

Department of Chemistry and Biochemistry

Chemistry 59-230/232

Time: 50 min.

Midterm #2

Nov. 17, 2008

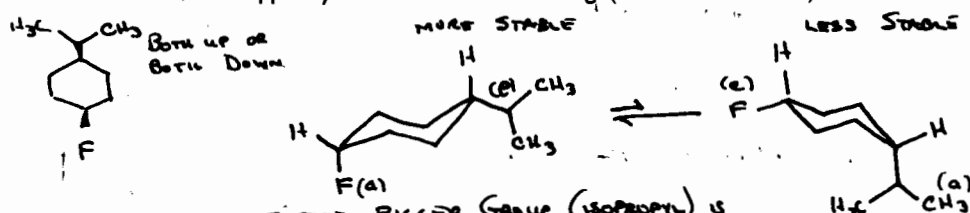
NAME _____ ID# _____

LAB SECTION (or TA/DAY/TIME) _____

Note: Please answer on the test paper. There is an extra sheet for rough work at the back, but it will not be marked unless asked. Tests written in pencil will be marked, but cannot be returned for remarking.

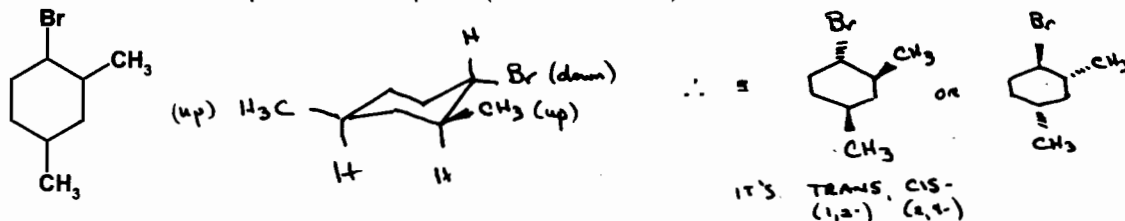
1. For the following questions the ranking in terms of group size is $C(CH_3)_3 > CH(CH_3)_2 > CH_2CH_3 > CH_3 > NH_2 > OH > F, Cl, Br, I > H$ (16 marks total)

- a. Draw the possible chair structures of cis-4-fluoro-1-isopropylcyclohexane. Indicate which is the more stable structure, and support your choice with reasoning. (10 of the 16 marks)



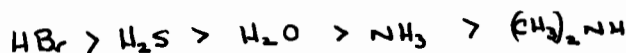
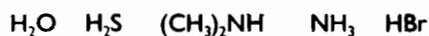
IN LEFT STRUCTURE THE BIGGER GROUP (ISOPROPYL) IS EQUATORIAL. EVEN THOUGH THE F GROUP IS AXIAL, IT'S A BETTER SITUATION THAN PUTTING THE F EQUATORIAL (RIGHT STRUCTURE) SINCE IT FORCES THE LARGER GROUP (ISOPROPYL) TO BE AXIAL

- b. Show the structure of the following compound in the most stable conformation of the most stable configuration. What are the stereochemical relationships between the substituents? A complete systematic name for the entire compound is not required. (6 of the 16 marks)

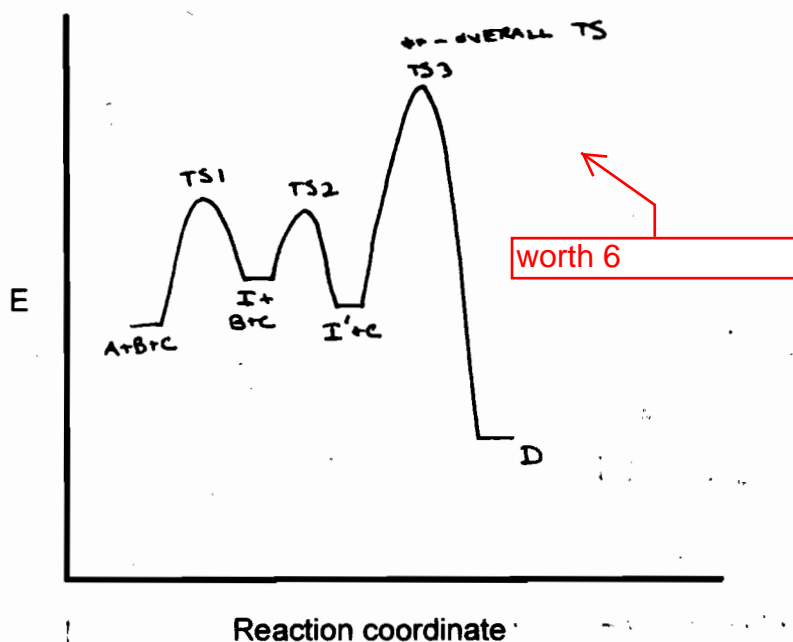


2. (Total 16 marks)

- a. Rank the following compounds in terms of acidity, from most to least acidic. (4 of the 16 marks)



