Circle one:         I wish to have my exam                    I wish to pick up
                    put in the rack.                          my exam.


Printed Name_____.
                    (Please print clearly)

Signature_____.

# CHEMISTRY 262

Exam I                                          February 5, 2013
100 Points                                          6:30 – 8:30 PM

This exam has <u>8 problems</u> on pages 2 through 8.

RULES

1.  The use of a calculator and model kits are **not** permitted.
2.  This exam is closed book and closed note. No aids other than writing implements are permitted.
3.  Answer the questions in the spaces provided on this exam.
4.  If you wish to ask a question about procedures or about a problem on the exam, raise your hand.


        1. _____              6. _____
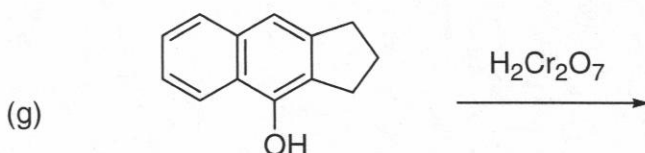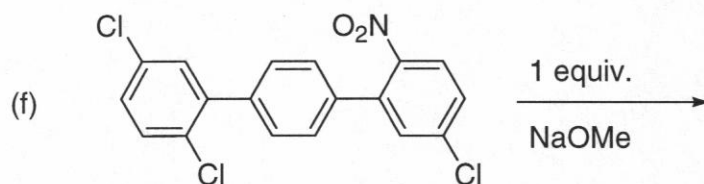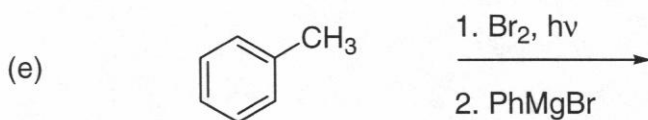
        2._____               7._____

        3._____               8. _____

        4. _____

        5. _____



                        TOTAL:       /100

1. Predict the major product or products (be inclusive) that you would expect to be formed in **five** of the following seven reactions. If you feel that no reaction will occur, then answer no reaction. Be sure to answer **only** five problems. If you answer more than five, then *only your first five will be graded.* (**10 points/ 2 pts. each**)

(a)

CO, HCl

AlCl$_3$, CuCl

(b)

1) Me—C(=O)—Cl , AlCl$_3$

2) Zn(Hg), HCl

(c)

hot KMnO$_4$

H$_2$O

(d)

Me—C(Me)(Me)—Cl

AlCl$_3$

(e)

1. Br$_2$, hv

2. PhMgBr

(f)

1 equiv.

NaOMe

(g)

H$_2$Cr$_2$O$_7$
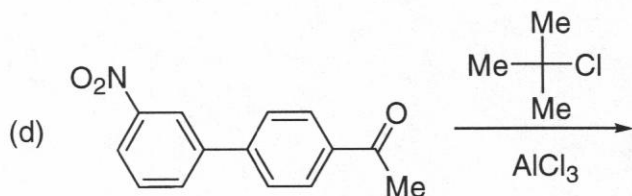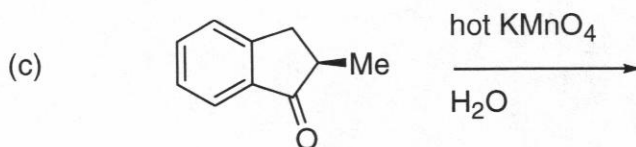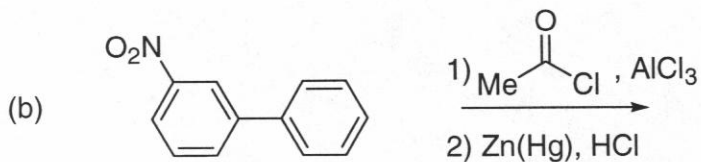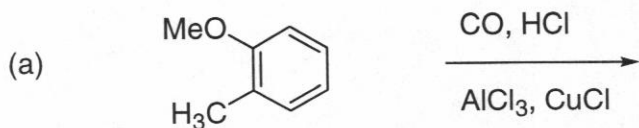
2. Fill in the reagents needed for accomplishing **two** of the three following transformations. More than one step is required. Remember that the order of the steps in a synthesis is important. Be sure to answer **only** two problems. (**6 points/ 3 pts. each**)

