CHEM 203

Final Exam
December 18, 2013

ANSWERS

Your name: ______________________________

This a closed-notes, closed-book exam

You may use your set of molecular models

This test consists of 10 pages

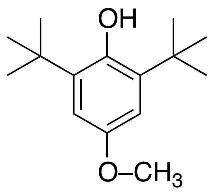
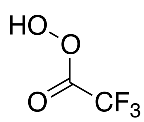
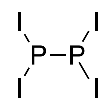
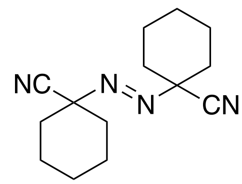
Time: 2h 30 min

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

TOTAL ________ / 250 = ________ / 100

This exam counts for 37.5% of your CHEM 203 grade

1. (20 pts.) The reagents shown below have not been discussed in class, but they are structurally related to reagents that have been covered in CHEM 203. On the basis of structural analogy, indicate the probable use of each of them (write your answers in the boxes):

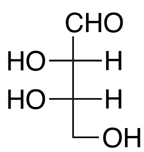
		probably used as/for:
a.		radical inhibitor
b.		epoxidation of alkenes
c.		conversion of prim. / sec. alcohols into alkyl iodides
d.		radical initiator

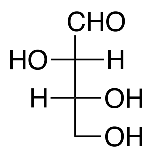
2 (20 pts) Check the appropriate box to indicate whether the following statements are true or false:

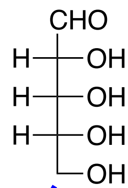
	true	false
a. An aqueous solution of H_2CrO_4 and H_2SO_4 oxidizes primary alcohols to aldehydes and secondary alcohols to ketones	☐	✓
b. An alkene will form the same epoxide upon treatment with either Br_2 and H_2O followed by base, or with MCPBA	✓	☐
c. Rearrangements may occur during S_N1 reactions, but not during S_N2 reactions	✓	☐
d. Rearrangements may occur during E2 reactions, but not during E1 reactions	☐	✓
e. Carbocations may add to alkenes	✓	☐
f. Radicals do not rearrange by the 1,2-shift mechanism typical of carbocations	✓	☐
g. A C–Si bond provides more effective hyperconjugative stabilization than a C–C bond	✓	☐
h. A bromohydrin is easily converted into a Grignard reagent upon reaction with metallic Mg	☐	✓
i. An acetal is a special type of ether	✓	☐
j. The Fischer-Kiliani synthesis of monosaccharide involves the addition of H–CN to an aldehyde	✓	☐

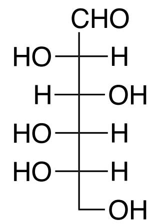
3. (30 pts.) Check the appropriate boxes to indicate whether:

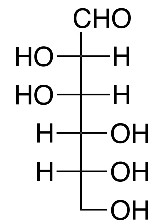
a. The following carbohydrates belong to the D or the L series:


D- [ ] L- [✓]

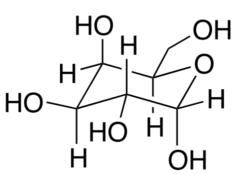

D- [✓] L- [ ]

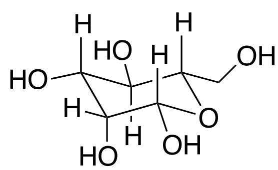

D- [✓] L- [ ]

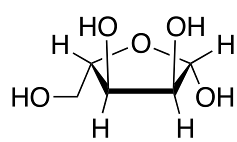

D- [ ] L- [✓]

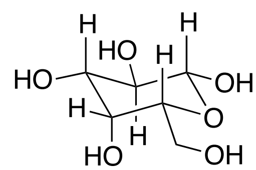

D- [✓] L- [ ]

b. The following carbohydrates possess the α- or the β-anomeric configuration:

