Problem Set 1

Following are the group assignments for group homework #1. The goals of this activity are to challenge you to work problems that are more complex and to practice working effectively in a group setting with people that you do not necessarily know well. The person with an 'O' after their name will be the organizer of the group and will be required to arrange meeting times and places to complete the assignment. The person with a 'W' after their name will be the person who prepares the final written assignment to be turned in for a grade. Groups will be re-assigned and roles will be changed for each set of homework, so that you have the opportunity to work with a variety of different people and in different roles throughout the semester.

On the next page is the 'grading' scale for each member of your group. After you have completed the homework assignment, please 'grade' the performance of each group member, including yourself, and turn in separately from the group homework for confidentiality purposes. A person who does not show up for the group meetings or does not participate in the problem solving process should receive an 'F' for the group grade. A person who contributes, asks questions, and helps the other group members to understand the problem and answer deserves an 'A'. A person who requires a little extra help and needs another group member to explain a topic **does not** deserve an 'F'. Their lack of understanding will help you as well because you will have to clearly explain the topic to him/her. If you choose to not turn in grades for your group members, I will assume 'average' participation for the entire group.

Submit only one set of answers per group. Please work with your assigned partners to prepare your final draft of answers. You may find it useful to xerox copies of the answer set, so that each group member may have it for reference. Please do not consult with anyone other than people in your group; you may consult me for question clarification only. You may use your textbooks and any other written references from the library. Do not copy anyone else's work. The honor code pledge is printed on the top of the "grading" scale page. By turning this page in, you are acknowledging that you have read and understand the privileges and responsibilities that this code bestows.

This is due Friday, October 14, at the beginning of class.

Benjamin D. Treichel Kari L. Maffitt (O) Stephanie J. Lewis Eric G. Nelson (W)	Arie J. DeGrio (W) Christopher T. Lund Sarah E. Erickson Alyssa C. Brooks (O) Trevor J. Wittwer	Emily J. Pelton (O) Matija Novakovic Michael S. Butterworth Lauren K. Hom Aaron A. Roessler (W)	Ellen E. Sauter Kyle R. Carlson (W) Nathan C. Bower Jeffrey M. Rock (O) Jennifer M. Paulsen
Nathan R. Erickson Leah A. Swanson (O) Morgan R. Wells (W) Fue F. Vang Emily K. Barnard	Rachel L. Roberg David J. Wray (O) Douglas R. Durand Kristen M. Burson Timothy Lamanna (W)	Jill K. Verchota (W) Rachel L. Elvebak Rachael M. Chaska (O) Nissa A. Hannemann Justin J. Hahn	Brian T. Castle (W) Christopher S. Leonard Brent McConahey Mackenzie Consoer (O) Andrew J. Bryan
Chris Ditlevson (W) Maari H. Hanson Nicholas J. Malm Zachary C. Walgenbach Krista M. Cruse (O)	Danielle J. Burras Brittany L. Murphy Marcus B. Perry (O) Daniel D. Freeman Micah S. Deitz (W)	Danielle R. Forstner Brianna E. Vaa Benjamin S. Levy (O) Douglas Schroeder (W) Jennifer A. Krantz	Scott J. Kyser (O) Krystal L. Long Jenna M. Kesty Aaron T. Insley Zach R. Alwine (W)
Stephen A. Howard Erik J. Kraska (O) Rachel A. Poppy Kelly Rozenboom Alexandra Burleigh (W)	Stephanie Soiseth (W) Matthew L. Hoke Chad T. Olson (O) Sunny P. Sonnabend Ryan Casper	Michael D. Stangler (W) Sarah L. Duncan Bridget L. Hoesley Amy J. Waldner (O) Matthew C. Royer	Alex Burum (W) Raychal N. Zupancich Bryce D. Gode (O) Erik A. Anderson Luis T. Valle
Kathryn Pesch (O) Holly Cooper (W) Connor Ziegler Erin Ge David Wold			

_____

Student ID #

Peer Evaluation Grading Sheet

On my honor, I pledge that I have not given, received, nor tolerated others' use of unauthorized aid in completing this work.

