CHEM 203

Final Exam
December 15, 2010

Your name: ANSWERS

This a closed-notes, closed-book exam

You may use your set of molecular models

This test contains 15 pages

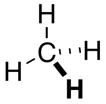
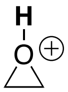
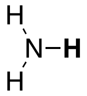
Time: 2h 30 min

1. ________ / 16
2. ________ / 15
3. ________ / 24
4. ________ / 35
5. ________ / 36
6. ________ / 36
7. ________ / 40
8. ________ / 48

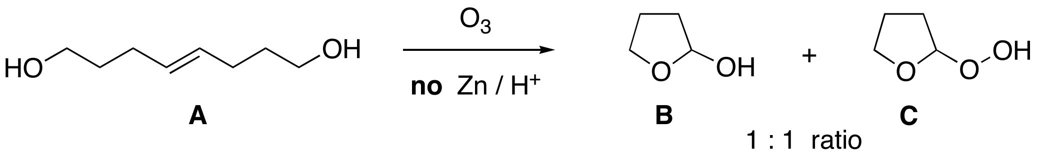
TOTAL ________ / 250 = ________ / 100

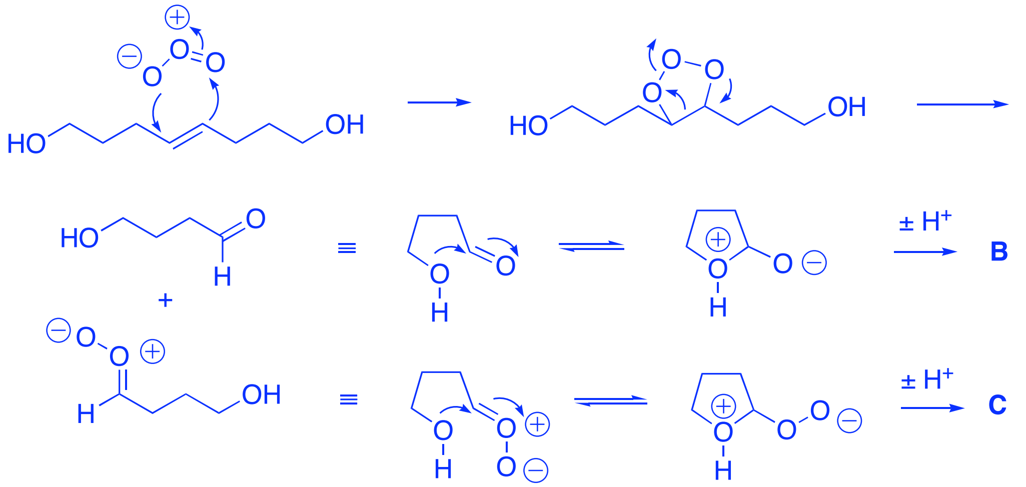
This exam counts for 45% of your CHEM 203 final grade

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)

			**H**–Br
50	– 3	35	– 8
CH_3–C≡C–**H**	**H**–OSO_2CF_3	**H**–H	CH_3–CH_2–O–**H**
25	– 10	40	17

2. (15 pts.) Write a detailed mechanism to account for the observation that treatment of compound **A** with ozone, but **without** the usual Zn/H^+ step, furnishes a 1 : 1 mixture of products **B** and **C**:

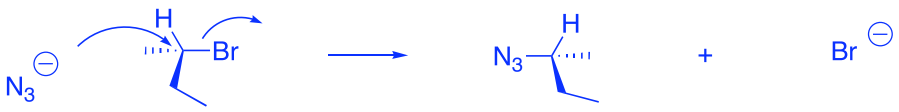




3. (24 pts.) Draw:

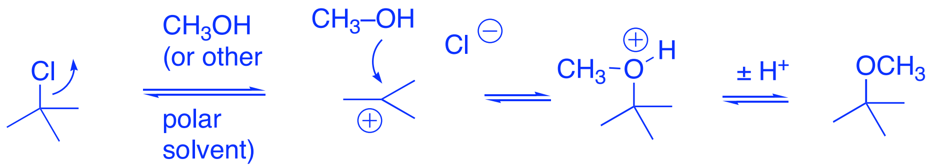
a. Accurate mechanisms for an example of S_N2 reaction and an example of S_N1 reaction:

S_N2:



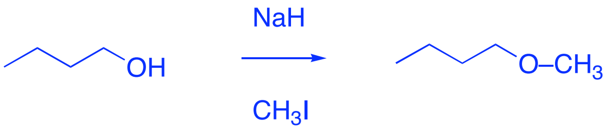
(other answers possible)

S_N1:



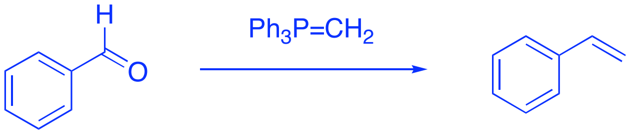
(other answers possible)

b. A chemical equation showing an example of Williamson reaction (without mechanism):



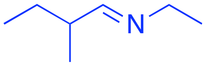
(other answers possible)

c. A chemical equation showing an example of Wittig reaction (without mechanism):



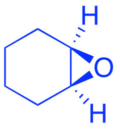
(other answers possible)

d. A chiral Schiff base:



(other answers possible)

e. An achiral epoxide that will react with aq. H_2SO_4 to form a chiral diol:

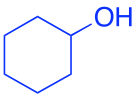
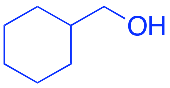


(other answers possible)

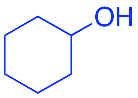
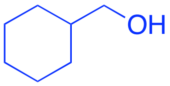
f. An olefin containing at least than 3 C atoms that will produce the same diol when treated either with OsO_4 followed by aq. $NaHSO_3$, or with MCPBA followed by aq. H_2SO_4.

