

LAST NAME: *Rogers*
FIRST NAME:
STUDENT ID:

CHEM 221 - ORGANIC CHEMISTRY I MIDTERM EXAMINATION

INSTRUCTIONS: PLEASE READ THIS BOX WHILE WAITING TO START YOUR EXAM.

- Check that your paper is complete: 4 pages (both sides).
- Note the (removable) reference data page: table of pK_a s, periodic table, electronegativities.
- Model kits and calculators are permitted. Cell phones & electronic dictionaries are not allowed.
- Read through the whole test quickly before starting.
- Please ask for clarification if you do not understand what a question is asking.
- You have 70 minutes to complete the test.

Mark breakdown:

	<u>Averages</u>	<u>%</u>
Ch. 1, 2 Page 2.	7.0 / 10	= 69.5 %
Ch. 2 Page 3.	7.7 / 11	= 70.3 %
Ch. 7, 4 Page 4.	4.4 / 10	= 44.3 %
Ch. 3, 4 Page 5.	4.9 / 10	= 49.1 %

TOTAL: **24.0** / 40 (maximum ⁴¹/40)

PERCENT: **60.1 %**

EARNED toward
FINAL GRADE: / 15

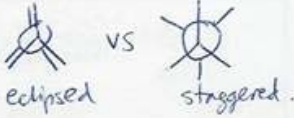
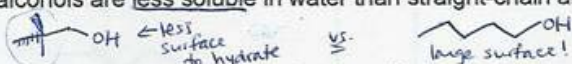
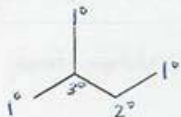
GENERAL COMMENTS:

- If > 70%, good basis to build on
- If < 70%: get Klein book
tutor
+ see me!

Everything builds upon
these foundations!

MOST PEOPLE NEED
WORK ON RXNS
+ MECHANISMS
(Ch. 4!)


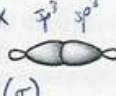
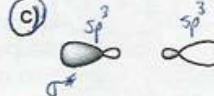

1. (5 marks) TRUE or FALSE? Circle T or F to describe the following statements.

- F T / F Eclipsed bonds produce less torsional strain than staggered bonds. 
- F T / F Branched alcohols are less soluble in water than straight-chain alcohols (assuming same # of Cs).
eg. 
- T / F Any molecule or atom described as a Lewis acid can also be described as an electrophile.
= e⁻-poor (d⁺ or open valence) = attracted to e⁻
- T / F Resonance delocalization occurs via the overlap of p-orbitals on adjacent atoms.
- F T / F The molecule shown here (at the right) contains three secondary carbons:


2. (1 mark) Which ONE of the following functional groups contains a π -bond?

- a) xalkoxy -OR
b) xamino -NR₂ (or -NH₂)
c) carbonyl -C=O
d) xhydroxyl -OH

3. (1 mark) The σ^* orbital for the C-Br bond in CH₃Br could be represented as:

- a) x  π
b) x  σ
c)  σ^*
d) x  σ

4. (1 mark) Each of the features below tends to decrease the stability of a resonance contributor, except

- a) x an atom with an incomplete octet decreases stability
b) a negative charge on the most electronegative atom increases eg. e⁻ on O vs. on N
c) x a negative charge not on the most electronegative atom decreases eg. e⁻ on N vs. on O
d) x charge separation decreases eg. R₂C=O⁻ vs. R₂C=O⁺

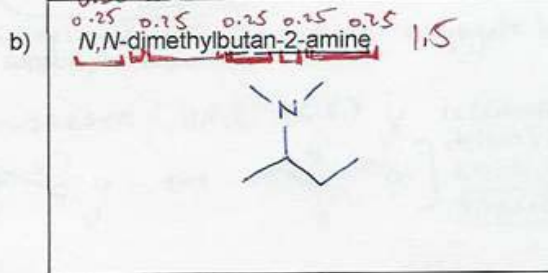
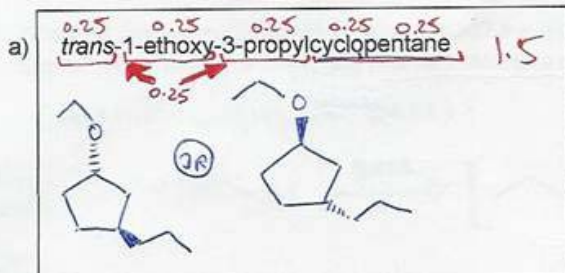
5. (2 marks) Which common base would be strong enough to deprotonate (CH₃)₂CHNH₂?

