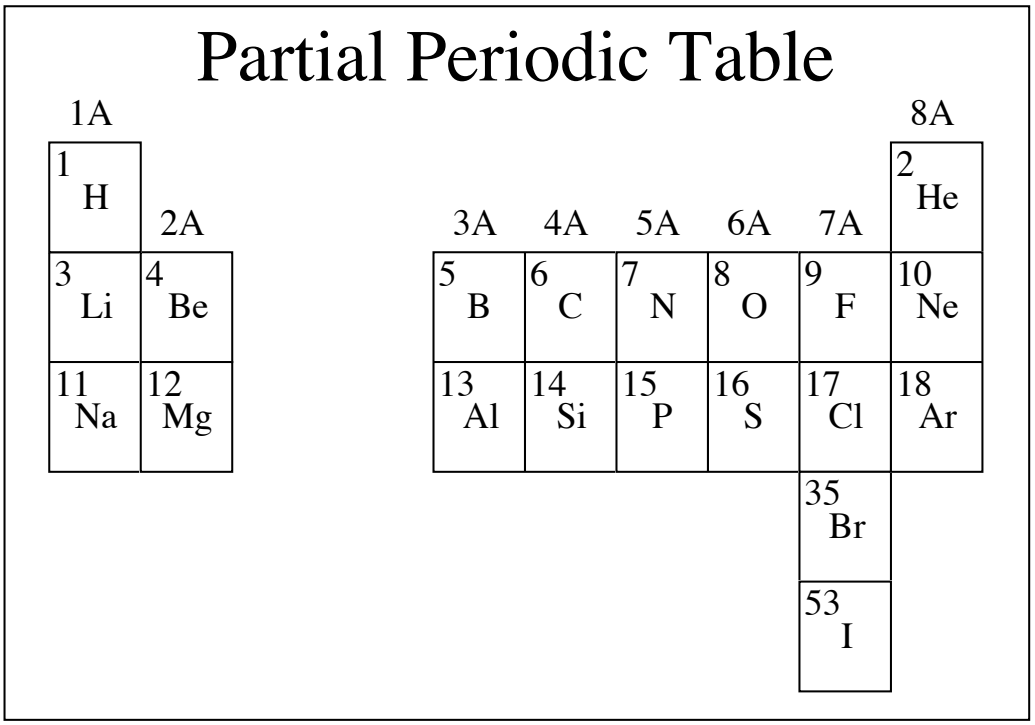
Recitation day and time: _____

This is a closed-book exam. The use of notes, calculators, scratch paper, or cell phones will not be allowed during the exam. You may use models brought in a clear ziplock bag. Please put all you answers on the test. Use the backs of the pages for scratch.

PLEASE read the questions very carefully!

*PLEASE **legibly** print your name on each page of the exam.*

Partial Periodic Table



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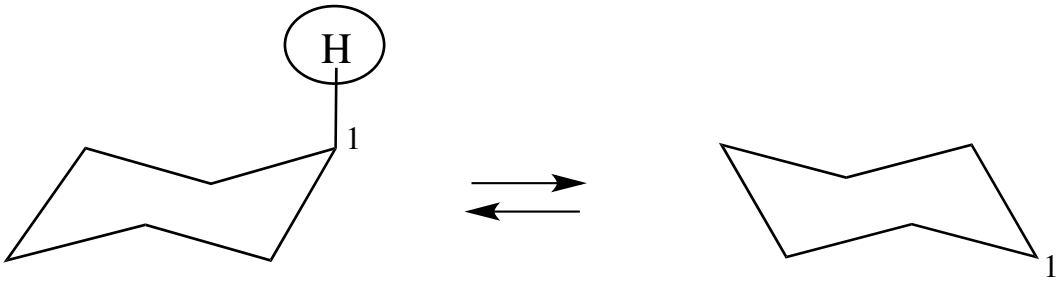
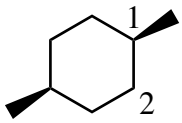
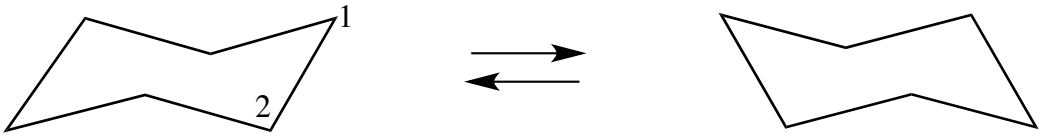
1 (20 pts) a) The carbon atoms of the two perspective chair ("flip chair") conformations of cyclohexane are given below. One of the carbons is labeled (carbon 1) in both structures, and one of the H atoms on carbon 1 is shown, and circled, in the structure on the left. **Carefully** complete the two structures showing **ALL** H atoms. Circle the H atom on the right structure corresponding to the H atom circled on the left structure. Use a "broken line" to indicate if a C—H is behind one of the C—C bonds, and make an unambiguously bold line if a C—H bond is in front of one of the C—C bonds.



