Name: ______________________________

CHEMISTRY 3351, Fall 1993
Professor Walba
First Hour Exam
September 27, 1993

scores:

1)

2)

3)

4)

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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 or scratch.

Partial Periodic Tal

1A	2A		3A	4A	5A	6A	7A	8A
		1 H						2 He
3 Li	4 Be		5 B	6 C	7 N	8 O	9 F	10 Ne

Name: ___________________________________

1) (25 pts) (a) Draw the most important valence bond structure for each of the following molecules (the connectivity should be obvious from the information given). Be sure to show all lone pairs and formal charges. You don't need to show geometry.

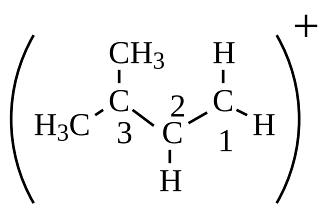
nitrous acid = $HONO_2$

Boron trifluoride = BF_3

ammonia/BF_3 complex = $H_3N—BF_3$

protonated formaldehyde = $(H_2C—O—H)^+$

(b) Draw the two most important resonance contributors to the structure of cation I.



I

Name: ___________________________________

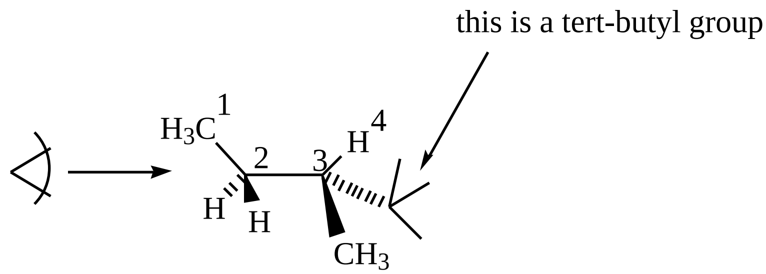
1) -continued-

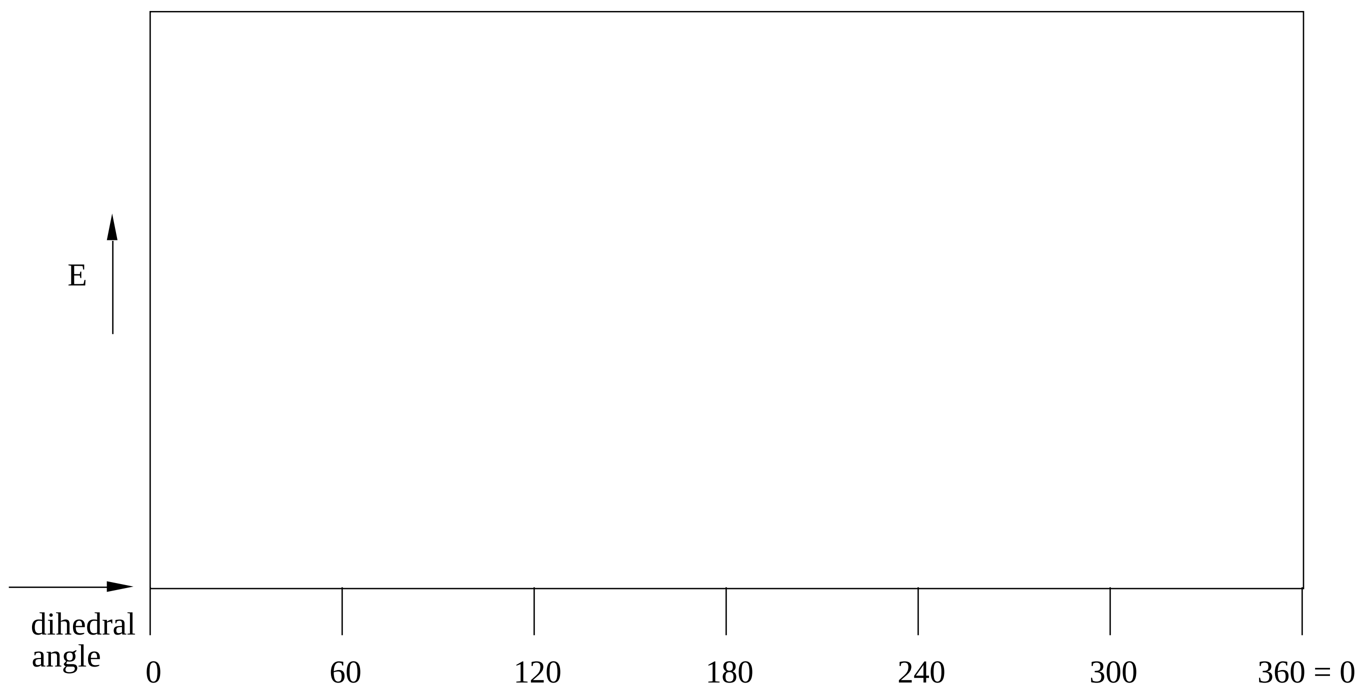
(c) Predict the C^1-C^2-C^3 bond angle for cation I and give the hybridization of the carbon 2.

(d) Do the two resonance structures contribute equally to the real structure? If you think they do then write "contribute equally" on your answer. If you think they don't, then circle the more important contributor.