(a)



(b)



(c)
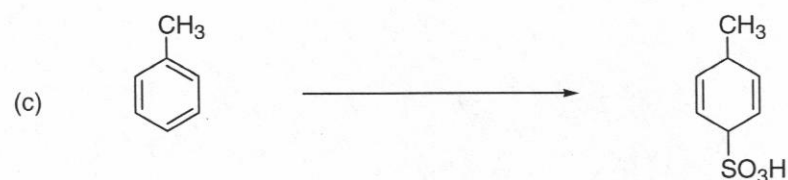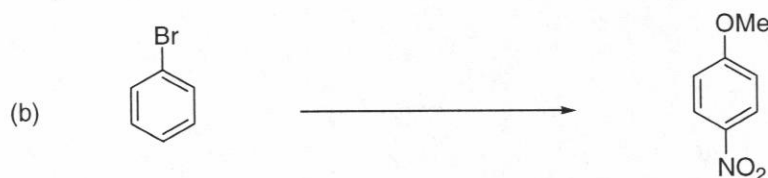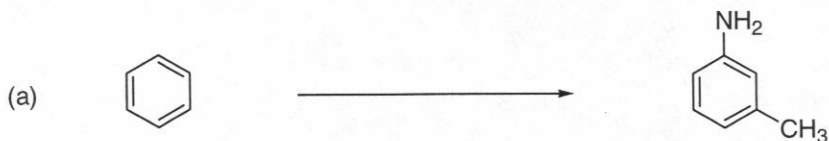


3.  **a.** What is the equilibrium constant for the following reaction? (**5 points**)



$$K_{eq} = ?$$

pKa (X = H) = 20

pKa = 35
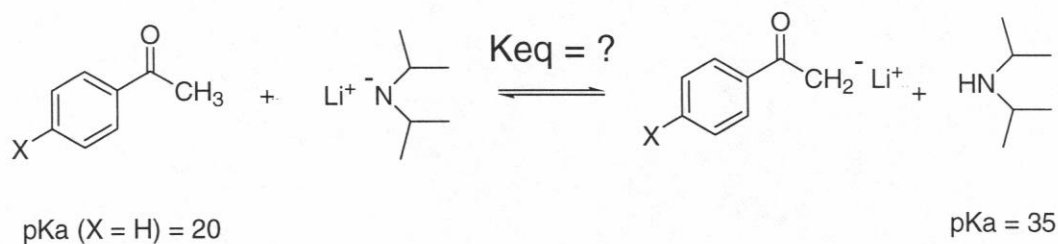
   **b.** The pKa given for the ketone was for a substrate where X = H. Would the pKa of the ketone be higher or lower than 20 if the substituent (X) was a nitro ($NO_2$) group? Why? (**4 points**)

**4.**     **a.** On several of the practice exams, you were asked about what would happen to an aromatic ring if you added or removed an electron from the π-system. Along the same lines, people have wondered what would happen if you added an electron to a system that is anti-aromatic. Does it become an aromatic ring? Show how you would answer this question with a consideration of cyclobutadiene (shown below). (**10 points**)



**b.** In part a, cyclobutadiene was pictured as a rectangle. Would the addition of an electron to cyclobutadiene to make the radical anion change this geometry? Why or why not? (**5 points**)

**5.** Suggest a synthetic scheme that would allow you to accomplish the following transformation. Make sure that you show your retrosynthesis – it will help. (**10 points**)
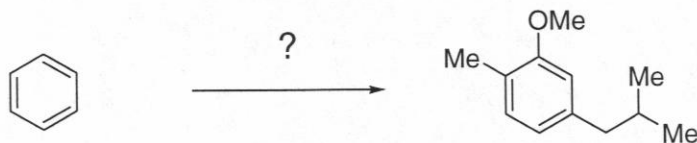


