

CHEM 3311 (300), Fall 2014  
 Professor Walba  
 Third Hour Exam  
 November 18, 2014

scores:

- 1) 20  
 2) 20  
 3) 20  
 4) 20  
 5) 20

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 100

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

Signature: Key

Recitation TA Name: \_\_\_\_\_

Recitation day and time: \_\_\_\_\_

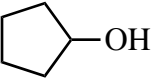
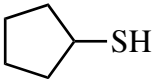
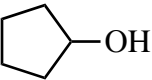
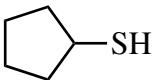
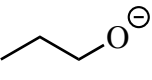
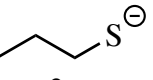
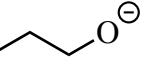
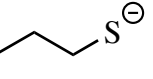
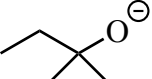
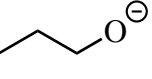
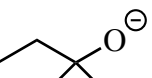
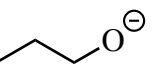
This is a closed-book exam. The use of notes, calculators, scratch paper, or cell phones will not be allowed during the exam. You may use models brought in a clear ziplock bag. Please put all your answers on the test in the appropriate place. Use the backs of the pages for scratch (there are two additional blank scratch sheets after the last page of the exam). DO NOT PUT ANSWERS ON THE SCRATCH SHEETS.

*PLEASE read the questions very carefully!*

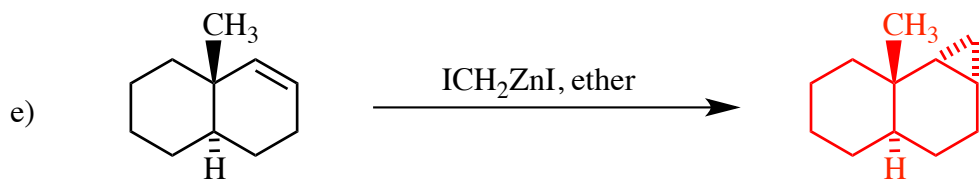
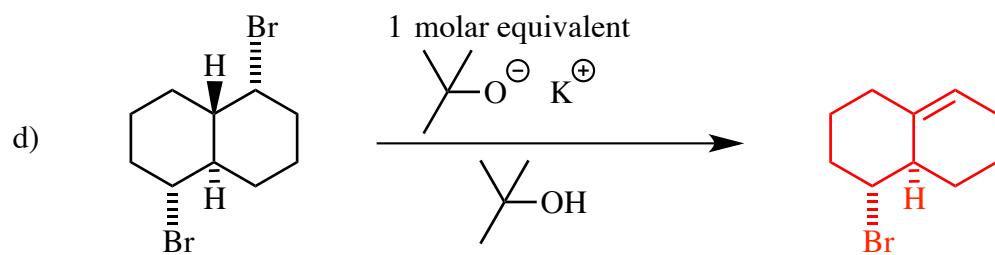
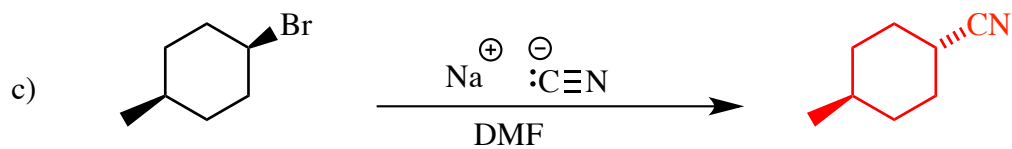
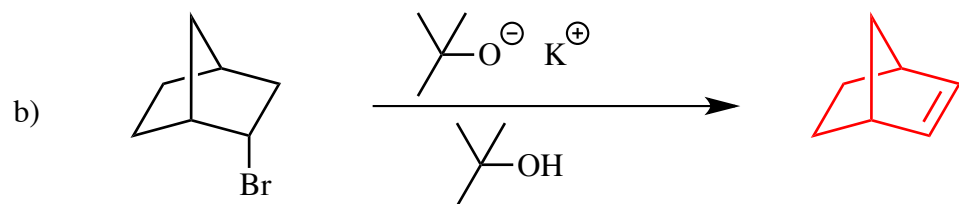
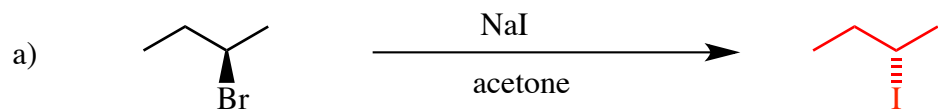
*PLEASE legibly print your name on each page of the exam.*