(other answers possible)

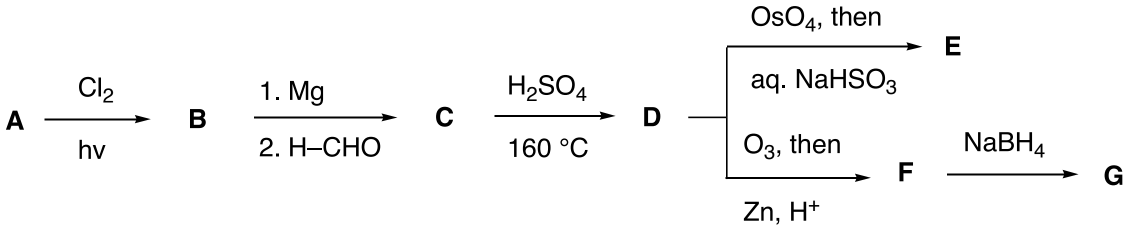
g. An alcohol containing at least 4 C atoms that is likely to undergo dehydration without rearrangement and one also containing at least 4 C atoms that is likely to undergo rearrangement during dehydration (write your answers in the appropriate boxes):

not likely to rearrange	**likely to rearrange**
 **(other answers possible)**	 **(other answers possible)**

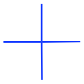
h. An alcohol that forms the same product when treated either with PCC or with the Jones reagent, and one that forms one product when treated with PCC, but a different product when treated with the Jones reagent (write your answers in the appropriate boxes):

gives the same product	**gives two different products**
 **(other answers possible)**	 **(other answers possible)**

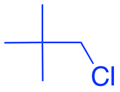
4. (35 pts.) The ^{1}H NMR spectrum of an alkane, **A**, exhibited only a singlet at 0.9 ppm. Treatment of **A** with Cl_2 / hv afforded a monochloro derivative, **B**, which upon reaction with metallic Mg followed by formaldehyde, H-CHO, produced compound **C**. The IR spectrum of **C** displayed a strong, broad absorption at 3340 cm^{-1}. The ^{1}H NMR spectrum of **C** is shown below. Reaction of **C** with H_2SO_4 at 160 °C yielded compound **D**. When substance **D** was treated with OsO_4 followed by aqueous $NaHSO_3$, compound **E** emerged. Furthermore, ozonolysis of **D** followed by Zn/H$^+$ produced only **F**, which upon treatment with $NaBH_4$ furnished **G**. The ^{1}H NMR spectra of **E** and **G** are also provided below. Deduce the structures of compounds **A** – **G** and write your answers in the appropriate boxes.