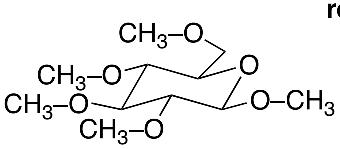
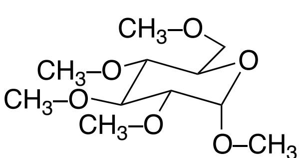
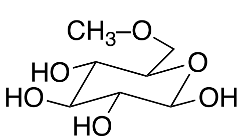

α- [✓] β- [ ]

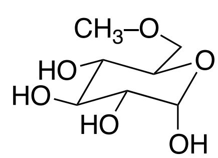
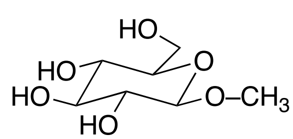
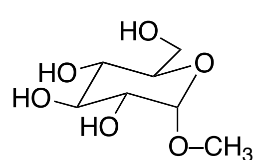

α- [ ] β- [✓]


α- [ ] β- [✓]


α- [ ] β- [✓]

c. The following derivatives of glucose are reducing or nonreducing:

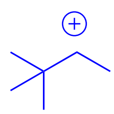
	reducing	nonreducing
	[ ]	[✓]
	[ ]	[✓]
	[✓]	[ ]

	reducing	nonreducing
	[✓]	[ ]
	[ ]	[✓]
	[ ]	[✓]

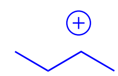
4. (30 pts) In the appropriate box, draw the structure of:

a. A carbocation that forms as the major product of protonation of an alkene and that is likely to undergo rearrangement, and one that also forms as the major product of protonation of an alkene, but that is not likely to undergo rearrangement:

likely to rearrange

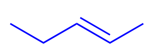


unlikely to rearrange

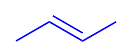


b. A *trans*-alkene that gives a chiral product upon reaction with Cl_2 and a *trans*-alkene that gives an achiral product upon reaction with Cl_2:

gives a chiral product

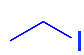


gives an achiral product

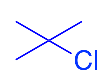


c. An alkyl halide that is likely to undergo substitution by the S_N2 mechanism, and one that is likely to undergo substitution by the S_N1 mechanism:

reacts by S_N2

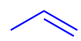


reacts by S_N1



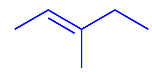
d. An alkene that is a good substrate for allylic bromination, and one that is a poor substrate for the same reaction:

good substrate



only 1 mono-bromo isomer can form

poor substrate

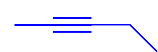


multiple mono-bromo isomers can form

e. An alkyne containing at least 3 carbon atoms, that produces an achiral diol when treated with H_2 and Lindlar catalyst, followed by OsO_4 and then aqueous $NaHSO_3$, or when treated with Na in liquid NH_3, followed by MCPBA and then aqueous H_2SO_4, and an alkyne also containing at least 3 carbon atoms that produces a chiral diol when treated under the same conditions:

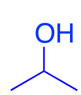
produces an achiral diol

produces a chiral diol

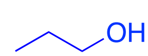


f. An alcohol that gives the same product when treated either with PCC or with the Jones reagent, and one that gives two different products under the same conditions:

gives the same product

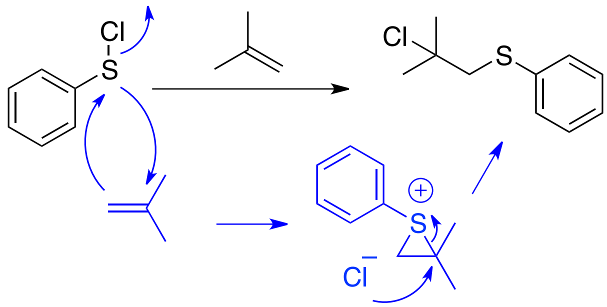


gives two different products

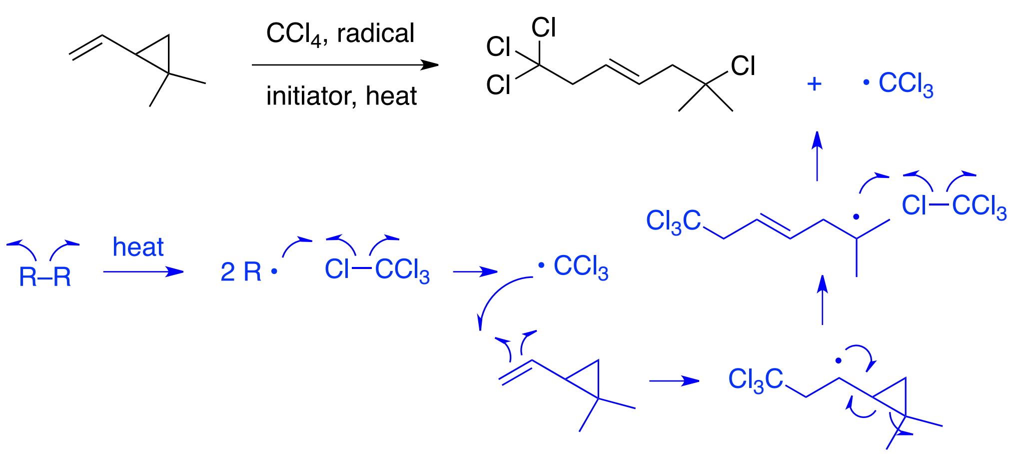


5. (30 pts) Write accurate mechanisms for the following known reactions:

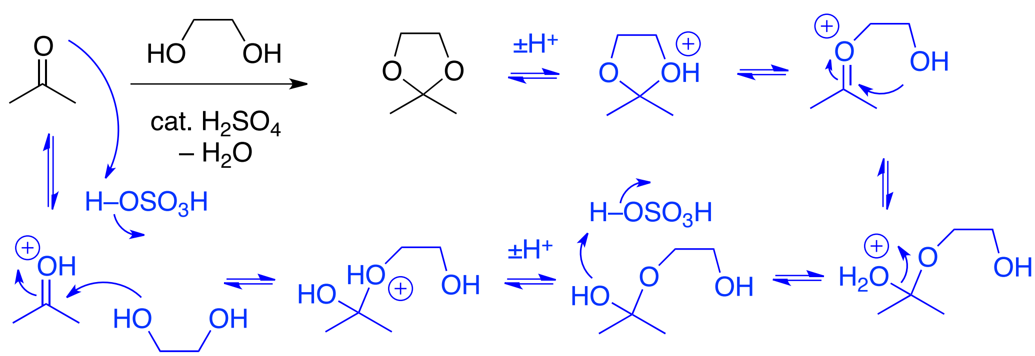
a.



b.

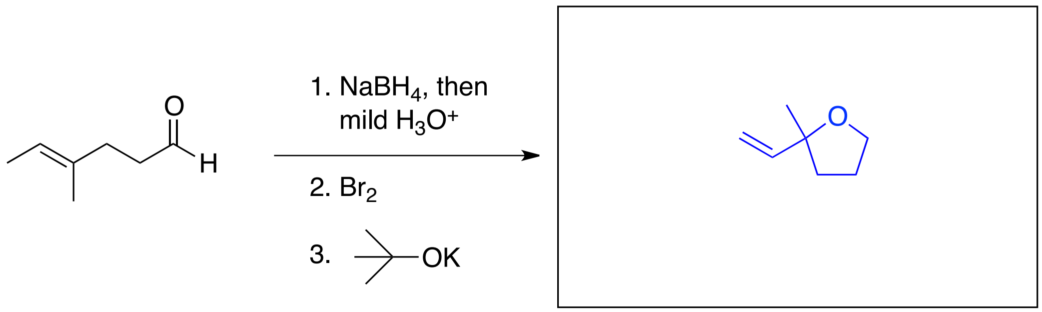


c.

