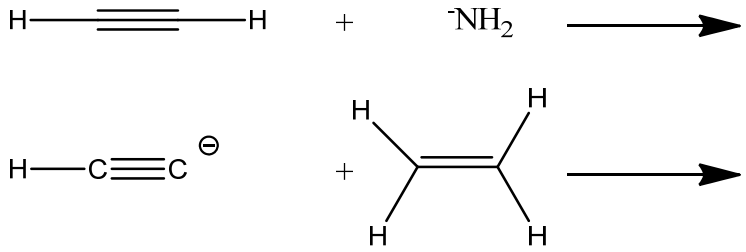
**Organic 211** Test # 4 December 5, 2013

Name:_____

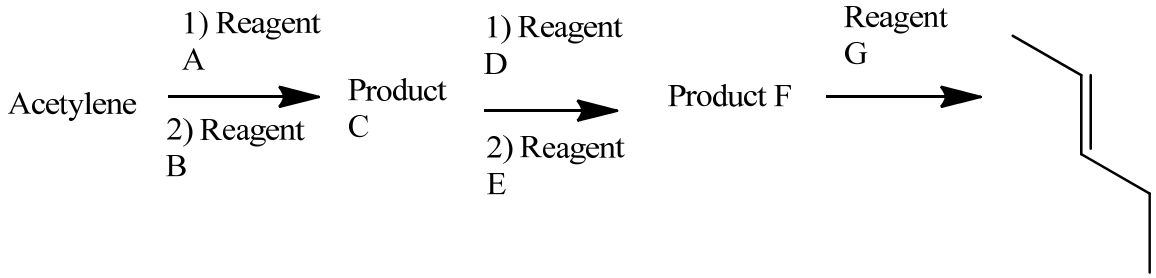
Directions: Work every question. NO CALCULATORS ALLOWED.

1) There are at least three six-carbon alkynes that can exist as diasteromers. Draw TWO of them. Your molecules should only contain carbon and hydrogen. (4 pts.)

2) Circle the reaction(s) [if any] that have a Keq > 1. (4 pts.)



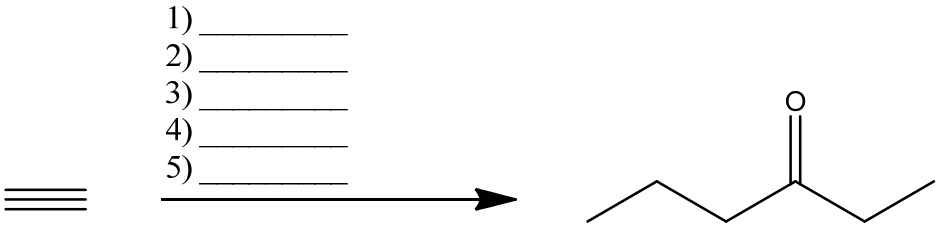

3) Give the missing reagents and products. (6 pts.)




A _____
B_____
C _____
D _____

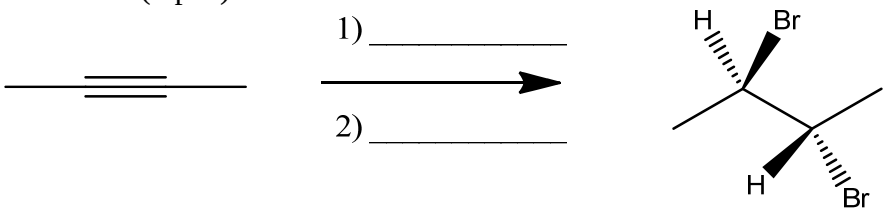
E _____
F _____
G _____

4) Put the correct letter for the reagent next to the number. A reagent may be used more than once. Carry out the steps so that the ketone shown is the ONLY product. (5 pts.)



