CHEM 203

Final Exam
December 10, 2011

Your name: ____

This a closed-notes, closed-book exam

You may use your set of molecular models

This test contains 11 pages

Time: 2h 30 min

1. ________ / 20
2. ________ / 24
3. ________ / 26
4. ________ / 30
5. ________ / 30
6. ________ / 40
7. ________ / 40
8. ________ / 40

TOTAL ________ / 250 = ________ / 100

This exam counts for 50% of the lecture component of your CHEM 203 grade

1. (20 pts.) Indicate the approximate pKa for the dissociation of the protons in boldface in the following molecules (write your answers in the appropriate boxes):

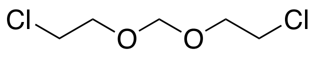
$\mathbf{H}{\equiv}CH_3$	$\mathbf{H}-H$	$\mathbf{H}-OSO_2CF_3$	$\mathbf{H}-CH_3$	$\mathbf{H}-\overset{\oplus}{O}H_2$
☐	☐	☐	☐	☐

$\mathbf{H}-Br$	$CH_3-COO-\mathbf{H}$	$\mathbf{H}-NH_2$	$\mathbf{H}-OH$	$\mathbf{H}-O-CH_2CH_3$
☐	☐	☐	☐	☐

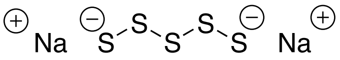
2 (24 pts) Check the appropriate box to indicate whether the following statements are true or false:

	true	**false**
i. A monosaccharide that exhibits mutarotation must necessarily be a reducing sugar	☐	☐
ii. Epoxide formation with MCPBA occurs with retention of olefin geometry	☐	☐
iii. Glycoside derivatives of monosaccharides react with aqueous ammonia to form glycosylamines	☐	☐
iv. Rearrangements are never seen in S_N1 reactions, but they may occur during S_N2 reactions	☐	☐
v. A bromohydrin cannot be converted into a Grignard reagent	☐	☐
vi. The Tollens reagent is a solution of $AgNO_3$ in aqueous NH_3	☐	☐
vii. Pyridinium chlorochromate (PCC) oxidizes primary alcohols to aldehydes and secondary alcohols to ketones	☐	☐
viii. Dichlorocarbene adds to alkenes in an *anti* mode	☐	☐

3. (26 pts) An early type of plastic polymer, which was useful as a substitute for natural rubber, was produced by heating compound **A** below with disodium pentasulfide:



A



= NaS–(S)$_3$–SNa

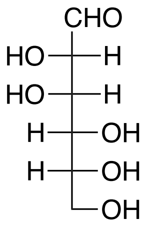
disodium pentasulfide

(i) Propose a method to prepare **A** starting with ethylene, $H_2C{=}CH_2$, and formaldehyde, $H_2C{=}O$ (show your synthesis as a flowchart with no mechanisms):

(ii) Draw the structure of a portion of the molecule of polymer that incorporates three units of **A** and two of disodium pentasulfide

4. (30 pts) Draw:

a. An accurate structure of the more thermodynamically favorable β-pyranose form of D-mannose (Fischer projection shown below):



D-mannose

b. A chiral epoxide that will react with aq. H_2SO_4 to form an achiral diol:

c. An alkene that will produce one diol when treated with OsO_4 followed by aqueous $NaHSO_3$, but a different diol when treated with MCPBA followed by aqueous H_2SO_4:

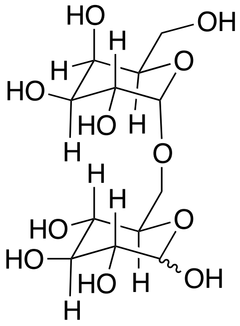
d. An alkene containing at least 5 C atoms that produces a chiral product when treated with Br_2, and one that furnishes an achiral product when treated with Br_2 (write your answers in the appropriate boxes):

gives a chiral product **gives an achiral product**

e. A chiral alcohol that will react with PCC to form a chiral product, and one that will react with PCC to form an achiral product (write your answers in the appropriate boxes):

gives a chiral product	**gives an achiral product**

f. The products obtained upon reaction of the disaccharide shown below with dilute aqueous H_2SO_4:



g. A carbonyl compound that can undergo addition of only one equivalent of a Grignard reagent, and one that can undergo addition of two equivalents of a Grignard reagent

reacts with one equivalent	**can react with two equivalents**

h. An alkene that is likely to undergo electrophilic addition of HCl without rearrangement and one that is likely to undergo electrophilic addition of HCl with rearrangement (write your answers in the appropriate boxes):

likely to rearrange **not likely to rearrange**

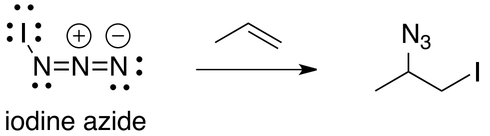
i. The structure of dibromocarbene and a chemical equation illustrating a method for its preparation:

j. An achiral alkene that gives a chiral product upon reaction with H_2 in the presence of finely divided Pd, and a chiral alkene that gives an achiral product under the same conditions (write your answers in the appropriate boxes):

