CHEM 203

Exam 2
November 17, 2010

Your name: _____

This a closed-notes, closed-book exam

You may use your set of molecular models

This test consists of 10 pages

Time: 1h 30 min

1. _____ / 9
2. _____ / 15
3. _____ / 16
4. _____ / 20
5. _____ / 20
6. _____ / 20

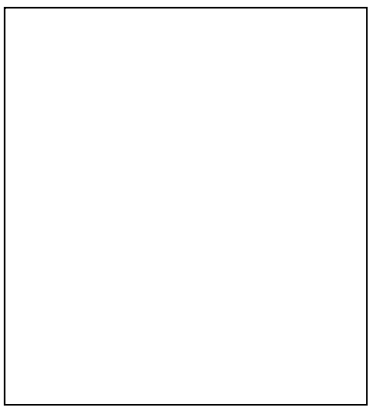
TOTAL _____ / 100

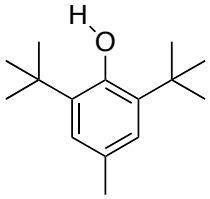
This exam counts for 15% of your CHEM 203 final grade

1. (9 pts.) In class, we discussed the reagents shown below. Provide a concise statement to indicate the purpose for which each compound is used (answer in the appropriate boxes).

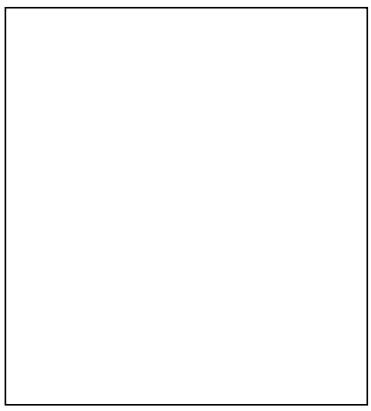
$NaNH_2$

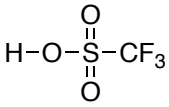
used for / as:



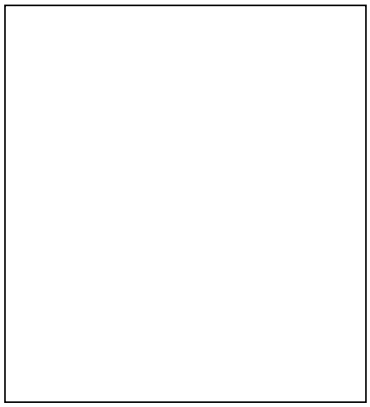


used for / as:



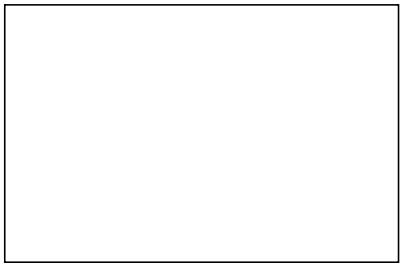


used for / as:

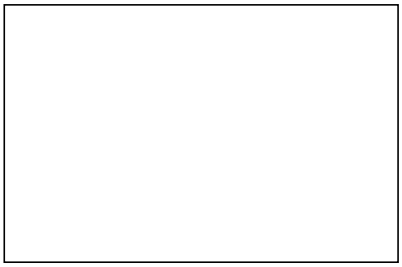


2. (15 pts.) Write accurate structures of:
   a. An alkyl halide that is likely to react with CH_3ONa to give a product of substitution, and one that is likely to react with CH_3ONa to give a product of elimination:

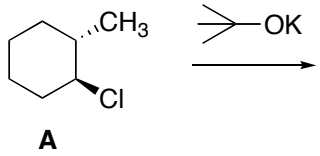
undergoes substitution



undergoes elimination



b. The product of E2 reaction of compound **A** below:



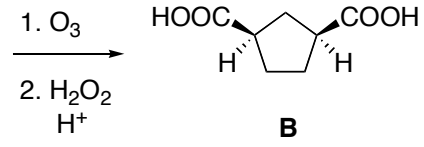
A

c. An alkane that is a good substrate for radical chlorination and one that is a poor substrate for the same reaction:

good substrate **poor substrate**

d. An olefin containing at least 3 carbon atoms that yields the same alcohol when treated either with BH_3 followed by H_2O_2 and aq. NaOH, or with H_2O and H_2SO_4

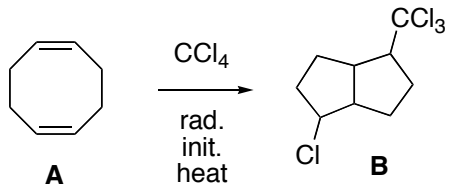
e. An olefin than shows no diagnostic IR absorptions besides C=C–H signals, and that gives only dicarboxylic acid **B** upon treatment with O_3 followed by H_2O_2 and acid:



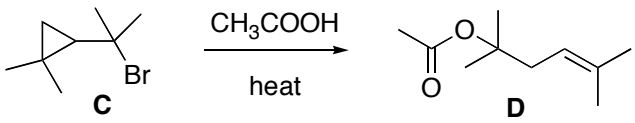
B

3. (16 pts.) Accounts for the following observations by writing accurate mechanisms for each transformation:

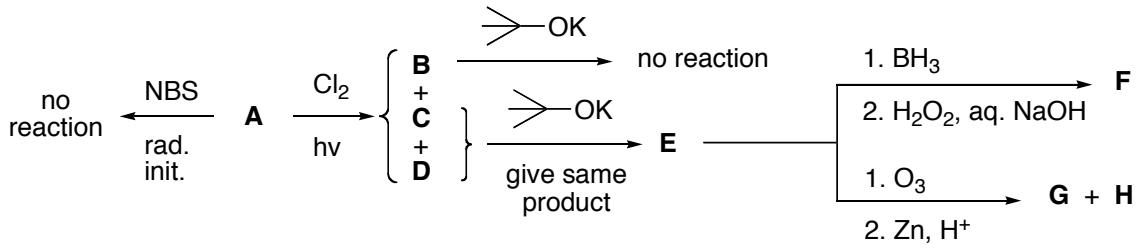
(i) treatment of alkene **A** with carbon tetrachloride, CCl_4, in the presence of a radical initiator gives compound **B**:

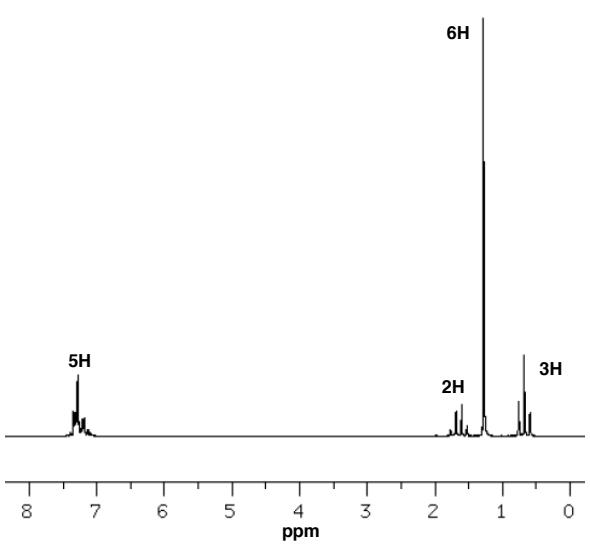


(ii) heating of alkyl halide **C** in acetic acid affords **D** as one of the products:

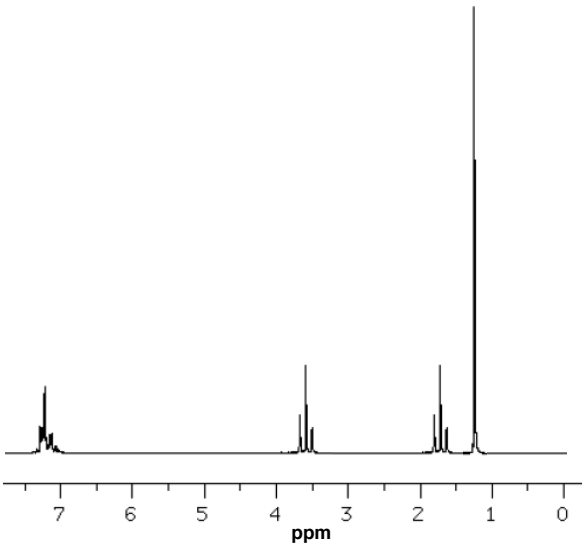


4. (20 pts). An unknown organic compound, **A**, had molecular mass equal to ca. 150 daltons and produced no characteristic absorptions in the IR spectrum. As shown in the reaction scheme below, **A** was recovered unchanged from treatment with NBS in the presence of a radical initiator; however, reaction with Cl_2 in the presence of light afforded three products of mono-chlorination: compounds **B**, **C**, and **D**. Treatment with potassium *tert*-butoxide had no