- a) sodium acetate: Na⁺ CH₃COO⁻ 4.7
b) potassium *tert*-butoxide: K⁺ (CH₃)₃CO⁻ 19
c) sodium hydride: Na⁺ H⁻ 35
d) *n*-butyl lithium: Li⁺ CH₃CH₂CH₂CH₂⁻ > 51
- ↑ pK_a ≈ 40
← only one with strongest conj. base to deprotonate acid of pK_a 40.
bases conjugate acid pK_a

10

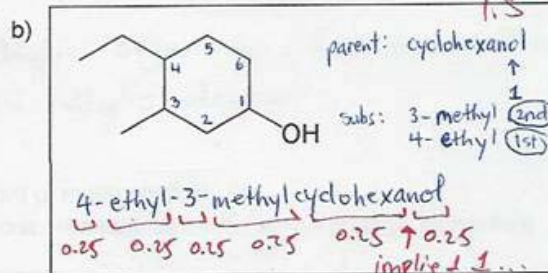
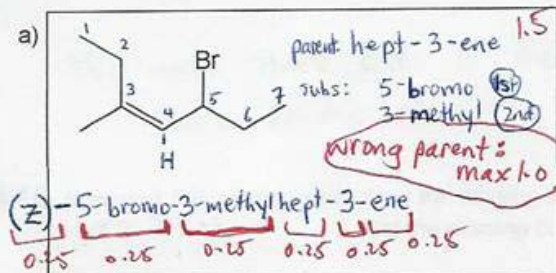
6. (3 Marks) Draw a line (skeletal) structure for the following compounds:
 -0.25 if not. (each!)

3



7. (3 Marks) Provide a systematic IUPAC name (including E/Z, if applicable) for the following compounds:

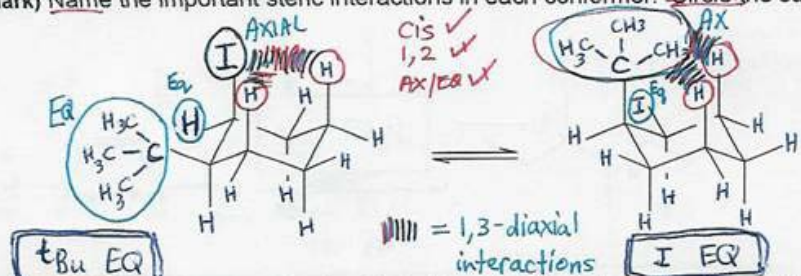
3



8. (5 marks) Shown below is an incomplete drawing of the ring-flipping equilibrium for cis-1-tert-butyl-2-iodocyclohexane (shown here at right).

2
1

a) (2 marks) To the chairs below: add the Hs and substituents tBu + I & label the substituents as axial ("ax") or equatorial ("eq").
 b) (1 mark) Name the important steric interactions in each conformer. Circle the substituents involved.



1,3-diaxial interactions are the only important steric effects + larger for tBu than for I

2

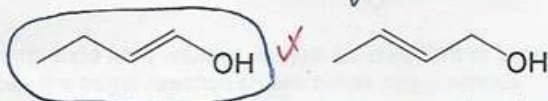
c) (2 marks) Imagine that a molecule of cis-1-tert-butyl-2-iodocyclohexane collides with a molecule of another compound "B" in a sample at room temperature. Which conformation of cis-1-tert-butyl-2-iodocyclohexane will molecule "B" most likely encounter? Why?