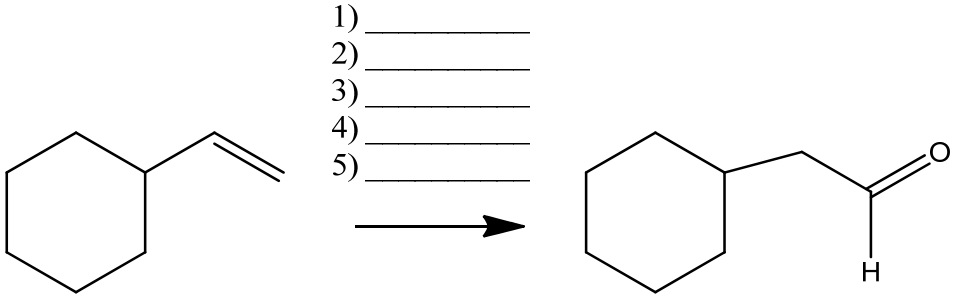

| | | |
|---|---|---|
| A __$CH_3I$__ | E _HBr (2 eq.)_ | I $BH_3/THF$ |
| B __$CH_3CH_2I$_ | F __$Br_2$ ( 2eq.)_ | J $NaNH_2$ |
| C __NaOH_____ | G __$Br_2$ (1 eq.)_ | K $HgSO_4/H_2O/H_2SO_4$ |
| D __HBr (1 eq.)_____ | H __$CH_3CH_2CH_2I$_ | L _$H_2$/Lindlar's catalyst |

5) Put the correct letter for the reagent next to the number. A reagent may be used more than once. (4 pts.)




| | | |
|---|---|---|
| A __$CH_3I$__ | E _HBr (2 eq.)_ | I $BH_3/THF$ |
| B __$CH_3CH_2I$_ | F __$Br_2$ ( 2eq.)_ | J $NaNH_2$ |
| C __NaOH_____ | G __$Br_2$ (1 eq.)_ | K $HgSO_4/H_2O/H_2SO_4$ |
| D __HBr (1 eq.)_____ | H __$Na/NH_3$_ | L _$H_2$/Lindlar's catalyst |

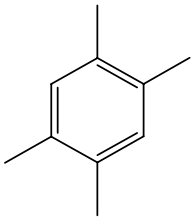
6) Put the correct letter for the reagent next to the number. A reagent may be used more than once. (5 pts.)

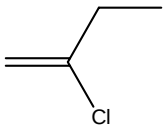


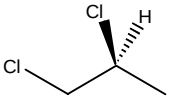

| | | |
|---|---|---|
| A __$H^+$____ | E _HBr (2 eq.)_ | I $(sia)_2BH$_ |
| B __$O_3/Zn$____ | F __$Br_2$ ( 2eq.)_ | J $NaNH_2$ |
| C __$H_2O_2/OH^-$_____ | G __$Br_2$ (1 eq.)_ | K $HgSO_4/H_2O/H_2SO_4$ |
| D __HBr (1 eq.)_____ | H __$Na/NH_3$_ | L _$H_2$/Lindlar's catalyst |

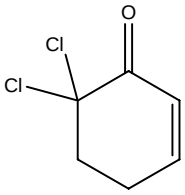
7) Give a molecular formula that fits the molecular weight of 275. NO CALCULATORS ALLOWED. SHOW YOUR WORK! (5 pts.)

8) How many different types of hydrogens do the following compounds show in the proton NMR? Assume all of spectra will be taken in an achiral solvent. (2 pts. each)

a) 

b) 

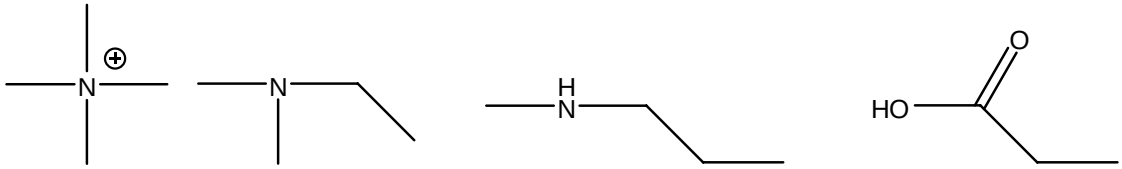

c) 


d) 

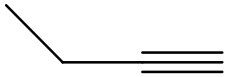
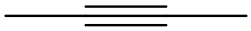

9) Compound A ($C_9H_{18}Cl_2$) has only one type of hydrogen. Compound A has three types of carbon. The locations in the carbon NMR are: δ 85 (singlet in proton-coupled), δ 20 (singlet in proton coupled) and δ 10 (quartet in proton coupled). Treatment of compound A with excess -$NH_2$ does not form an alkyne. Give the structure of A. (4 pts.)

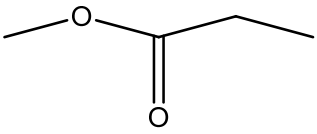
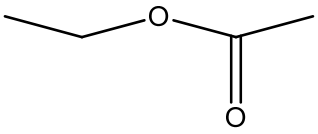
10) Compound B has the molecular formula $C_5H_{12}$ and has only one peak in the proton NMR which is a singlet. Give a structure for compound B. (4 pts.)

