

Polytechnic Tutoring Center Midterm II REVIEW – CM 2223, Spring 2022

Disclaimer: This mock exam is only for practice. It was made by tutors in the Polytechnic Tutoring Center and is not representative of the actual exam given by the Academic Department.

Problem 1:

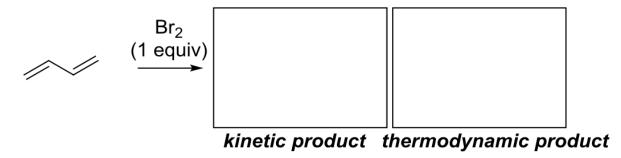
a)	Draw the complete arrow-pushing mechanism for the reaction of 2-methyl-1,3-butadiene
	(isoprene) with 1 equivalent of Hbr to produce 1-bromo-3-methylbut-2-ene. Make sure to
	include all lone pairs and non-zero formal charges.

b) Is 1-bromo-3-methylbut-2-ene the *kinetic* or *thermodynamic* product? Explain.

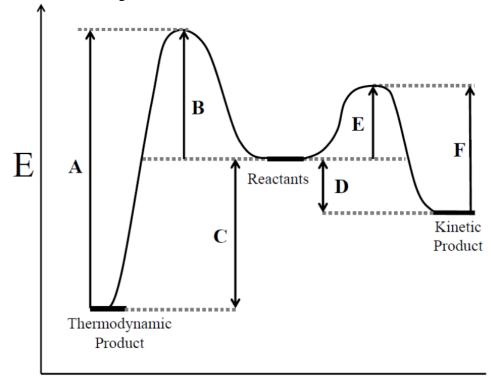
c) Draw the structures of any other products that you expect to form in this reaction.

Problem 2:

a) Draw the structures of the products of this reaction in the boxes provided.



The reaction coordinate diagram for this reaction is show below:

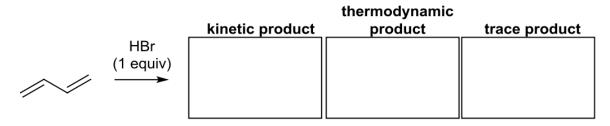


Circle the correct terms:

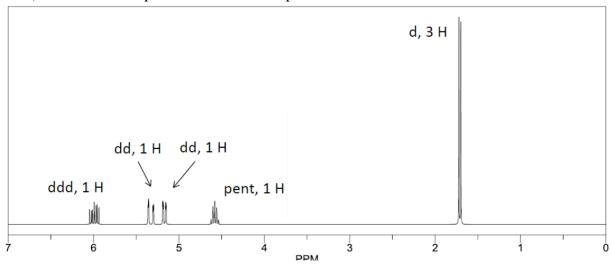
- b) At LOW/HIGH temperatures, the thermodynamic product is favored.
- c) At LOW/HIGH temperatures, there is enough energy to overcome barrier **E** but not **F** or **B**.
- d) The formation of the thermodynamic and kinetic products is both ENDOTHERMIC/EXOTHERMIC
- e) At LOW/HIGH temperatures, there is enough energy to overcome barriers **E**, **F**, and **B**, but not **A**.
- f) The reaction to form the KINETIC/THERMODYNAMIC product proceeds at a higher rate at all temperatures.
- g) The KINETIC/THERMODYAMIC product is more stable because the alkene is more substituted.

Problem 3: Treatment of 1,3-butadiene with one equivalent of HBr leads to three products. One product is major, one is minor, and one is formed in only trace amounts (less than 1%). Which product is favored (kinetic or thermodynamic) depends on the reaction temperature.

a) Draw in the products of this reaction.



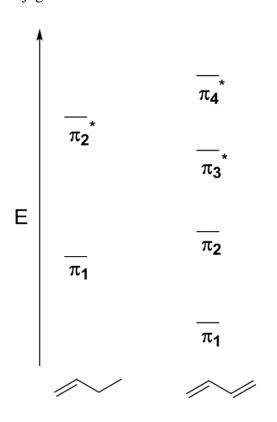
b) The ¹H NMR spectrum of one of the products is shown below.



Which product is this? Explain your answer.

Problem 4: Consider these molecular orbital diagrams. Notice that the relative energies of the MOs are shown, but the actual shapes of the MOs are omitted.

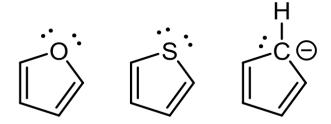
One of these diagrams is for the π bond in an isolated alkene, and the other diagram is for a conjugated diene.



- a) Fill in the electrons and label HOMO and LUMO on each diagram.
- b) What effect does conjugation have on the relative energy of the HOMO?
- c) What effect does conjugation have on the HOMO-LUMO gap?

d) In the Diels-Alder reaction, the dieneophile needs to be conjugated to an electron-withdrawing group for the reaction to proceed at a reasonable rate. Considering that the Diels-Alder reaction occurs via overlap of the filled HOMO on the diene with the empty LUMO on the dienophile, do you think the presence of the EWG raises or lowers the energy of the LUMO dienophile? Explain.

Problem 5: Furan and thiophene are aromatic heterocycles that are similar in structure to the cyclopentadienyl anion.



- a) Which of the following statements are trye for all three compounds?
 - i. They are aromatic
 - ii. All of the atoms in the ring are sp² hybridized
 - iii. They are 4pi electron systems
 - iv. They are weak bases
- A) I, II, and III B) II and III C) III and IV D) II only E) I, II and IV b) Draw the conjugate acid of each compound in the boxes provided.



- c) Which of the structures from part b) are aromatic? Explain.
- d) Which of the structures from part b) are nonaromatic? Explain.
- e) Are any of the structures from part b) antiaromatic? Explain.