b) Complete the two flip-chair conformations for cis-1,4-dimethylcyclohexane, using the carbon atom numbering scheme indicated. Do not put in the H atoms on the rings, but use "CH_3" to indicate the methyl groups. In the boxes below the structures, write the estimated strain energy for each conformation in units of "GB" = Gauche Butane interactions ≈ a single 1,3-diaxial CH_3 – H interaction.





GBs of strain

GBs of strain

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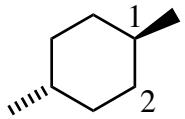
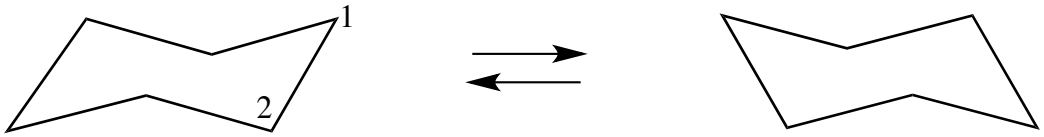
1) –continued-

c) Complete the two flip-chair conformations for trans-1,4-dimethylcyclohexane and give the strain energy of the two conformations as in part b) above.



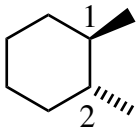


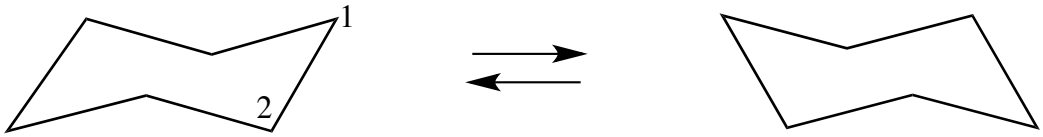
GBs of strain

GBs of strain

d) Which stereoisomer of 1,4-dimethylcyclohexane is more stable, cis or trans?

e) Complete the two flip-chair conformations for trans-1,2-dimethylcyclohexane and give the strain energy of the two conformations as in part c) above.





GBs of strain

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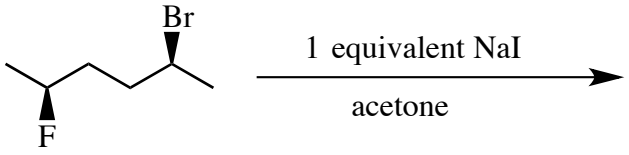
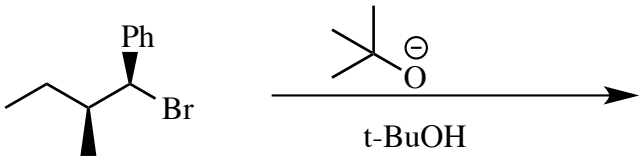
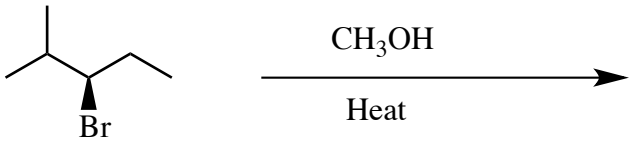
2) (20 pts) Give the single major product for each of the following reactions (two major product for part e), carefully showing stereochemistry using wedges and dashes. If a racemate is formed, show only one enantiomer and label it "rac." Assume chiral starting materials are single pure enantiomers unless they are labeled "rac." NOTE: Ph = phenyl group = benzene ring.

a) 

b) 

c) 

d) 

e) 