Partial Periodic Table									
1A							8A		
1 H							2 He		
	2A	3A	4A	5A	6A	7A			
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne		
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar		
						35 Br			
						53 I			

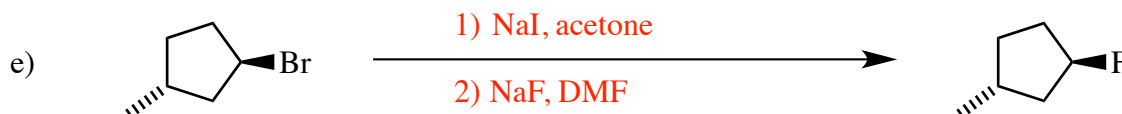
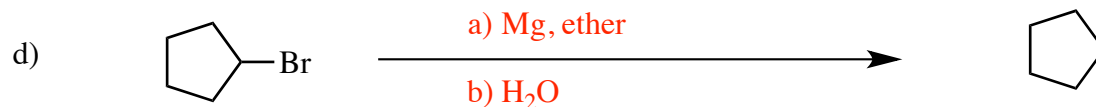
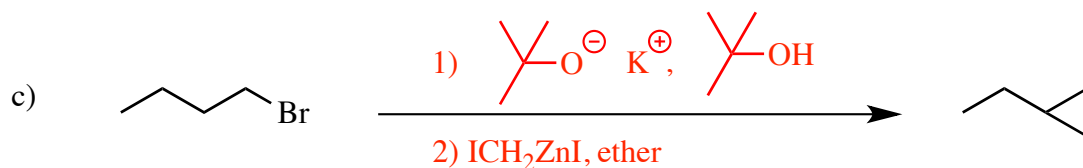
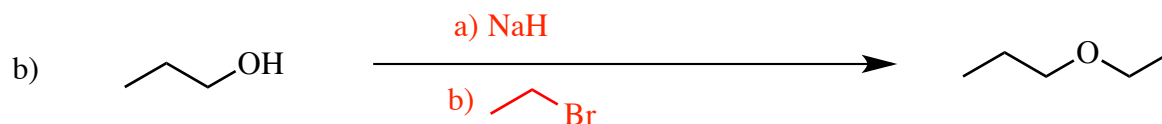
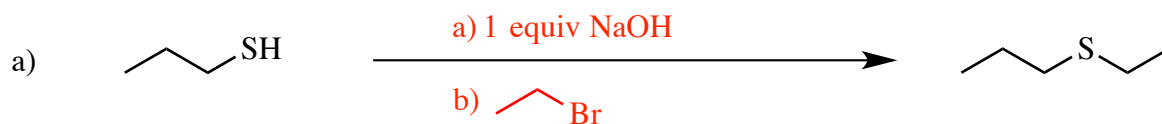
1 (20 pts) For each of the following pairs of structures, propose an answer to the questions indicated in the boxes in the right hand column using the compound numbers (1 or 2). (DMF = dimethylformamide)

$\text{H}_3\text{C}-\overset{\cdot\cdot}{\underset{\text{H}}{\text{N}}}-\text{CH}_3$ 1	$\text{H}_3\text{C}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{CH}_3$ 2	Stronger Brønsted acid in any solvent  1
 1	 2	Stronger Brønsted acid in CH <sub>3</sub> OH solvent  2
 1	 2	Stronger Brønsted acid in DMF solvent  2
 1	 2	Stronger nucleophile in propanol solvent  2
 1	 2	Stronger nucleophile in DMF solvent  1
 1	 2	Stronger Brønsted base in propanol solvent  1
 1	 2	Stronger Brønsted base in gas phase  2
$\text{Br}^\ominus$ 1	$\text{F}^\ominus$ 2	Stronger Brønsted base in propanol solvent  2
$\text{Br}^\ominus$ 1	$\text{F}^\ominus$ 2	Stronger nucleophile in propanol solvent  1
$\text{Br}^\ominus$ 1	$\text{F}^\ominus$ 2	Stronger nucleophile in DMF solvent  2

2) (20 pts) Give the **single major product** for each of the following reactions, 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."

