Name:_____Key_____

CHEMISTRY 3311, Fall 2001
Professor Walba
First Hour Exam
September 27, 2001

scores:

1) 20

2) 20

3) 15

4) 20

5) 20

6) 5

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100

This is a closed-book "open model" exam. You may use models, but no notes or books. Please put all your answers on the test. Use the backs of the pages for scratch.

PLEASE read the questions carefully!

Partial Periodic Table

1A							8A
1 H	2A	3A	4A	5A	6A	7A	2 He
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	

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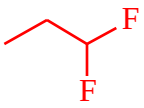
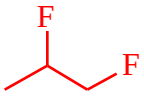
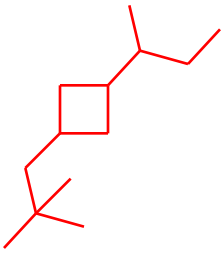
1 (20 pts) a) Draw all of the possible constitutional isomers with the molecular formula $C_3H_6F_2$. Draw each isomer only once. Use bond-line formulas (molecular graphs) to show the structures without geometrical cues (no wedges and dashes). DO NOT indicate any stereoisomerism.

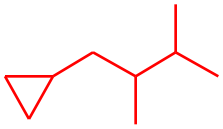




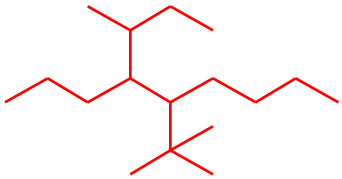
b) Draw a bond-line structure for each of the following molecules above its name using wedges and dashes to indicate stereochemistry if necessary.



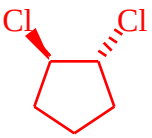
cis-1-*sec*-butyl-3-neopentylcyclobutane



(2,3-dimethylbutyl)cyclopropane



4-*sec*-butyl-5-*tert*-butylnonane



trans-1,2-dichlorocyclopentane

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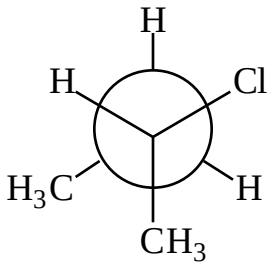
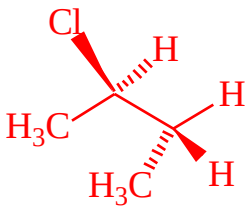
2) (20 pts) A Newman projection of one of the staggered conformations of 2-chlorobutane is shown below.



a) Carefully draw a bond-line structure for this conformation using wedges and dashes to indicate geometry. For this problem, you should put in the hydrogen atoms.



b) What is the dihedral angle between the C2-chlorine bond the C3-C4 bond?