Give the TWO major products for part e

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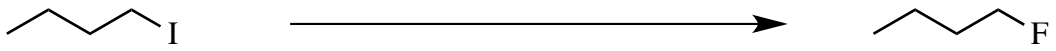
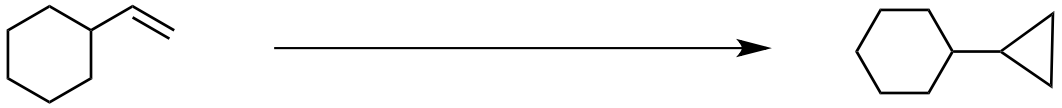
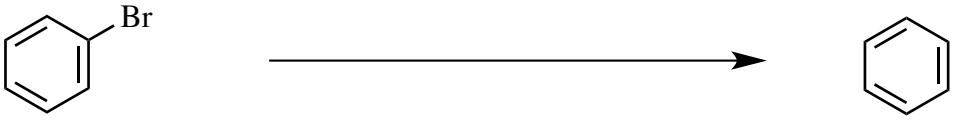
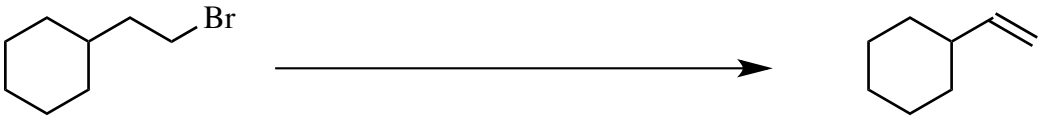
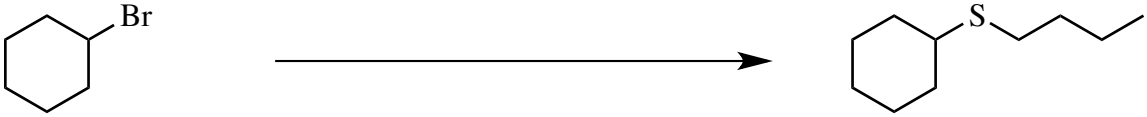
3) (20 pts) Propose reagents for accomplishing each of the following reactions. Make your reaction efficient (i.e. the target product should be the major product). Assume chiral starting materials and products are single pure enantiomers unless they are labeled "rac." If the solvent is important to obtain the product, then include the solvent along with the reagents. If you need an organometallic reagent, you can use it without showing how to make it.

a) 

b) 

c) 

d) 

e) 

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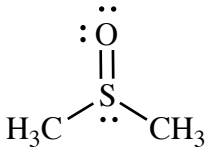
4) (20 pts) Dimethyl sulfoxide (DMSO) is a favorite solvent for organic reactions. The structure is typically written as follows.



This is NOT a valid valence bond structure, but rather an historical holdover that refuses to go away.

a) Draw a valid valence bond structure for DMSO, showing all lone pairs and formal charges.

b) Categorize DMSO as a solvent (choose from: polar or apolar: protic or aprotic; donor or non-donor).

c) What is the hybridization of the S atom in DMSO?

d) Which is the stronger nucleophile in DMSO, sodium methoxide or sodium thiolate?

e) Which is the stronger nucleophile in methanol solvent, sodium methoxide or sodium thiolate?

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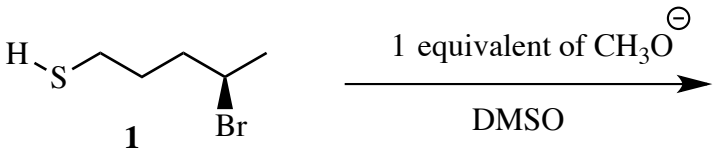
4) –continued-

f) When the bromothiol **1** is treated with one equivalent of methoxide in DMSO, one product is formed in high yield. The product has molecular formula $C_5H_{10}S$, and there is **no double bond**. Also, as you can tell from the molecular formula of the product, there is **no oxygen atom**. Carefully draw the structure of the product, showing stereochemistry if appropriate.



1

g) The fact that the CH_3O group did not end up in the product is interesting. Give a very brief explanation for why there is very little substitution with methoxide in this reaction.