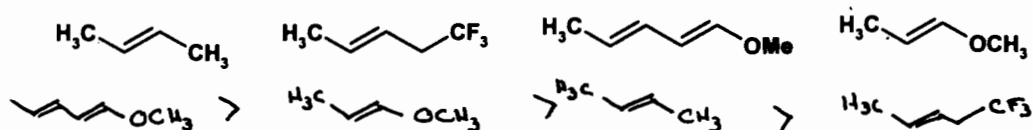
- b. Consider a three step reaction, where $A+B+C \rightarrow D$, and where: A is consumed in the 1st step; B is consumed in the 2nd step; C is consumed in the 3rd step. If the 3rd step has the highest transition state energy, draw the reaction profile and indicate the overall rate equation for the process. Include in the drawing the intermediates, and label the transition states for each step (TS1, TS2 etc.) and the overall transition state (star (*) it). (8 of the 16 marks)



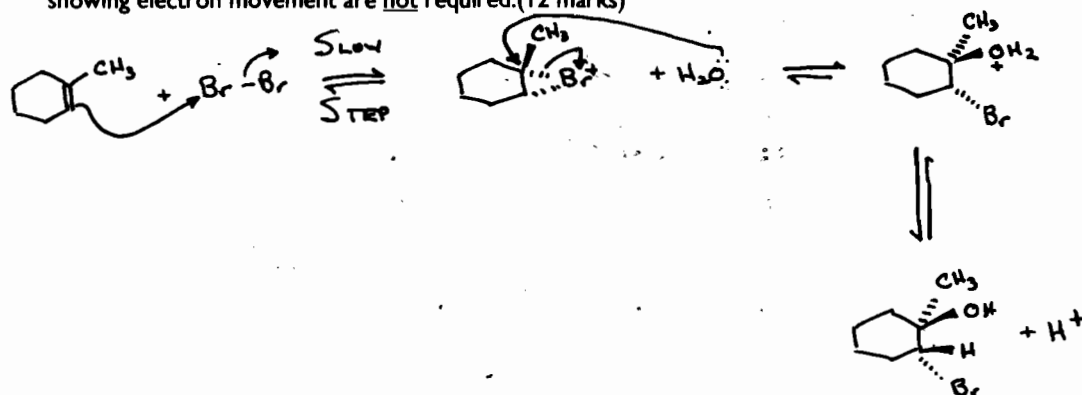
$$(\text{rate}) \propto [A][B][C]$$

← worth 2

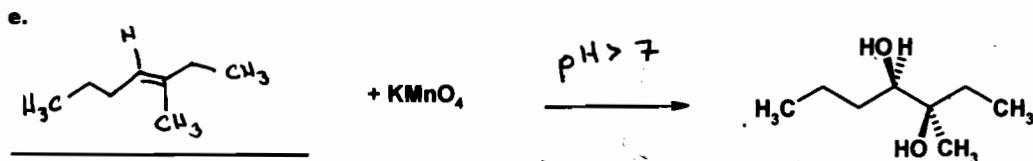
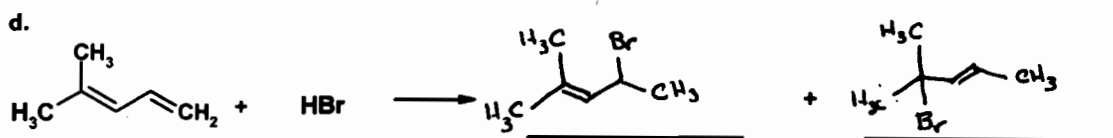
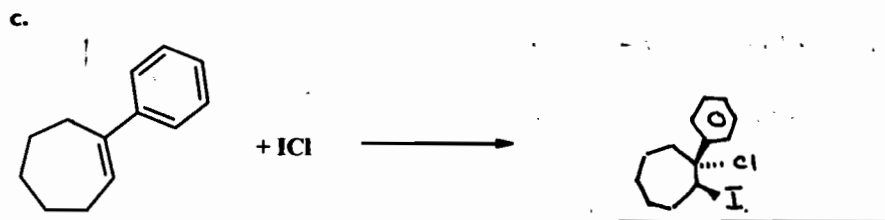
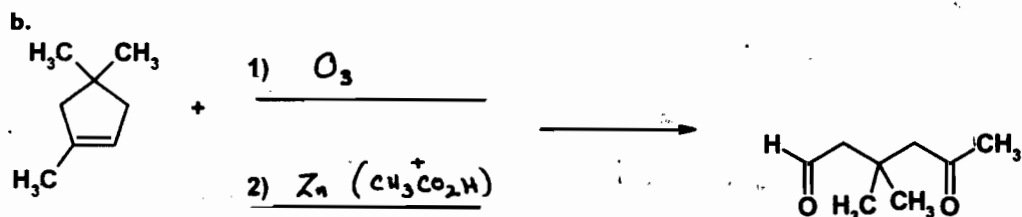
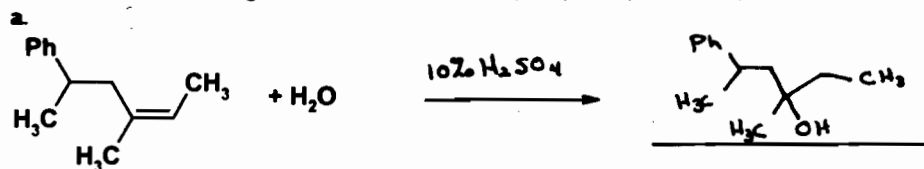
c) Rank the following compounds in terms of their rate of reaction with HCl, from fastest to slowest. You do not need to draw the products of the reaction (4 of the 16 marks).