↳ i.e., most common conformation adopted by the molecule of cis-tBu-2-iodocyclohexane

i.e., the most STABLE conformer = the chair with tBu in the equatorial position, because tBu is HUGE + about 4500 x more likely to be EQ vs. AX. due to 1,3-diaxial interactions with Hs.

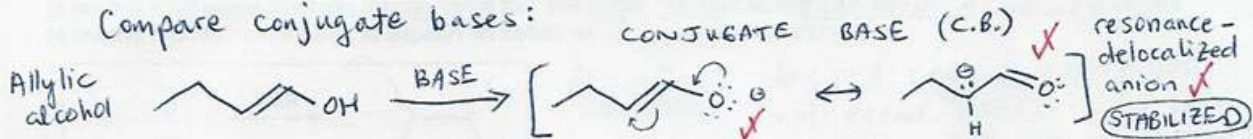
11

9. (4 marks) Two isomeric alcohols are shown here:



Which of the two compounds is more acidic? ← the compound with the weaker conjugate base. Explain your choice, and include relevant structures to support your arguments.

Compare conjugate bases:



4



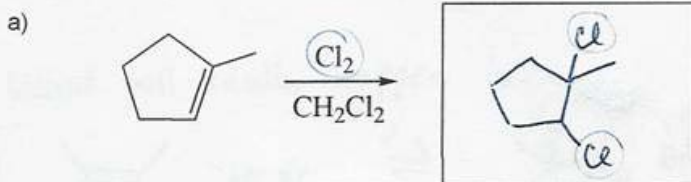
The more stable C.B. is the allylic oxyanion, which means the more acidic alcohol is the allylic alcohol.

CB strength

all-or-none

10. (6 marks) Fill in the boxes: draw the missing reactant or major product OR

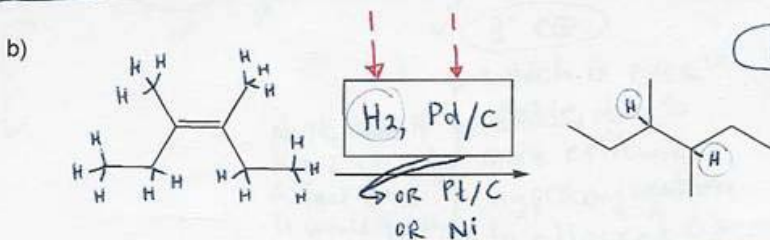
list the missing conditions: reagent, catalyst, solvent (if critical for reaction)



2

step-wise electrophilic addition

- of "Cl⁺" to form halonium⁺
- then Cl⁻ (attacks anti)
- no C⁺ int ∴ no rearranging

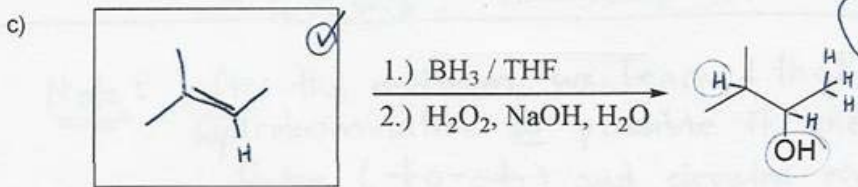


2

hydrogenation

Notice: C₈H₁₆ → C₈H₁₈ ADDED H₂

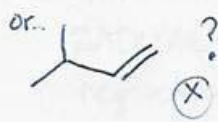
- count atoms to reveal what rxn occurred...



2

Concerted 1st step = electrophilic addition

- attack BH₃ ("B⁺")
- OH replaces B
- anti-Markovnikov addition of H-OH
- no rearranging.



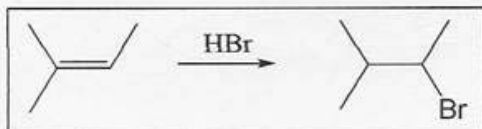
but that would be Markovnikov, ∴ not using the above reagents!

