CHEM 203

Midterm Exam 2
November 18, 2008

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.	________	/ 15
3.	________	/ 15
4.	________	/ 15
5.	________	/ 20
6.	________	/ 20
TOTAL	________	/ 100

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

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

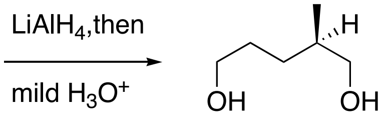
1. An alkyl halide that is likely to undergo nucleophilic substitution by the S_N2 mechanism, and one that is likely to undergo nucleophilic substitution by the S_N1 mechanism (write your answers in the appropriate boxes):

likely to react by S_N2 mechanism **likely to react by S_N1 mechanism**

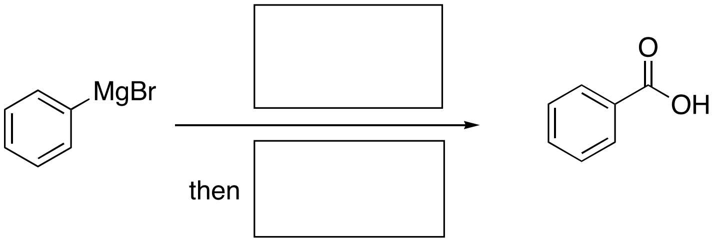
2. A chiral alkyne that produces a chiral product upon reaction with metallic Na in liquid NH_3 but an achiral product upon reaction with H_2 in the presence of metallic Pt.

3. The organic compound of formula $C_6H_{10}O_4$ that reacts with $LiAlH_4$ followed by mild H_3O^+ to yield the product shown below:

$C_6H_{10}O_4$

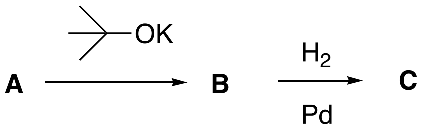


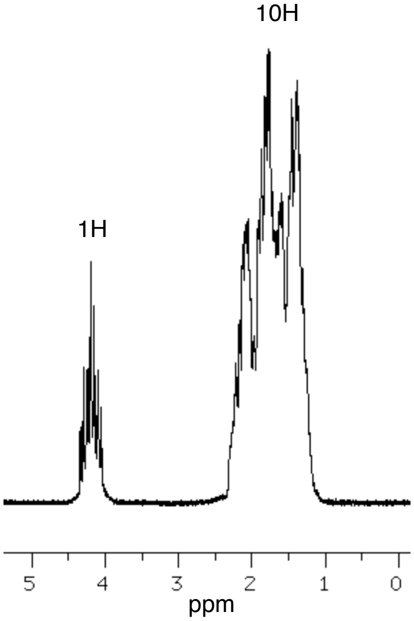
4. The reagents necessary to achieve the conversion of phenylmagnesium bromide into benzoic acid (complete the reaction diagram below):



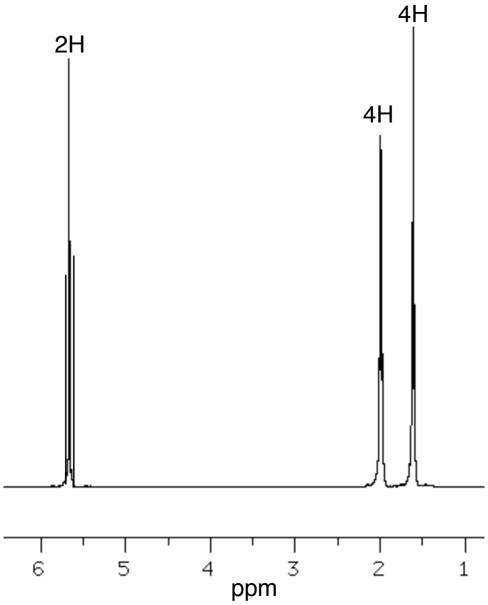
5. An alkyl halide containing at least 3 carbon atoms that CANNOT undergo E2 reaction

2. (15 pts.) Appropriate analytical techniques determined that an unknown organic compound **A** contained bromine and had a molecular mass between 160 and 170 daltons. Treatment of **A** with potassium *tert*-butoxide as per the scheme below produced **B**, hydrogenation of which furnished **C**. The ^{1}H NMR spectra of **A** – **C** are shown below. Deduce the structures of the three compounds and write your answers in the appropriate boxes.

