

CHEM 3371, Spring 2015  
 Professor Walba  
 First Hour Exam  
 March 10, 2015

scores:

- 1) 20  
 2) 20  
 3) 20  
 4) 20  
 5) 20

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 100

CU Honor Code Pledge: On my honor, as a University of Colorado at Boulder Student, I have neither given nor received unauthorized assistance.

Name (printed): \_\_\_\_\_ **Key**

Signature: \_\_\_\_\_

Recitation TA: \_\_\_\_\_ Patrick Chaffey or Carley Little  
 (circle your TAs name)

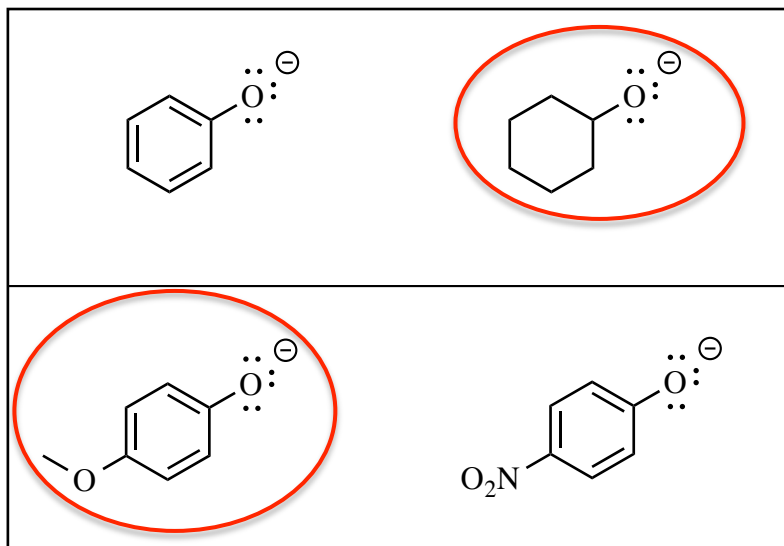
Recitation day and time: \_\_\_\_\_

This is a closed-book exam. The use of notes, calculators, scratch paper, or cell phones will not be allowed during the exam. You may use models brought in a clear ziplock bag. Please put all you answers on the test in the appropriate place. Use the backs of the pages for scratch (there are two additional blank scratch sheets after the last page of the exam). DO NOT PUT ANSWERS ON THE SCRATCH SHEETS.

*PLEASE read the questions very carefully!*

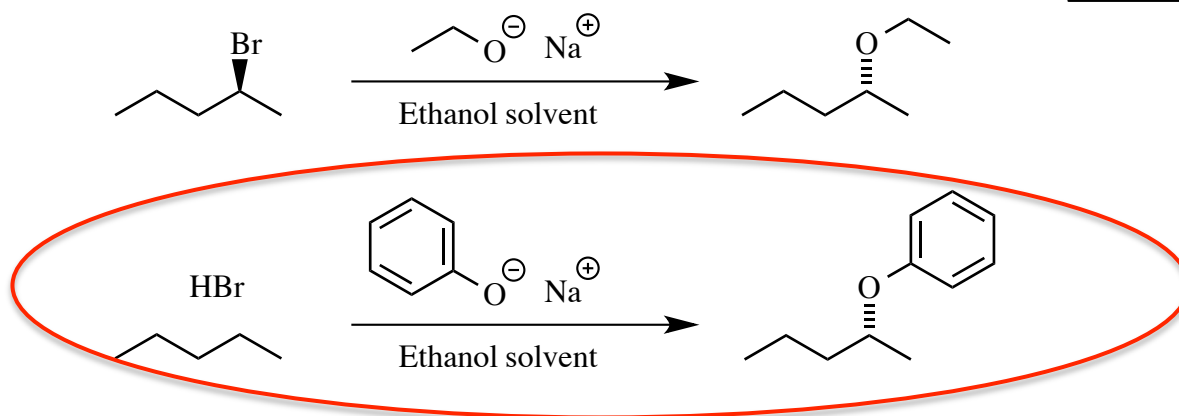
| Partial Periodic Table |          |          |          |         |         |          |          |  |  |
|------------------------|----------|----------|----------|---------|---------|----------|----------|--|--|
| 1A                     |          |          |          |         |         |          | 8A       |  |  |
| 1<br>H                 |          |          |          |         |         |          | 2<br>He  |  |  |
|                        | 2A       | 3A       | 4A       | 5A      | 6A      | 7A       |          |  |  |
| 3<br>Li                | 4<br>Be  | 5<br>B   | 6<br>C   | 7<br>N  | 8<br>O  | 9<br>F   | 10<br>Ne |  |  |
| 11<br>Na               | 12<br>Mg | 13<br>Al | 14<br>Si | 15<br>P | 16<br>S | 17<br>Cl | 18<br>Ar |  |  |
|                        |          |          |          |         |         | 35<br>Br |          |  |  |
|                        |          |          |          |         |         | 53<br>I  |          |  |  |

