CHEM 203

Final Exam
December 11, 2008

Your name: ANSWERS

This a closed-notes, closed-book exam

You may use your set of molecular models

This exam contains 13 pages

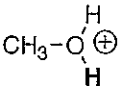
Time: 2h 30 min

1. _____ / 16
2. _____ / 24
3. _____ / 20
4. _____ / 30
5. _____ / 40
6. _____ / 40
7. _____ / 40
8. _____ / 40

TOTAL _____ / 250 = _____ / 100

This exam counts for 45% of your CHEM 203 final grade

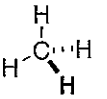
1. (16 pts.) Indicate the approximate pKa's for the Bronsted dissociation of the proton in boldface in the following molecules (write your answers in the appropriate boxes)



-3

H–Cl

-7



50

H–OSO$_3$H

-5

CH_3–C≡C–H

25

35

H–F

4

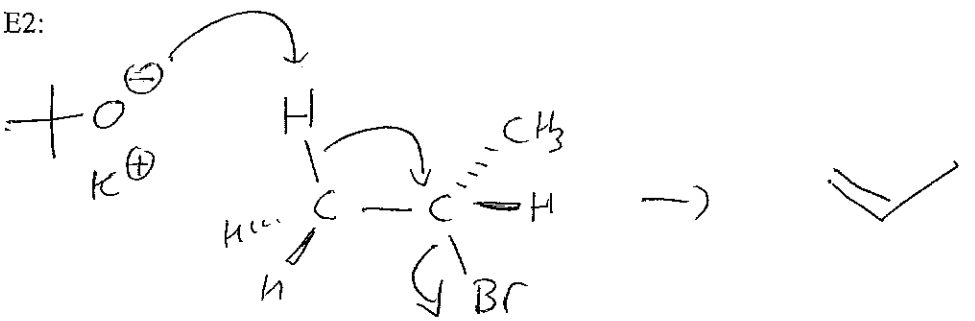
CH_3–CH_2–O–H

18

2. (24 pts.) Draw:

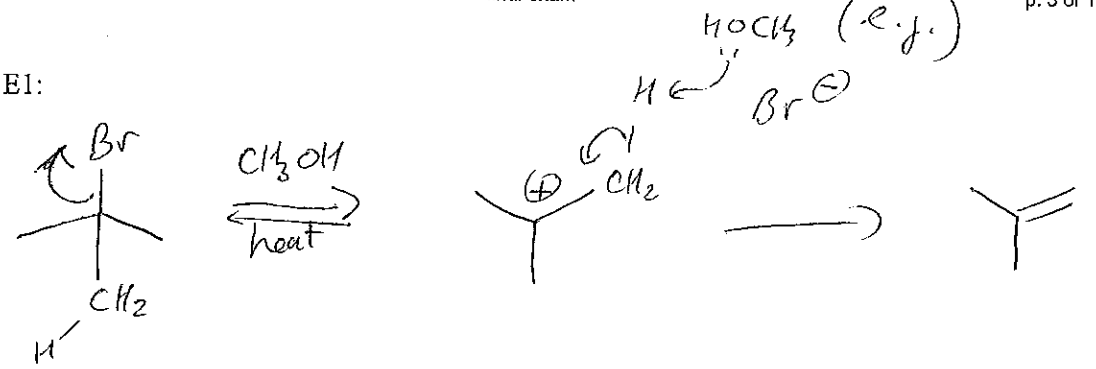
a. Accurate mechanisms for an example of E2 reaction and an example of E1 reaction:

E2:

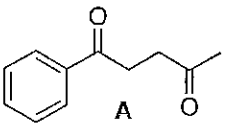


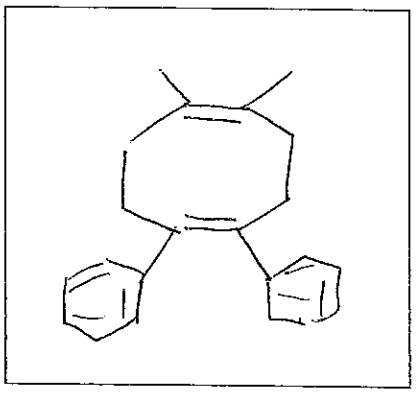
(β - anti elimination)

E1:

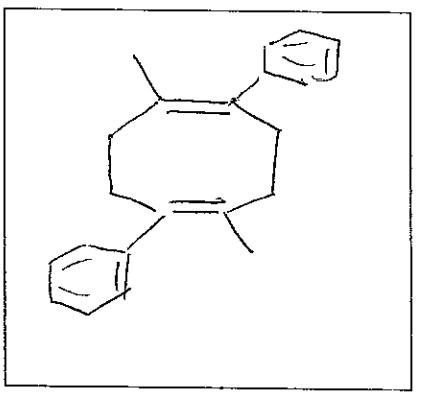


b. **Two** isomeric alkenes that furnish only compound **A** upon treatment with O_3 followed by Zn / H^+ (write your answers in the appropriate boxes):