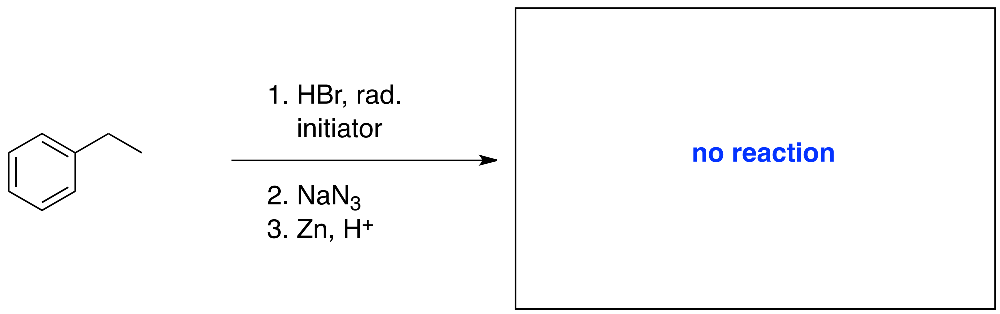


6. (40 pts.) Draw the structure of the major product expected from the following reactions (write your answer in the boxes). If no change is predicted, answer "**NO REACTION.**"

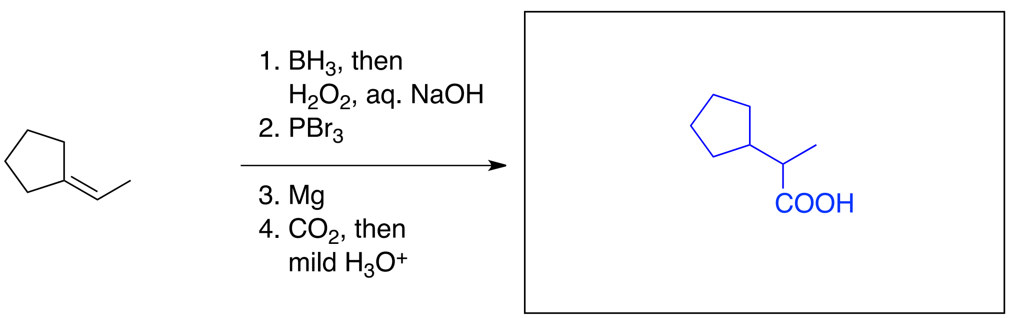
a.



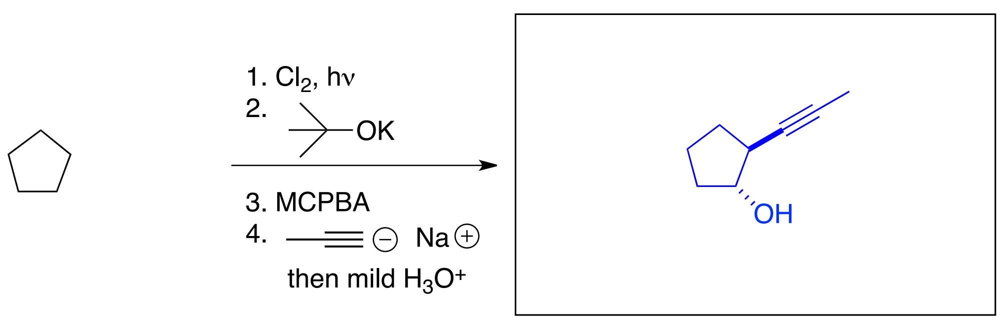
b.



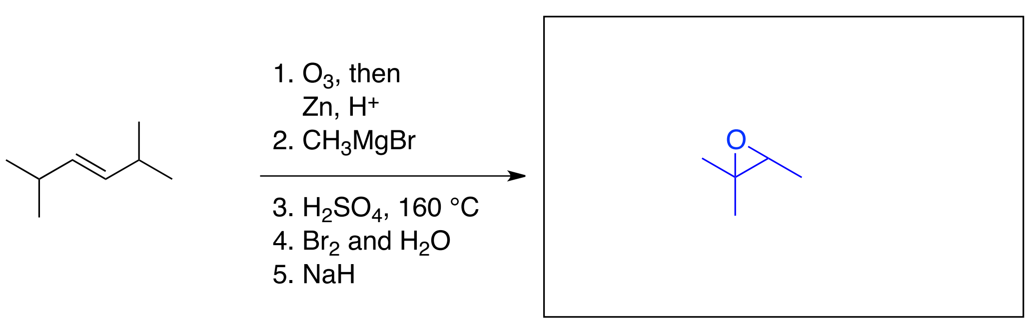
c.



