

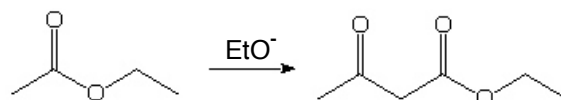
Chemistry 125 Final Examination
May 2, 2006

Name _____

1. (36 min) How do you know? Provide **experimental** evidence to support **six** (6 ONLY) of the following 10 assertions. Be as specific as possible.
- a) The pentavalent carbon in an S_N2 substitution is a transition state, not an intermediate.
 - b) A hydrogen is rearranging during the rate-determining transition state of a reaction.
 - c) S_N1 substitution involves a carbon cation intermediate.
 - d) A methyl group can rearrange rapidly from one ring carbon to the next in the heptamethylcyclohexadienyl cation.
 - e) A ring system can be "aromatic" with $4n+2$ π electrons when $n \neq 1$.
 - f) It is possible to discriminate between Z and E alkene isomers spectroscopically.
 - g) S_N2 substitution involves inversion of configuration at carbon.
 - h) The trend in bond dissociation energies for alkane C-H bonds might NOT be due to differences in radical stability.
 - i) One can use a "trick" to isomerize a long-chain alkyne to its least stable isomer.
 - j) "Electrophilic" addition to an alkene can involve an important nucleophilic component.

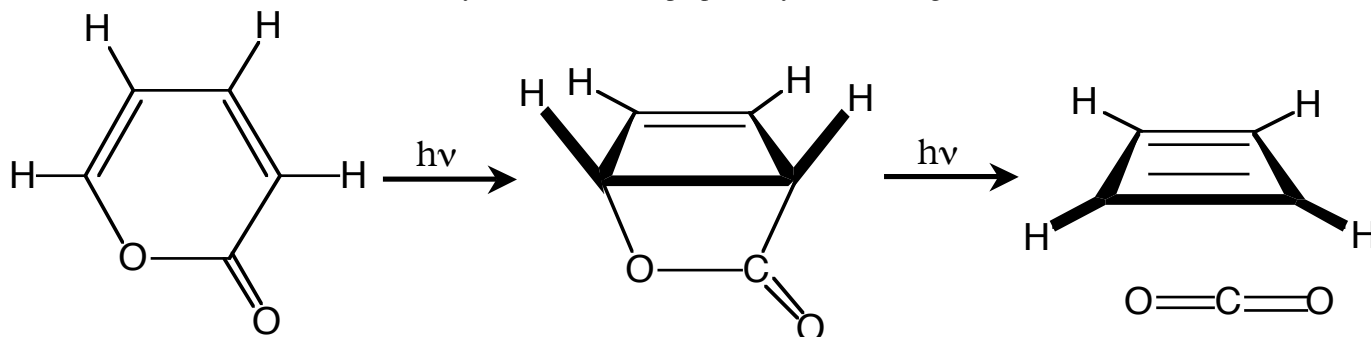
2. (7 min) **Draw a mechanistic scheme** for the propagation steps in the anti-Markovnikov addition of HBr to an alkene in order to **explain why it fails** for HCl and HI.

3. (7 min) Esters undergo the “Claisen condensation,” a reaction analogous to the aldol reaction, to give β -ketoesters. [This kind of reaction is key in the biosynthesis of fatty acids.] **Draw a mechanism** for this reaction. **AND** explain how a **property of the β -ketoester** should drive the equilibrium toward product in the presence of EtO^- .

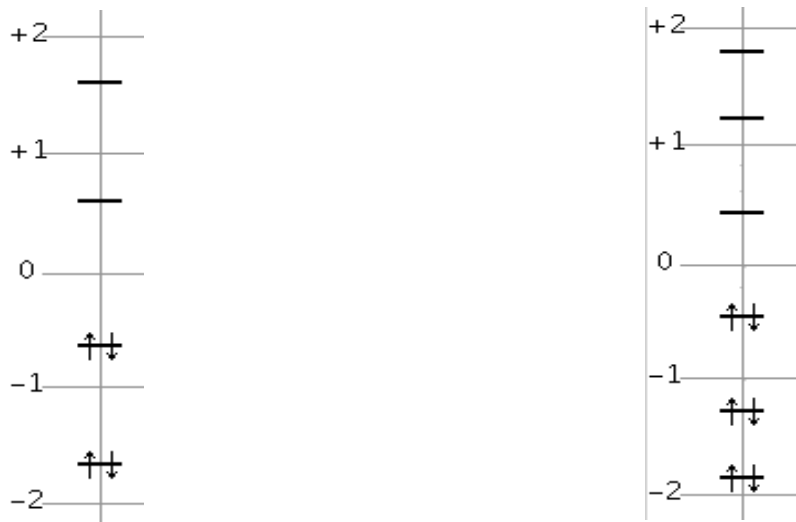


Preparation of Cyclobutadiene

In 1991 the elusive molecule cyclobutadiene was prepared by the following two transformations:



4. (1 min) Draw curved arrows in the first and second structures to show the change in bonding electrons during the two reactions.
5. (6 min) Note that the first reaction involves partial rotation about the two double bonds to allow the tops of the p-orbitals on the ends of the butadiene to touch and form the new σ bond. **Complete the diagrams** below to explain in terms of orbital energies why the *transition state* for this process should not be as favorable as that for a seemingly analogous reaction in which hexatriene closes to form cyclohexadiene [Do NOT try to be quantitatively precise].

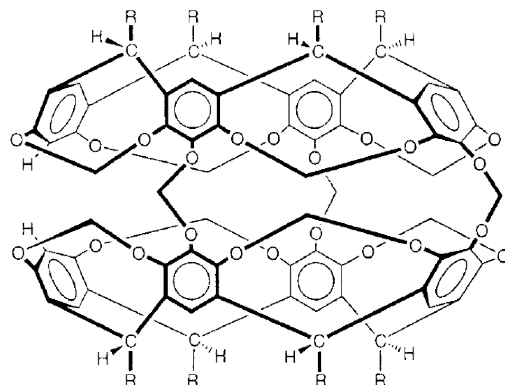


6. (7 min) The unfavorability described in the previous question was circumvented by using ultraviolet light that is absorbed by the substituted cyclohexadiene. Explain **TWO WAYS** in which absorption of light favors the reaction.

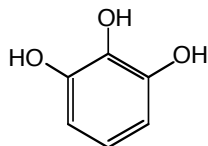
7. (5 min) Should the light absorbed by the cyclohexadiene in the first transformation be **longer or shorter** in wavelength than that absorbed by the cyclobutene in the second transformation? Answer in terms of **orbital energies**, and **explain** the relationship of your answer to the beautiful **red color** in the wings of the *Tichodroma muraria* (the wallcreeper).

8. (4 min) Why is cyclobutadiene so hard to isolate?

9. (6 min) Explain how the “spherical” molecule on the right was helpful in preparing and studying cyclobutadiene.

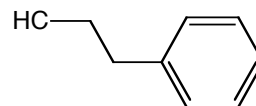


Note that the spherical molecule above, whose synthesis we are about to discuss, is made from three repeating elements:



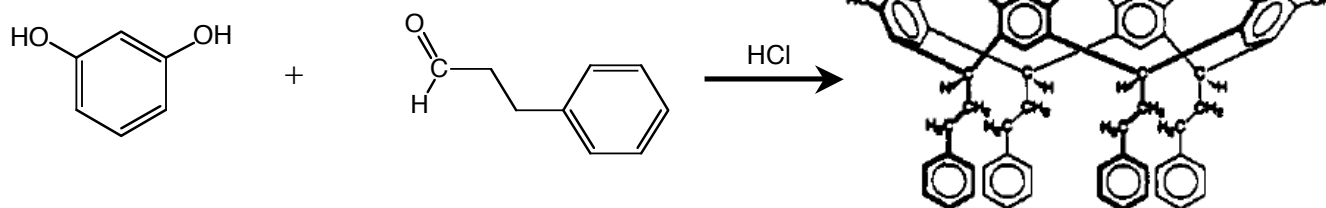
benzene “triols”

CH_2 “bridging groups”
between oxygens



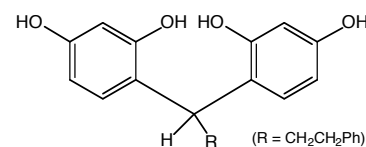
CHR groups between benzenes

Synthesis of the “sphere” involved first beginning a “hemisphere” by acid-catalyzed reaction of a diol and an aldehyde:



10. (7 min) Show how the **aldehyde** in the center above may be prepared beginning with reaction of two simpler aldehydes, followed by a common reaction of alkenes. [No detailed mechanism or curved arrows necessary. Just show **starting aldehydes**, isolable intermediate product(s), and the **reagent(s)** which lead(s) to the aldehyde above.]