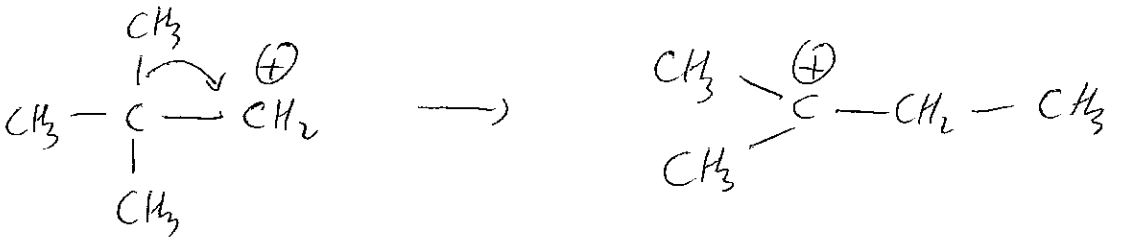




and

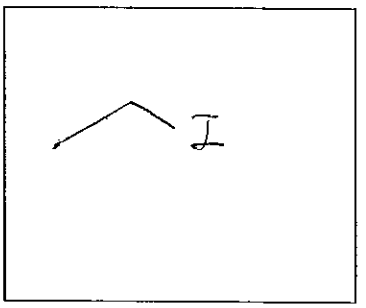


c. A carbocation that is stabilized by **NO** hyperconjugative interactions with C–H bonds, and that will rearrange to form a new carbocation stabilized by eight hyperconjugative interactions with C–H bonds:

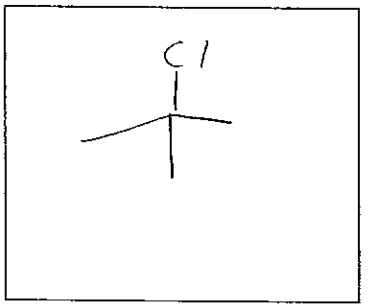


d. An alkyl halide that is likely to react with CH_3ONa to give a product of substitution, and one that is likely to react with CH_3ONa to give a product of elimination:

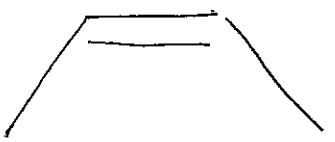
undergoes substitution



undergoes elimination



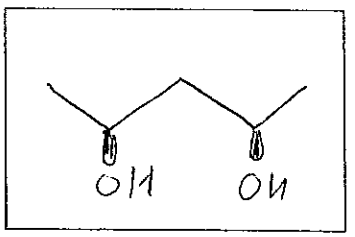
e. An alkene that produces an achiral diol when treated with OsO_4 followed by aqueous $NaHSO_3$, but a chiral diol when treated with MCPBA followed by aqueous H_2SO_4:



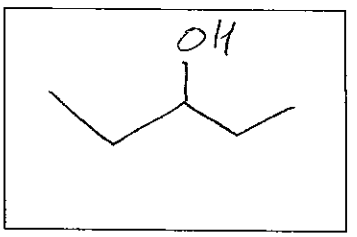
(other answers possible)

f. An achiral molecule that is a meso form, and an achiral molecule that is not a meso form:

achiral and meso



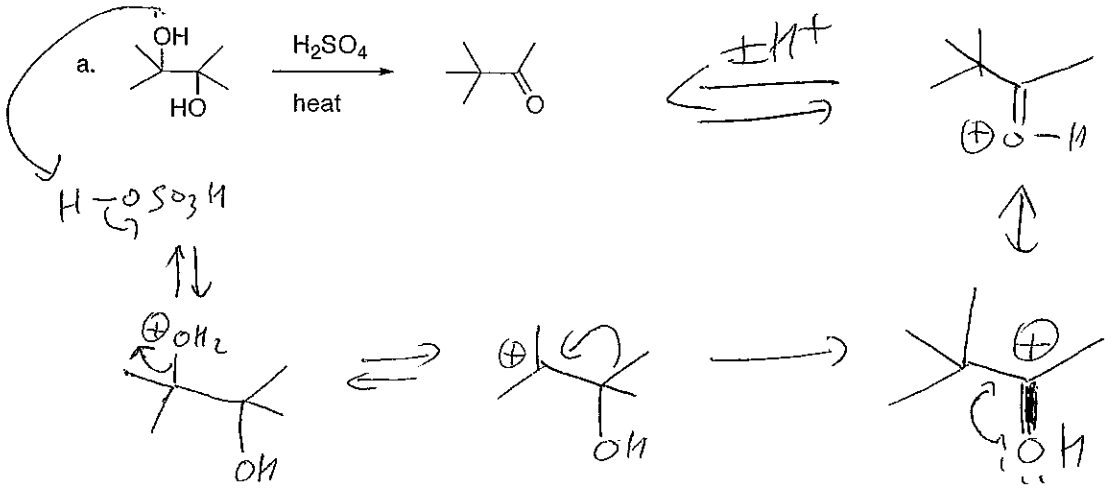
achiral, but not meso



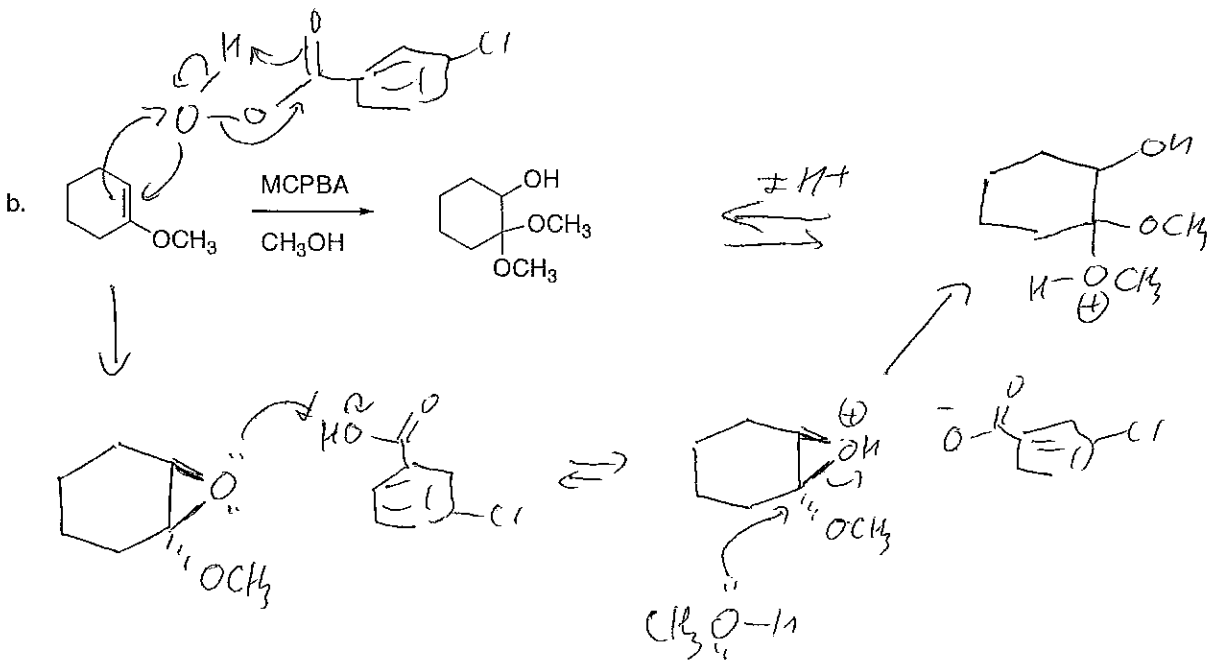
(other answers possible)

3. (20 pts.) Write an accurate mechanism for the following known reactions:

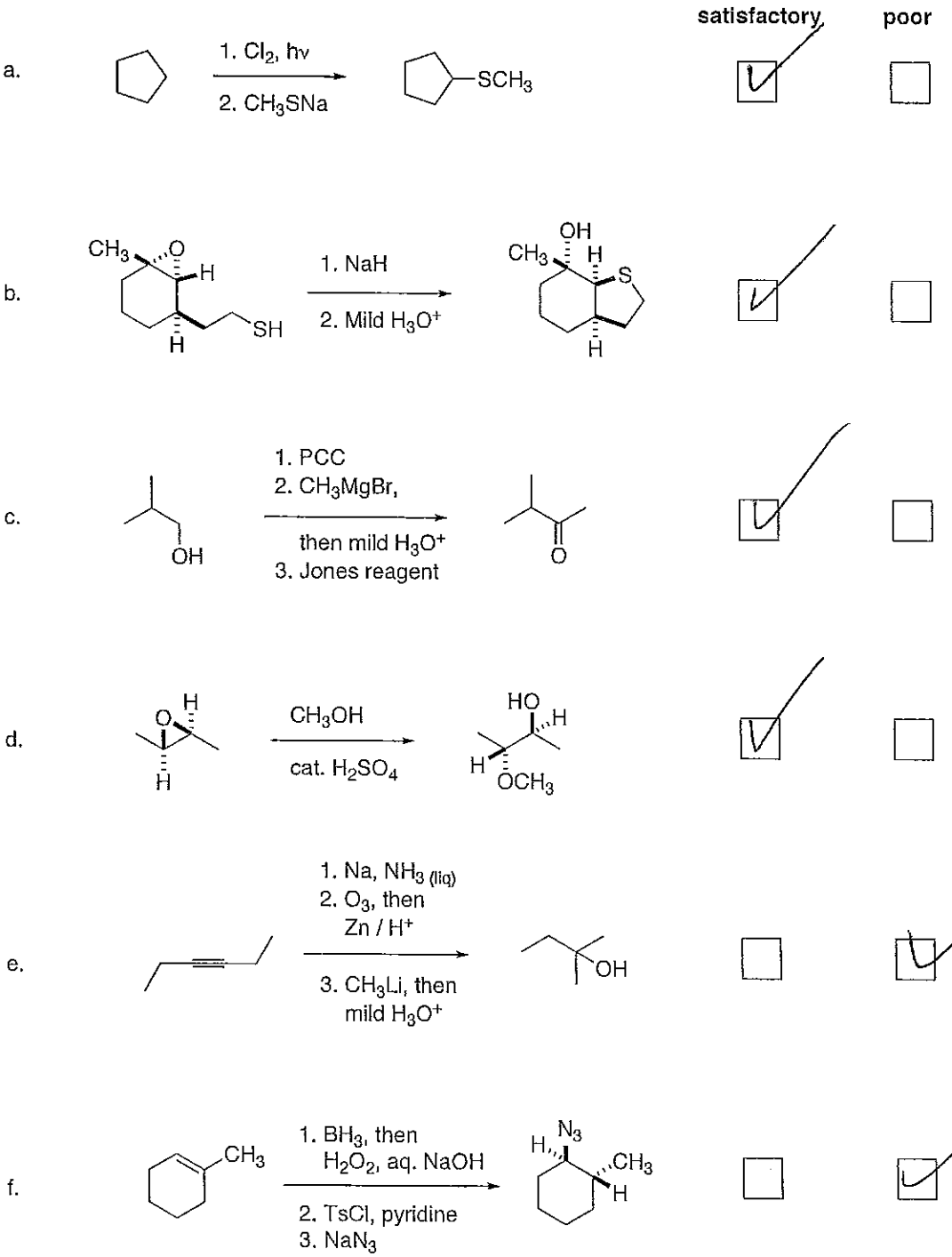
a.



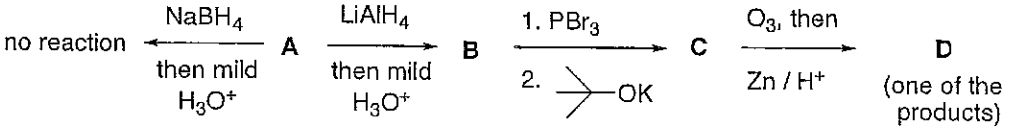
b.



4. (30 pts.) Check the appropriate box to indicate whether the following procedures represent satisfactory or poor methods for the preparation of the compounds shown:

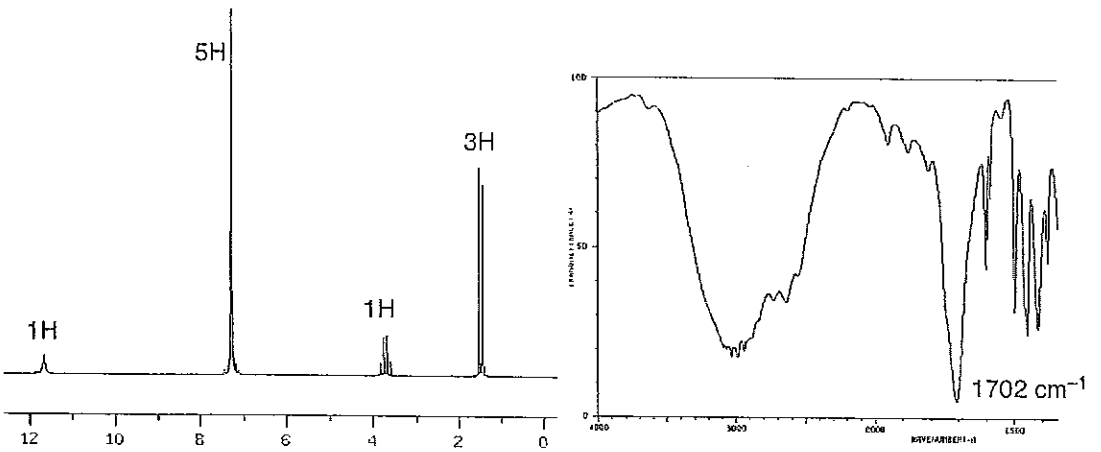


5. (40 pts.) An unknown organic compound, **A**, was found to be possess appreciable anti-inflammatory activity. As indicated in the scheme below, **A** was recovered unchanged from a treatment with $NaBH_4$; however, it reacted with $LiAlH_4$ to furnish substance **B**. Reaction of **B** with PBr_3 and treatment of the resultant with potassium tert-butoxide yielded **C**, which upon ozonolysis followed by Zn / H^+ afforded **D** as one of the products.