10

11. (10 marks) When planning the synthesis of one compound from another, it's just as important to know what *not* to do as to know what to do. For example, the target reaction shown below has a serious drawback to it. Your task here is to explain what is wrong with this approach.

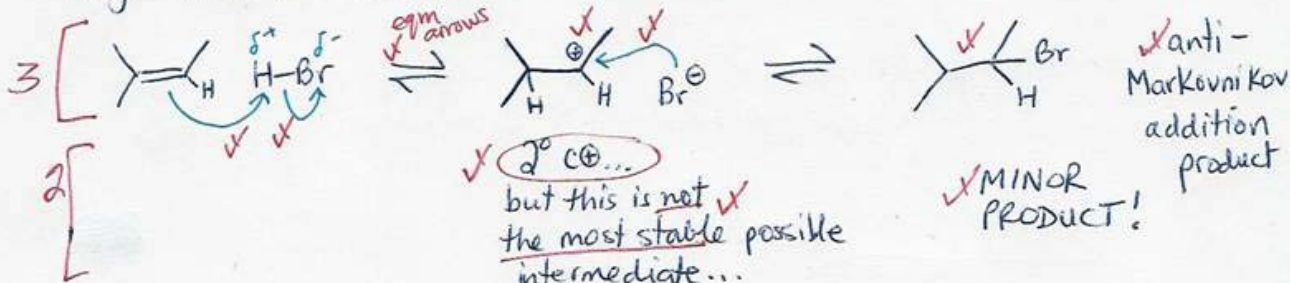
Your explanation must include:

(6 marks) • full arrow-pushing mechanisms for: the target reaction vs. the pathway that will actually dominate
 (4 marks) • written comments to explain (in detail) what causes this difference.

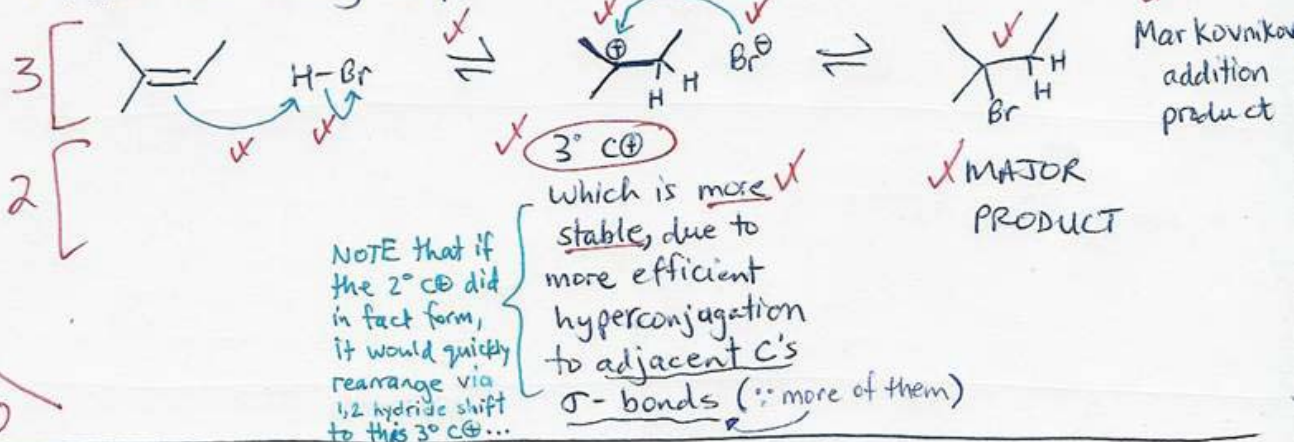


PROBLEM: desired regiochemistry will not occur under these rxn conditions (i.e. HBr only reagent)

• Target reaction's mechanism would need to be:



• What will really happen is:



Note: after the midterm, we learned that antiMarkovnikov hydrobromination IS possible if one uses a radical initiator (to-ot) and elevated temperature or light. RADICAL hydrobromination does give the above target regiochemistry.