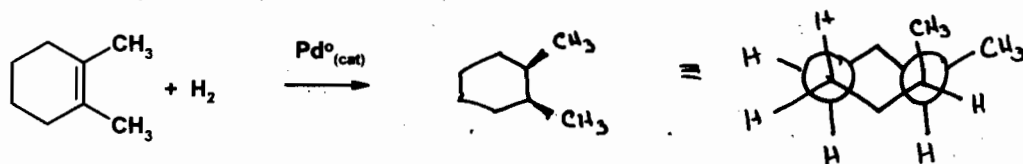
3. Draw the complete mechanism of the reaction of Br₂ addition to 1-methylcyclohexene in H₂O solvent. Show all accurate intermediates, and indicate which is the slow (rate determining) step. Curved arrows showing electron movement are not required. (12 marks)



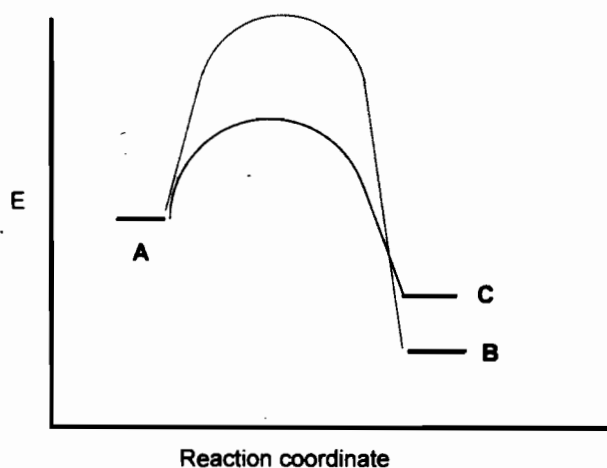
4. For each of the following reactions, fill in the blank with the structural formula of the required chemical. Show any required catalysts or conditions over the reaction arrow. Be sure to include stereochemistry where it is important. Note: Every reagent may not be shown by me, and there may be more than one reagent or more than one step required per blank. (Total 30 marks (6 each))



5a) (Total 14 marks). Draw the most stable conformation of the product of the following reaction as a Newman projection. (8 of the 14 marks).



b) Consider the following set of competing reactions ($A \rightarrow B$ and $A \rightarrow C$) (6 marks overall of the 14).



i. Which product is formed predominantly under kinetic conditions?

C

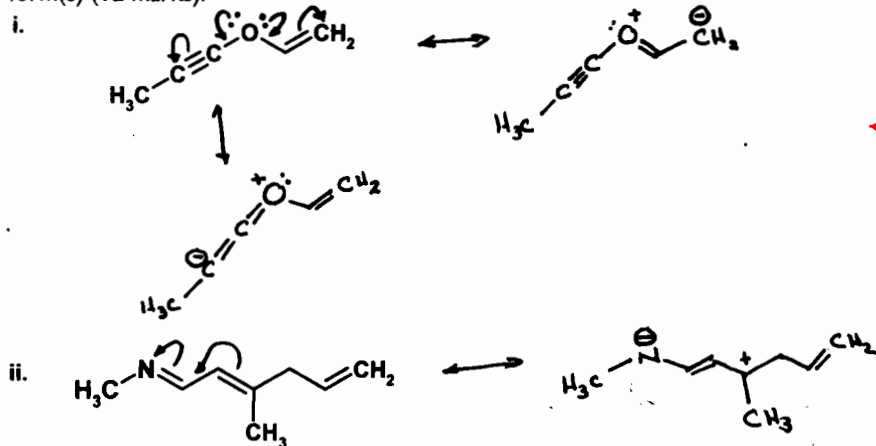
ii. Which is formed predominantly under thermodynamic conditions?

B

iii. Yes or no. Is it ever possible (not necessarily in this reaction scheme) to have a situation where the same product is both the kinetic and thermodynamic product?

YES

6. Draw all reasonable resonance forms for the following structures. For each of these, show the appropriate use of curved arrows demonstrating the electron movement leading to the other resonance form(s) (12 marks).



each worth 4,
8 total

worth 4

MOVING ARROWS THE OTHER WAY WOULD GIVE
A BAD RESONANCE FORM.

Bonus. We have seen that enols (indicated below) rapidly isomerizes (this specific case is called tautomerization) to ketones. Assuming there is always a trace of H^+ present with the enol, can you suggest a reasonable mechanism for this transformation? (up to 5 marks) Indicate if the answer is continued on the back.