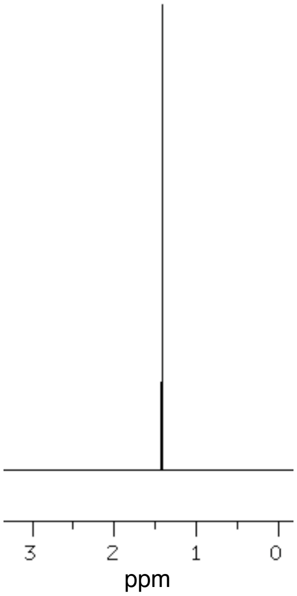




A



B



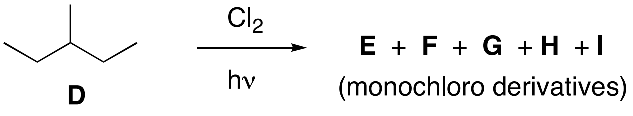
C

structure of compound A

structure of compound B

structure of compound C

3. (15 pts.) Radical chlorination of 3-methylpentane, **D**, afforded a complex mixture of products, from which five different substances, **E** – **I**, of formula $C_6H_{13}Cl$ were isolated. Appropriate analytical methods revealed that **E** and **F** were achiral, while **G**, **H**, and **I**, were racemic mixtures. Write the structures of compounds **E** – **I** in the boxes below.



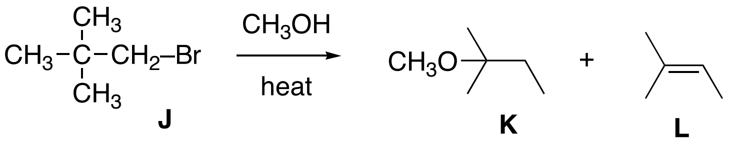
achiral products

structure of product E **structure of product F**

racemic products

structure of product G **structure of product H** **structure of product I**

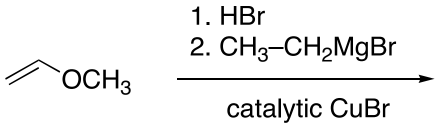
4. (15 pts.) Write a detailed reaction mechanism to account for the fact that heating a solution of **J** in CH_3OH causes the formation of **K** and **L**.



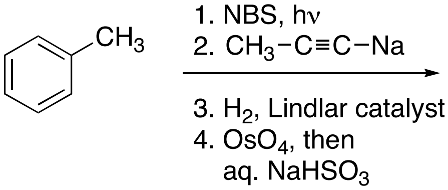
5. (20 pts.) Provide the structure of the major product expected from the following reaction sequences. **Important**: compounds incorporating multiple stereogenic centers must be drawn with the correct relative configuration.

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

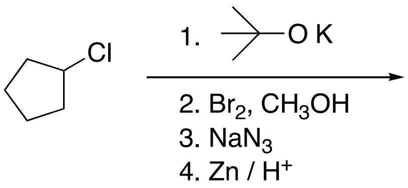
a.



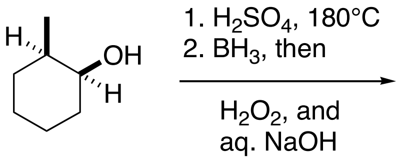
b.



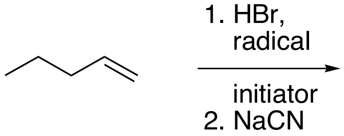
c.



d.



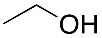
e.



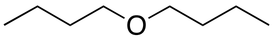
6. (20 pts.) Propose a method for the preparation of compounds a. – e. below starting ONLY with 1-butene as the source of carbon atoms. You may use any additional reagent that might be needed (e.g., borane, HCl, Mg, H_2O_2, potassium tert-butoxide, etc.). Present your answer as a clear flowchart that shows all intermediate steps and products. Substances obtained in one sequence may be used as components of a later sequence.

It is not necessary to draw mechanisms

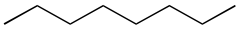
a.

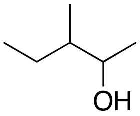


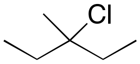
b.



c.



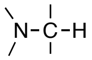
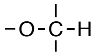
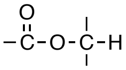
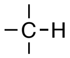
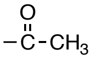
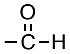
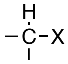
d. 

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 – 4.8
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