1 (20 pts) a) Circle the stronger base for each of the following pairs of anions.



b) For the reactions given below, what is the name of the mechanism for the reactions?

$S_N2$



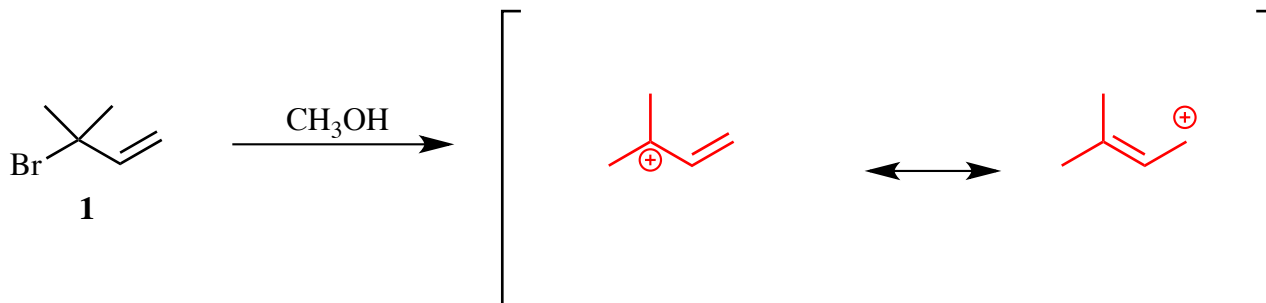
c) Circle the reaction given in part b) that is faster.

d) The slower reaction in part b) actually produces a different product as the major product. Draw the structure of the major product of the slower reaction.



1 – Continued

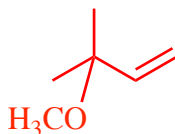
e) When 3-bromo-3-methyl-1-butene (**1**) is dissolved in methanol, a reactive intermediate is formed. Give the two major resonance contributors to the structure of this intermediate.



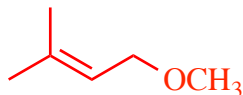
f) The reaction shown in part e) above produces two major products. Draw the structure of the two products.



