CHEM 203

Midterm Exam 1

October 21, 2010

Your name: ANSWERS

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. _____ / 12
3. _____ / 15
4. _____ / 18
5. _____ / 20
6. _____ / 20

TOTAL _____ / 100

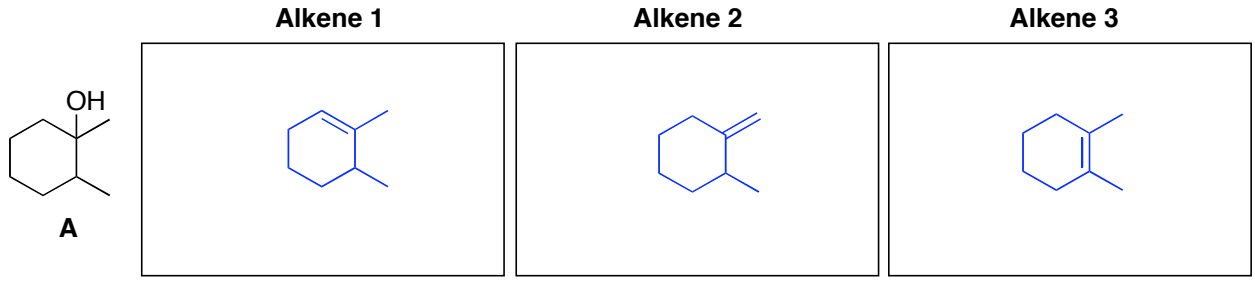
This exam counts for 15% of your CHEM 203 final grade

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

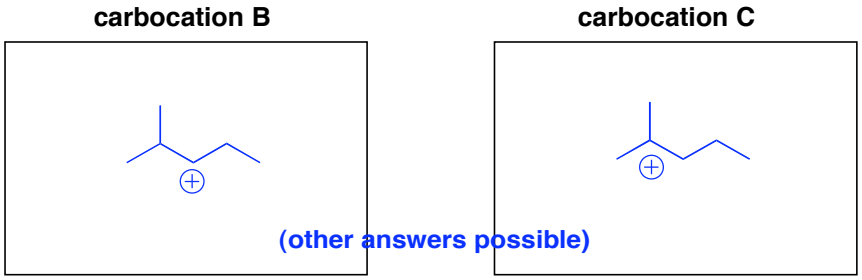
   a. An achiral alkene that produces a chiral alkyl chloride upon reaction with HCl

   eg:  **(other answers possible)**

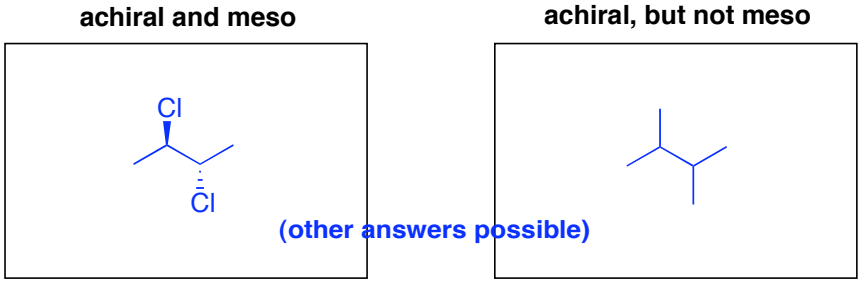
   b. Three isomeric alkenes that produce alcohol **A** as the major product of reaction with H_2O and H_2SO_4 (write your answers in the appropriate boxes):



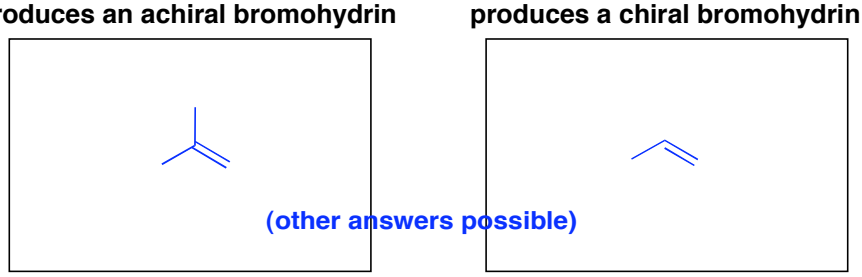
   c. A carbocation, **B**, that is stabilized by 3 hyperconjugative interactions with C–H bonds and that is likely to rearrange to form a new carbocation, **C**, stabilized by 8 hyperconjugative interactions with C–H bonds (write your answers in the appropriate boxes):