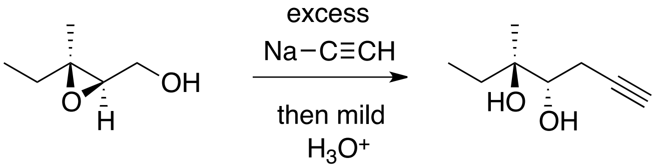
achiral alkene that gives chiral product **chiral alkene that gives achiral product**

5. (30 pts) Write accurate mechanisms for the following known reactions:

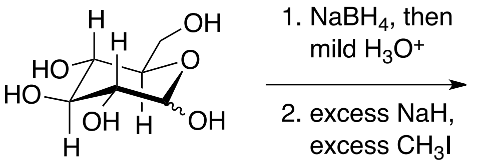
a.

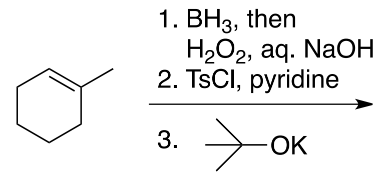


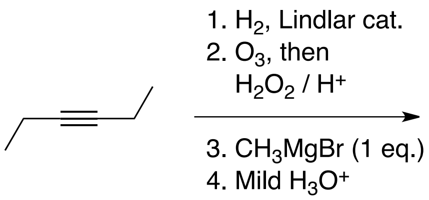
b.

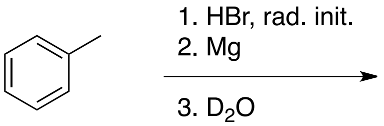


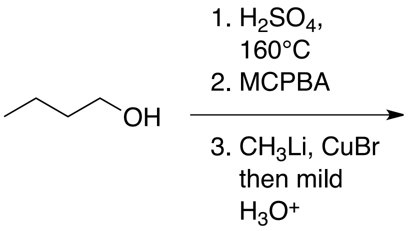
6. (40 pts.) Draw the structure of the major product expected from the following reactions (write your answer in the boxes). If no overall change is predicted, answer "**NO REACTION.**" **Important**: where needed, molecules must be drawn with the correct configuration.





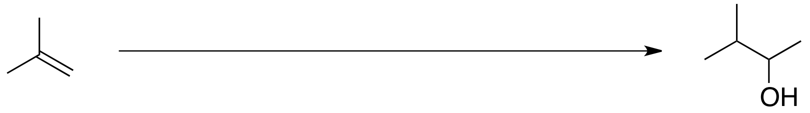






7. (40 pts.) Indicate all the reagents, catalysts, etc., in the correct order, that are necessary to induce the transformations shown below. List such reagents above / below the reaction arrows. **NOTE**: aqueous workups are understood and do not need to be shown.

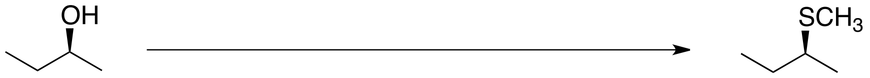
a.



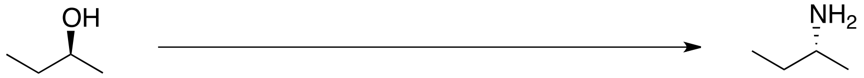
b.

c.

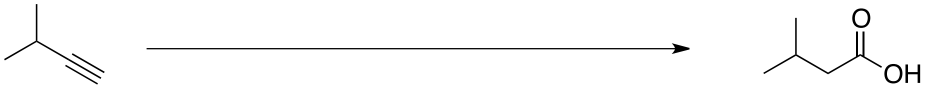
d.



e.

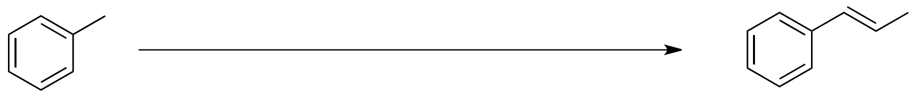


f.



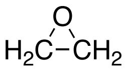
g.

h.



8. (40 pts.) Propose a good synthesis of the molecules shown below using **only methanol**, **acetylene** and **ethylene oxide** (see below) as the sources of carbon atoms. Intermediates / products obtained during an earlier sequence may be employed in a subsequent procedure. Assume the availability of all necessary reagents (such as bases, acids, BH_3, Mg, TsCl, PCC, PBr_3, MCPBA, etc.).

methanol: CH_3OH acetylene: $H-C\equiv C-H$ ethylene oxide:

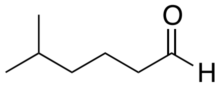


Important:

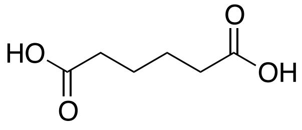
i. aqueous workups at the end of each reaction are understood and need not to be shown.

ii. It is not necessary to write mechanisms

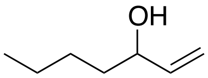
a.



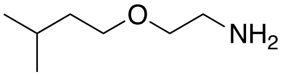
b.



c.



d.



Happy Holidays!