FINAL EXAMINATION
Organic Chemistry 130AL
Instructor: Mouser
December 7, 1998

Name: _____

Signature: _____
(MANDATORY)

CS24

10 point deduction for being in the wrong room

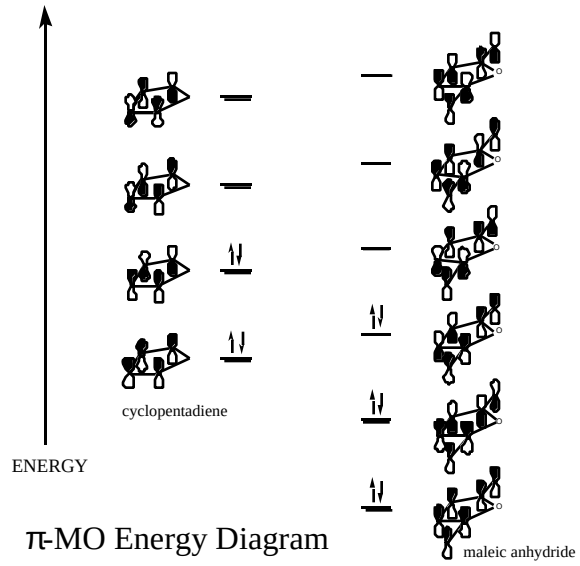
Place in this box the initial of your last name

Do Not Open This Exam Until Instructed To Do So!

Problem	Possible Points	Points Scored	Grader
1	10 points		
2-3	12 points		
4	14 points		
5	12 points		
6	10 points		
7-8	20 points		
9-10	25 points		
11	25 points		
12	10 points		
13	15 points		
14	36 points		
Total	189 points		

1. (4 points) Propose structures only for the ***major*** products **A** and **B**.

(6 points) At low temperature product **A** is formed. Explain using FMO theory **and the appropriate drawing(s).**