Compound **A**

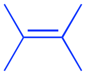


Compound **B**

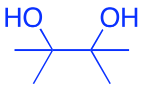


Compound **C**

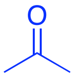
Compound **D**



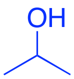
Compound **E**

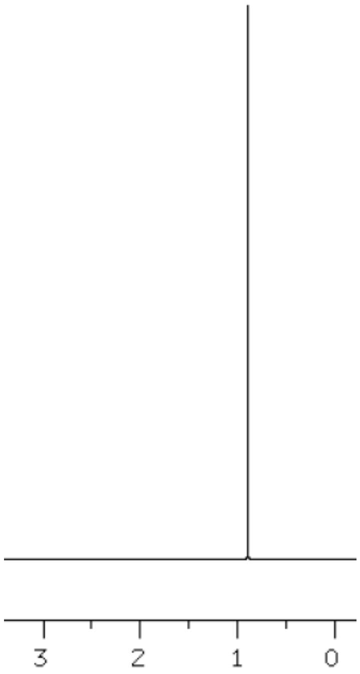


Compound **F**

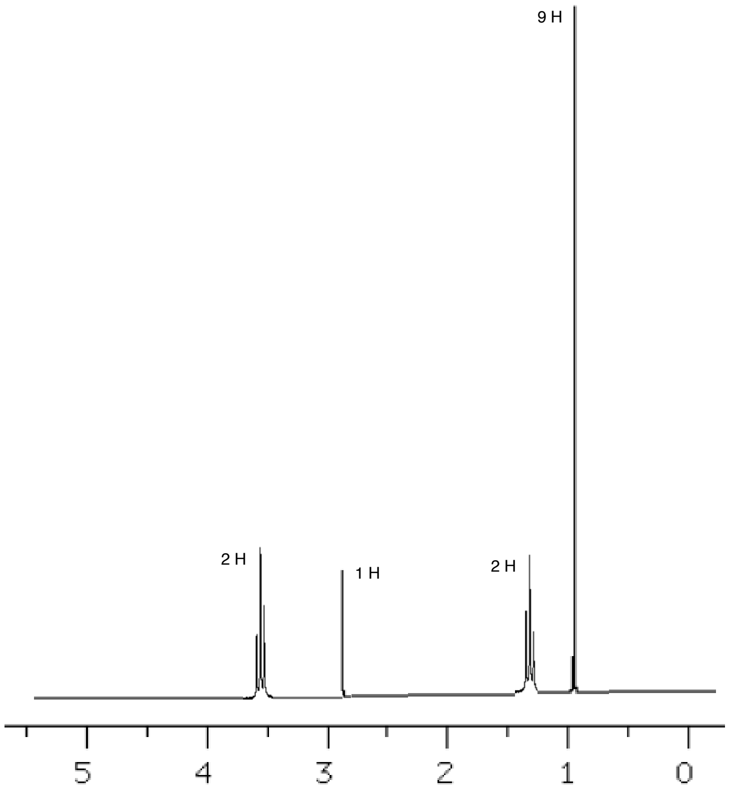


Compound **G**

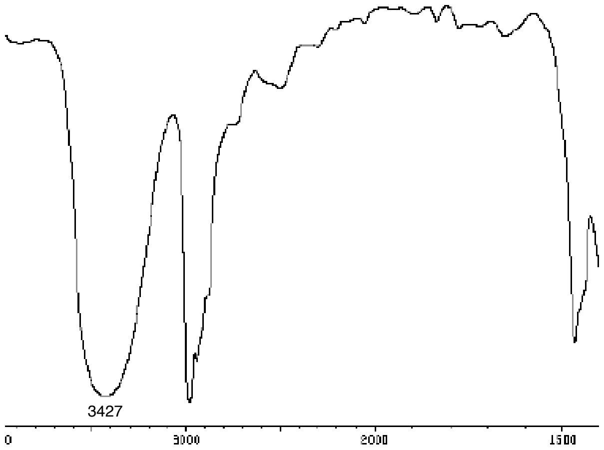




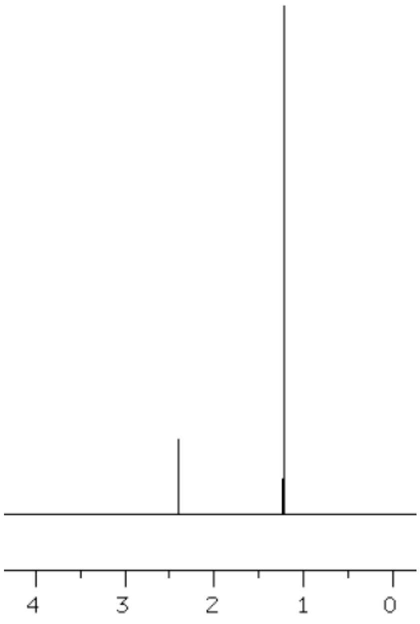
^{1}H NMR spectrum of **A**



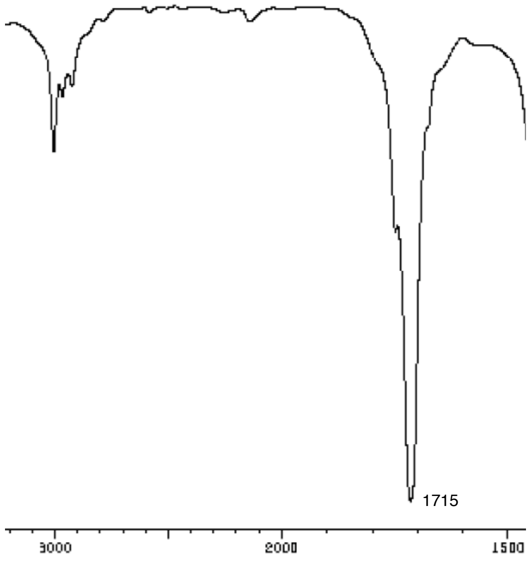
