CHEM 203

Midterm Exam 1
October 31, 2008

ANSWERS

Your name: _____

This a closed-notes, closed-book exam

You may use your set of molecular models

This exam contains 8 pages

Time: 1h 30 min

1. _____ / 15
2. _____ / 16
3. _____ / 11
4. _____ / 18
5. _____ / 20
6. _____ / 20

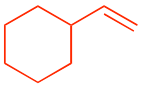
TOTAL _____ / 100

This exam counts for 15% of your CHEM 203 final grade

1. (15 pts.) Write accurate structures of:

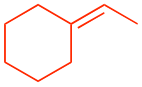
   1. An alkene containing at least 7 C atoms that is likely to undergo rearrangement upon reaction with HCl, and an alkene also containing at least 7 C atoms that is not likely to undergo rearrangement under the same conditions (write your answers in the appropriate boxes):

likely to undergo rearrangement

e.g. 

many other answers are possible

NOT likely to undergo rearrangement

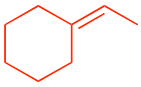
e.g. 

many other answers are possible

   2. An achiral alkene that produces a chiral diol upon reaction with OsO_4 followed by aq. $NaHSO_3$ solution, as well as a chiral dichloride upon reaction with Cl_2:

e.g.  (many other answers are possible)

   3. An achiral alkene that produces a chiral alcohol upon reaction with BH_3 followed by aq. NaOH and H_2O_2, but an achiral alcohol upon reaction with H_2SO_4 and H_2O:

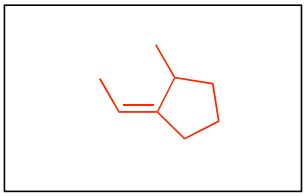
e.g.  (many other answers are possible)

   4. An alkene that contains at least 6 C atoms, and that produces the same alcohol when treated either with BH_3 followed by H_2O_2 and aq. NaOH, or with H_2SO_4 / H_2O:

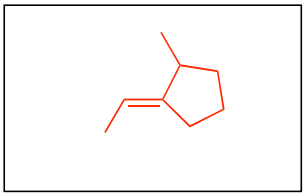
e.g.  (many other answers are possible)

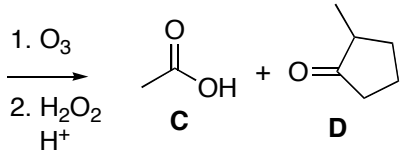
   5. <u>Two</u> isomeric alkenes, **A** and **B**, that produce a 1:1 mixture of compounds **C** and **D** upon reaction with O_3 followed by H_2O_2 and acid:

Alkene A



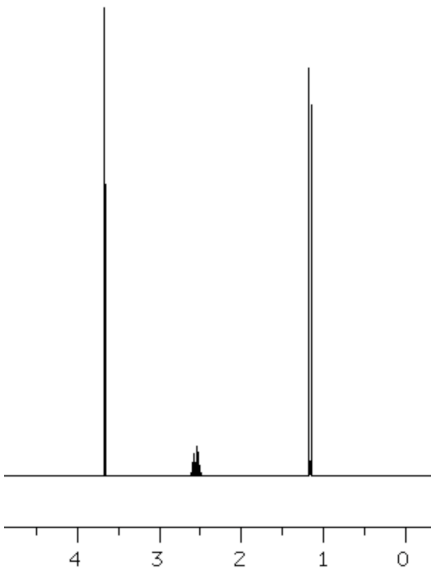
Alkene B



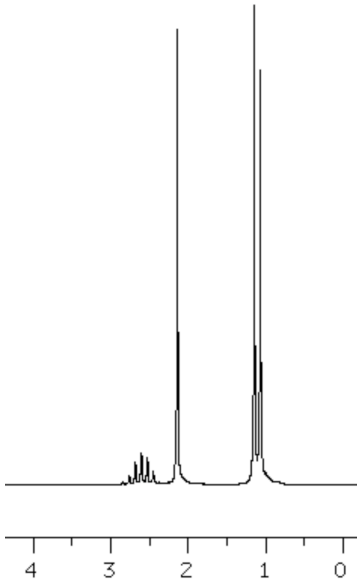


C **D**

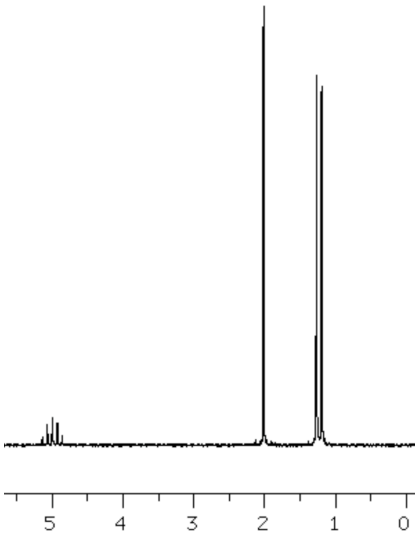
2. (16 pts.) Correlate the four ^{1}H NMR spectra shown below with compounds **E-H** (write your answer in the appropriate box).