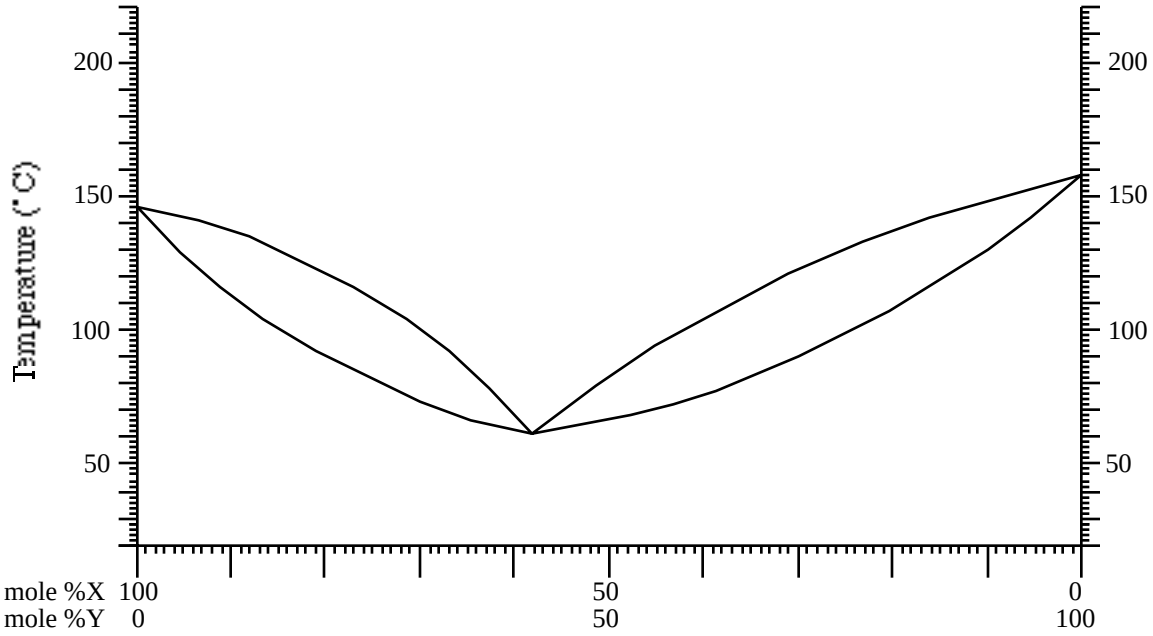


π-MO Energy Diagram

2. (6 points) Product **B,** from the previous problem, was recrystallized by a student. However, the student wasn't too careful and carried out the recrystallization in a wet (i.e., water contamination) flask. They isolated a white crystalline product with a sharp melting point at about 175°C. They also noted that this final product was soluble in 5% $NaHCO_3$(aq). **Propose a structure for this product.**

3. (6 points) In the Diels-Alder reaction the term "cracking" was used both in my lecture and in the text. What does "cracking" mean? **Give an example reaction with a very brief explanation for full credit.**

4. Refer to the below melting point–composition curve and answer the following questions.



a. (3 points) Melting point of pure compound **Y =** _____

b. (3 points) On a mole-per-mole basis what is the Eutectic composition?

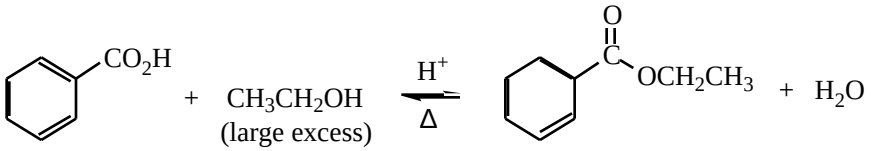
c. (4 points) Assuming compound **Y** as a 5% contaminant in **X** (on a mole-per-mole basis), what is the theoretical melting point range of compound **X** = _____

d. Assuming compound **X** is the expected product and compound **Y** is an impurity, if a ***sharp*** melting point is observed could it be certain that compound **X** is nearly pure? ***(circle)***

Yes or No

(4 points) ***Briefly explain your answer.***

5. (12 points) Benzoic acid is refluxed in excess ethanol in the presence of concentrated H_2SO_4 (catalysis) until equilibrium is reached (refer to the below equation). **Outline a separation scheme** for the isolation of *dry* ethyl benzoate (use any needed solvent and reagents). Note that ethyl benzoate is a liquid.



START HERE!

6. **(10 points)** Compound **W** is water insoluble. Referring to the below table, how many moles of **W** codistills with every mole of water at atmospheric pressure.

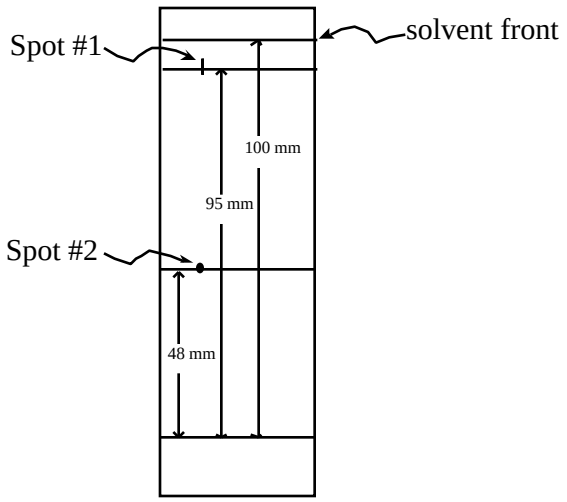
	Vapor Pressure (mm Hg)	
temperature(°C)	**Water**	**Compound W**
93	588	45
94	611	46
95	634	47
96	657	49
97	682	51
98	707	53
99	733	56

7. a. (6 points) If a 6.0 mL aqueous solution contained 600 mg of **Compound X** and was extracted with 6.0 mL of CH_2Cl_2, how much **X** would be in the organic layer? **Show your work for full credit.**

Given: Solubility of **X** in water at room temperature = 120 mg/mL
Solubility of **X** in CH_2Cl_2 at room temperature = 120 mg/mL

b. (6 points) What if instead, the solution was extracted with **three** 2.0 mL portions of CH_2Cl_2, how much of **X** would be in the combined organic layers? **Show your work for full credit.**

8. (8 points) Calculate the R_f value for both Spot #1 and #2.