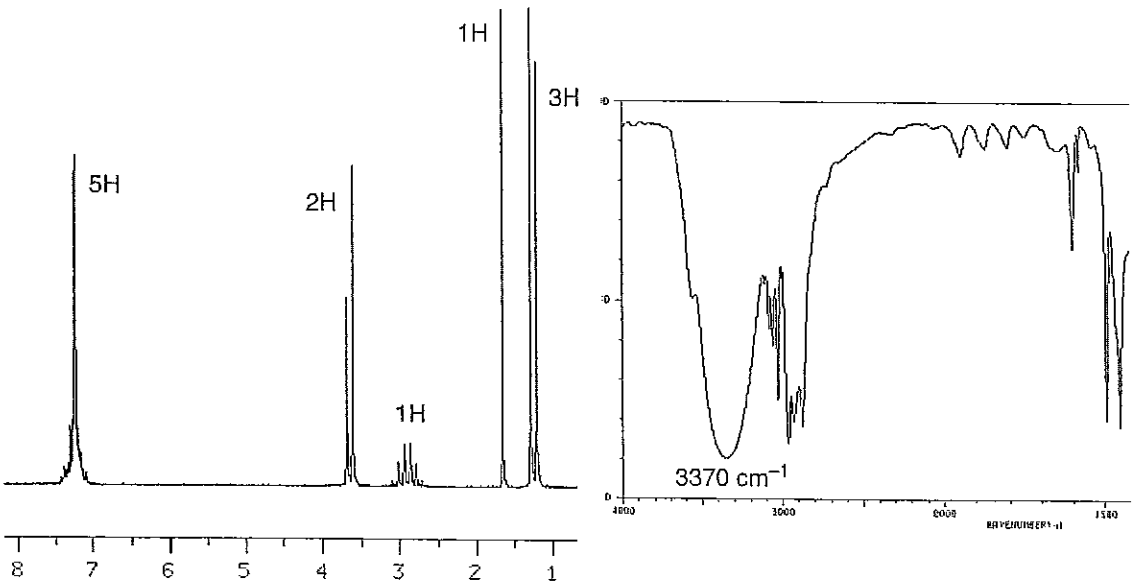


The spectra of **A**, **B**, and **D** are shown below. Deduce the structures of compounds **A**, **B**, **C**, and **D** and write your answers in the appropriate boxes.