^{1}H NMR spectrum of **C**



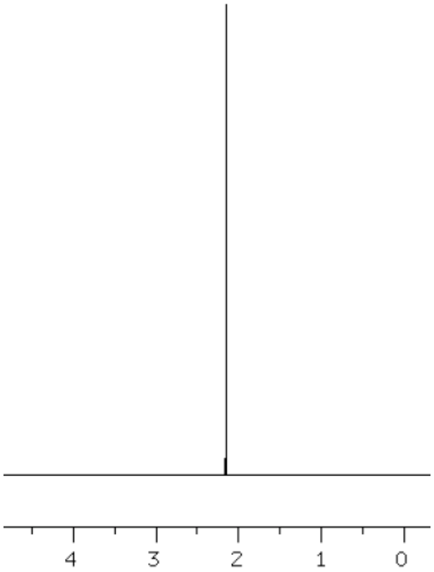
IR spectrum of **E**



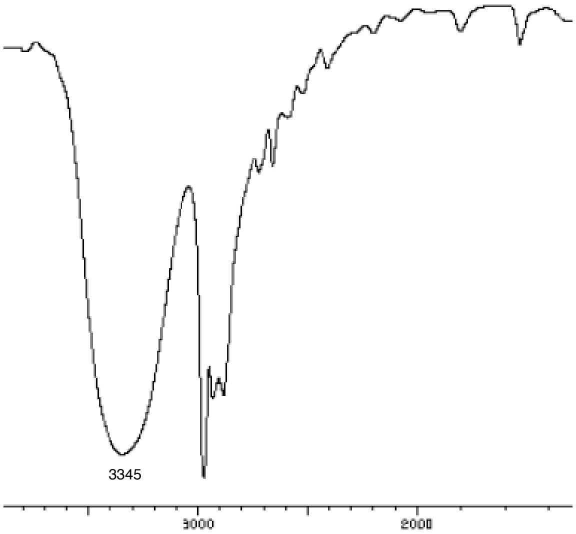
^{1}H NMR spectrum of **E**



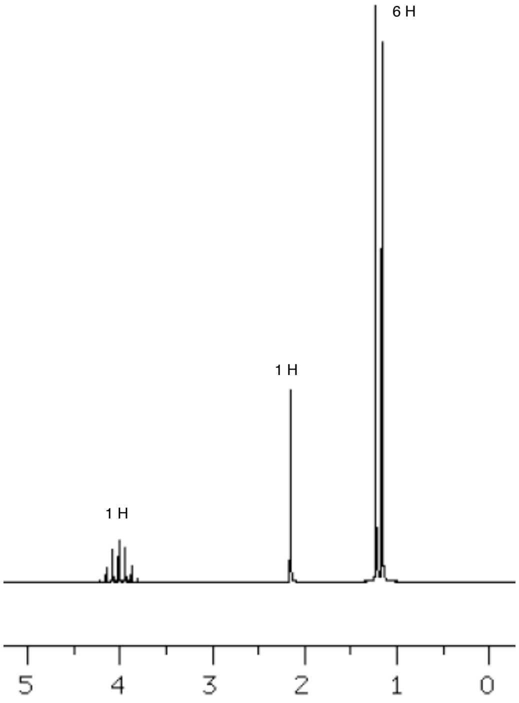
IR spectrum of **F**



^{1}H NMR spectrum of **F**

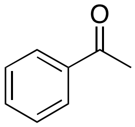


IR spectrum of **G**

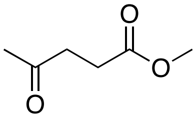


^{1}H NMR spectrum of **G**

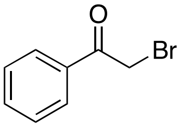
5. (36 pts.) Indicate which among compounds **a**-**j** produce the spectra shown below:



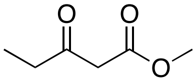
a



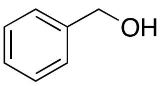
b



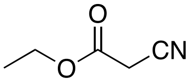
c



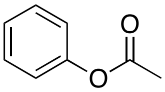
d



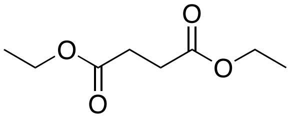
e



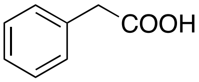
f



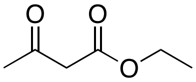
g



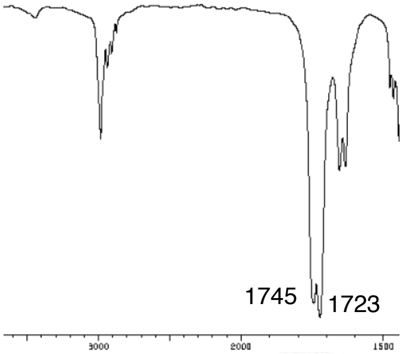
h

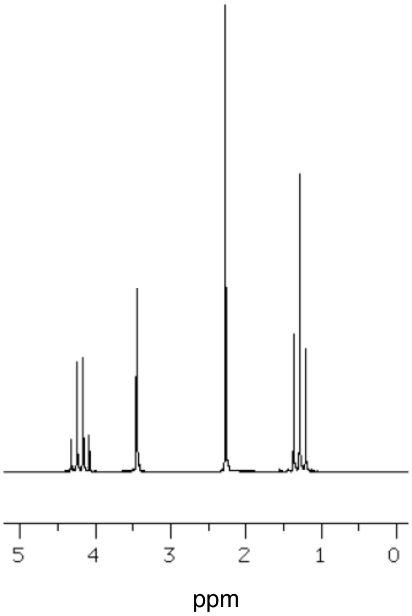


i



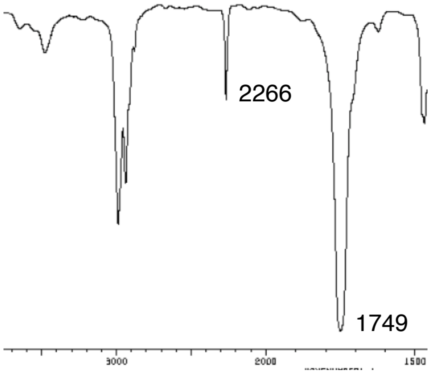
j

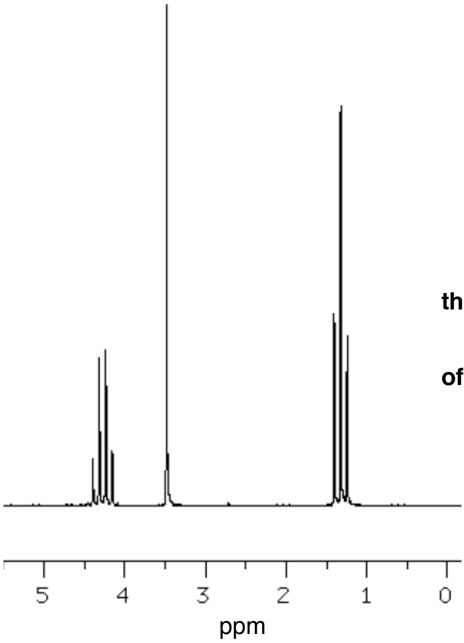




these are the spectra

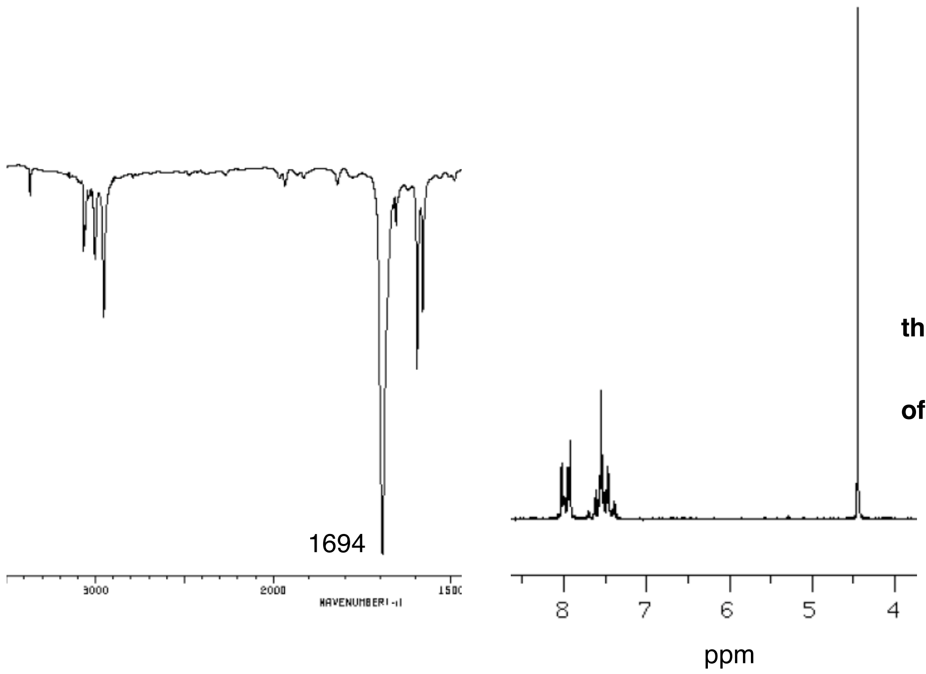
of compound: j





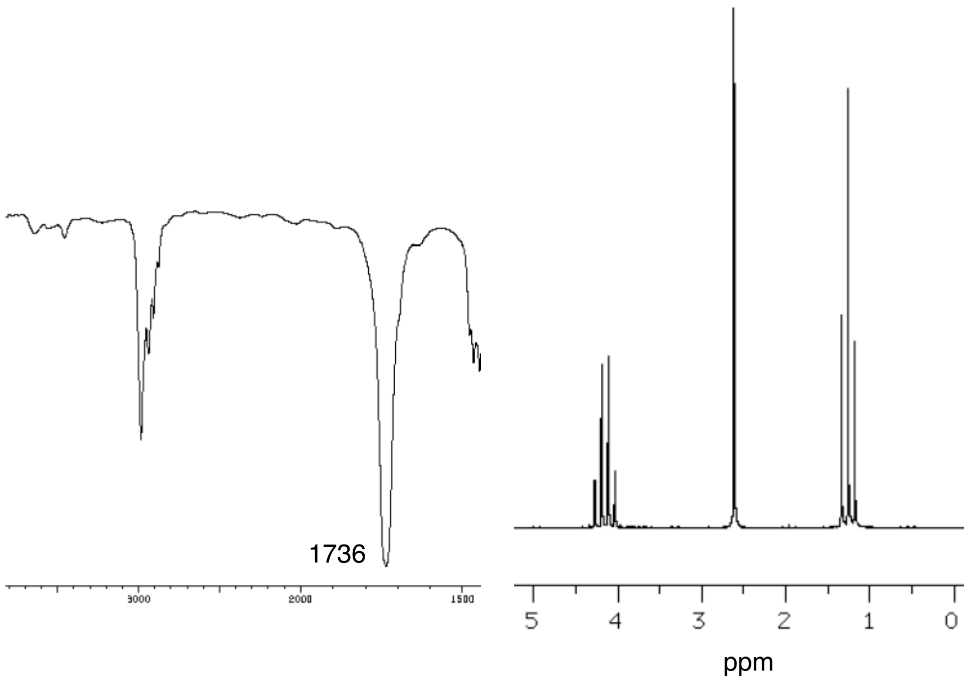
these are the spectra

of compound: f



these are the spectra

of compound: c

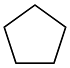


these are the spectra

of compound: h

6. (36 pts.) Draw the structure of the major product expected from each of the following reactions. If no overall change is predicted, answer "**NO REACTION.**" **Important**: where appropriate, molecules must be drawn with the correct configuration

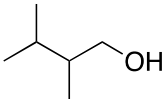
a.



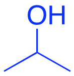
1. HBr, rad. init.
2. $CH_3-C\equiv C-Na$ then mild H_3O^+
3. Na. $NH_{3(liq)}$

NO REACTION

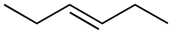
b.



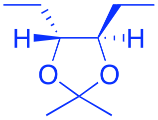
1. H_2SO_4, heat
2. O_3, then Zn / H^+
3. $NaBH_4$, then mild H_3O^+



c.

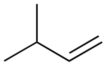


1. OsO_4, then aq. $NaHSO_3$
2. acetone, cat. H_2SO_4, 60 °C, removal of H_2O

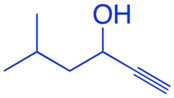


(or enantiomer)

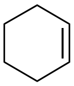
d.



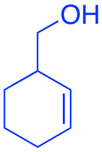
1. BH_3, then H_2O_2, aq. NaOH
2. PCC
3. $HC\equiv C-Na$ then mild H_3O^+



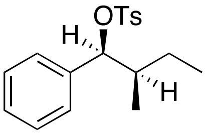
e.