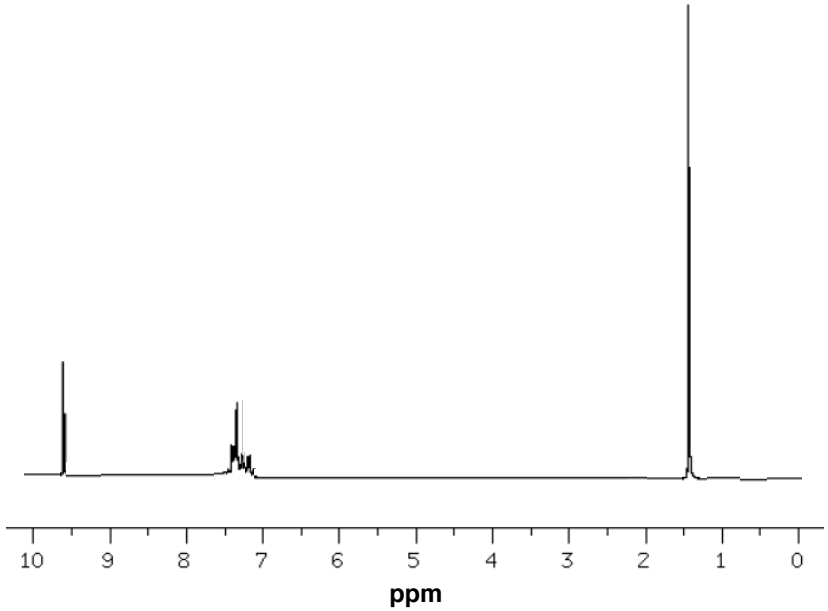




NMR spectrum of: compound **A**



compound **F**



NMR spectrum of: compound **G**

compound **H**

effect on **B**, but it converted substances **C** and **D** to the same product, **E**. The reaction of **E** with BH_3 followed by H_2O_2 / aq. NaOH afforded product **F**, while its reaction with O_3, followed by Zn/H^+ provided substances **G** and **H**. The spectra of **A**, **F**, **G**, **H** are provided. Determine the structures of compounds **A**-**H** and write your answers in the appropriate boxes provided below.

Structure of A:

Structure of B:

Structure of C:

Structure of D:

Structure of E:

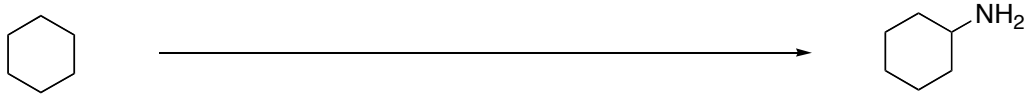
Structure of F:

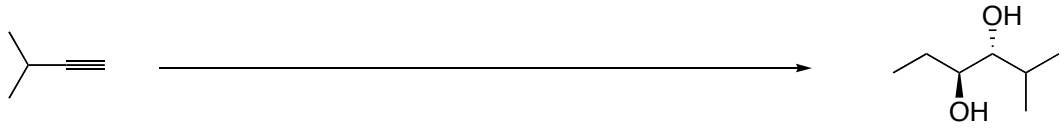
Structure of G:

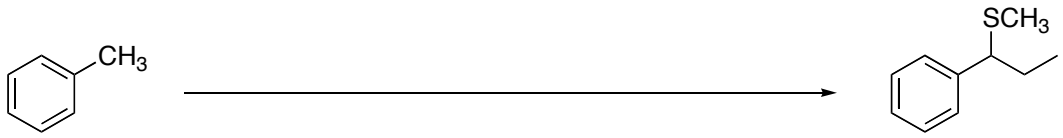
Structure of H:

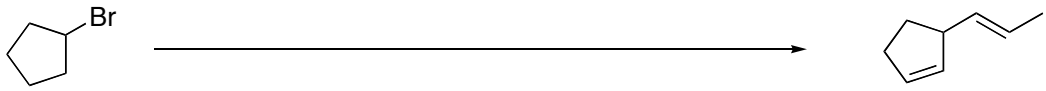
5. (20 pts.) Propose a method to achieve the transformations shown below. Indicate all the reagents, in the correct order, that are required to induce each transformation. Present your answer as a numbered list displayed above / below each reaction arrow.

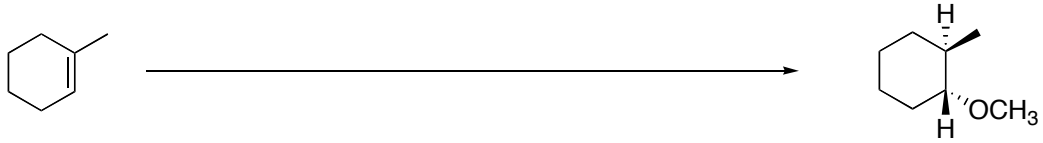
Note: it is understood that chiral compounds will be obtained as racemic mixtures.

a. 

b. 

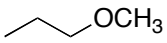
c. 

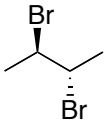
d. 

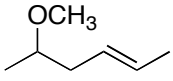
e. 

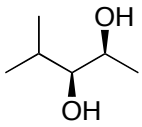
6. (20 pts.) Propose a method for the preparation of compounds a. – e. below starting ONLY with methane and propyne, $H–C{\equiv}C–CH_3$, as the source of carbon atoms. You may use any additional reagent that might be needed (e.g., borane, HCl, Mg, H_2O_2, *tert*-BuOK, etc.). Present your answer as a clear flowchart that shows all intermediate steps and products. Substances obtained in one sequence may be used as components of a later sequence.

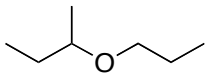
It is not necessary to draw mechanisms

a. 

b. 

c. 

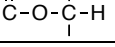
d. 

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		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 – 4.8
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 – 2.5	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 – 4.5	Carboxylic acid	–COOH	11.0 – 12.0