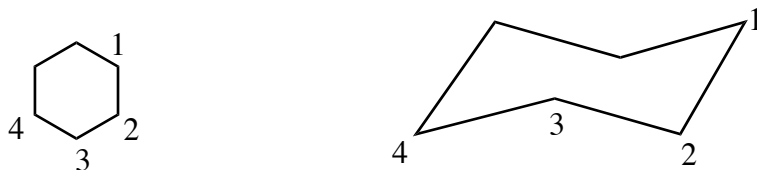


3) (20 pts) Propose reagents for accomplishing each of the following transformations. Make your synthesis efficient (i.e. the target product should be the major product). Be careful to indicate sequential addition of reagents for a single reaction using letters. For these syntheses, more than one reaction **may** be required. If more than one reaction is required, use numbers to indicate the reactions in your sequence. If the solvent is key to making a reaction work, please indicate the solvent.

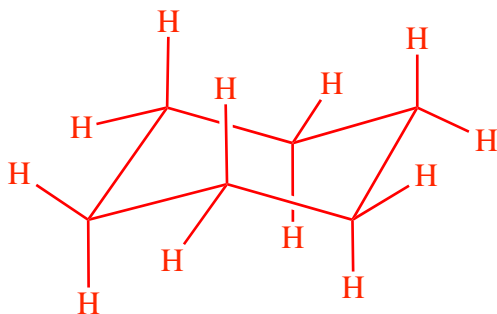


Printed Name: \_\_\_\_\_

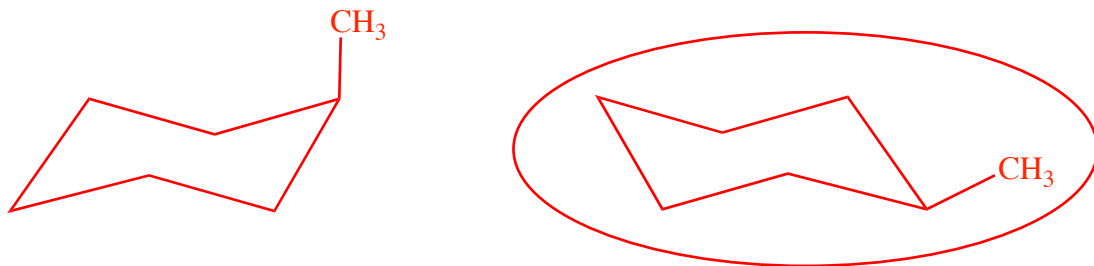
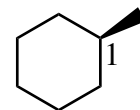
4) (20 pts) For this problem, use the cyclohexane carbon numbering given below (of course I've only drawn one of the two possible flip-chair conformations of the cyclohexane ring).



a) Re-draw the chair conformation given above (with C1 at the far right and "up") carefully showing all of the hydrogen atoms.



b.1) Carefully draw **both** flip-chair conformations of methylcyclohexane ("wedges and dashes" structure given at right), using the same convention for orientation of the rings indicated above (i.e. carbon 1 is the farthest right carbon in both chairs). DO NOT include H atoms in these drawings.



b.2) Circle the most stable conformation of 1-methylcyclohexane above.

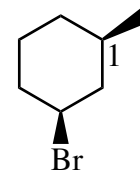
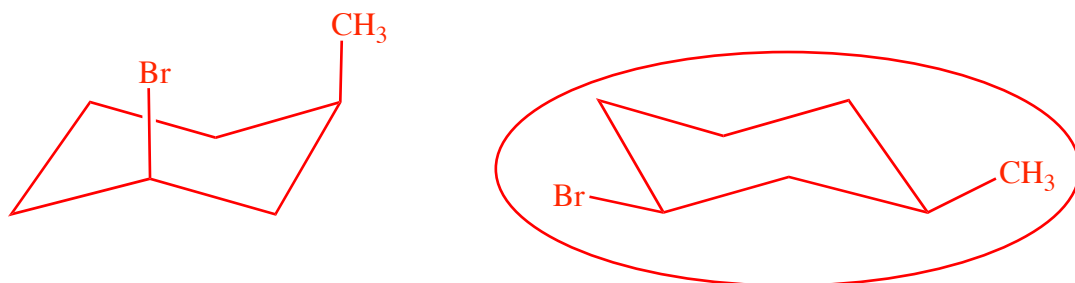
b.3) Give the difference in energy of the two conformations in units of "gauche butane interactions" (GBs)