_____ A B C D F

Group member #1

_____ A B C D F

Group member #2

_____ A B C D F

Group member #3

_____ A B C D F

Group member #4

_____ A B C D F

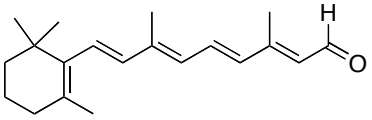
Group member #5

Comments:

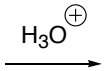
Believe it or not, you already know enough chemistry to understand many important biochemical processes. The following examples are designed to help you both to understand the organic chemistry mechanisms that allow living systems to manipulate energy and to view organic chemistry from a different perspective. For our purposes, the biology is interesting, but the details of the biology are not test material for CHE-251. Focus on understanding the reaction mechanisms.

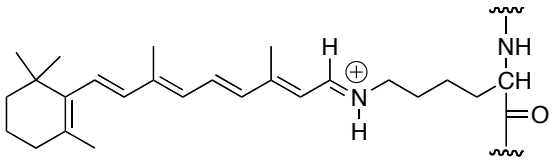
1) (10 pts) Bacteriorhodopsin is one of the best-characterized and most well-studied *integral membrane proteins* (proteins that are tightly bound to cellular membranes through hydrophobic interactions). This protein comes from bacteria that grow in salty places such as the Dead Sea. Under low oxygen conditions, the bacteria grows 0.5 μm wide patches of purple membrane with only bacteriorhodopsin as the protein component. The protein acts as a light driven proton pump (it forces protons from one side of the membrane to the other) to establish a pH gradient. This pH gradient then is used by the bacteria to drive the synthesis of ATP (adenosine triphosphate, nature's energy currency). The purple color, and the light absorbing element, is due to a covalent bonding of retinal (compound **1**) with a lysine residue in the protein (shown, in part, by compound **2**). A similar covalent complex forms with rhodopsin and forms photoreceptors in the human eye.

Using curved arrow notation, show an acid catalyzed mechanism for the formation of the retinal-rhodopsin complex (compound **3**).

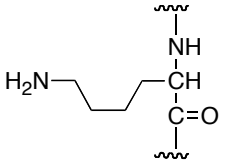


retinal
(1)





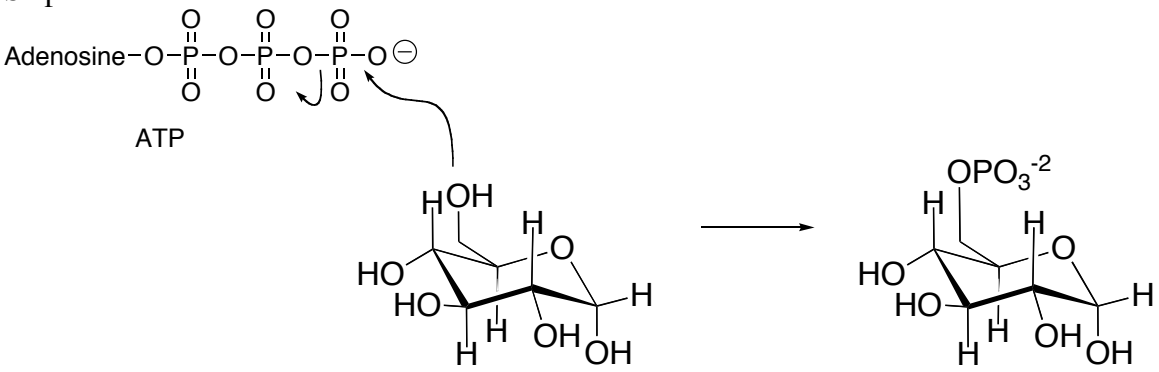
rhodopsin-retinal complex
(3)



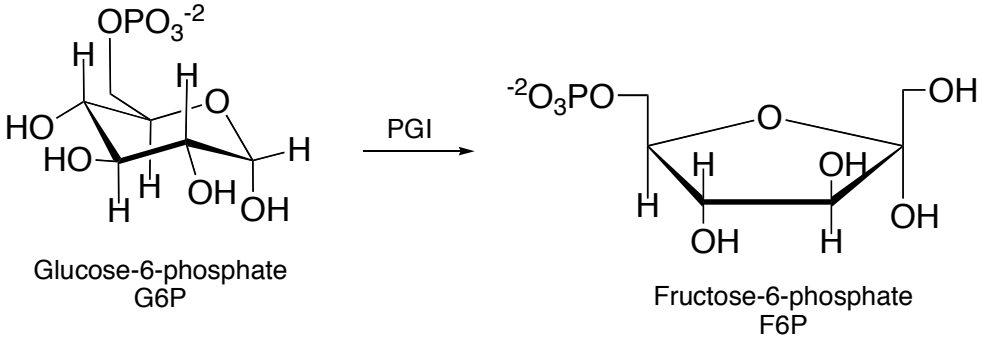
lysine residue
(2)

