

ANSWER KEY

Practice Exam #2 Chemistry 5.12 Organic Chemistry

- Midterm exam #2 will be held on Friday, March 14, from 12–1pm.
- Notes and calculators will not be allowed in the exam.
- You will be free to use molecular models during the exam.
- You will be given a periodic table and a table of BDEs.
- The exam will cover reading (Ch. 3–5, 6.1–6.8) and lecture material through Monday, March 10th. Material from the first three weeks is still fair game.
- Dr. Tabacco will give a review session at 7pm on Tuesday, March 11, Please download the review handout to bring to the review session.
- Additional suggested problems from the book (some of these were already suggested during lecture): 3-42–44,46; 4-35–37,39–42,44,46,48,54; 5-30,31,34–36,38.
- For best results, take this test as if it were your exam. That way, you'll know which areas need extra work before you get to the real exam. (Don't worry, it's a bit longer than your actual exam.)

1. Circle the correct answer.

a) The lowest energy conformer of butane is:

gauche **anti** eclipsed

b) Molecules that have internal mirror planes are always:

chiral **achiral** meso

c) Thalidomide was sold to consumers as a:

racemate painkiller teratogen

d) If the transition state is product-like, the reaction is:

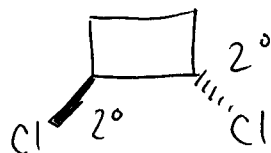
exothermic kinetic **endothermic**

e) CH_2I_2 is a _____ halide.

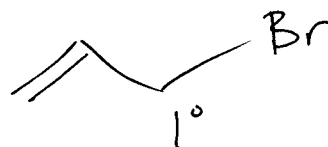
vicinal secondary **geminal**

2. a) Provide structures for the following alkyl halides.

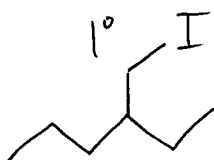
b) Label each halide as 1° , 2° , or 3° .



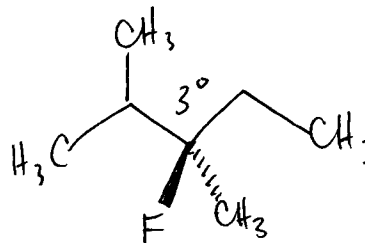
trans-1,2-dichlorocyclobutane



allyl bromide



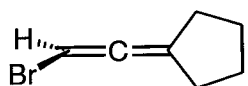
4-(iodomethyl)hexane



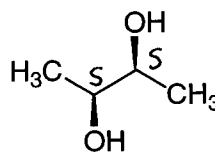
(*R*)-3-fluoro-2,3-dimethylpentane

3. a) Label each molecule as **chiral** or **achiral**.
 b) Label each stereocenter with its **R** or **S** configuration.
 c) Circle any **meso** compounds.

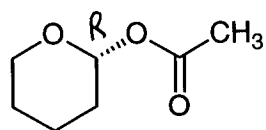
this molecule has an internal mirror plane in the plane of the paper



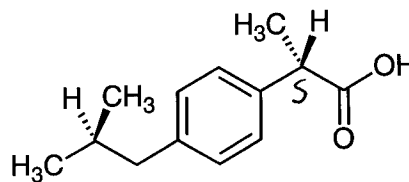
achiral



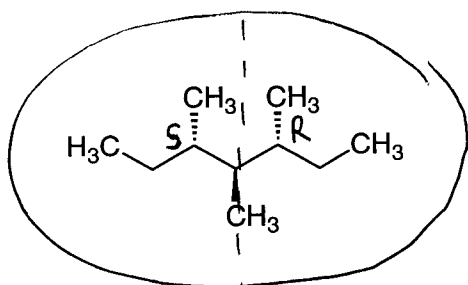
chiral



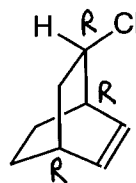
chiral



chiral



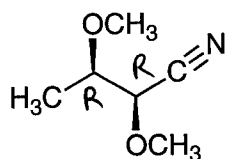
achiral
(meso)



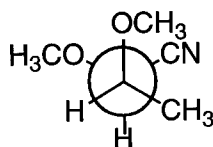
chiral

4. Label each pair as **enantiomers**, **diastereomers**, or **same molecule**.

It might help to assign R/S!

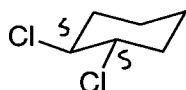


and

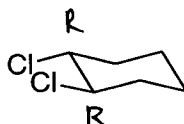


front = R
back = S

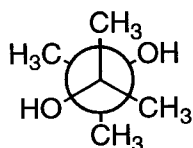
diastereomers



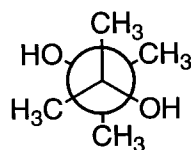
and



enantiomers



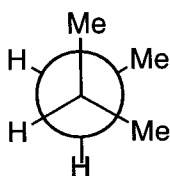
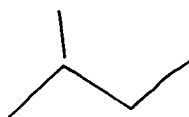
and



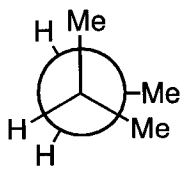
same molecule

no stereocenters!