**6.** Consider each of the following mechanism questions:

**a.** Initially, it seems surprising that acylium ions form so easily during a Friedel-Crafts acylation. However, a consideration of orbitals can provide a nice rationale for this observation. With this in mind, draw the σ*-orbital for the C-Cl bond and the use your drawing to illustrate why acylium ions are so easy to generate. (**5 points**)
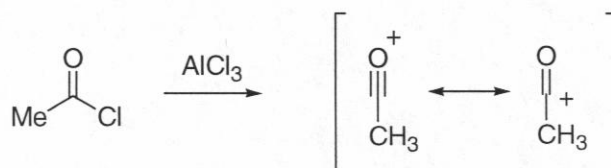
**b.** Write a "curved-arrow" mechanism for the following transformation. (**5 points**)
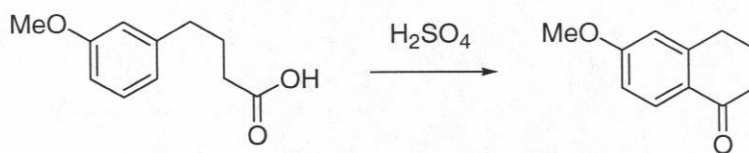


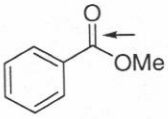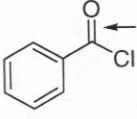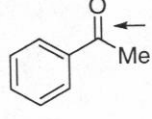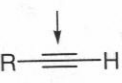**c.** Write a "curved-arrow" mechanism for the following transformation. (**5 points**)
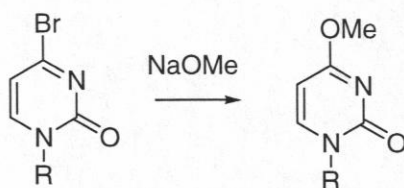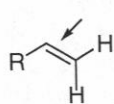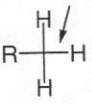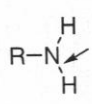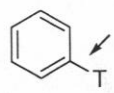


**d.** Would the equilibrium constant for the reaction illustrated below be less than or greater than one? In other words, which side of the equilibrium would favored? Why? (**5 points**)

**7. Parts a – e.** For each series of molecules illustrate below an arrow points to a bond. Rank the wavenumber that would be associated with the bond indicated from the highest (assign the number 1) to the lowest (assign the number 3) value. (**10 points**)
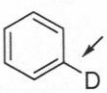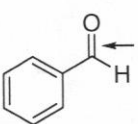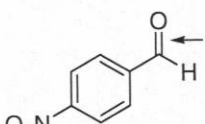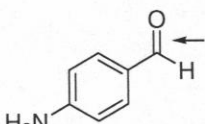
Answers for part f below:

a.

b.

c.

d.

(T = tritium)

e.

**f.** For each molecule that you labeled with a 1 in parts a – e, indicate the region of the IR spectrum (an approximate wave number or range of wave numbers) where you would find the stretch for the bond indicated. Write the number or range of numbers in the right hand margin next to the series above. (**5 points**)

**g.** For part e above, which aldehyde would have the most intense signal? Why? (**5 points**)

**8.**   **a.** In the following reaction only one of the two aromatic rings will be brominated in order to form either products A or product B. How could you use mass spectrometry to prove which ring brominated? (**5 points**)

1 equiv. Br₂

FeBr₃

+

**A**

OR

**B**
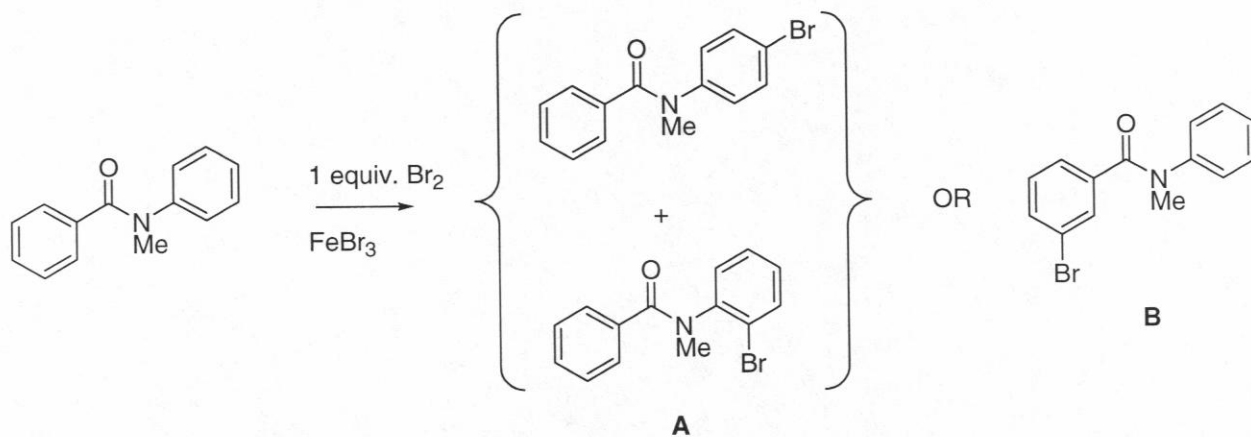
**b.** You can also use mass spectrometry in two different ways to determine if the reaction accidently adds two bromines to the substrate. One way is to simply measure the mass of the product. The other is to look at the parent peak for the product. How many lines would be observed for the parent peak of a product having two bromine atoms? What would the intensity of those lines be? (**5 points**)