180°

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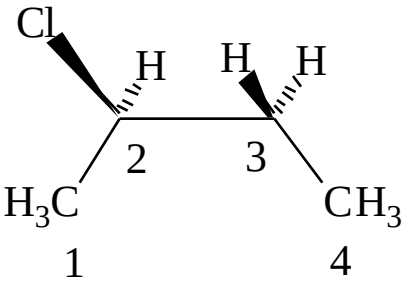
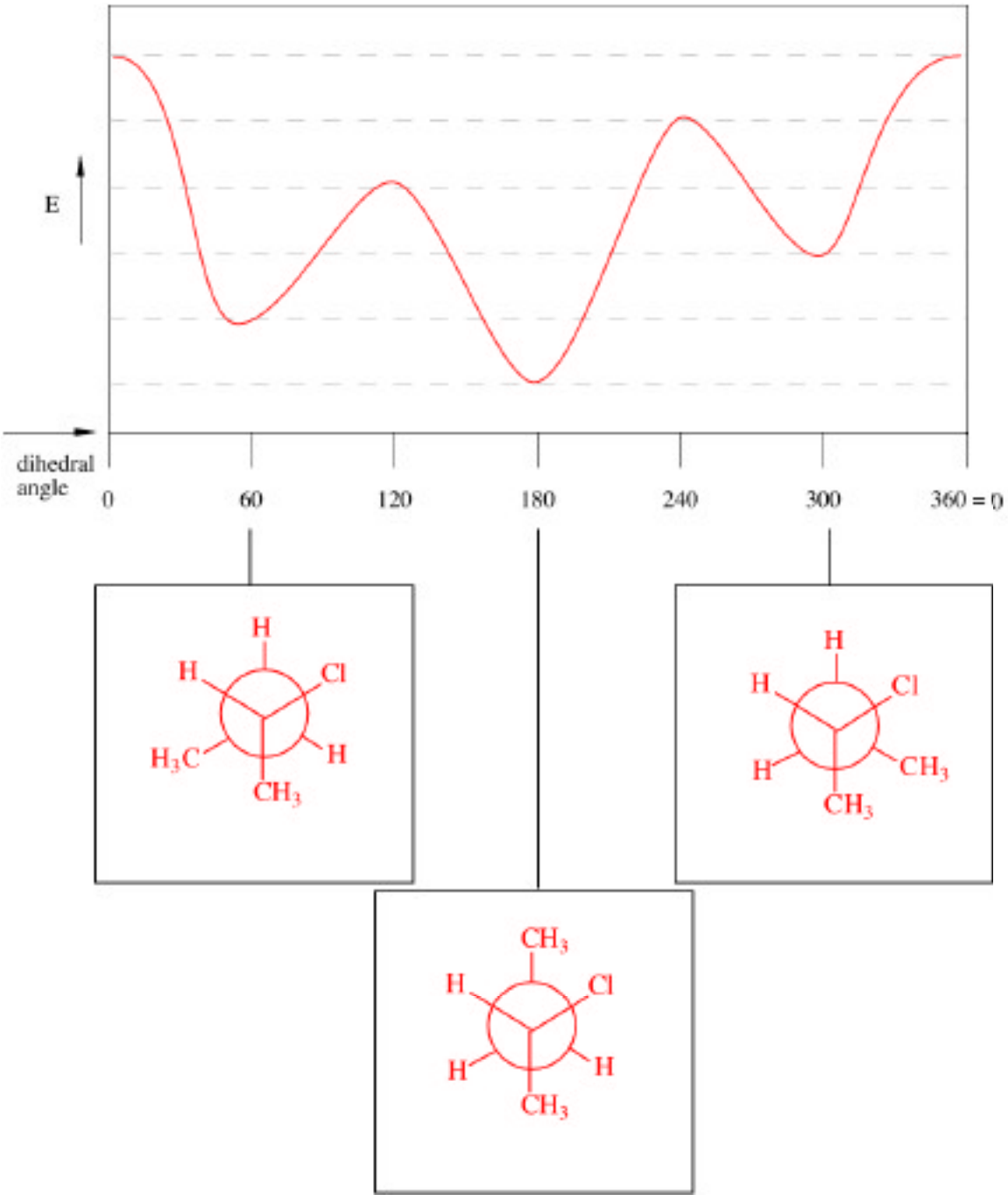
2 – continued

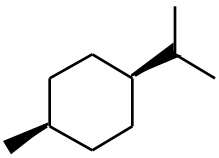
c) An eclipsed conformation of 2-chlorobutane is indicated in the wedges and dashes structure shown to the right. Given that a chlorine atom bonded to carbon is considerably larger than a hydrogen atom, but smaller than a methyl group, complete the following energy diagram for rotation about the C2-C3 bond of this molecule. Use the conformation shown, sighting down the C2-C3 bond with C3 in back, as the conformation with dihedral angle = 0° = 360°. Please rotate the back carbon (C3) clockwise to generate your conformations. Carefully show the relative energies of all the conformational wells and transition states (of course, no numbers are required), and fill in the rest of the energies with smooth curves. Also, draw Newman projections of the conformations with C1C2-C3C4 dihedral angles = 60°, 180°, and 300° in the boxes.