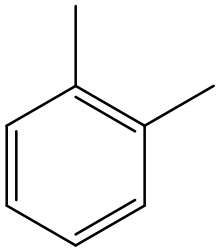
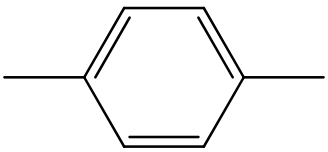
11) Circle the molecule(s) (if any) below that will have a peak disappear upon stirring with $D_2O$. (4 pts.)




12) Using the method indicated, describe how you would tell the molecules apart. (3 pts. each)

a)  vs.  IR

b)  vs.  $^{1}$H NMR

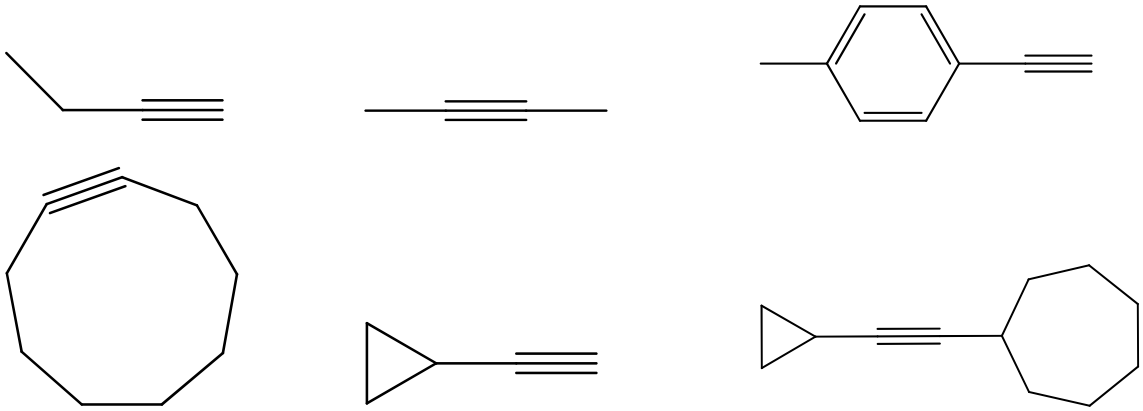
c)  vs.  $^{13}$C NMR

d) Ethyl chloride vs. Ethyl bromide Mass Spectrum

13) What does an IR spectrum tell you? (4 pts.)

14) What is the transformation seen in a UV spectrum? (4 pts.)

15) Circle the terminal alkyne(s) [if any] below. ( 4 pts.)



For the following three combined spectra problems, give a structure that will give all of the spectra. Partial credit will be given so indicate as much information as possible.

16) (6 pts.)

17) (6 pts.)

18) ( 6 pts.)

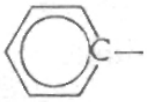
19) Free question: Give me something that you will remember about Organic I. (5 pts.)

**TABLE 13.1** Approximate Proton Chemical Shifts

| TYPE OF PROTON | CHEMICAL SHIFT, DELTA, PPM |
|---|---|
| 1° Alkyl, $RCH_3$ | 0.8–1.0 |
| 2° Alkyl, $RCH_2R$ | 1.2–1.4 |
| 3° Alkyl, $R_3CH$ | 1.4–1.7 |
| Allylic, $R_2C{=}C(R){-}CH_3$ | 1.6–1.9 |
| Benzylic, $ArCH_3$ | 2.2–2.5 |
| Alkyl chloride, $RCH_2Cl$ | 3.6–3.8 |
| Alkyl bromide, $RCH_2Br$ | 3.4–3.6 |
| Alkyl iodide, $RCH_2I$ | 3.1–3.3 |
| Ether, $ROCH_2R$ | 3.3–3.9 |
| Alcohol, $HOCH_2R$ | 3.3–4.0 |
| Ketone, $RC(=O)CH_3$ | 2.1–2.6 |
| Aldehyde, $RC(=O)H$ | 9.5–9.6 |
| Vinylic, $R_2C{=}CH_2$ | 4.6–5.0 |
| Vinylic, $R_2C{=}CH(R)$ | 5.2–5.7 |
| Aromatic, $ArH$ | 6.0–9.5 |
| Acetylenic, $RC{\equiv}CH$ | 2.5–3.1 |
| Alcohol hydroxyl, $ROH$ | 0.5–6.0[a] |
| Carboxylic, $RC(=O)OH$ | 10–13[a] |
| Phenolic, $ArOH$ | 4.5–7.7[a] |
| Amino $R{-}NH_2$ | 1.0–5.0[a] |

[a]The chemical shifts of these groups vary in different solvents and with temperature and concentration.

