Final Exam - Long Island University ANSWER KEY



2. Assign the absolute configuration to each chirality center in the following molecules. <u>In (b) be</u> sure to number your carbons. (15 pts)



3. Give the relationship between the following pairs of molecules. They may be the same molecule, enantiomers, diastereomers, or constitutional isomers. (10 pts)



4. Which molecule would have the **LOWER** heat of combustion? To answer this question you must make careful three-dimensional chair drawings of **BOTH** conformations of each molecule, showing clearly the ring flip. (20 pts)



So, molecule **A** is lower in energy than **B**, since it has a conformation in which all the groups are equatorial.



These two conformations are about equal, though the conformation **B2** in which the largest group, the Br, is equatorial is slightly lower than **B1**.

Two groups are axial, two are equatorial.

5. For the following reaction, there is only one major product. (a) Give the product, showing the complete reaction mechanism. (b) Calculate the overall energy change for this reaction using the given bond dissociation energies (BDE). (c) Explain, using an energy diagram and the Hammond Postulate for the SLOW step why there is only one major product formed. (20 pts)



(c) For bromination the first step is endothermic, so there is a late transition state and a relatively large difference in energy between the transitions states as postulated by Hammond. In chlorination the first step is exothermic and so there is an early transition state and a relatively small difference in energy in the transitions states.

6. Give the product(s) of the following reactions, showing the major and minor products where appropriate. (15 pts each, 90 pts)





7. For the following reaction **FOUR** products are formed. (a) Show them and show the complete reaction mechanism by which each is formed. (b) Two of the products are favored at lower temperature and two at higher temperatures. Indicate which products these are and briefly explain your reasoning. (25 pts)





(b) The more stable carbocation intermediate is favored at lower temperatures since it forms faster. The carbocation leading to C is the most stable since it is tertiary and allylic and benzylic and also the carbocation leading to B is tertiary allylic and would befavored over the carbocation leading to C. The more stable products are favored at higher temperature. These would be the more substituted double bonds, D and A. Both of these are benzylic and tetrasubstituted.

8. Only one product is formed in the following reaction. (a) Show this product and show the complete reaction mechanism by which it is formed. (b) Using resonance structures show why this product (*ortho* or *para* or *meta*) is formed in preference to the other possible products. (20 pts)



The bulky diisopropyl amino group blocks the ortho position

9. Synthesize **THREE** of the following **FOUR** molecules form the starting materials given on the LEFT. Do all **four** for extra credit. (30 pts)