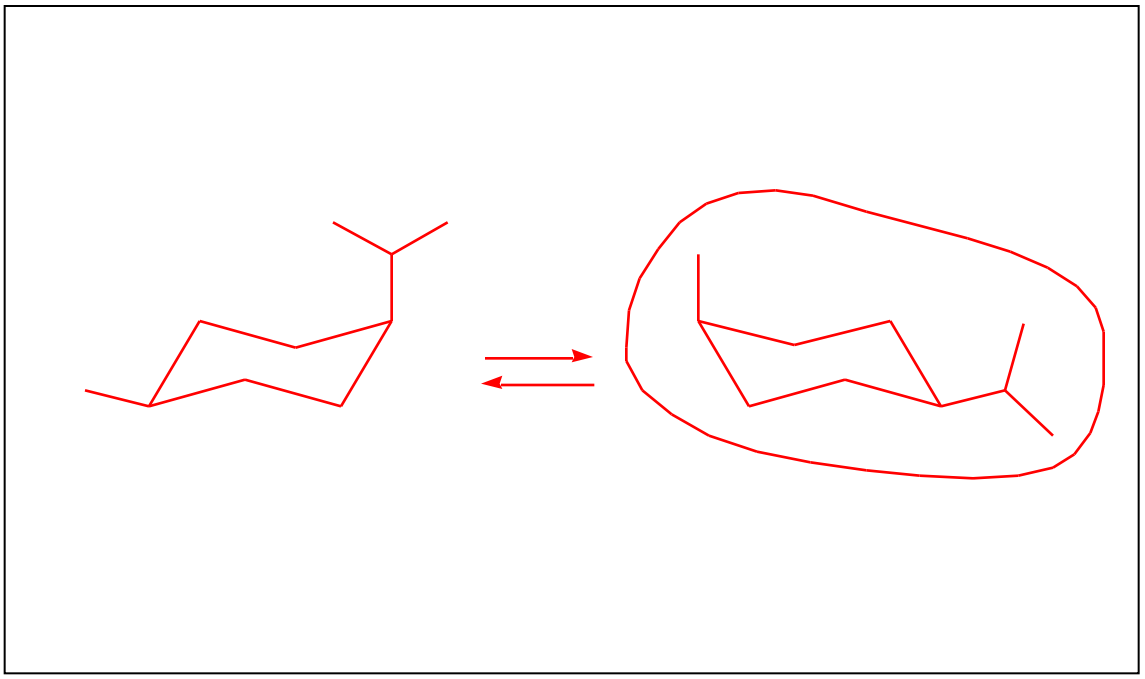


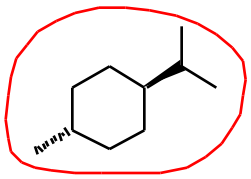


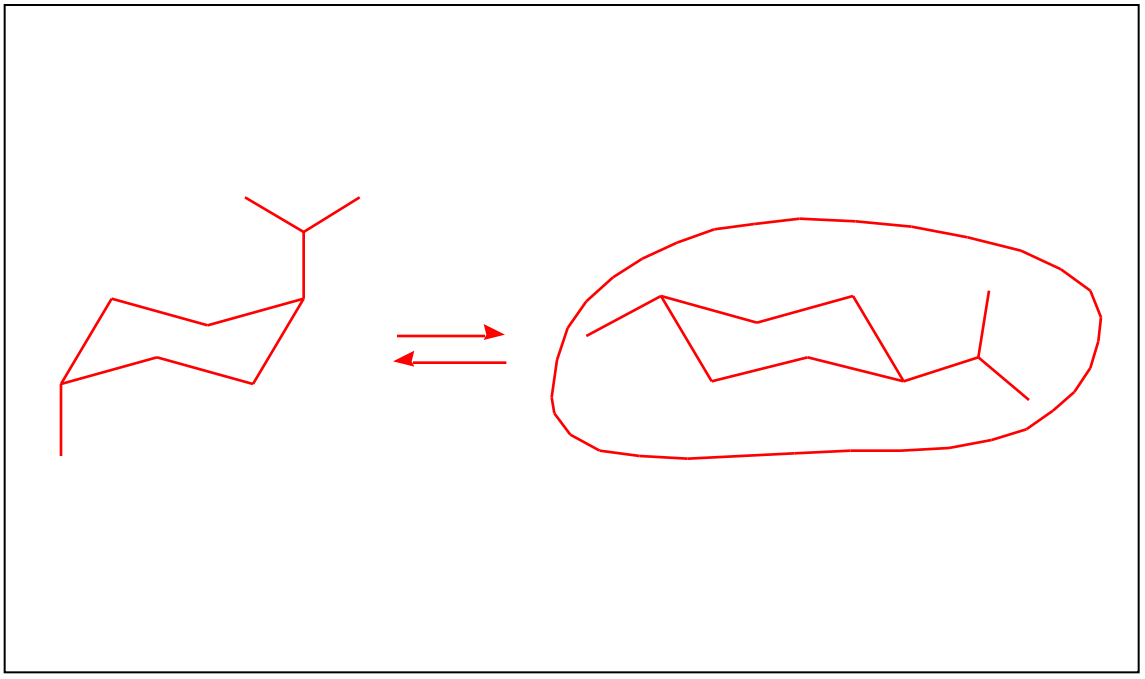
Name:_____Key_____

3) (15 pts) a) For the following substituted cyclohexane isomers (cis and trans 1-methyl-4-isopropylcyclohexanes), carefully draw the two possible chair conformations for each isomer (that means you should have four perspective chair structures drawn, two equilibrating structures in each box). DO NOT put H atoms on the rings. For each pair of conformations, circle the more stable conformation. If the two conformations have the same energy, label that pair "same". ALSO, CIRCLE THE MORE STABLE ISOMER (i.e. one of the two structures on the left should be circled).