9. (9 points) In the aldol experiment, TLC was carried out on the starting material and final product. What were the relative R_f values for these three compounds? (supply structures and rank them according to increasing R_f values).

(6 points) For full credit, referring to the physical properties of the particular compounds explain the differences in the R_f values.

10. In the aldol experiment, the final product was recrystallized in a 1:1 mixture of toluene and ethanol.

a. **(6 points)** Why was a mixed solvent system used? Explain (and supply any appropriate diagram(s)).

b. **(4 points)** Why not recrystallize from toluene only? Explain.

11. Referring to Gas Chromatography, supply a diagram depicting the interaction of a 2-component system with the stationary phase in a gc column.

place diagram here

(**4 points**)

a. **(4 points)** In the above diagram, identify the stationary phase and solid support.

b. **(4 points)** Name two common carrier gases used in GC analysis.

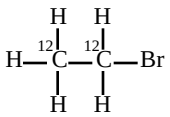
c. **(5 points)** If the flow rate was too high, what affect would this have on the separation of the above two component system? **Briefly Explain.**

d. **(4 points)** If a polar stationary phase column was used, rank the following components in increasing order of retention times: anisole, diethyl ether, methylene chloride, *ortho*-xylene.

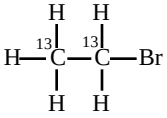
e. **(4 points)** If a nonpolar stationary phase column was used, rank the following components in increasing order of retention times: anisole, diethyl ether, methylene chloride, ortho-xylene.

12. (4 points) How many signals would the $^{13}C\{^{1}H\}$ NMR spectrum of ethyl bromide have?

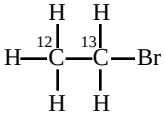
(6 points) The natural abundance of Carbon-12 is 99% and Carbon-13 is 1%. Given the below possible isotopic combinations (**A-D**), designate which molecule(s) would be responsible for the *singlet* signals in the $^{13}C\{^{1}H\}$ NMR spectrum of ethyl bromide (CIRCLE).



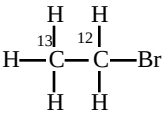
A



B

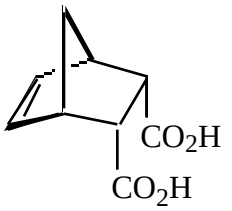


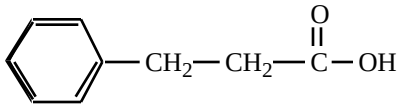
C

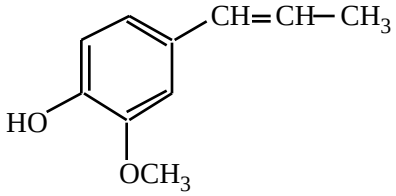


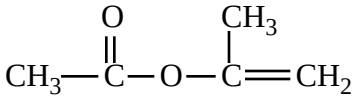
D

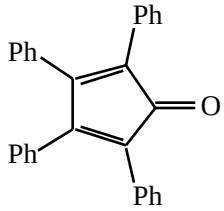
13. Match the appropriate compound with the below IR spectrum (**CIRCLE YOUR ANSWER**). (**15 points**) Justify your selection.