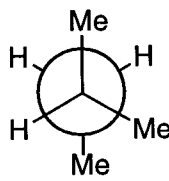
5. Provide a line drawing for the alkane represented by the following Newman projections and predict the relative energies of the conformers.



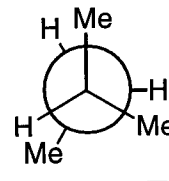
$E_{rel} =$
1.8



$E_{rel} =$
6.3



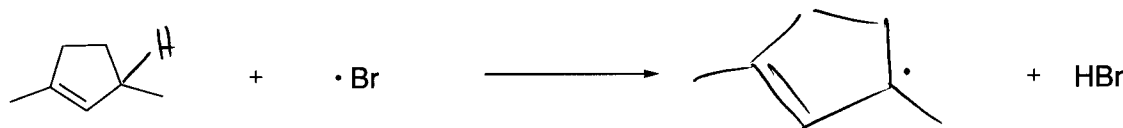
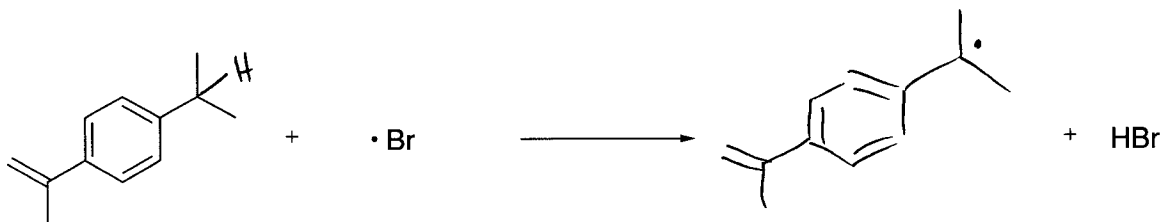
$E_{rel} =$
0.9



$E_{rel} =$
3.9

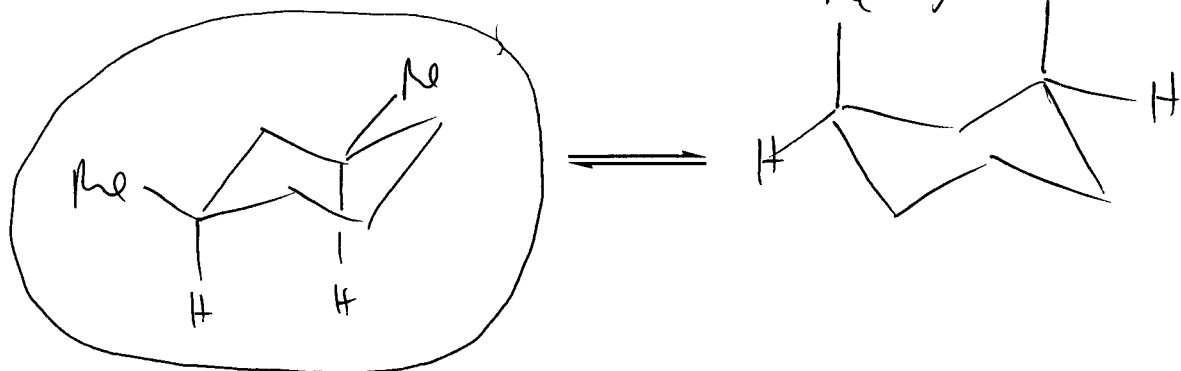
6. Hydrogen abstraction with bromine radical is generally very selective. In each case, draw the radical that you would expect to be formed.

Make sure you understand the reasoning behind each of these!