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

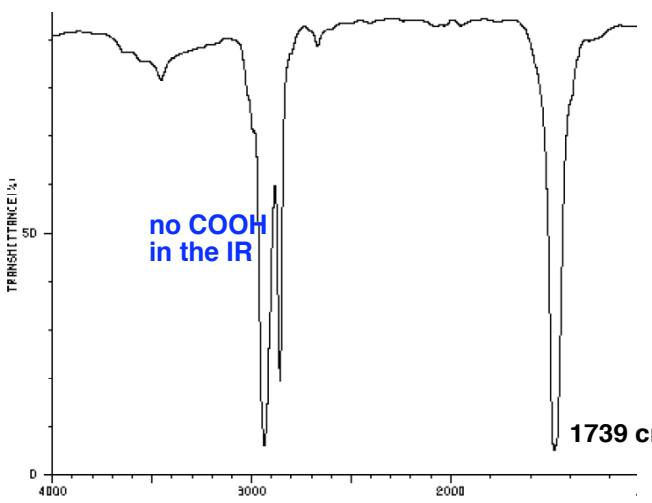


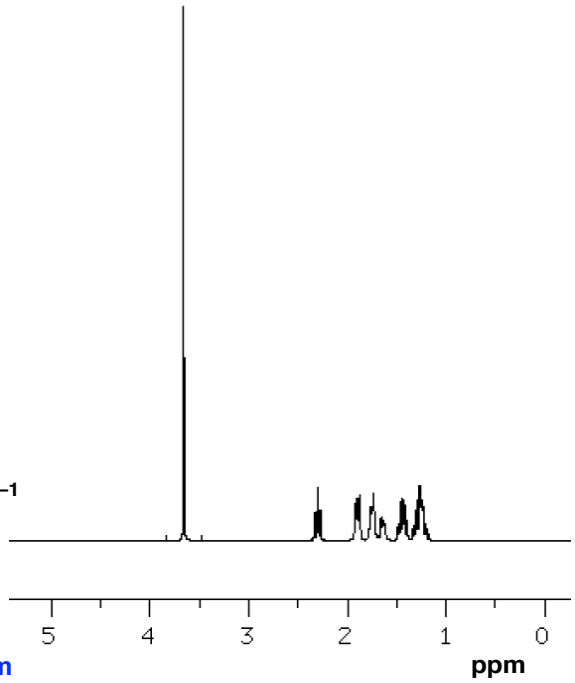
   e. An alkene that produces an achiral bromohydrin upon reaction with Br_2 and H_2O, and one that produces a chiral bromohydrin upon reaction with Br_2 and H_2O.

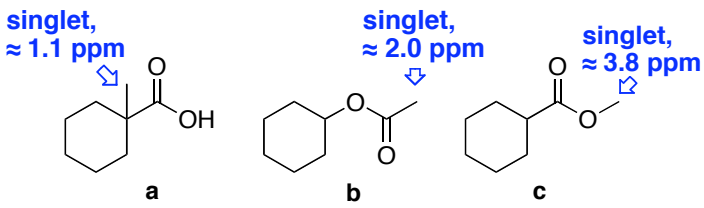


2. (12 pts.) Consider the following two sets of IR and ^{1}H NMR spectra. Each set is produced by one of the three isomeric compounds that appear below the IR spectrum. Deduce which compound produces each spectral set (write your answers in the appropriate boxes):