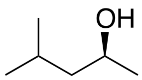
d.



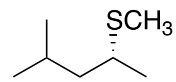
e.

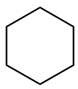


7. (40 pts.) Indicate all the reagents, catalysts, etc., in the correct order, that are necessary to induce the transformations shown below. List such reagents above / below the reaction arrows. **NOTE**: aqueous workups are understood and do not need to be shown.

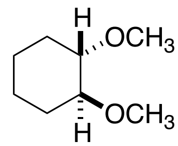
a. 

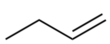
1. TsCl, pyridine
2. CH_3SNa



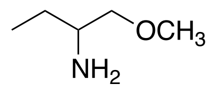
b. 

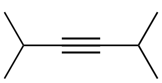
1. Cl_2, hv
2. tert-BuOK
3. MCPBA
4. aq. H_2SO_4
5. NaH, CH_3I



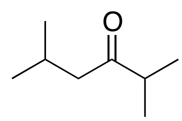
c. 

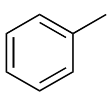
1. MCPBA
2. CH_3ONa
3. TsCl, pyridine
4. NaN_3
5. Zn, H^+



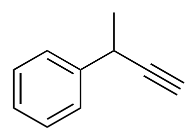
d. 

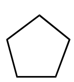
1. H_2, Lindlar
2. BH_3
3. H_2O_2, aq. NaOH
4. PCC



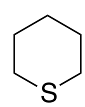
e. 

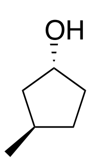
1. NBS, hv
2. CH_3Li, CuBr
3. NBS, hv
4. $H\text{-}C{\equiv}C^- \, Na^+$



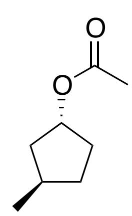
f. 

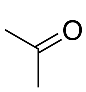
1. Cl_2, hv
2. tert-BuOK
3. O_3, then Zn / H^+
4. $NaBH_4$
5. TsCl, pyridine
6. Na_2S



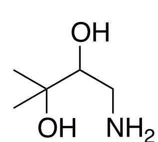
g. 

1. PBr_3
2. $CH_3\text{-}COO^- \, Na^+$

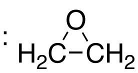


h. 

1. $H\text{-}C{\equiv}C^- \, Na^+$
2. H_2, Lindlar catalyst
3. MCPBA
4. NaN_3 followed by Zn / H_+