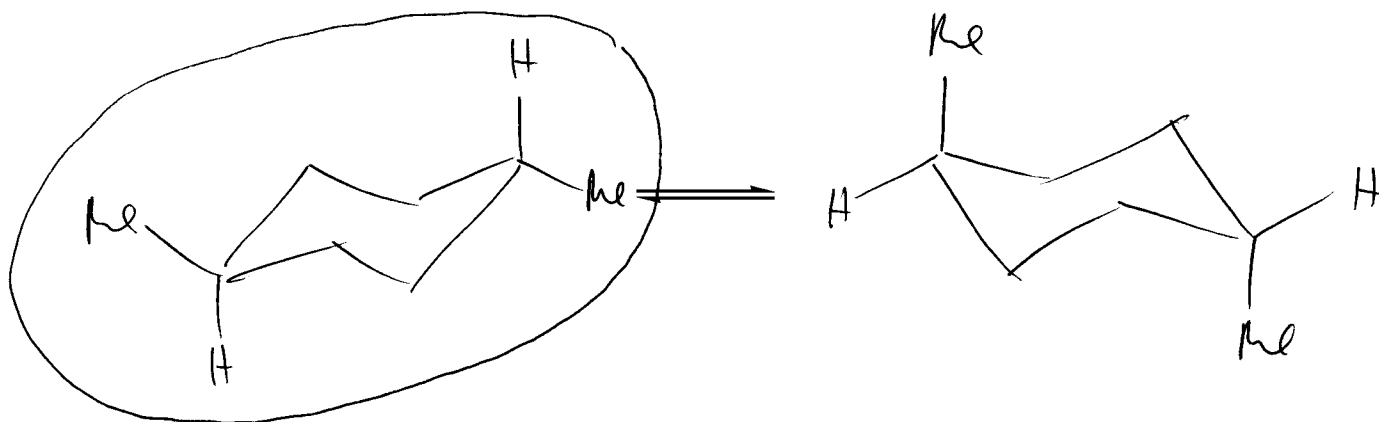


7. For each molecule, draw the two possible chair conformers and circle the preferred conformer.

a) *cis*-1,3-dimethylcyclohexane



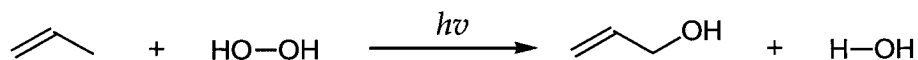
b) *trans*-1,4-dimethylcyclohexane



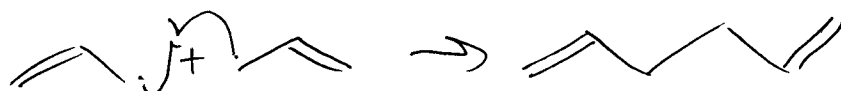
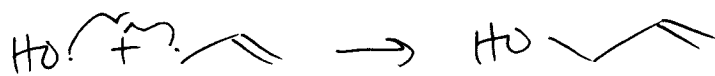
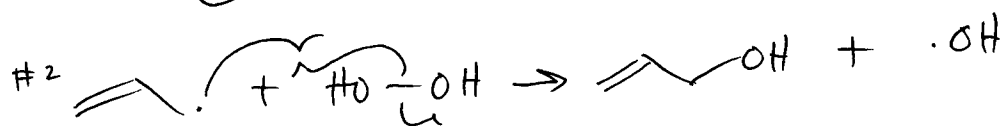
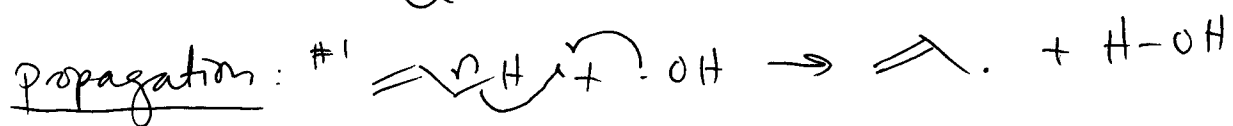
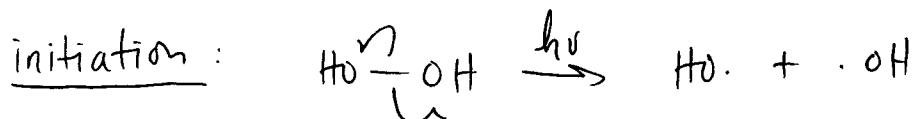
c) The energy difference between the two chair conformers is greater in part a than in part b. Why?

In part a), the high energy conformer is further destabilized by a Me/Me 1,3-diaxial interaction. This interaction is not present in the high energy diaxial conformer in part b).

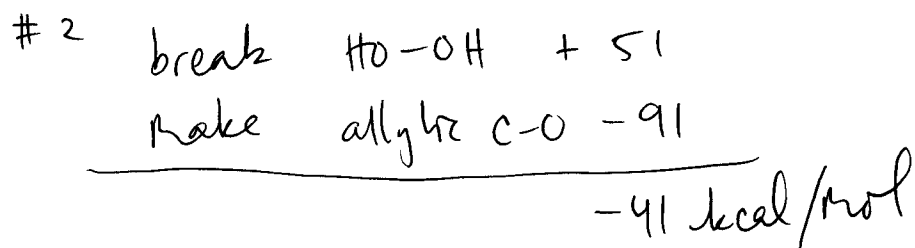
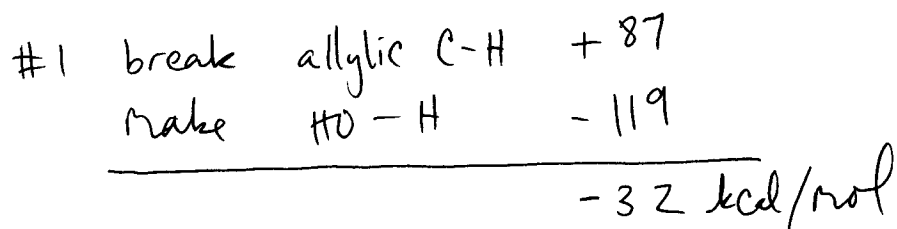
8. The oxygen-oxygen bond in hydrogen peroxide (HO-OH) is very weak (BDE = 51 kcal/mol). As a result, radical oxidation proceeds by a similar mechanism as radical halogenation.