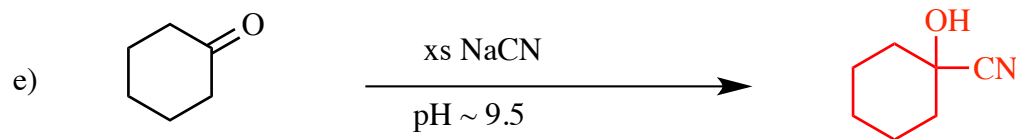
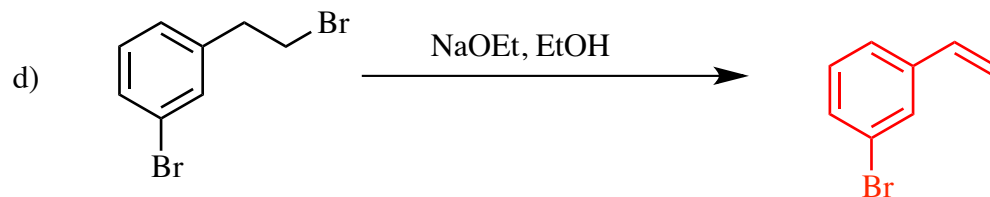
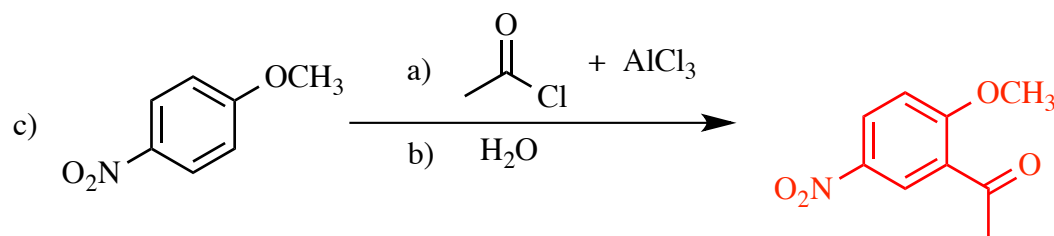
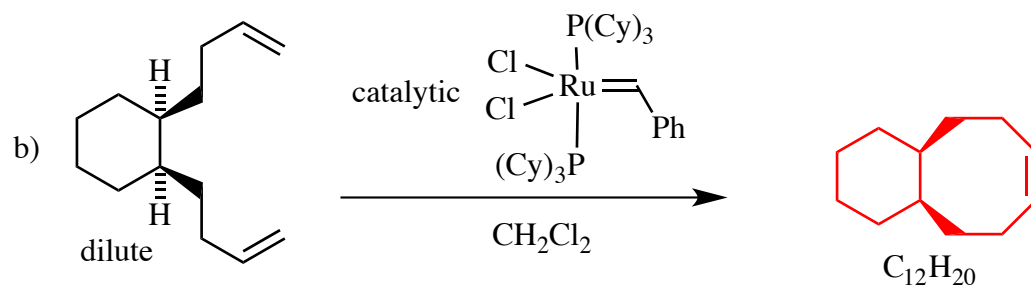
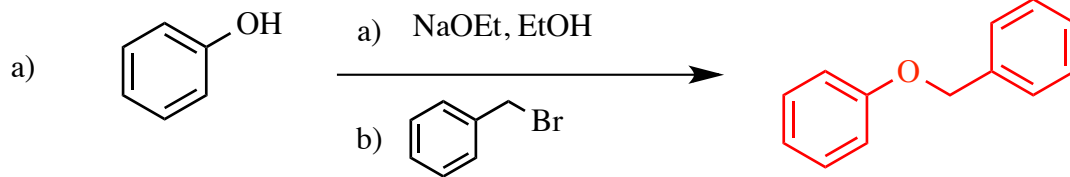
g) For the reaction in part e), the single major product changes depending upon conditions. Give the single major product expected if the reaction is run as indicated, with no acid added (to be safe, assume there is an insoluble "acid scavenger" such as  $\text{Na}_2\text{CO}_3$  in the reaction mixture).