Set 1

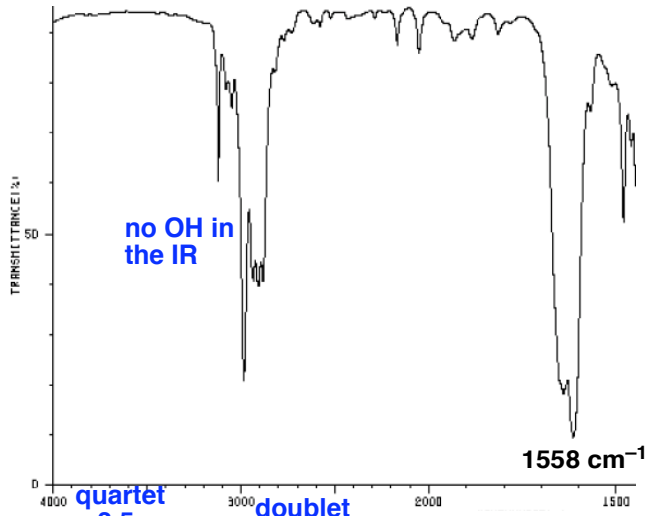


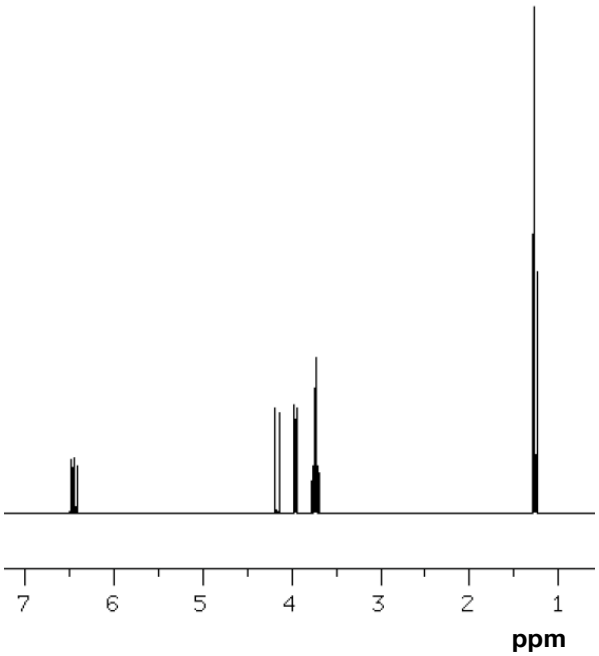


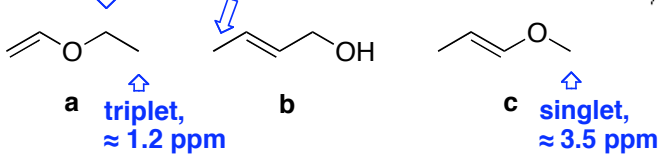


these spectra are produced by compound: **C**

Set 2

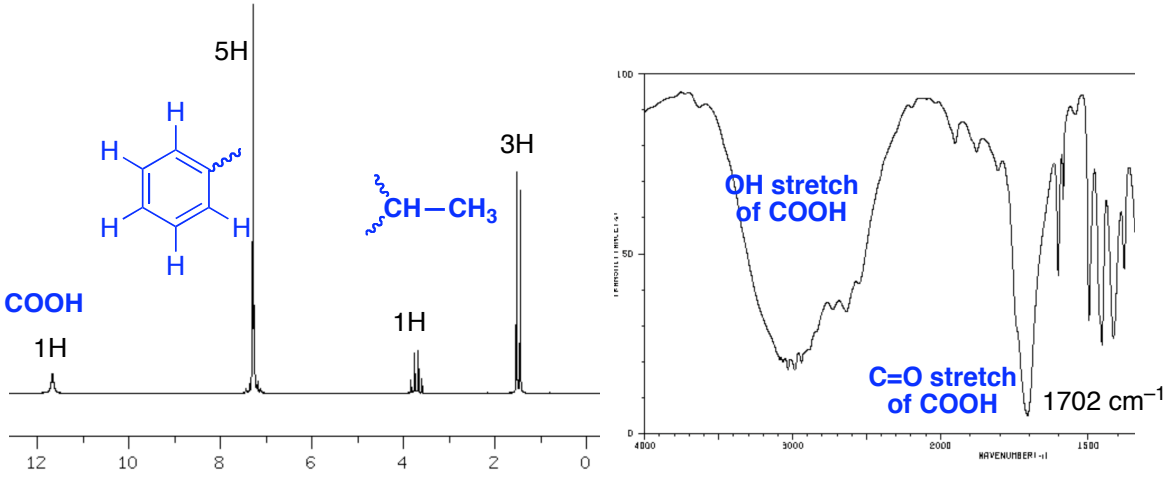






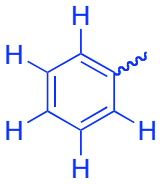
these spectra are produced by compound: **A**

3. (15 pts.) An unknown organic compound, **A**, was found to possess anti-inflammatory activity. This substance was sparingly soluble in water, but the pH of its aqueous solution was determined to be about 5. Various measurements suggested that the molecular mass of the compound had to be between 140 and 160 Dalton. The ^{1}H NMR and IR spectra of the material are shown below. Deduce the structure of **A** (write your answer in the box provided below).



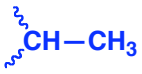
the structure of compound A is:

so, the molecule contains:



COOH

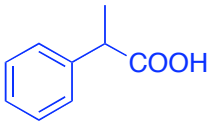
mass = 45



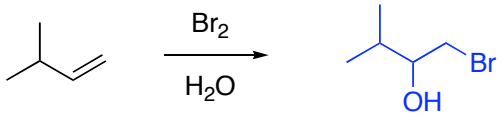
mass = 77

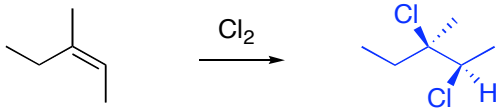
mass = 28

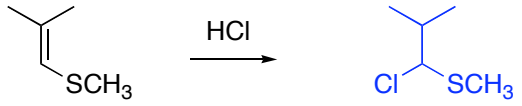
total mass = 150 -- OK

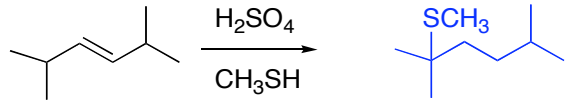


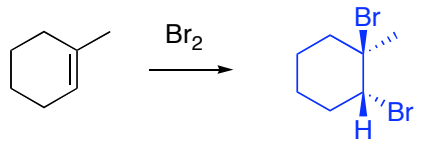
4. (18 pts.) Provide the structure of the major product expected from the following reactions. If no reaction is expected, answer "NO REACTION." **Important**: compounds incorporating multiple stereogenic centers must be drawn with the correct relative configuration. It is understood that chiral compounds will be obtained as racemic mixtures.