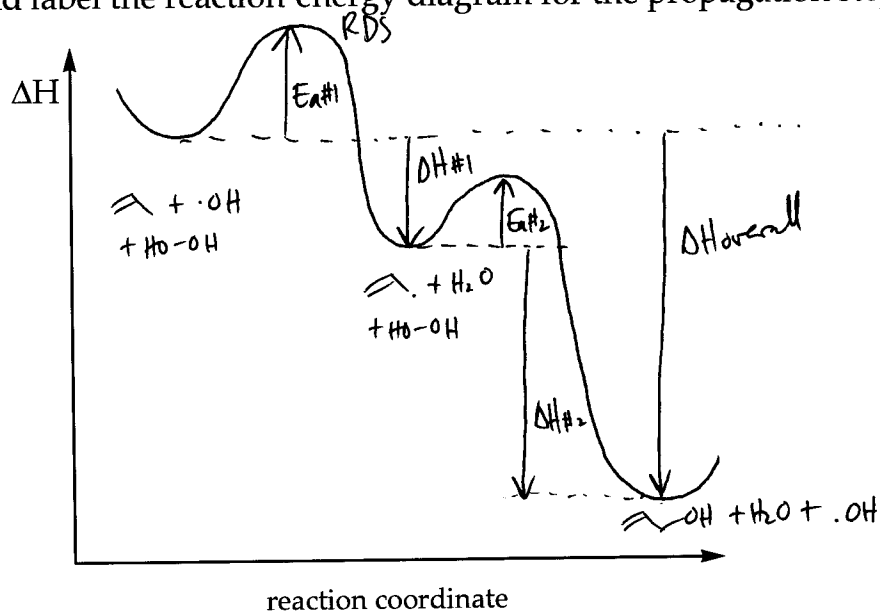
a) Provide a complete and detailed reaction mechanism for the above reaction. Include at least two possible termination steps.



b) Calculate ΔH° for each of the propagation steps.



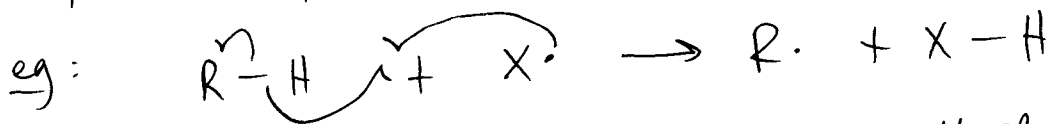
c) Draw and label the reaction-energy diagram for the propagation steps from part b.



Bonus Question: Given the following trend in bond strengths, how would you expect the selectivity of radical oxygenations to compare to the analogous chlorination and bromination reactions?

HO-H	119 kcal/mol
Cl-H	103 kcal/mol
Br-H	88 kcal/mol

In each of these rxns, the first propagation step determines the selectivity. The first propagation step always involves formation of an X-H bond (X = Br, Cl, HO.).



The stronger the X-H bond, the more exothermic this step will be. As a rxn becomes more exothermic, the transition state looks more and more like the reactants. In these propagation rxns, the reactants are always the same, regardless of the possible products. Therefore, as the X-H bond strengthens (HO-H > Cl-H > Br-H), the competing transition states become less selective. closer in energy = the selectivity: bromination > chlorination > oxygenation

Bond-Dissociation Energies for Homolytic Cleavage (kcal/mol)

H—H	104	°1 C—H	98	°1 C—Br	68
F—F	38	°2 C—H	95	°2 C—Br	68
Cl—Cl	58	°3 C—H	91	°3 C—Br	66
Br—Br	46	allylic C—H	87	°1 C—I	53
I—I	36	benzylic C—H	85	°2 C—I	53
HO—OH	51	°1 C—F	107	°3 C—I	50
H—F	136	°2 C—F	106	°1 C—OH	91
H—Cl	103	°3 C—F	106	°2 C—OH	91
H—Br	88	°1 C—Cl	81	°3 C—OH	91
H—I	71	°2 C—Cl	80	allylic C—OH	91
H—OH	119	°3 C—Cl	79	benzylic C—OH	91