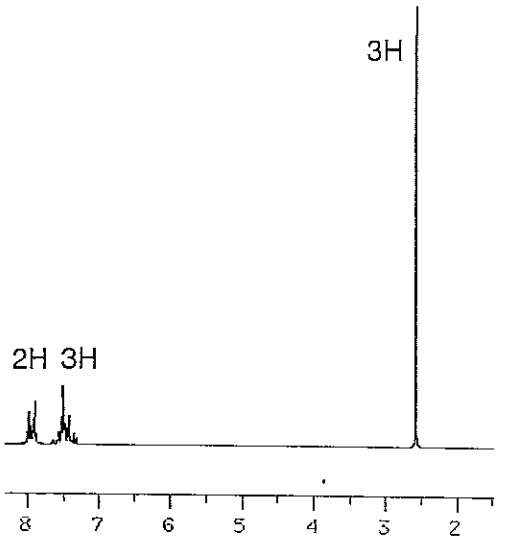
spectra of A

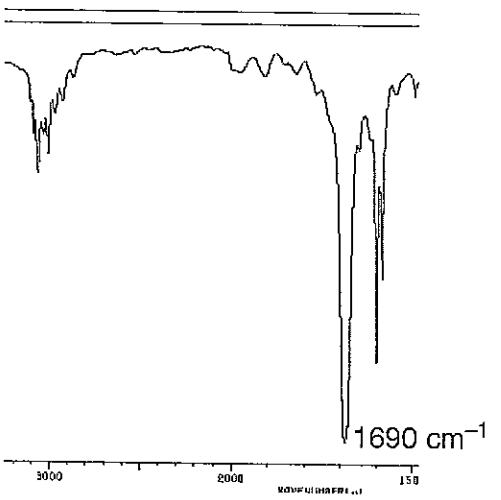


spectra of B

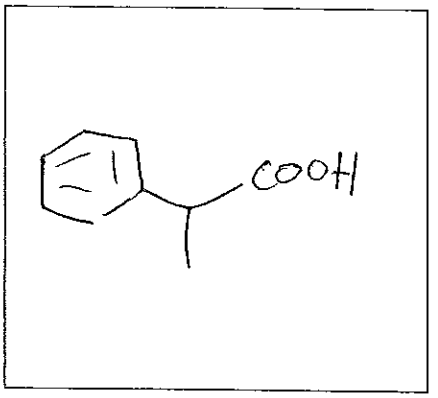


spectra of D

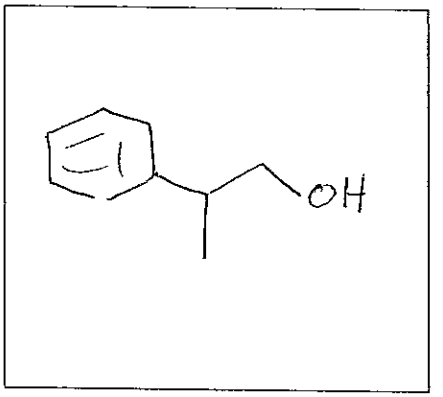




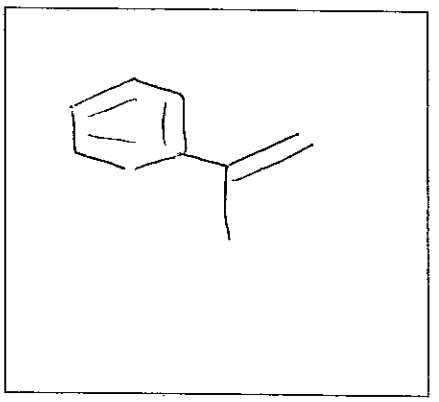
structure of A



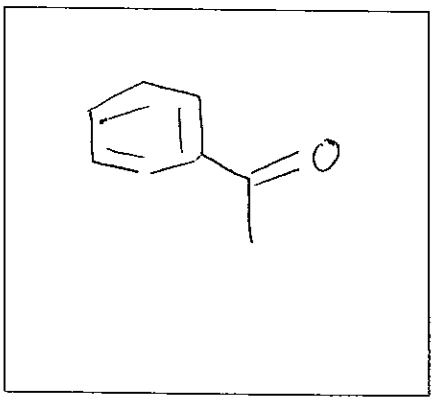
structure of B



structure of C

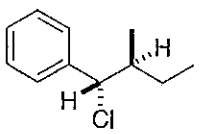


structure of D

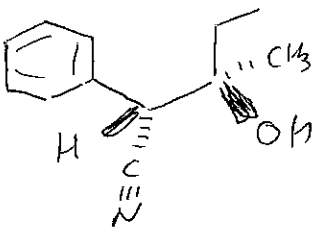


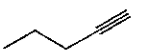
6. (40 pts.) Draw the structure of the major product expected from each of the following reactions. Write your answers in the appropriate boxes. If you should conclude that a given substrate will not react with the reagent(s) shown, write "**NO REACTION**" in the box.

Important: where appropriate, molecules must be drawn with the correct configuration

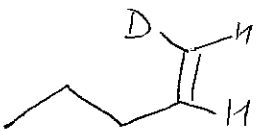
a. 

1. 
2. MCPBA
3. NaCN, then mild H_3O^+



b. 

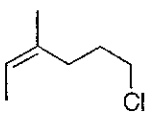
1. CH_3MgBr
2. D_2O
3. H_2, Lindlar catalyst



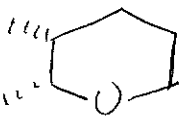
c. 

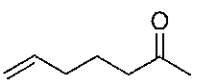
1. HBr
2. $CH_3-C\equiv C-Na$
3. Na. $NH_{3(liq)}$

NO REACTION

d. 

1. BH_3
2. H_2O_2, aq. NaOH
3. NaH



e. 

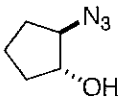
1. OsO_4
2. aq. $NaHSO_3$
3. cat. H_2SO_4, 60 °C, removal of H_2O

this product has formula $C_7H_{12}O_2$

7. (40 pts.) Indicate all the reagents, catalysts, etc., in the correct order, that are necessary to induce the transformations outlined below. List such reagents above / below the reaction arrows. If a product does not appear to be available from the substrate shown by any method known to you, write "**INACCESSIBLE**" on the reaction arrow.

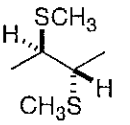
a. 

1. Cl_2, hν
2. +OK
3. MCPBA
4. NaN_3, then mild H_3O^+



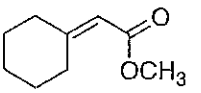
b.