# PERIODIC TABLE OF THE ELEMENTS

## Periodic Table

| 1 H 1.0079 | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3 Li 6.941 | 4 Be 9.0122 | | | | | | | | | | | 5 B 10.811 | 6 C 12.011 | 7 N 14.007 | 8 O 15.999 | 9 F 18.998 | |
| 11 Na 22.990 | 12 Mg 24.305 | | | | | | | | | | | 13 Al 26.982 | 14 Si 28.086 | 15 P 30.974 | 16 S 32.066 | 17 Cl 35.453 | |
| 19 K 39.098 | 20 Ca 40.078 | 21 Sc 44.956 | 22 Ti 47.88 | 23 V 50.942 | 24 Cr 51.996 | 25 Mn 54.938 | 26 Fe 55.847 | 27 Co 58.933 | 28 Ni 58.69 | 29 Cu 63.546 | 30 Zn 65.39 | 31 Ga 69.723 | 32 Ge 72.61 | 33 As 74.922 | 34 Se 78.96 | 35 Br 79.904 | |
| 37 Rb 85.468 | 38 Sr 87.62 | 39 Y 88.906 | 40 Zr 91.224 | 41 Nb 92.906 | 42 Mo 95.94 | 43 Tc (98) | 44 Ru 101.07 | 45 Rh 102.91 | 46 Pd 106.42 | 47 Ag 107.87 | 48 Cd 112.41 | 49 In 114.82 | 50 Sn 118.71 | 51 Sb 121.75 | 52 Te 127.60 | 53 I 126.90 | |
| 55 Cs 132.91 | 56 Ba 137.33 | 71 Lu 174.97 | 72 Hf 178.49 | 73 Ta 180.95 | 74 W 183.85 | 75 Re 186.21 | 76 Os 190.2 | 77 Ir 192.22 | 78 Pt 195.08 | 79 Au 196.97 | 80 Hg 200.59 | 81 Tl 204.38 | 82 Pb 207.2 | 83 Bi 208.98 | 84 Po (209) | 85 At (210) | |
| 87 Fr (223) | 88 Ra (226) | 103 Lr (260) | 104 Unq (261) | 105 Unp (262) | 106 Unh (263) | 107 Uns (262) | 108 Uno (265) | 109 Une (266) | 110 Uun (269) | 111 Uuu (272) | | | | | | | |

### Lanthanides

| 57 La 138.9 | 58 Ce 140.1 | 59 Pr 140.9 | 60 Nd 144.2 | 61 Pm (145) | 62 Sm 150.4 | 63 Eu 152.0 | 64 Gd 157.3 | 65 Tb 158.9 | 66 Dy 162.5 | 67 Ho 164.9 | 68 Er 167.3 | 69 Tm 168.9 | 70 Yb 173.0 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|

### Actinides

| 89 Ac (227) | 90 Th 232.04 | 91 Pa 231.04 | 92 U 238.03 | 93 Np (237) | 94 Pu (244) | 95 Am (243) | 96 Cm (247) | 97 Bk (247) | 98 Cf (251) | 99 Es (252) | 100 Fm (257) | 101 Md (258) | 102 No (259) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|