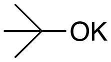
1. NBS, rad. initiator
2. Mg
3. H-CHO, then mild H_3O^+



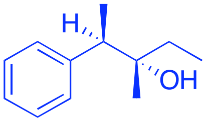
f.



1.



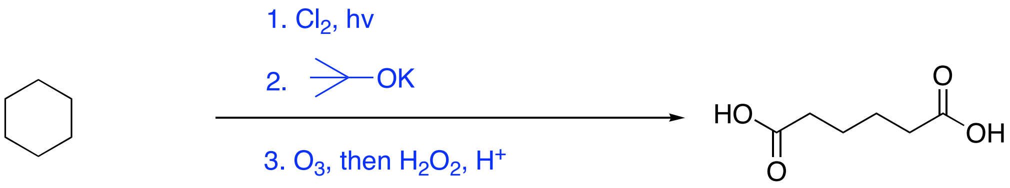
2. MCPBA
3. CH_3MgBr, CuBr, then mild H_3O^+



(or enantiomer)

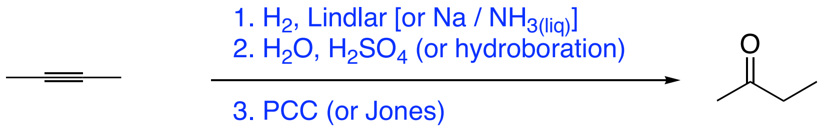
7. (40 pts.) Indicate all the reagents, catalysts, etc., in the correct order, that are necessary to induce the transformations shown below. List such reagents above / below the reaction arrows. If a product does not appear to be available from the substrate shown by any method known to you, write "**INACCESSIBLE**"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

a.



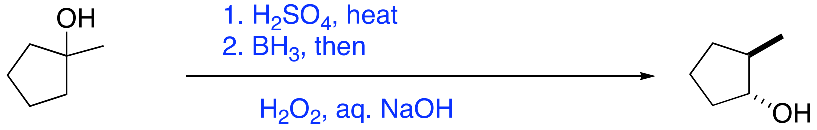
1. Cl_2, hv
2. OK
3. O_3, then H_2O_2, H^+

b.



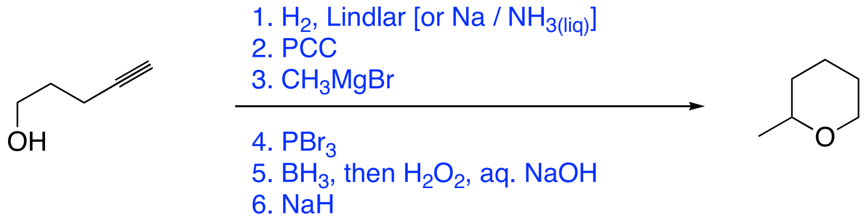
1. H_2, Lindlar [or Na / $NH_{3(liq)}$]
2. H_2O, H_2SO_4 (or hydroboration)
3. PCC (or Jones)

c.



1. H_2SO_4, heat
2. BH_3, then H_2O_2, aq. NaOH

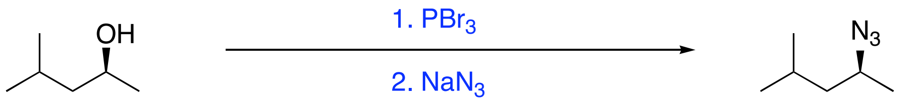
d.



1. H_2, Lindlar [or Na / $NH_{3(liq)}$]
2. PCC
3. CH_3MgBr
4. PBr_3
5. BH_3, then H_2O_2, aq. NaOH
6. NaH

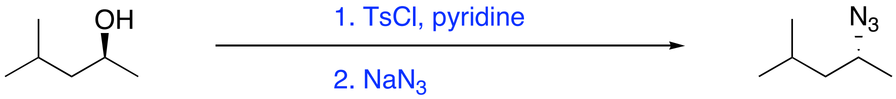
(other anwers possible)

e.



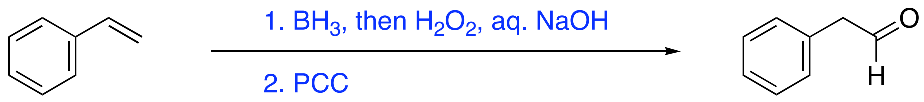
1. PBr_3
2. NaN_3

f.



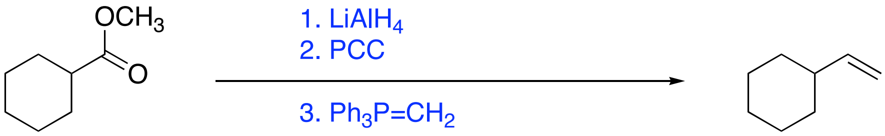
1. TsCl, pyridine
2. NaN_3

g.



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

h.

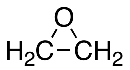


1. $LiAlH_4$
2. PCC
3. $Ph_3P{=}CH_2$

8. (48 pts.) Propose a good synthesis of the molecules shown below using **only methanol**, **NaCN**, **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, BH_3, Mg, TsCl, PCC, PBr_3, MCPBA, etc.).