2) (15pts) Glycolysis (from the Greek *glykos*, sweet; *lysis*, loosening) is the metabolic pathway by which glucose is converted to pyruvate with the concomitant generation of 2 mol of ATP/mol of glucose. The first step involves the hexokinase-mediated reaction of ATP with glucose (**4**) to give glucose-6-phosphate (G6P). The second step is the phosphoglucose isomerase (PGI) catalyzed isomerization of G6P to fructose-6-phosphate (F6P).

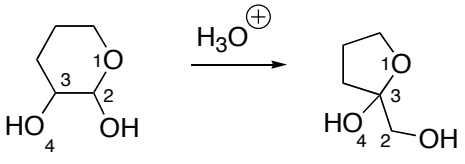
Step 1:



Step 2:

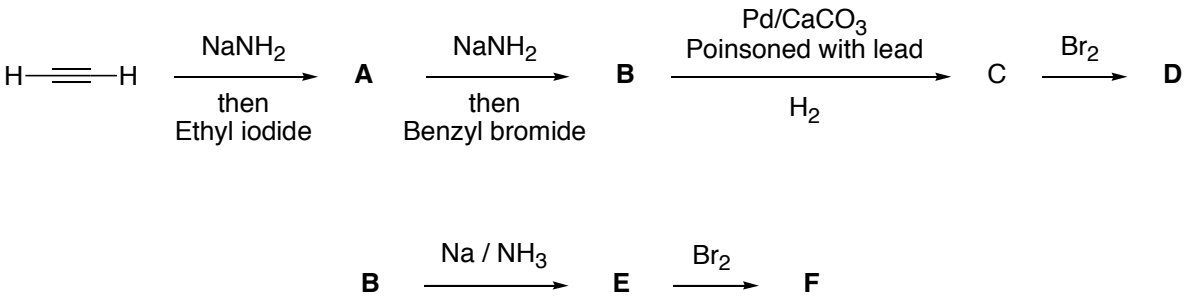


A simplified version of this second reaction is shown below by the acid catalyzed conversion of **5** to **6**. Note that some of the atoms are labeled: O(1), C(2), C(3), O(4). The atoms labeled in compound **5** map onto the similarly labeled atoms in compound **6**. That is, the carbon labeled "3" in compound **5** is the same carbon labeled "3" in compound **6**. For this problem, provide a mechanism, using curved arrow notation, that accounts for the transformation of **5** to **6**. Show all proton transfers. As a hint, think about keto-enol tautomers.



5 **6**

3) (25 pts total) Consider the following reaction scheme:



A) (3 pts each) Fill in the missing products:

Compound **A**: Compound **B**:

Compound **C**: Compound **D**:

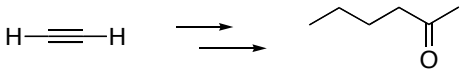
Compound **E**: Compound **F**:

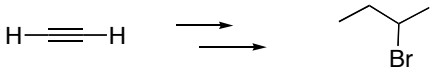
B) (2 pts) In the convertion of **B** to **C**, what is the common name for the palladium catalyst?

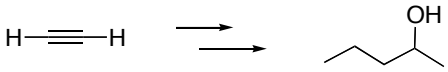
C) (2 pts) What is the stereochemical relationship between compounds **D** and **F?**

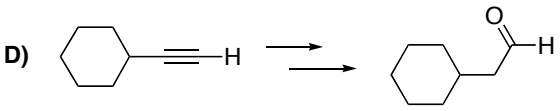
D) (3 pts) Provide a mechanism, using curved arrow notation, for the conversion of **B** to **E**.

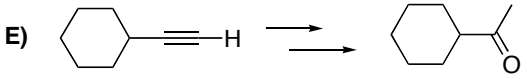
4) (5 pts each) Show how each of the following compounds could be prepared using the given starting material, any necessary inorganic reagents, and any necessary organic compounds containing no more than four carbon atoms.