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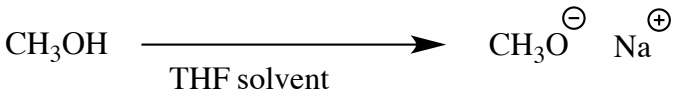
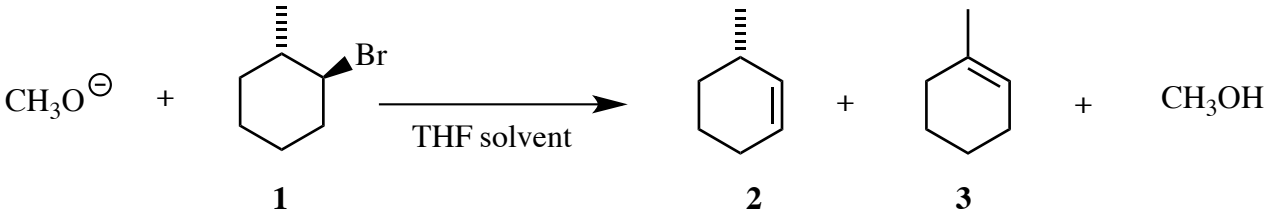
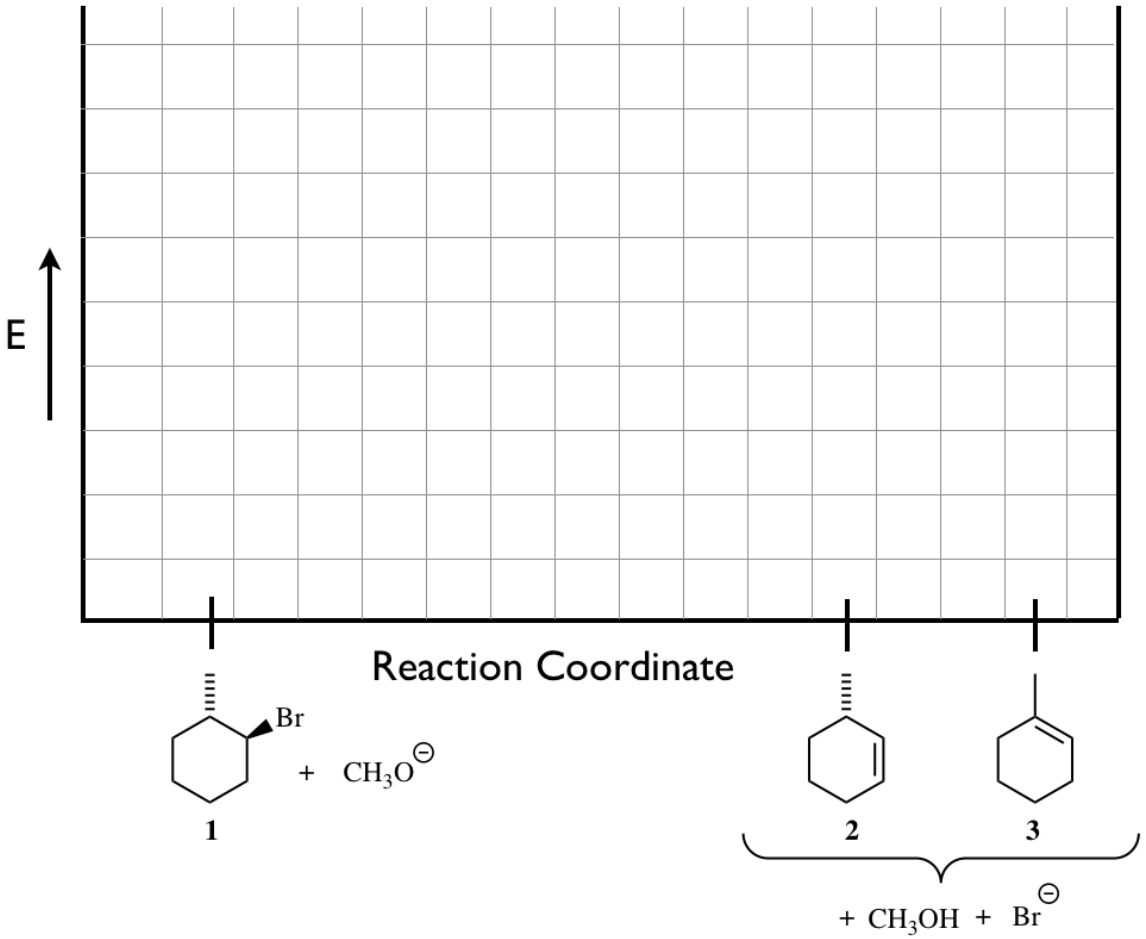
5) (20 pts) a) Give a reagent for converting methanol in THF solvent to sodium methoxide in THF.



b) Treatment of (1S,2S)-1-bromo-2-methylcyclohexane (**1**) with sodium methoxide in THF gives two products: Alkenes **2** and **3**. Circle the major product.



c) Carefully complete the energy diagram below, showing the energetics of the system leading from starting material **1,** to products **2** and **3**.



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