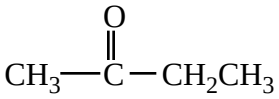


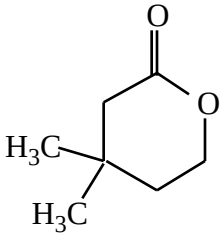


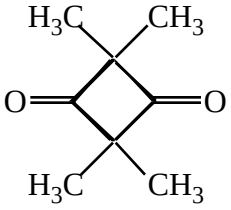


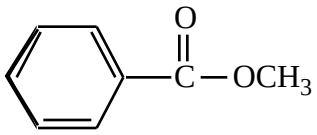


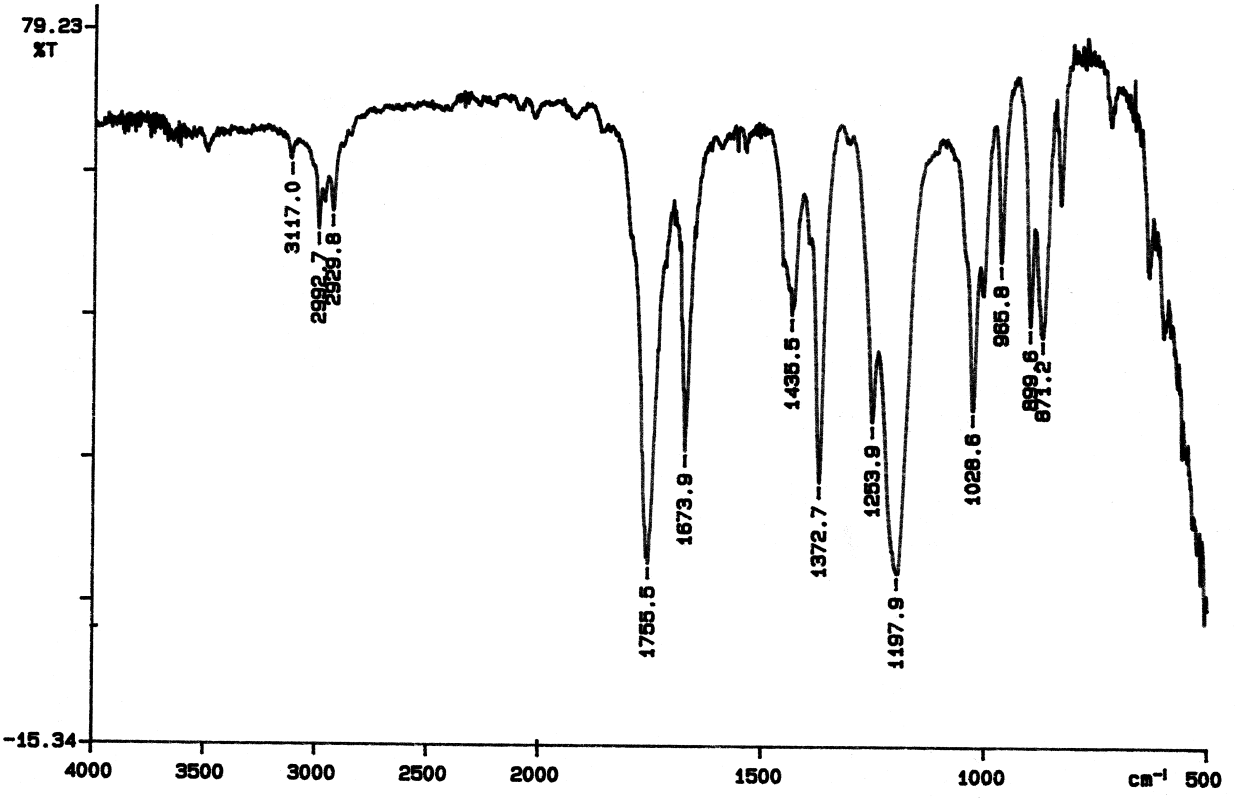




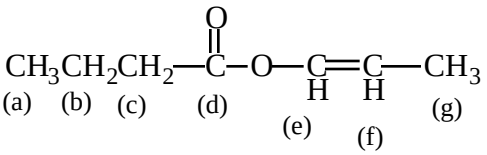


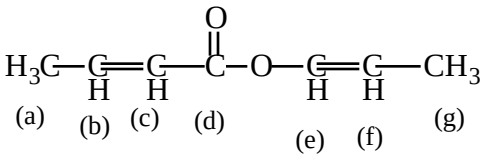


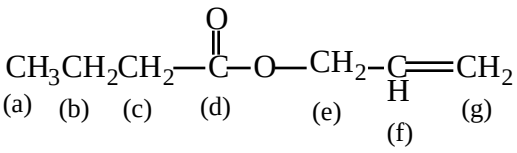