A) 

B) 

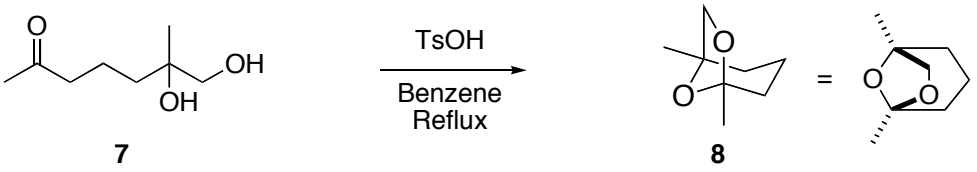
C) 

D) 

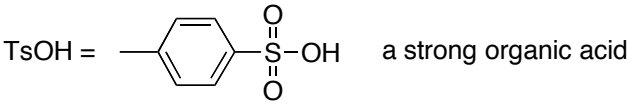
E) 

5) Frontalin (**8**) is an insect pheromone responsible for aggregation of Southern Pine Beetles, one of the most destructive insects in pines forest of the southeastern United States. The aggregation mechanism of these insects isn't perfectly known but it seems that compounds (terpenes like α-pinene) produced by the trees attract some female insects. The females secrete (-)-frontalin, among other pheromones, that attract a lot of male (and female) insects.

A) (7 pts) Using curved arrow notation, provide a plausible mechanism for the conversion of **7** to frontaline under the conditions indicated. Be careful to show all steps (including proton transfers), and use equilibrium arrows between distinct mechanistic steps. You may use H-A and B: as generic acid/base reagents for proton transfers.



7 **8**

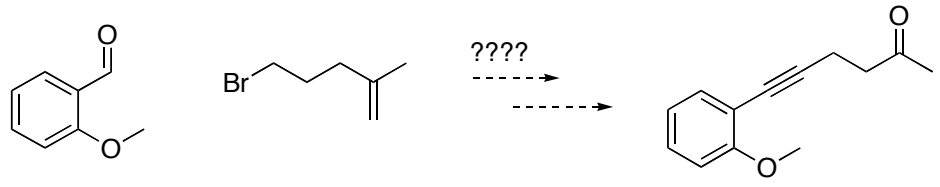


a strong organic acid

B) (1 pt) How does one drive the equilibrium in the desired direction (i.e. toward **8**)?

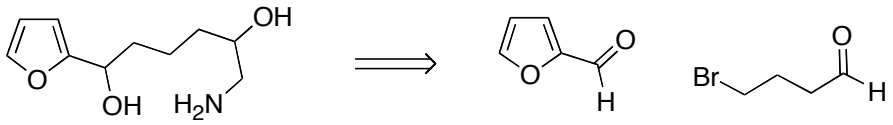
C) (2 pts) What is the required stoichiometry (based upon **7**) of TsOH?

6) (10 pts) Show how you would make compound **11** starting from benzaldehyde derivative **9** and 5-bromo-2-pentanone (**10**). You may use any inorganic reagent you with, and any organic reagent of 2 carbons or less.



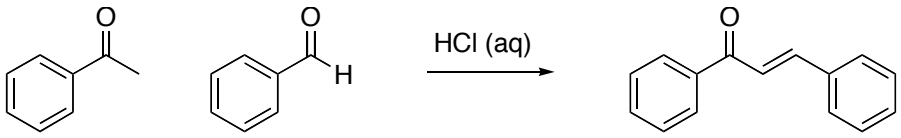
9 **10** **11**

7) (5 pts) The biochemists at the Pharmaceutical company for which you work have just found an interesting calcium-binding drug lead to help in the fight against high blood pressure. They have figured out its structure (**12**), and need you to make this compound for further testing. In your lab, you have furfural (furan aldehyde, **13**), 4-bromo-butanal (**14**), any inorganic reagent you might need, and any organic reagent that contains two or less carbons. (The cheap-skates. You need to find a better company to work for!) How would you make compound **12** from these chemicals?



12 **13** **14**

Extra Credit (10 pts) It is known that when acetophenone (**15**) and benzaldehyde **(16**) are stirred with aqueous HCl, they react to give **17**.



15 **16** **17**

Provide a mechanism, using curved arrow notation, that accounts for this transformation. Be sure to include all proton transfers.