TABLE 13.2 Approximate Carbon-13 Chemical Shifts

| TYPE OF CARBON | CHEMICAL SHIFT, DELTA, PP |
|---|---|
| 1° Alkyl, $RCH_3$ | 0–40 |
| 2° Alkyl, $RCH_2R$ | 10–50 |
| 3° Alkyl, $RCHR_2$ | 15–50 |
| Alkyl halide or amine, $-\overset{|}{\underset{|}{C}}-X$ (X = Cl, Br, or $-\overset{|}{N}-$) | 10–65 |
| Alcohol or ether, $-\overset{|}{\underset{|}{C}}-O$ | 50–90 |
| Alkyne, $-C\equiv$ | 60–90 |
| Alkene, $\diagdown C=$ | 100–170 |
| Aryl,  | 100–170 |
| Nitriles, $-C\equiv N$ | 120–130 |
| Amides, $-\overset{O}{\overset{\|\|}{C}}-\overset{|}{N}-$ | 150–180 |
| Carboxylic acids, esters, $-\overset{O}{\overset{\|\|}{C}}-O$ | 160–185 |
| Aldehydes, ketones, $-\overset{O}{\overset{\|\|}{C}}-$ | 185–215 |

## TABLE 13.3 Characteristic Infrared Absorptions of Functional Groups

| GROUP | | FREQUENCY RANGE $cm^{-1}$ | INTENSITY[a] |
|---|---|---|---|
| **A. Alkyl** | | | |
| C—H (stretching) | | 2853–2962 | (m-s) |
| Isopropyl, $-CH(CH_3)_2$ | | 1380–1385 | (s) |
| | and | 1365–1370 | (s) |
| *tert*-Butyl, $-C(CH_3)_3$ | | 1385–1395 | (m) |
| | and | ~1365 | (s) |
| **B. Alkenyl** | | | |
| C—H (stretching) | | 3010–3095 | (m) |
| C=C (stretching) | | 1620–1680 | (v) |
| $R-CH=CH_2$ | (out-of-plane C—H bendings) | 985–1000 | (s) |
| | and | 905–920 | (s) |
| $R_2C=CH_2$ | | 880–900 | (s) |
| *cis*-RCH=CHR | | 675–730 | (s) |
| *trans*-RCH=CHR | | 960–975 | (s) |
| **C. Alkynyl** | | | |
| ≡C—H (stretching) | | ~3300 | (s) |
| C≡C (stretching) | | 2100–2260 | (v) |
| **D. Aromatic** | | | |
| Ar—H (stretching) | | ~3030 | (v) |
| Aromatic substitution type (C—H out-of-plane bendings) | | | |
| Monosubstituted | | 690–710 | (very s) |
| | and | 730–770 | (very s) |
| *o*-Disubstituted | | 735–770 | (s) |
| *m*-Disubstituted | | 680–725 | (s) |
| | and | 750–810 | (very s) |
| *p*-Disubstituted | | 800–840 | (very s) |
| **E. Alcohols, Phenols, Carboxylic Acids** | | | |
| OH (alcohols, phenols, dilute solns) | | 3590–3650 | (sharp, v) |
| OH (alcohols, phenols, hydrogen bonded) | | 3200–3550 | (broad, s) |
| OH (carboxylic acids, hydrogen bonded) | | 2500–3000 | (broad, v) |
| **F. Aldehydes, Ketones, Esters, and Carboxylic Acids** | | | |
| C=O stretch | | 1630–1780 | (s) |
| aldehydes | | 1690–1740 | (s) |
| ketones | | 1680–1750 | (s) |
| esters | | 1735–1750 | (s) |
| carboxylic acids | | 1710–1780 | (s) |
| amides | | 1630–1690 | (s) |
| **G. Amines** | | | |
| N—H | | 3300–3500 | (m) |
| **H. Nitriles** | | | |
| C≡N | | 2220–2260 | (m) |

[a]Abbreviations: s = strong, m = medium, w = weak, v = variable, ~ = approximately.