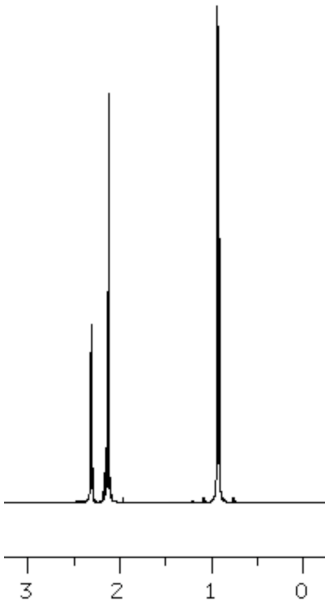
is the ^{1}H spectrum of **F**



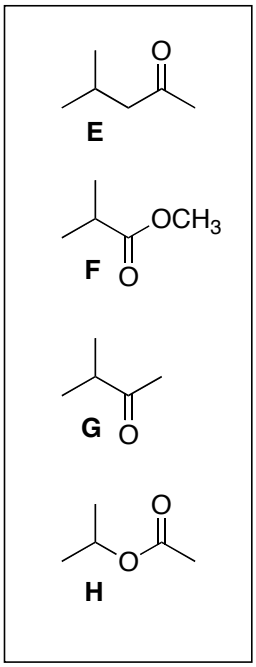
is the ^{1}H spectrum of **G**



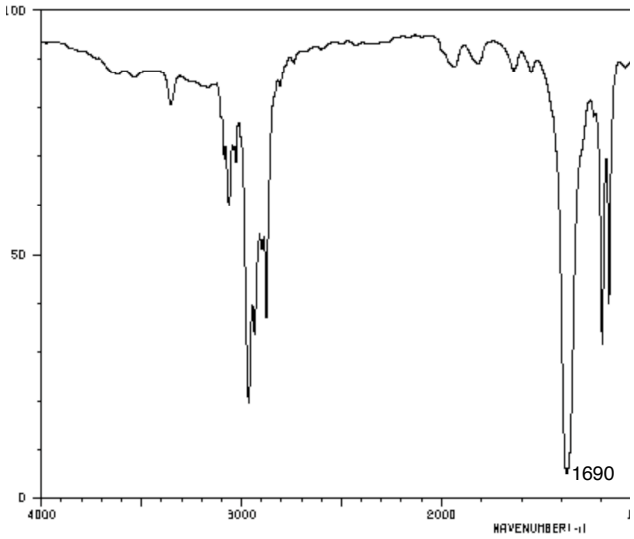
is the ^{1}H spectrum of **H**



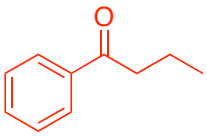
is the ^{1}H spectrum of **E**

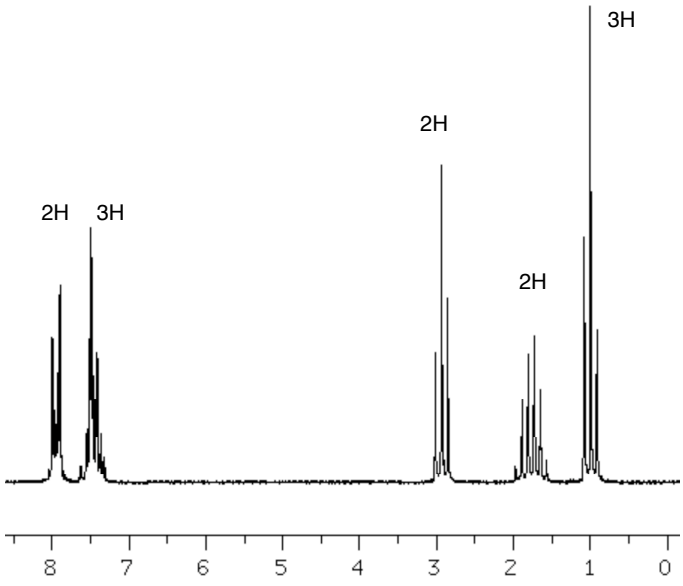


3. (11 pts.) A compound **I** of formula $C_{10}H_{12}O$ produces the IR and ^1H NMR spectra shown below. Propose a reasonable structure for **I** (write your answer in the box):



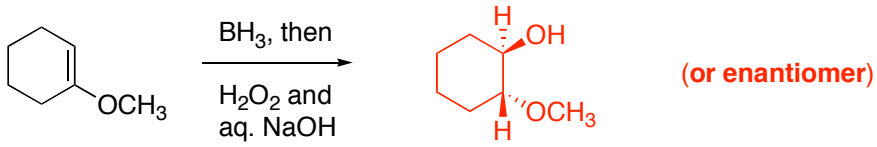
the structure of compound I is:



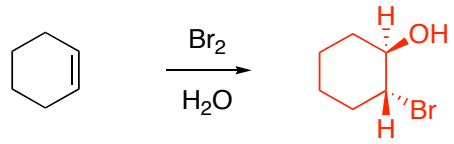


4. (18 pts.) Provide the structure of the major product expected from the following reactions. **Important**: compounds incorporating multiple stereogenic centers must be drawn with the correct relative configuration.

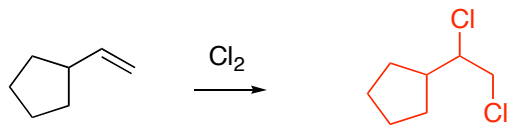
Note: it is understood that chiral compounds will be obtained as racemic mixtures.

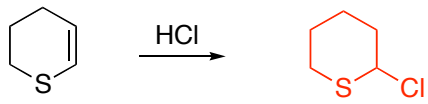
a. 

(or enantiomer)

b. 

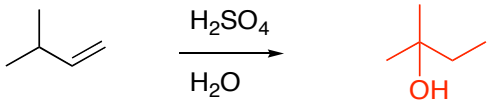
(or enantiomer)

c. 

d. 

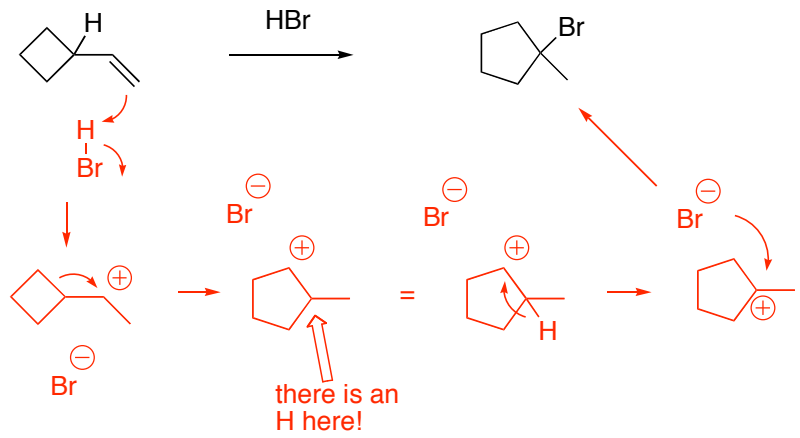
e. 