11. (10 min) Use curved arrows to draw the mechanism by which one aldehyde is bonded to the two adjacent diols to give the product shown at the right. [Repetition of this process gives the product at top right.]

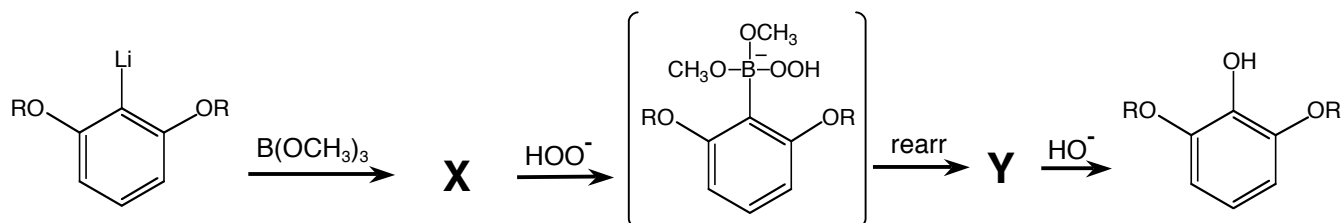
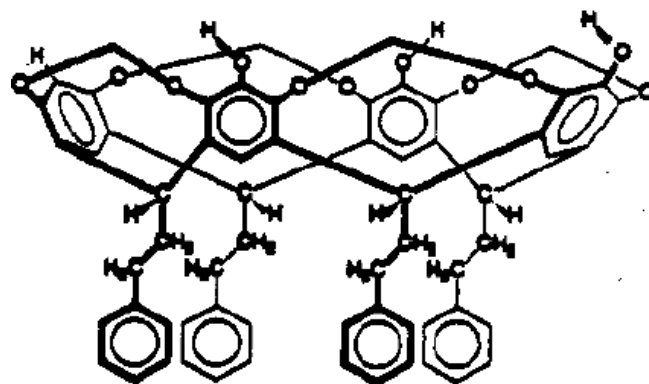


12. (3 min) The reaction at the top of the page initially gave a mixture of four configurational stereoisomers (and perhaps larger rings with different numbers of constituents as well). What **lucky break** gave a 69% yield of the compound shown?

13. (8 min) To prepare for forming three bridges between the two hemispheres of the desired spherical molecule, bromine atoms were substituted for hydrogen on the three carbons denoted by arrows in the figure at the top right of the previous page. **Suggest a REAGENT** that might yield "Br⁺" to begin each substitution, **AND** draw formula(s) to help **explain why the substitution takes place between the oxygen atoms** of each ring rather than on the opposite side of the rings (between carbon substituents) or somewhere on phenyl rings at the "bottom" of the hemisphere.
14. (5 min) Four CH₂ groups were next introduced to bridge between the oxygen atoms of adjacent rings to complete the "upper rim" of the hemisphere (shown below). **Identify a reagent and name the type of reaction** that would be suitable for this transformation. (You don't need to draw the actual mechanism.)

Now the bridged tribromide was converted to the bridged triol, the complete "hemisphere," which needs only 3 CH₂ bridges of the same kind to link to another hemisphere and complete synthesis of the final "sphere."

To make this triol each of the three bromines was replaced with Li (by treating with BuLi), and the lithiated product was treated with B(OCH₃)₃ to give **X**. **X** was then treated with HOO⁻ (probably a D/A substitution at B), after which the unstable intermediate, shown in brackets, rearranged to **Y**. **Y** then reacted with OH⁻ to generate a product with an OH group where the original Br had been.



Although we did not study any of these reactions explicitly, they are probably mechanistically analogous to reactions we did study. You will demonstrate the analogies in the the last five questions of this exam.

15. (8 min) Show how the mechanism for the first reaction to give **X** *might* be analogous to electrophilic aromatic substitution.
16. (8 min) Show how the mechanism of converting **X** to the unstable intermediate in brackets might be analogous to a reaction involving carbon instead of boron. **Explain** how the properties of **B** and its substituents would facilitate this process.
17. (7 min) Describe one specific experiment that suggests that the carbon analogue has the mechanism you have discussed in question M.

18. (7 min) Where did we encounter a rearrangement analogous to that from the unstable intermediate to **Y**?
19. (8 min) Show how the last reaction of **Y** with OH^- is analogous to that between an ester of a carboxylic acid and OH^- .