CH_3OH methanol

H–C≡C–H acetylene



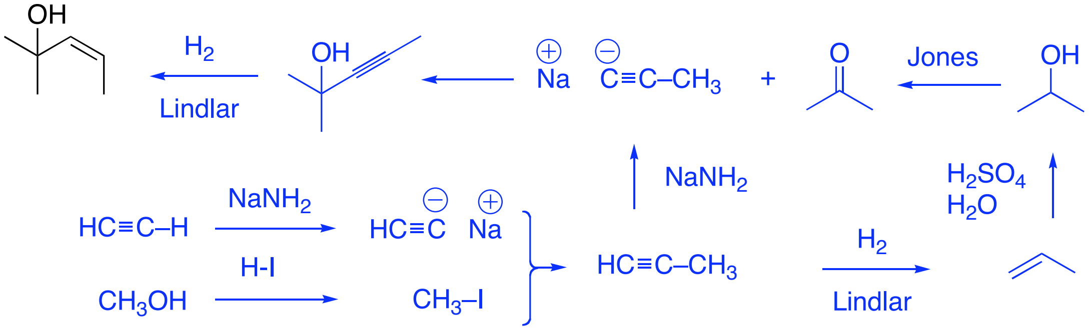
$H_2\overset{O}{C-C}H_2$

ethylene oxide

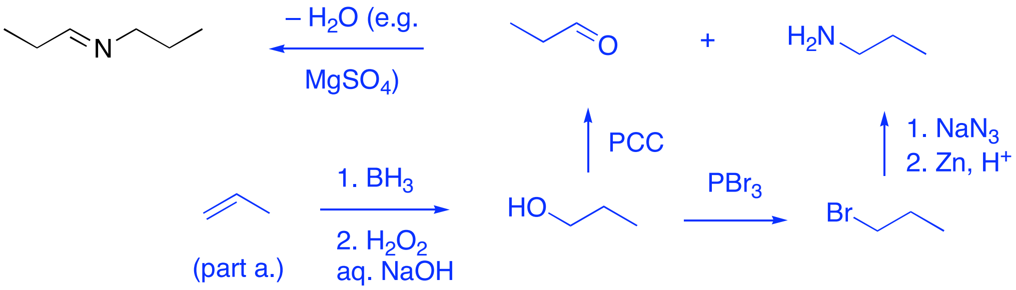
Important: **Note: answers other than the ones given below are possible**

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

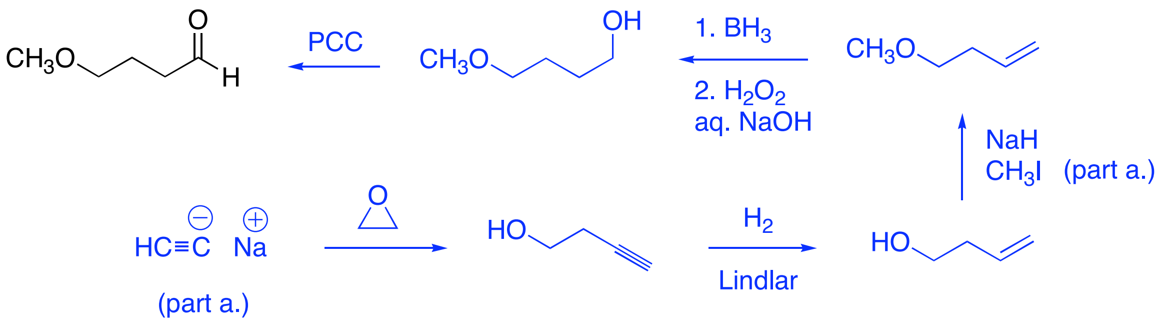
a.



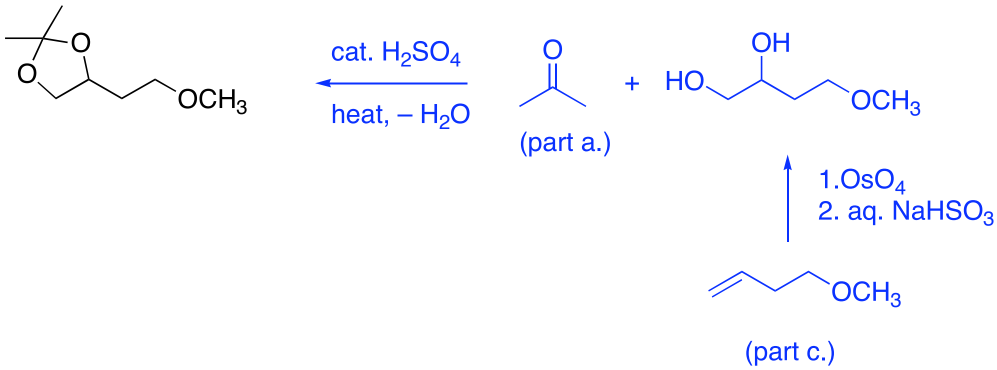
b.



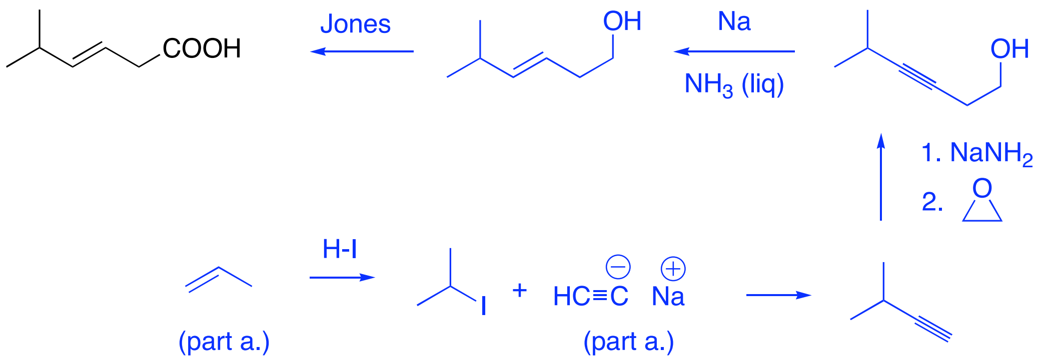
c.