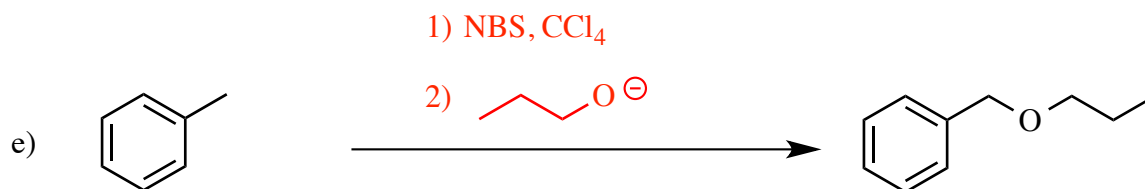
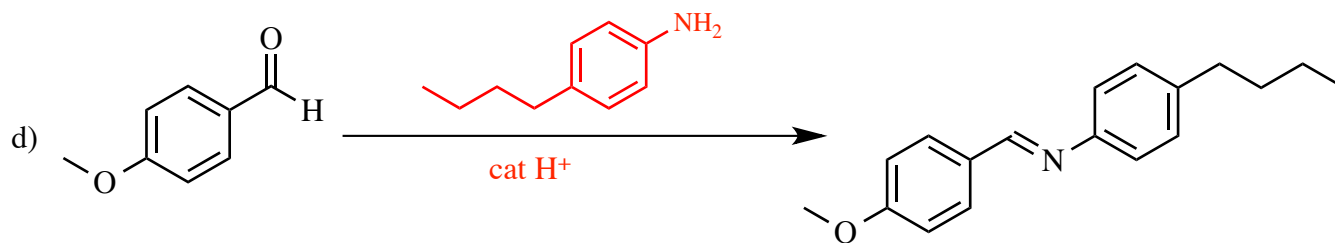
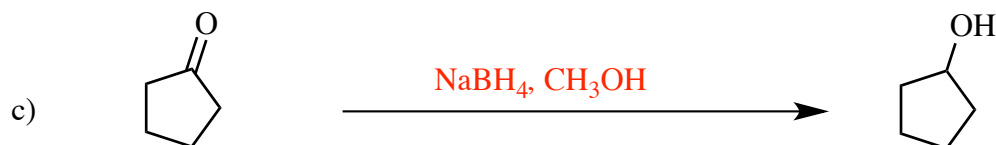
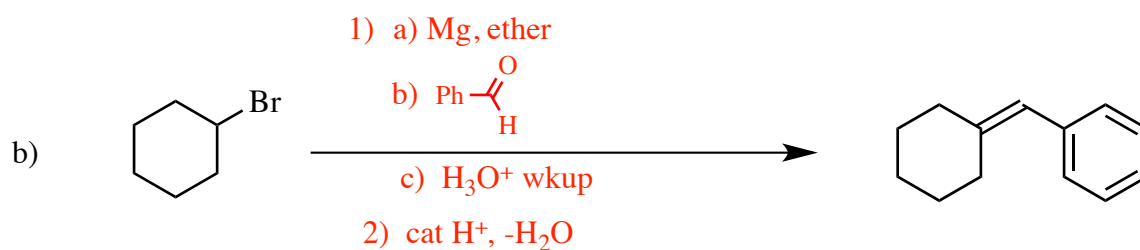
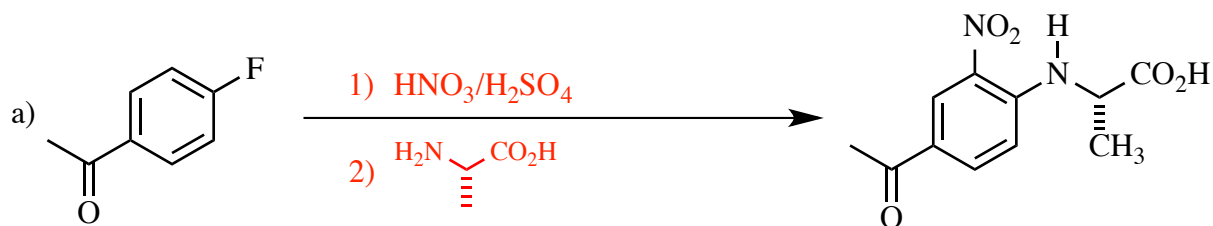
h) For the reaction in part e), give the major product you would expect if catalytic sulfuric acid is added to the reaction mixture.



2) (20 pts) Give the single major product for each of the following reactions, carefully showing stereochemistry using wedges and dashes where appropriate. If a racemate is formed, show only one enantiomer and label it "rac."