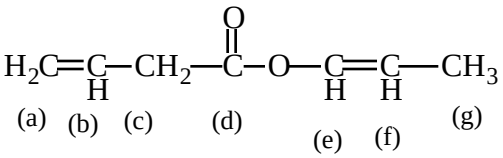


14. (**5 points**) Given the IR, $^{13}C\{^{1}H\}$, and DEPT spectra for compound **X** select the appropriate structure below (**CIRCLE**).









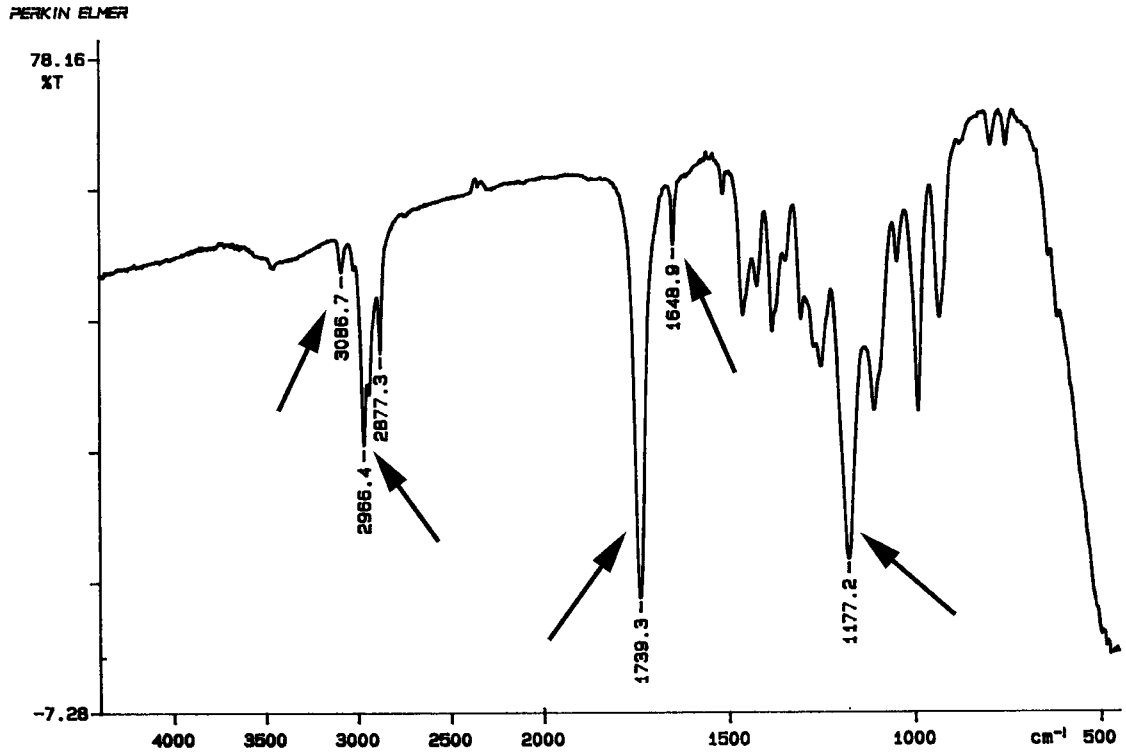
Do the following:

a. (10 points) In the below IR spectrum, assign the functional groups to all below vibrations designated by an arrow.