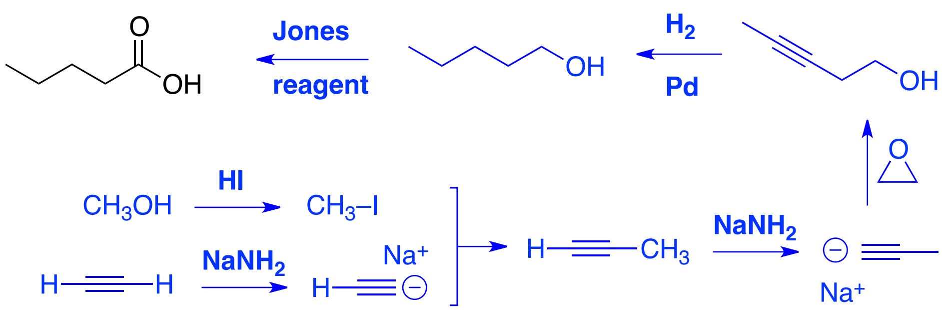


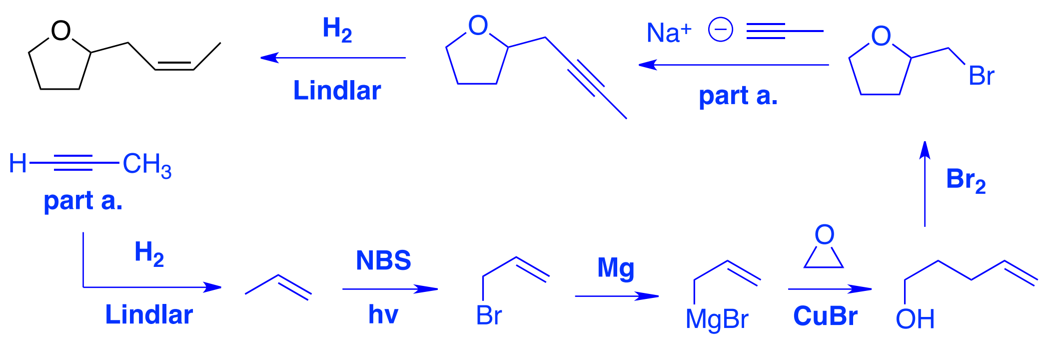
8. (40 pts.) Propose a good synthesis of the molecules shown below using **only methanol**, **acetylene** and **ethylene oxide** (see below) as the sources of carbon atoms. Intermediates / products obtained during an earlier sequence may be employed in a subsequent procedure. Assume the availability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

methanol: CH_3OH acetylene: H−C≡C−H ethylene oxide: 

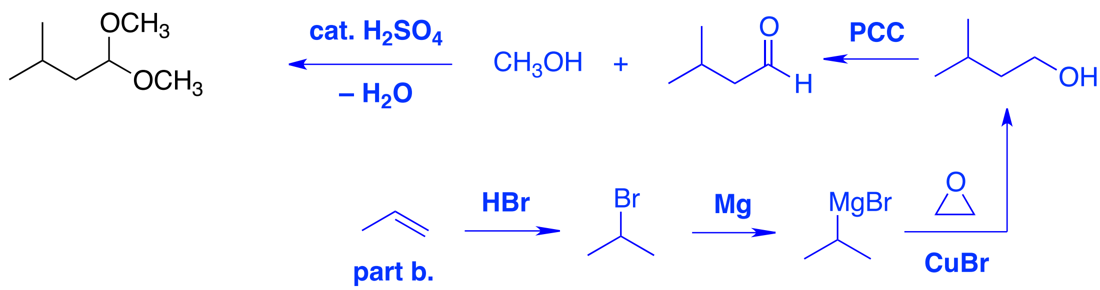
Important:

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.

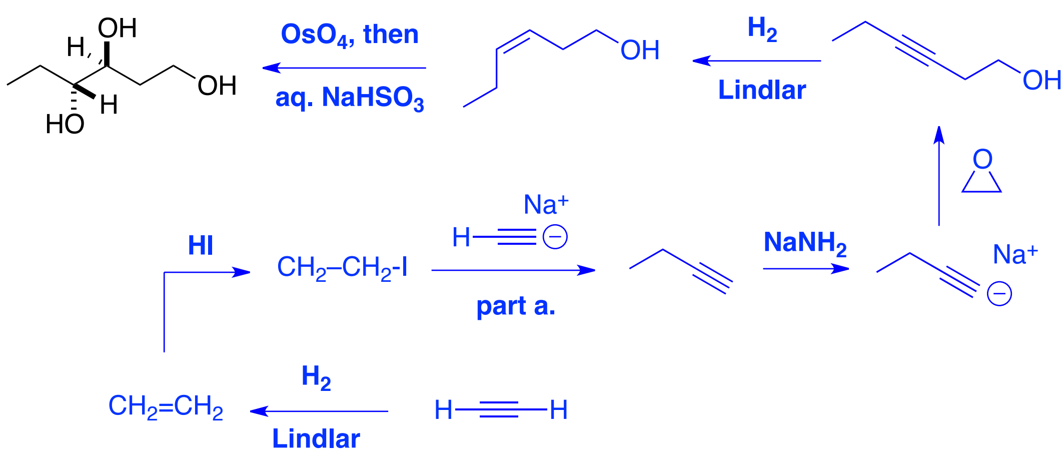
a. 

b. 

c.



d.



Happy Holidays!