CHEM 203

Midterm Exam 1

October 16, 2008

Your name: ____

This a closed-notes, closed-book exam

You may use your set of molecular models

This exam contains 7 pages

Time: 1h 30 min

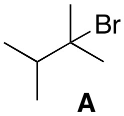
1.	________ / 15
2.	________ / 15
3.	________ / 12
4.	________ / 18
5.	________ / 20
6.	________ / 20
TOTAL	________ / 100

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

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

a. A chiral alkene that produces an achiral alkane upon hydrogenation:

b. Three isomeric alkenes that produce alkyl bromide **A** as the major product of reaction with HBr (write your answers in the appropriate boxes):



A

Alkene 1 **Alkene 2** **Alkene 3**

c. A carbocation, **B**, that is stabilized by 4 hyperconjugative interactions with C–H bonds and that is likely to rearrange to form a new carbocation, **C**, stabilized by 7 hyperconjugative interactions with C–H bonds (write your answers in the appropriate boxes):

carbocation B **carbocation C**

d. An alkene that contains at least 5 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. An alkene that contains at least 5 C atoms, and that produces one alcohol when treated with H_2SO_4 / H_2O, but an isomeric alcohol when reacted with BH_3 followed by H_2O_2 and aq. NaOH:

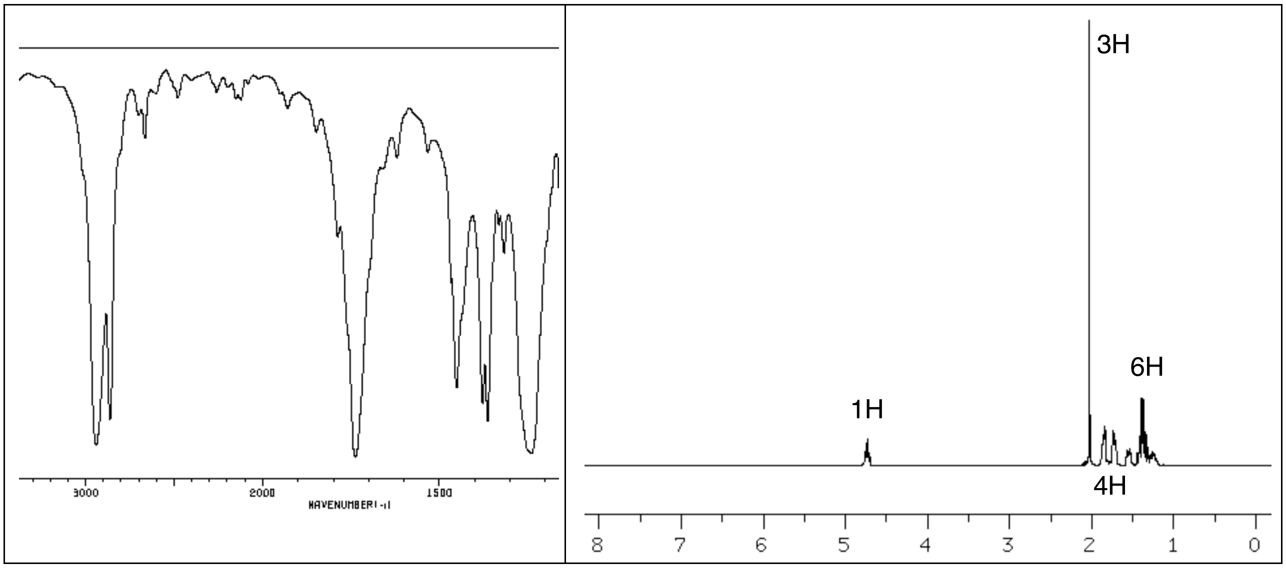
2. (15 pts.) Two isomeric compounds, **A** and **B**, possess formula $C_6H_{12}O$. The IR and ^1H NMR spectra of **A** and **B** are very similar and display the following signals:

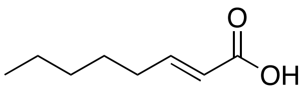
   IR (cm^{-1}): 3400 (strong, broad), 3100, 2950, 1650, 1180
   NMR (δ): 5.68 (m, 2H); 2.54 (broad s, 1H); 1.71 (d, 3H); 1.36 (s, 6H)

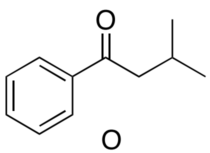
   Reaction of **A** with H_2 in the presence of Pt metal yields a compound **C** of formula $C_6H_{14}O$ with release of 22.9 kcal/mol of energy. Reaction of **B** under the same conditions also provides compound **C**, but with release of 25.0 kcal/mol of energy. Deduce the structure of **A**, **B**, and **C**. Write these structures in the appropriate boxes below.