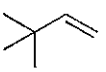
1. Na / NH_3 (liq)
2. $BrCl$
3. CH_3SNa



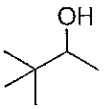
c. 

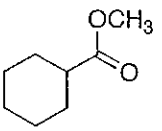
1. H_2O, cat. H_2SO_4
2. Jones rgt.
3. $Ph_3P{=}CHCOOCH_3$



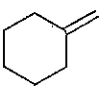
d. 

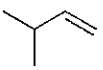
1. O_3, then Zn/H+
2. CH_3MgBr, then mild H_3O^+



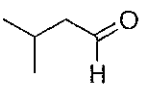
e. 

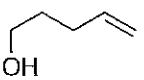
1. LiAlH4, then mild H_3O^+
2. TsCl, Pyridine
3. +OK



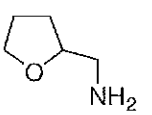
f. 

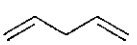
1. BH_3
2. H_2O_2, aq. NaOH
3. PCC



g. 

1. $BrCl$
2. NaN_3
3. Zn / H+



h. 

1. BH_3
2. H_2O_2, aq NaOH
3. TsCl, Pyr.
4. Na_2S

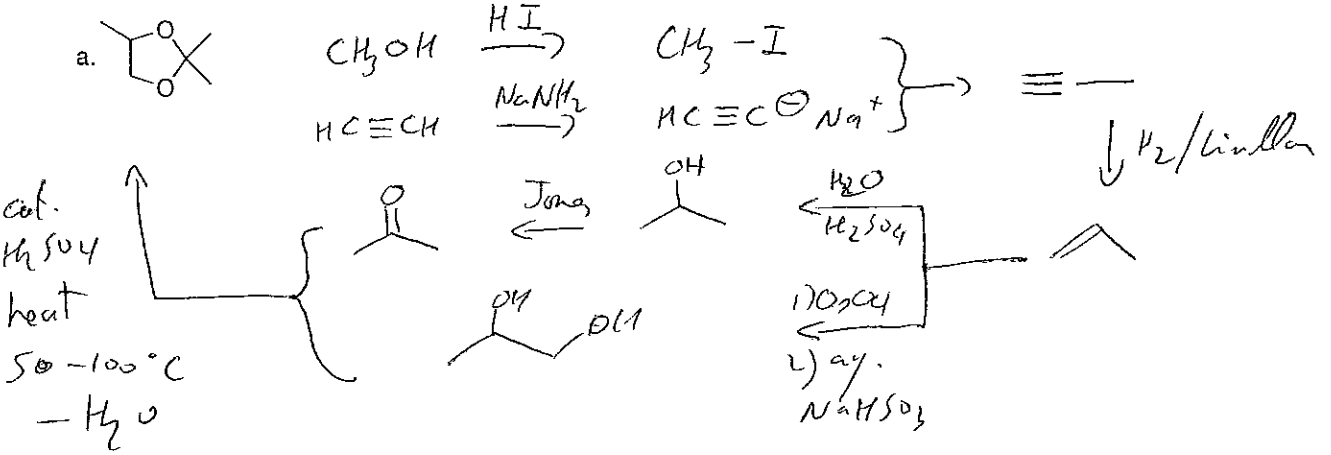
(other answers may be OK)

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, without showing their preparation again. Assume the availability of all necessary reagents (such as bases, acids, KCN, Mg, TsCl, PCC, PBr_3, MCPBA, etc.).

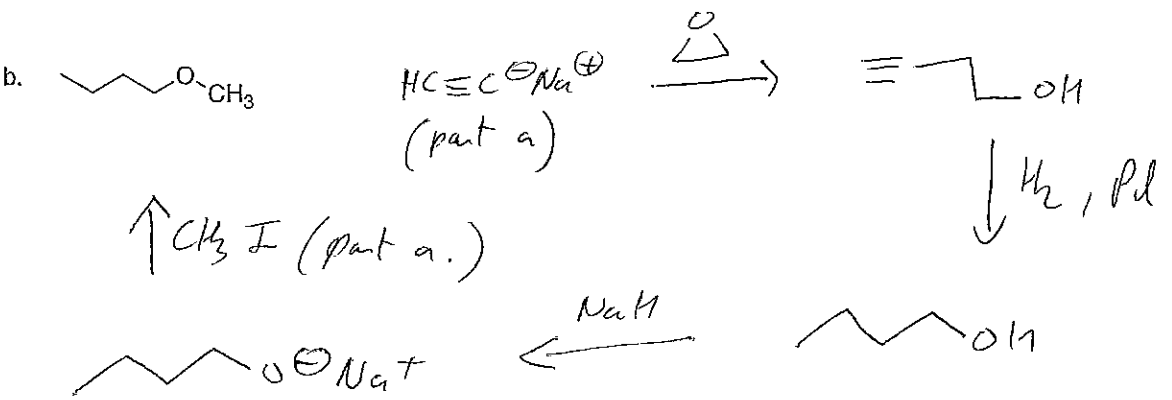
CH_3OH	H–C≡C–H	$H_2C(O)CH_2$
methanol	acetylene	ethylene oxide