2 GBs

4. – continued

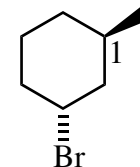
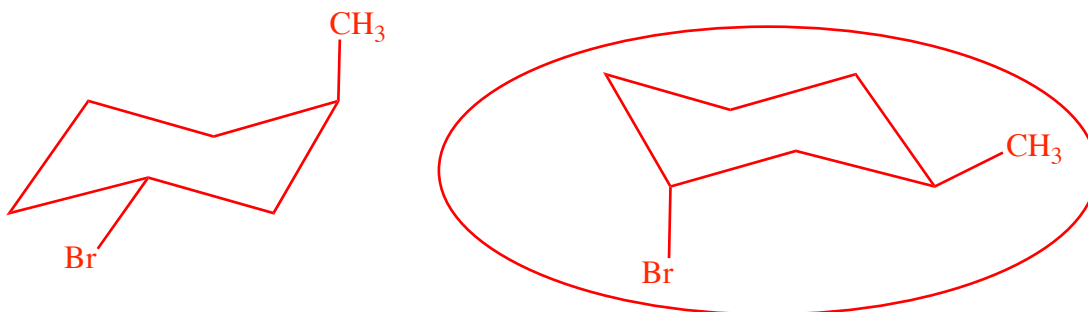
c) As we learned on the first hour exam, a bromine atom is quite large in atomic radius. However, for 1-bromopropane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ ), if the bromine atom is **gauche** with respect to the methyl group, sterically the Br behaves as if it were substantially smaller than a methyl but much larger than an H (this is due to the long C-Br bond). This fact is true for substituted cyclohexane conformational analysis as well.

c.1) Draw the two flip-chair conformations for cis-3-bromo-1-methylcyclohexane (structure and carbon atom numbering given at right), again putting C-1 at the far right in both chairs.



c.2) Circle the more stable conformation of cis-3-bromo-1-methylcyclohexane. If both conformations have the same energy, then label them “same.”

d.1) Draw the two flip-chair conformations of trans-3-bromo-1-methylcyclohexane (structure and carbon atom numbering given at right), again putting C-1 at the far right in both chairs.

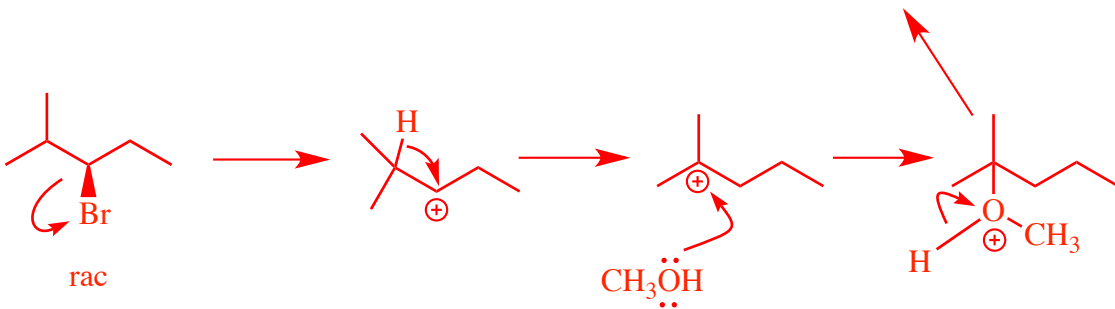
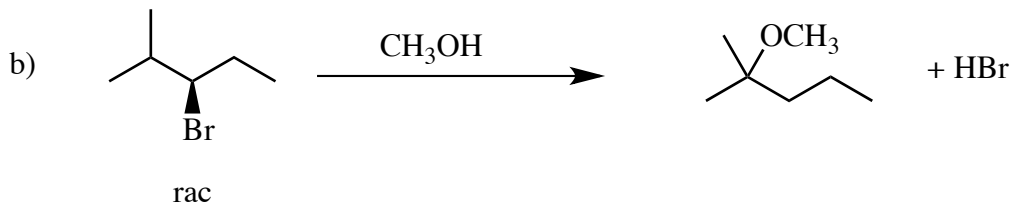
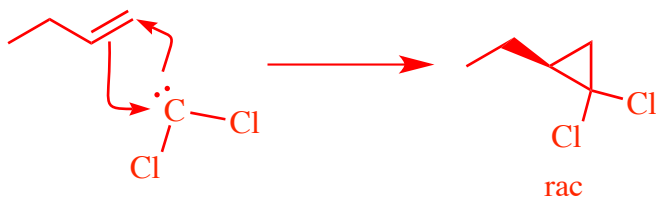
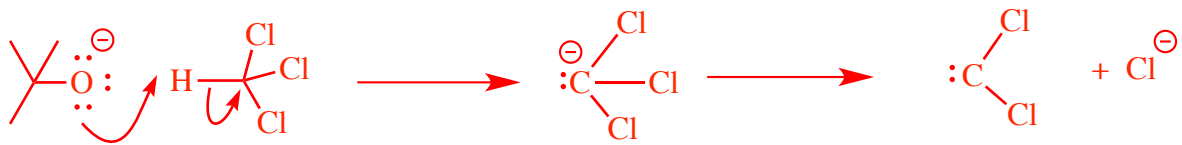
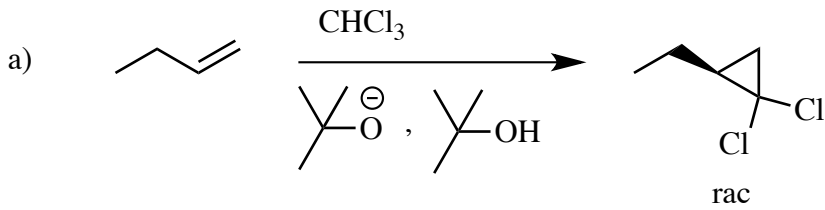