(or enantiomer)

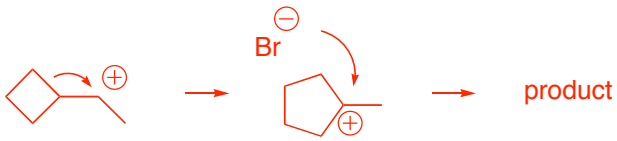
f. 

5. (20 pts.) Write an accurate mechanism for the following known reactions:

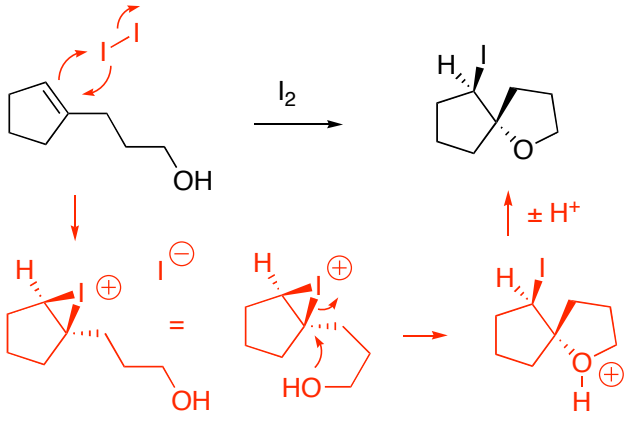
a.



Note: you will still receive full credit on this question if you omitted the second rearrangement, i.e., if you showed:

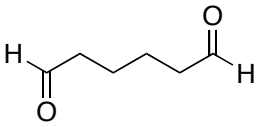


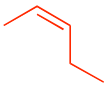
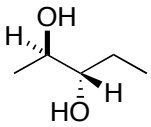
b.

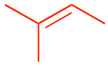
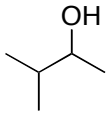


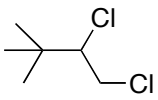
6. (20 pts.) Propose a method for the preparation of compounds a. – e. below starting from appropriate alkenes. Draw a clear structure of your proposed starting olefin on the left side of the reaction arrow. Above/below the reaction arrow, list all reagents / catalysts, in the correct order, that are required to induce the desired transformation. **Important**: the desired compound must be the major product of your reaction(s). If a product does not appear to be available by any reaction known to you, write "INACCESSIBLE" on the reaction arrow.

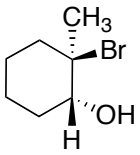
Note: it is understood that chiral compounds will be obtained as racemic mixtures.

a.  1. O_3 / 2. Zn / H^+ 

b.  1. OsO_4 / 2. aq. $NaHSO_3$ 

c.  1. BH_3 / 2. H_2O_2, aq. NaOH 

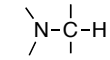
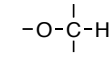
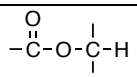
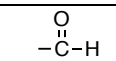
d.  Cl_2 (no rearrangement b/c reaction DOES NOT involve carbocations) 

e. INACCESSIBLE 

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		2.3 – 3.0
Alkane, primary	$-CH_3$	0.7 – 1.3	Alcohol, ether		3.3 – 4.0
Alkane, secondary	$-CH_2-$	1.2 – 1.4	Ester		3.7 – 4.2
Alkane, tertiary		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		2.1 – 2.4	Aldehyde		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)		2.5 – 4.0	Carboxylic acid	–COOH	11.0 – 12.0