It is not necessary to write mechanisms

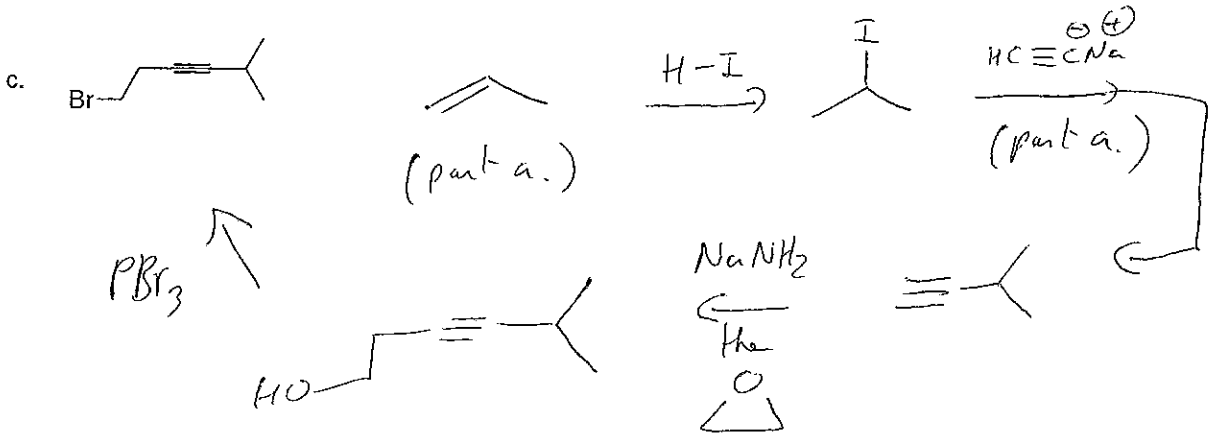
a.



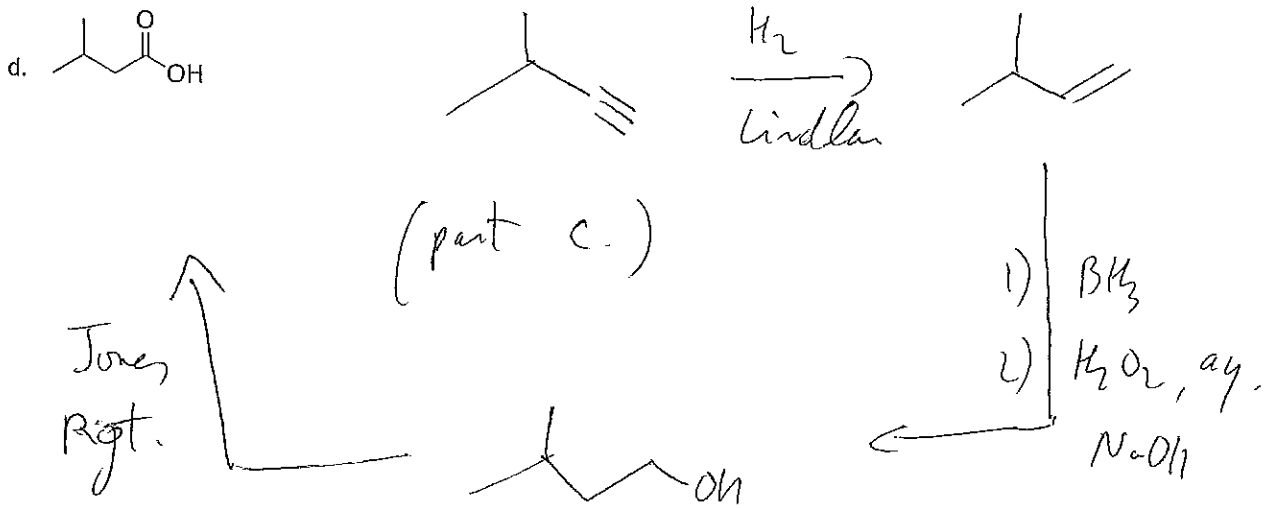
b.



c.


Br
(part a.)
H–I
I
HC≡CNa
(part a.)
PBr3
HO
NaNH2
the
O

d.


O
OH
H2
Lindlar
(part c.)
1) BH3
2) H2O2, aq. NaOH
Jones
Rgt.
OH