Name: ____________________________________

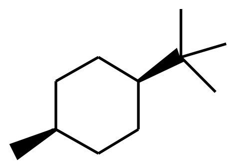
2) (25 pts) A wedges and dashes picture of an eclipsed rotamer of a trimethylpentane isomer is given below. Define the C^1-C^2-C^3-H^4 dihedral angle for this rotamer as 0° = 360°. Do a conformational analysis for rotation about the C^2—C^3 bond by completing the energy diagram. In the complete diagram you should show a curve indicating qualitatively (i.e. no numbers) the relative energies of all the rotamers, and give a Newman projection showing the structure corresponding to each well and each barrier top. In your conformational analysis please rotate carbon 3 (i.e. the "back" carbon) clockwise starting at the 0° dihedral strucutre in your conformational analysis.



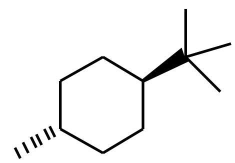


Name: ____________________________________

3) (25 pts) (a) Carefully draw perspective chair strucutres for the single most stable conformation for cis-1-tert-butyl-4-methylcyclohexane (II) and trans-1-tert-butyl-4-methylcyclohexane (III). Circle the <u>more stable</u> isomer.



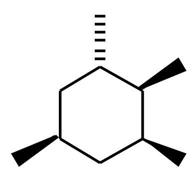
II



III

(b) Which isomer (II or III) would have a higher heat of combustion?

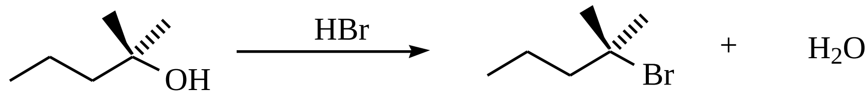
(c) Draw the two chair-flip conformations for the 1,2,3,5-tetramethylcyclohexane isomer IV . Circle the more stable conformation.



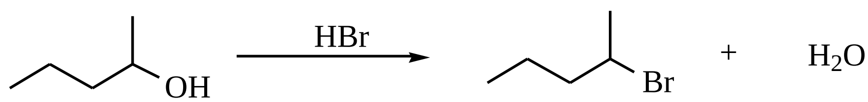
IV

Name: ___________________________________

4) (25 pts) (a) Propose an arrow-pushing mechanism for the reaction shown below. Be sure to show all lone pairs and formal charges for each step in your mechanism. All of your structures should be valid valence bond structures, but you don't need to show geometry.

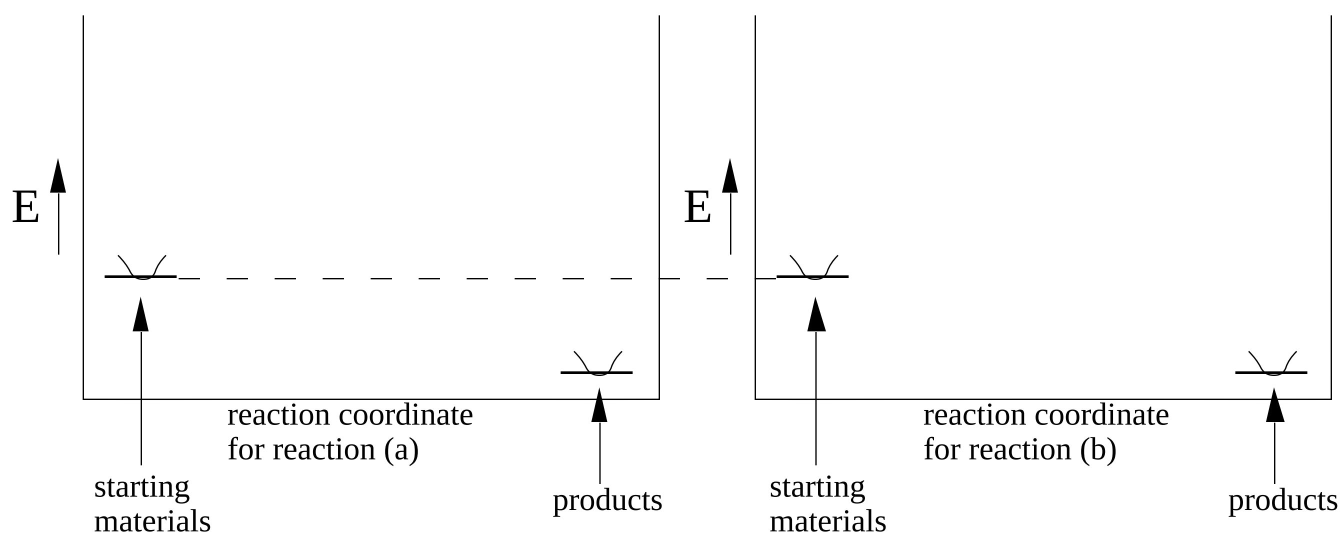


(b) Would the reaction in part (a) be faster, slower, or the same rate as the reaction shown below.



Name: ________________________________

(c) Complete the two energy diagrams for the reactions in part (a) and part (b). In these diagrams we're normalizing the energy scale so that the starting materials are at the same energy. For the sake of simplicity assume that the final products are also at the same energy, and the products are more stable than the starting materials, as shown. Please show the structure of the key intermediate (this is a hint, folks) for both reactions.



(d) What is Hammond's postulate? How did you use this concept to help construct your energy diagrams?