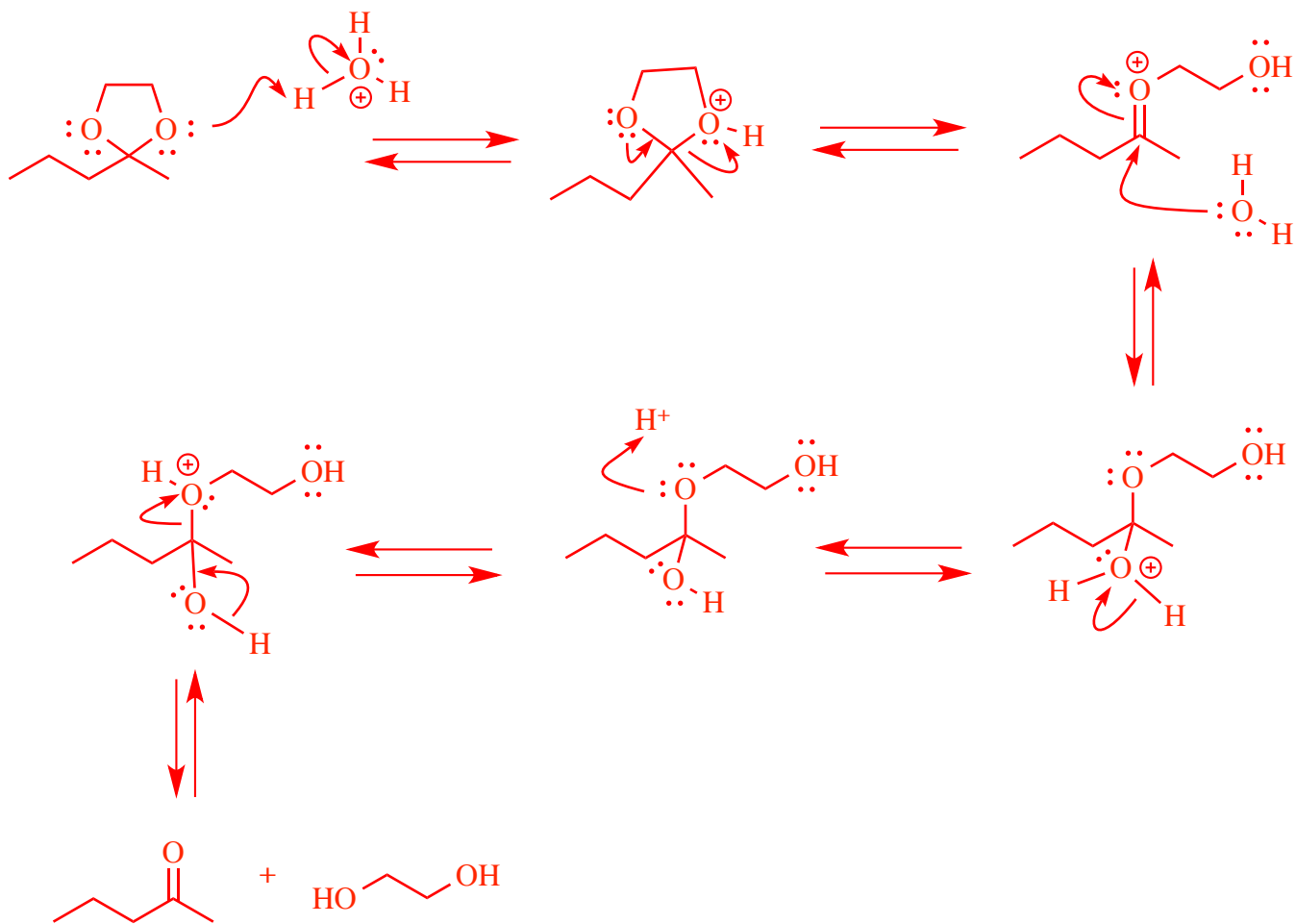
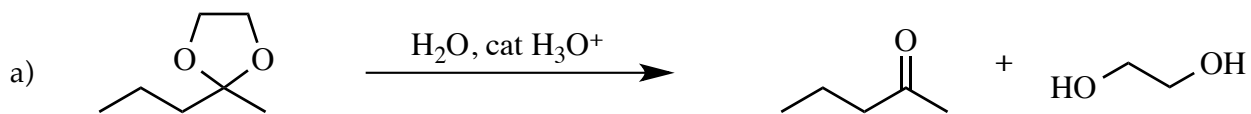


3) (20 pts) Propose reagents for accomplishing each of the following transformations. Make your reactions efficient (i.e. the target product should be the major product). Some of these transformations may require more than one step with isolation of intermediate products in between. Use letters to indicate sequential addition of reagents for one step, and use numbers to indicate multiple steps.