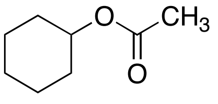
compound A **compound B** **compound C**

3. (12 pts.) Indicate which one among compounds a.-f. below produces the following IR and ^1H NMR spectra (write your answer in the box):

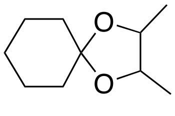


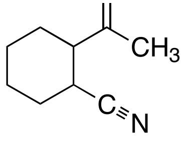
a.


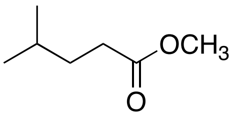
b.


c.


Answer

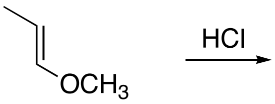
d.


e.


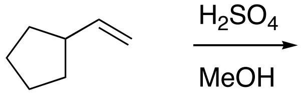
f.


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.

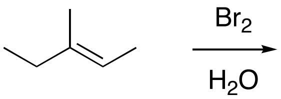
a.



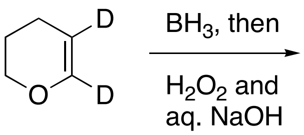
b.



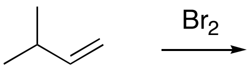
c.



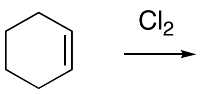
d.



e.

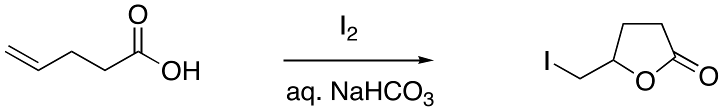


f.

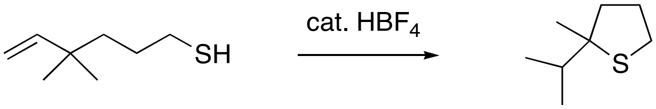


5. (20 pts.) Write an accurate mechanism for the following known reactions:

a.



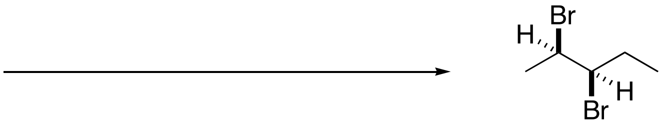
b.



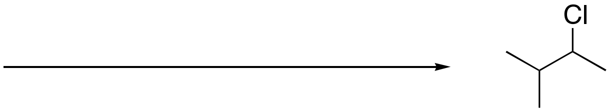
6. (20 pts.) Propose a method for the preparation of compounds a. – e. below starting from appropriate alkenes. Draw a clear structure of your proposed starting olefin on the left side of the reaction arrow. Above/below the reaction arrow, list all reagents / catalysts, in the correct order, that are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

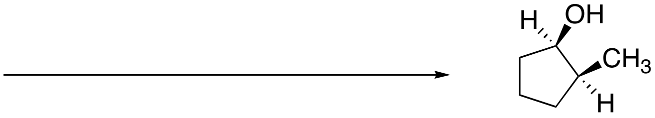
a.



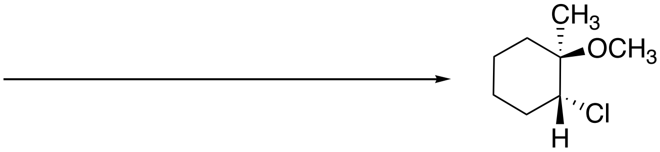
b.



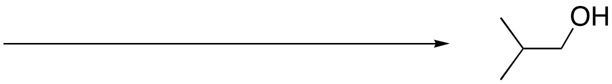
c.



d.



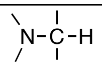
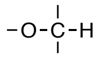
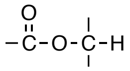
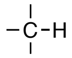
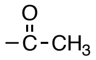
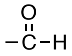
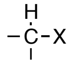
e.



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 – 4.2
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 – 2.4	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 – 4.0	Carboxylic acid	–COOH	11.0 – 12.0