d.2) Circle the more stable conformation of trans-3-bromo-1-methylcyclohexane. If both conformations have the same energy, then label them “same.”

d.3) Which isomer is more stable, the cis, or the trans 3-bromo-1-methylcyclohexane?

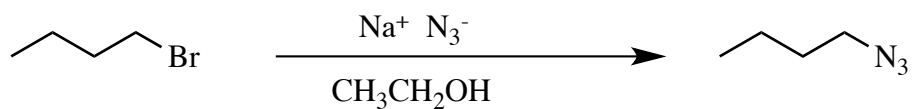
**Cis-3-bromo-1-methylcyclohexane is more stable**

5) (20 pts) Propose arrow-pushing mechanisms for the two transformations on this page. Show **all** intermediates in your mechanisms, but do not show transition states. Be sure structures are complete, including all lone pairs.

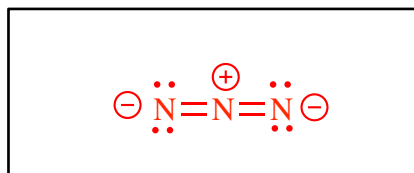


5. – continued

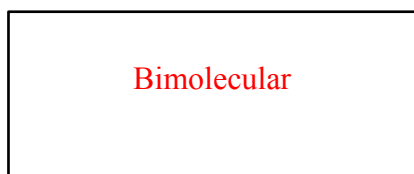
c) Referring to the following reaction:



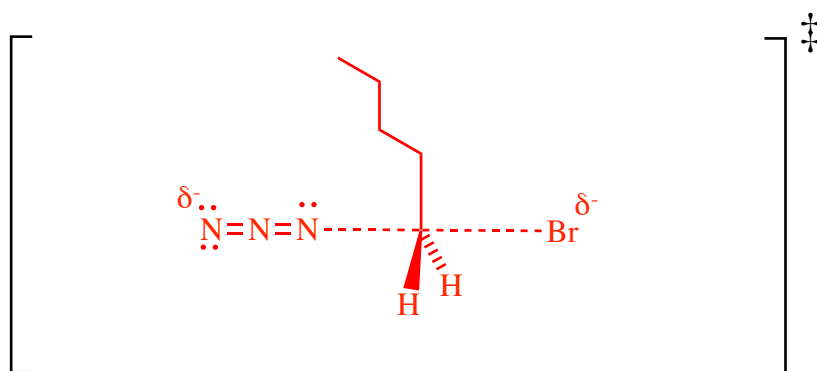
c.1) Draw a valid valence bond structure for the azide ion ( $\text{N}_3^-$ ).



c.2) Is this reaction unimolecular or bimolecular?

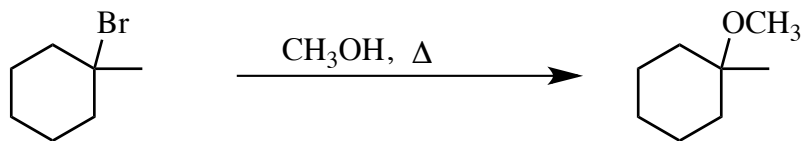


c.3) Draw the structure of the **transition state for the rate determining step** of this reaction.





d) Referring to the following reaction:



d.1) Is this reaction unimolecular or bimolecular?

Unimolecular

d.2) Draw the structure of the **transition state for the rate determining step** of this reaction.