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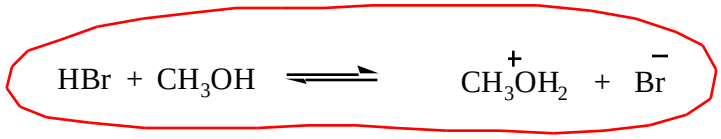
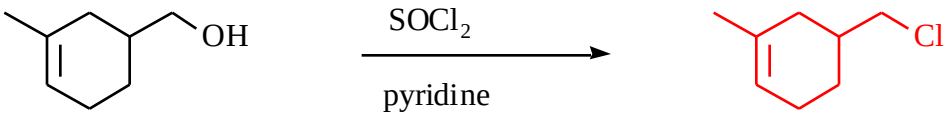
4) (20 pts) a) HBr is a stronger acid than HCl. Circle the reaction below with the larger equilibrium constant.



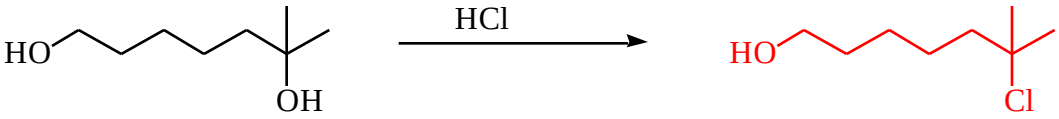
Give the single major organic product (or two products if so indicated) for each of the following transformations.

a)

b)



c)



Molecular formula $C_8H_{17}OCl$

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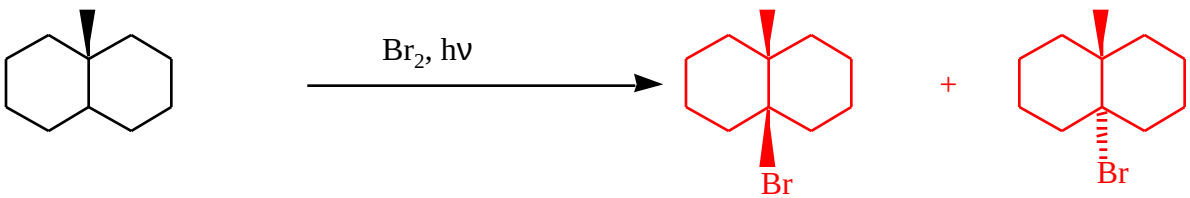
d)



TWO products, both with the molecular formula $C_{11}H_{19}Br$

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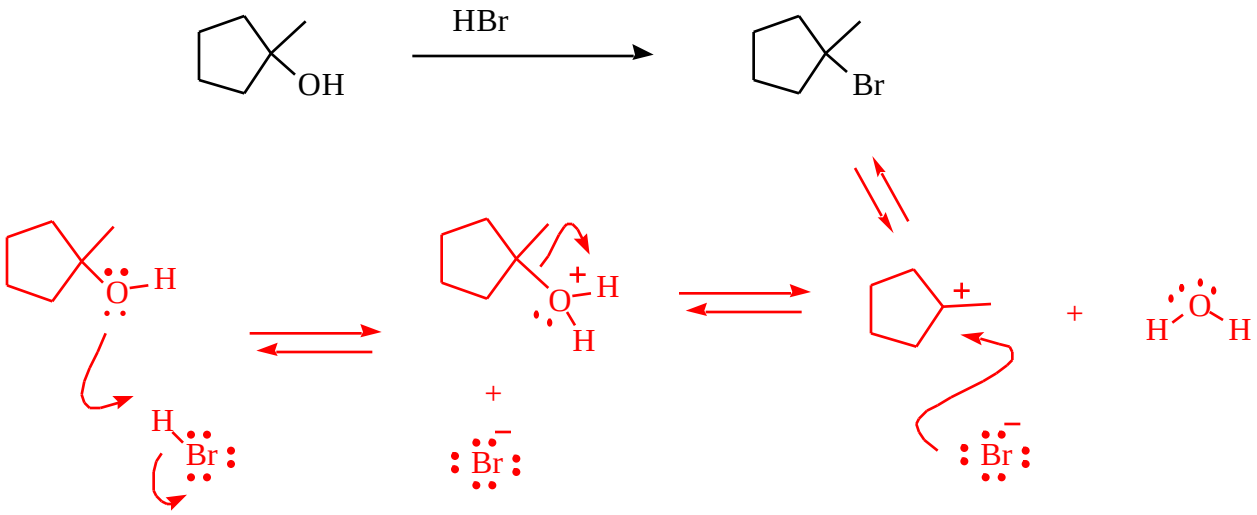
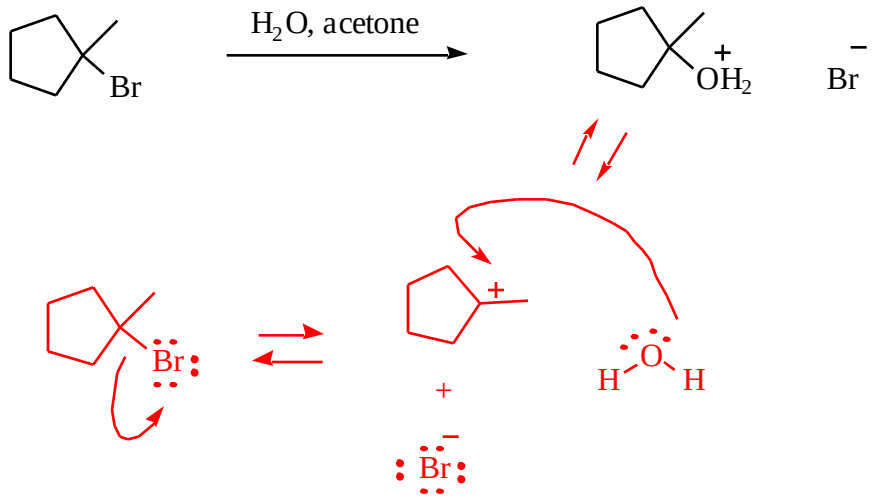
5) (20 pts) a) Propose an arrow-pushing mechanism for the following transformation. Show all lone pairs in your structures, and carefully show the structures of all intermediates in your mechanism. DO NOT show transition states.



