

Chemistry 124 Sixth Examination
February 26, 2010

Name _____

The exam budgets 50 minutes, but you may have 60 minutes to finish it. Good answers can fit in the space provided. Question values correspond to allotted time. Don't waste too much time on cheap questions.

1. (6 min) Provide an approximate value in kcal/mole for the energy change of the following processes:

ethylene + H₂ → ethane _____

benzene + H₂ → 1,3-cyclohexadiene _____

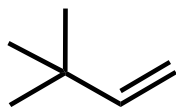
cis-2-butene → trans-2-butene (activation energy without catalysis) _____

s-cis-1,3-butadiene → s-trans-1,3-butadiene (activation energy without catalysis) _____

2. (3 min) The isomeric n-butyl and t-butyl cations differ in energy by 37 kcal/mole in the gas phase. Explain whether you would expect the difference to be larger or smaller in solution.

3. (1 min) Why did Prof. Siegel recommend memorizing the pseudo-word "FONCLBRISCH"?

4. (3 min) If it is possible to add H₂O to an alkene like 3,3-dimethyl-1-butene with simple acid catalysis, why might one choose to use the more complicated, indirect sequence of reaction with Hg(OAc)₂ and water followed by reduction with NaBH₄ to achieve H₂O addition to the alkene?



5. (9 min) Two new bonds to carbons (involving two electron pairs) are formed simultaneously in reaction of Cl_2 with ethylene, in reaction of BH_3 with ethylene, and in reaction of O_3 with ethylene. Position each reagent properly with respect to the ethylenes below (two frames for each reagent; one for each electron pair), draw their relevant LCAO-MOs (with signs and HOMO/LUMO labels) to show how these three reactions are analogous

Reaction with Cl_2



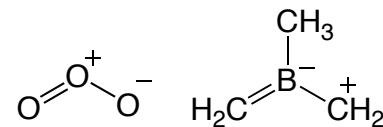
Reaction with BH_3



Reaction with O_3

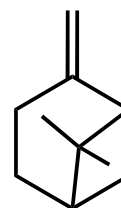
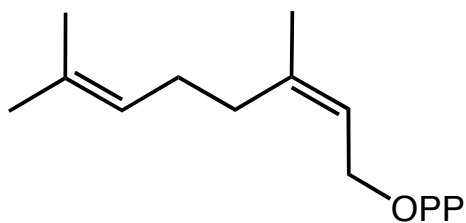


6. (2 min) Explain why the hypothetical reagent $\text{CH}_3\text{B}(\text{CH}_2)_2$ should not react like O_3 in the reaction of Question 4, even though their dipolar formulae look similar



7. (8 min) By choosing different reagents 2-butyne can be converted selectively to either isomer of 2-butene.
- A. Give the reagent(s) for forming cis-2-butene :
 - B. Give the reagent(s) for forming trans-2-butene :
 - C. Draw a mechanistic sequence (curved arrows and all) to explain how **ONE** of these processes occurs (either A or B).
8. (5 min) Explain how cross-linking natural rubber (by vulcanization) can both keep it from becoming brittle in the cold and from becoming runny when hot.

9. (9 min) Draw a reasonable reaction sequence (with curved arrows) for converting neryl pyrophosphate to β -pinene.



10. (5 min) What is the mechanistic significance of the fact that addition of DCl to 1,3-pentadiene at -78°C gives three times as much of the 1,2- as of the 1,4-addition product? [It might help to draw the reaction intermediate.]