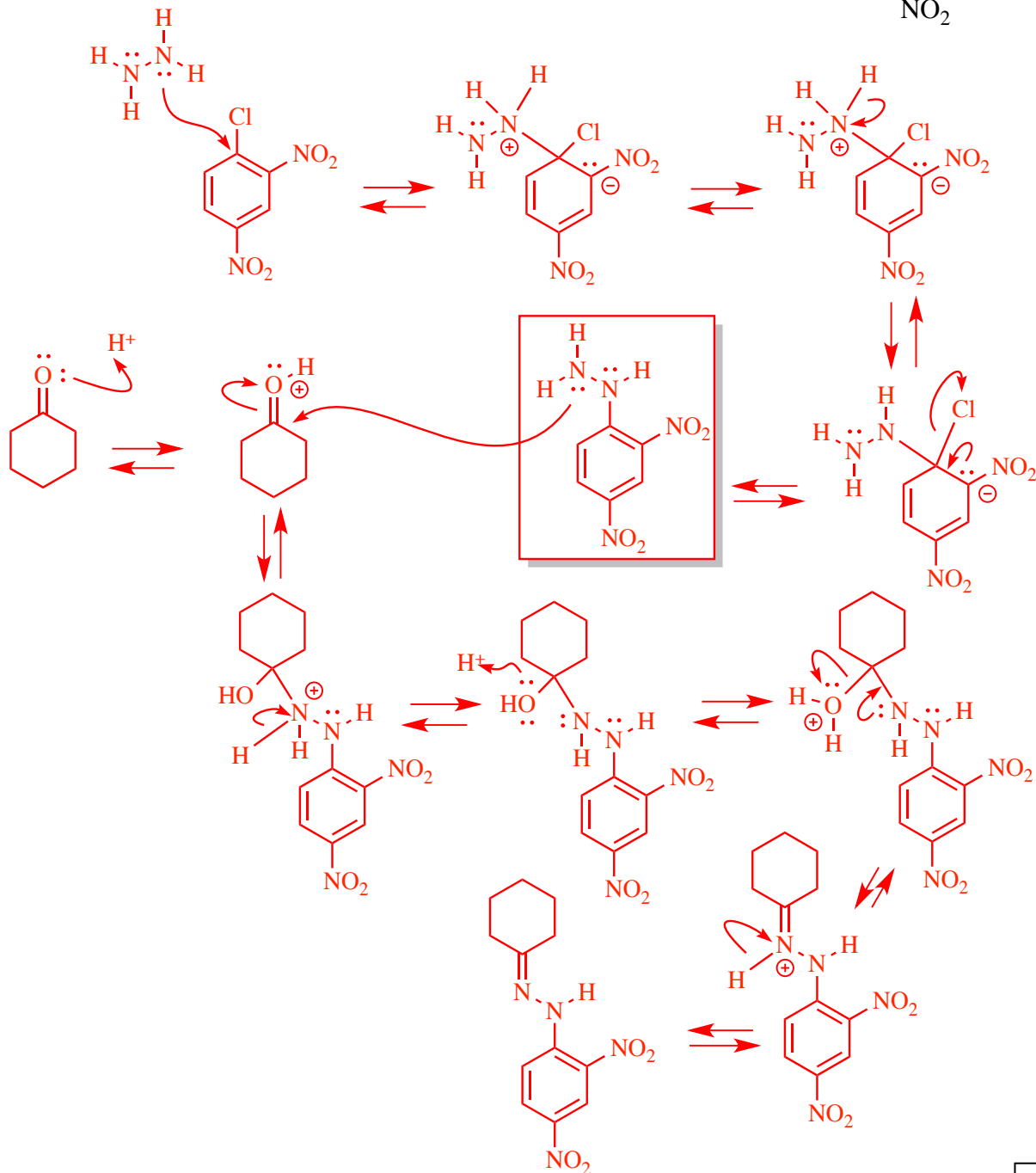
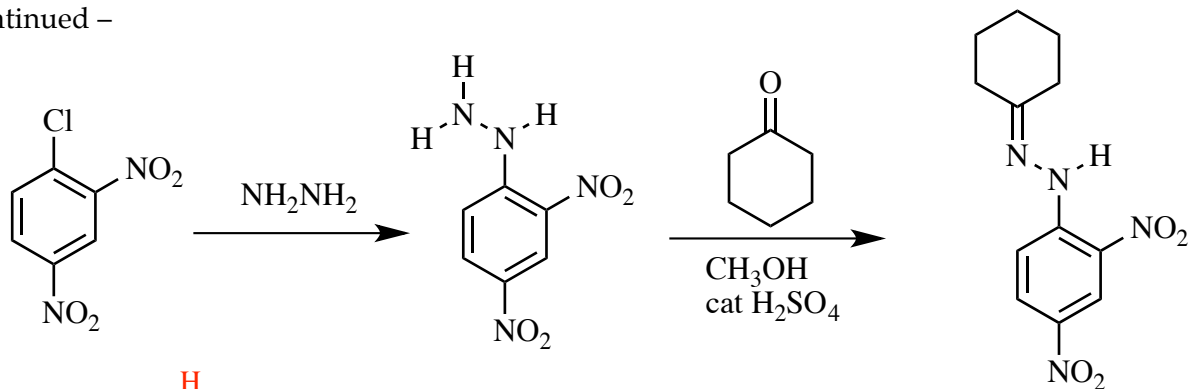
note: for the NBS bromination solvent is important

4) (20 pts) Propose an arrow-pushing mechanism for both of the following reactions. Note that 4b is actually a reaction sequence. Give the mechanism for both of the reactions in the sequence.