CH3O
O
H
PCC
CH3O
OH
1. BH3
2. H2O2
aq. NaOH
CH3O
NaH
CH3I (part a.)
HC≡C Na
(part a.)
O
HO
H2
Lindlar
HO

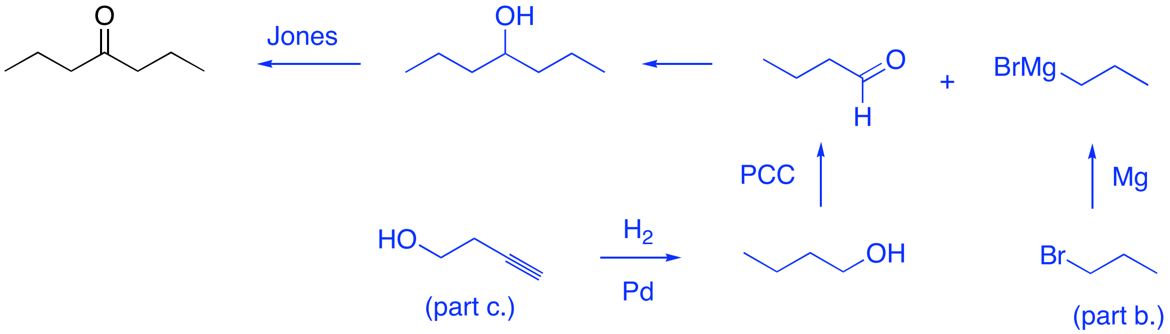
d.


O
O
OCH3
cat. H2SO4
heat, – H2O
O
(part a.)
+
HO
OH
OCH3
1.OsO4
2. aq. NaHSO3
OCH3
(part c.)

e.


COOH
Jones
OH
Na
NH3 (liq)
OH
1. NaNH2
2. O
H-I
(part a.)
I
+
HC≡C Na
(part a.)

f.


O
Jones
OH
O
H
+
BrMg
PCC
Mg
HO
(part c.)
H2
Pd
OH
Br
(part b.)

Characteristic Infrared Absorptions of Common Functional Groups

Functional Group	Bond	Frequency Range (cm^{-1})	Functional Group	Bond	Frequency Range (cm^{-1})
Alcohol	O–H	3400 – 3650 (s, broad)	Nitrile	C≡N	2210 – 2260 (w – m)
	C–O	1050 – 1150 (s)	Carboxylic acid	O–H	2500-3100 (s, broad)
Ether	C–O	1000 – 1260		C=O	1700 – 1720 (s)
Amine	N–H	3300 – 3350 (m)	Ester	C=O	1710 – 1750 (s)
Alkane	C–H	2850 – 2950 (m – s)	Acyl halide	C=O	1770 – 1820 (s)
Alkene	=C–H	3020 – 3100 (m)	Acid anhydride	C=O	1740 – 1790 (s)
	C=C	1640 – 1680 (m)			1800 – 1850 (s)
Alkyne	≡C–H	3270 – 3330 (s)	Amide	C=O	1630 – 1700 (s)
	C≡C	2100 – 2260 (w – m)	Aldehyde, ketone	C=O	1680 – 1730 (s)

Characteristic Proton (^1H) NMR Chemical Shifts

Type of Hydrogen	Structure	Chemical Shift δ (ppm)	Type of Hydrogen	Structure	Chemical Shift δ (ppm)
Reference	$(CH_3)_4Si$	0.00	Amines	$>N-\overset{\vert}{\underset{\vert}{C}}-H$	2.3 – 3.0
Alkane, primary	$-CH_3$	0.7 – 1.3	Alcohol, ether	$-O-\overset{\vert}{\underset{\vert}{C}}-H$	3.3 – 4.0
Alkane, secondary	$-CH_2-$	1.2 – 1.4	Ester	$-\overset{O}{\overset{\Vert}{C}}-O-\overset{\vert}{\underset{\vert}{C}}-H$	3.7 – 4.8
Alkane, tertiary	$-\overset{\vert}{\underset{\vert}{C}}-H$	1.4 – 1.7	Olefinic	C=C-H	5.0 – 6.5
Allylic, primary	$C=C-CH_3$	1.6 – 1.9	Aromatic	Ar–H	6.5 – 8.0
Methyl carbonyl	$-\overset{O}{\overset{\Vert}{C}}-CH_3$	2.1 – 2.5	Aldehyde	$-\overset{O}{\overset{\Vert}{C}}-H$	9.7 – 10.0
Aromatic methyl	$Ar-CH_3$	2.5 – 2.7	Amine	$-NH_2$	1 – 5, variable
Alkyne	≡C–H	2.5 – 2.7	Alcohol	–OH	1 – 5, variable
Alkyl halide (X = Cl, Br, I)	$-\overset{H}{\underset{\vert}{C}}-X$	2.5 – 4.5	Carboxylic acid	–COOH	11.0 – 12.0