b) If one simply mixes 1-bromo-1-methylcyclopentane with water, the following reaction occurs by the S_N1 mechanism (acetone is used as a co-solvent to make the bromide dissolve, but acetone isn't involved in the mechanism). Propose an arrow-pushing mechanism for this reaction.



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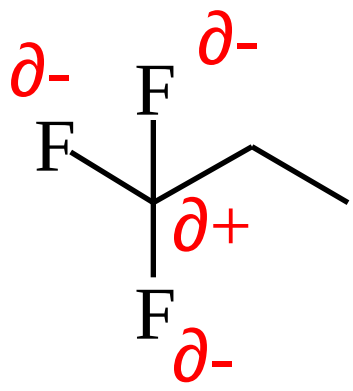
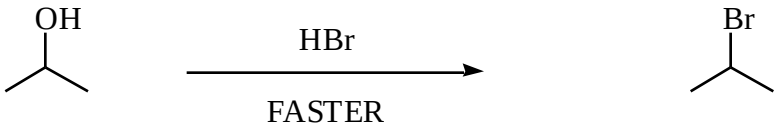
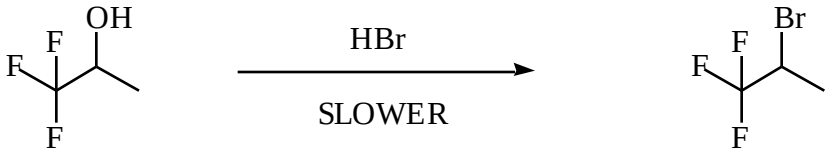
6) (5 pts) a) Using the ∂+ and ∂- notations, indicate the main partial charges on atoms of the 1,1,1-trifluoropropane structure given below (you should have partial charges on only four atoms).



b) 1,1,1-trifluoro-2-propanol reacts much more slowly than 2-propanol with HBr, as indicated below. Give a SHORT explanation for why this might be the case. [NOTE: OK – this is nontrivial, but lighten up, it's only five points!]





[This answer is longer than what you would have needed to get full credit] The rate-determining step is the one where the water falls off to give a carbocation. The activation energy of this step is determined by the stability of the carbocation (the transition state looks mostly like the carbocation). The fluorine atoms cause the carbon at C1 of the trifluoropropanol to have a lot of positive charge. In the carbocation from the trifluoropropanol, there are two adjacent atoms with positive charge (the carbocation at C2, and the C1 carbon connected to the electronegative fluorine atoms). Having two atoms with positive charge next to each other is a high-energy (unstable) situation due to Coulomb's law. The carbocation from the trifluoropropanol is much less stable than the carbocation from the propanol, even though they are both 2° carbocations. Therefore, the activation energy for the rate determining step in the reaction of HBr with trifluoropropanol is much higher, and the rate is much slower, than that of 2-propanol.