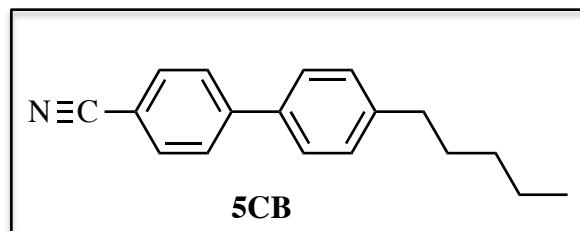
4) – Continued –

b)

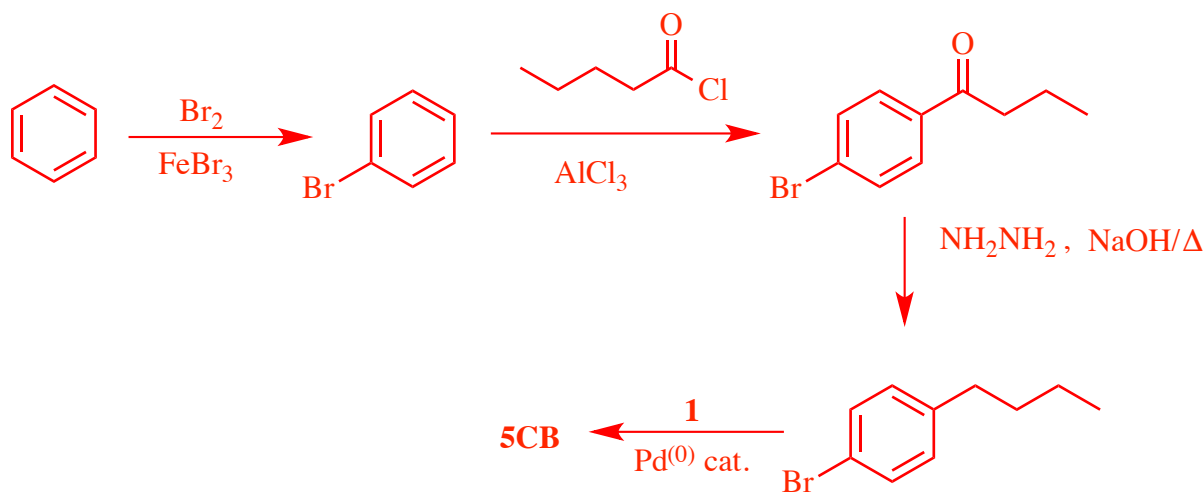
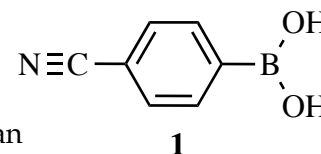


5) (20 pts) Propose a synthesis for each of the following targets. Allowed starting materials include benzene and/or any other organic molecules containing **five (5) carbons or less**. You may use any necessary inorganic reagents. Try to make your syntheses efficient (i.e. the target should be produced in the highest possible yield). More than one step will be required. Please show all the intermediate **products** in your synthesis (not reactive intermediates involved in the mechanisms, but actual isolated molecules on the path from starting material to product). Please do not put multiple reactions over one arrow. (Continued on next page)

a) The target for question 5a is a prototype of the family of cyanobiphenyl liquid crystals, known as 5CB (structure given at right). These were the first materials useful for fabrication of laptop LC displays, and are still the subject of scientific investigations and the foundation to new tech such as LC-based biosensors. A SciFinder Scholar structure search for 5CB turns up 5,853 papers since the synthesis and characterization was first reported by George Gray in 1973, and 101 commercial sources (!).



For this synthesis, in addition to the allowed starting materials given in the first paragraph of question 5, you can use 4-cyanobenzeneboronic acid (compound 1). Sigma-Aldrich, a major research chemical vendor, lists 807 commercial arylboronic acids. Compound 1 retails for \$54/gm – expensive, but probably less expensive than student labor and materials required to synthesize it in acceptably pure form.





5) - Continued

b) For this question, remember that benzylic alcohols are very sensitive to strong or intermediate strength acids, including Lewis acids. They are stable to weak acids.