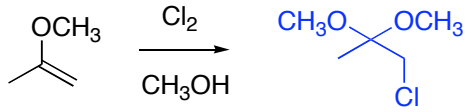
a. 

b. 

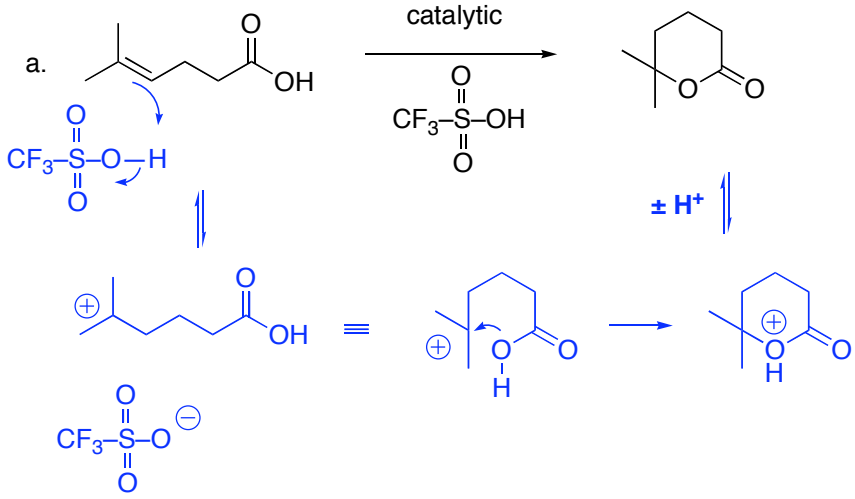
c. 

d. 

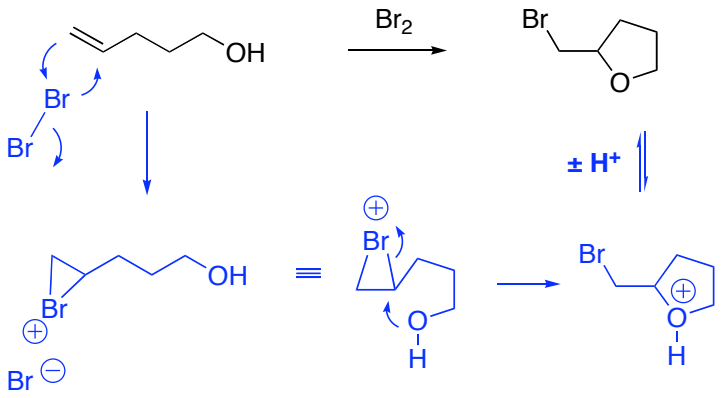
e. 

f. 

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

a. 

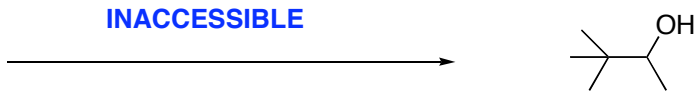
b.

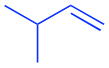
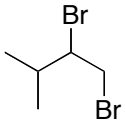


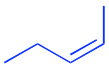
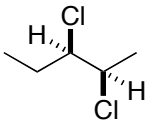
6. (20 pts.) Propose a method for the preparation of compounds a. – e. below starting from appropriate alkenes. Draw a clear structure of your proposed starting olefin on the left side of the reaction arrow. Above/below the reaction arrow, list all reagents / catalysts, in the correct order, that are 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.

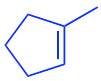
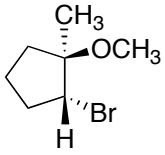
Note: it is understood that chiral compounds will be obtained as racemic mixtures.

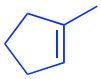
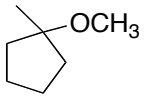
a.



b.  $\xrightarrow{Br_2}$ 

c.  $\xrightarrow{Cl_2}$ 

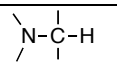
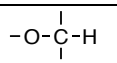
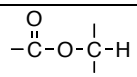
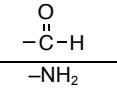
d.  $\xrightarrow[CH_3OH]{Br_2}$ 

e.  $\xrightarrow[H_2SO_4]{CH_3OH}$ 

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