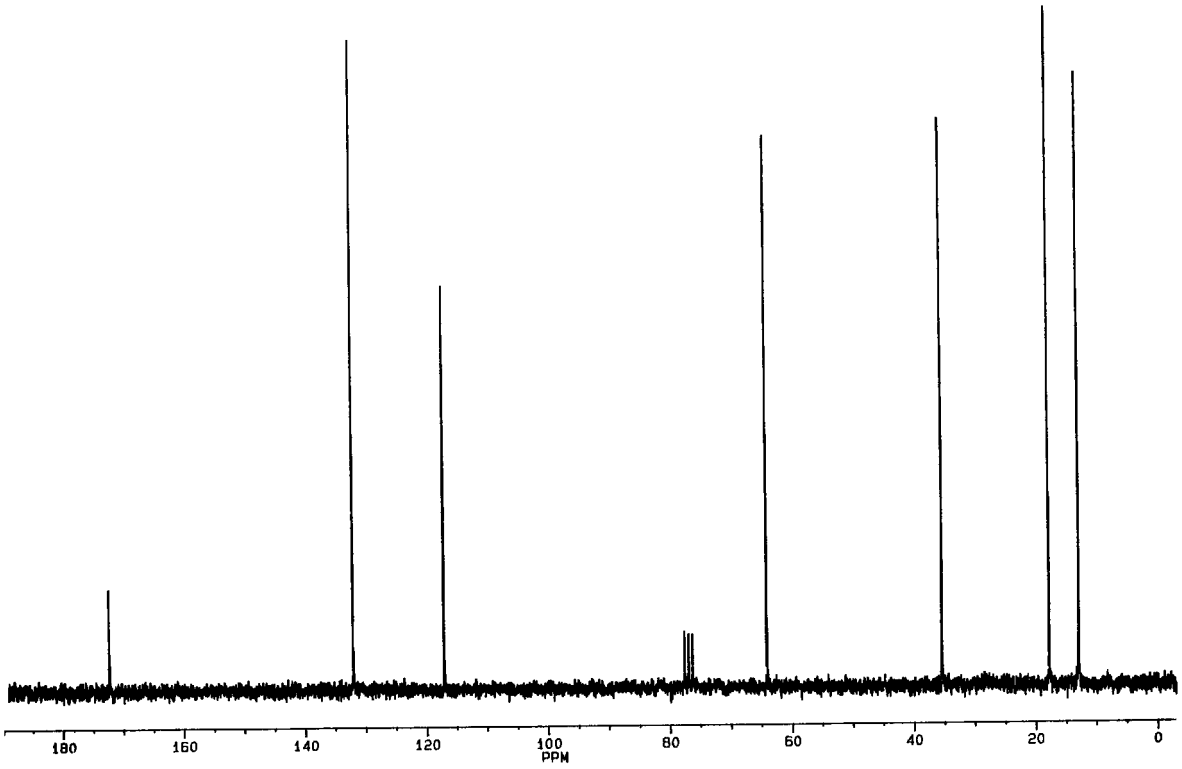
b. (14 points) Assign all signals in the $^{13}C\{^{1}H\}$ NMR on the next page. [Use the supplied lettering scheme (a) through (g).]

c. (7 points) Below the $^{13}C\{^{1}H\}$ NMR predict and draw the ^{13}C NMR spectrum.

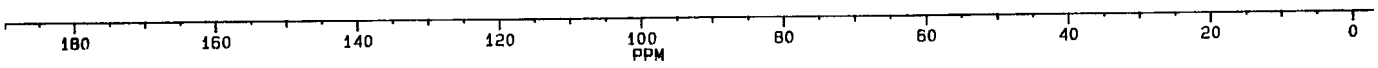
Note: DEPT is given on the page 11. You do not need to assign signals in the DEPT.



$^{13}C\{^{1}H\}$ NMR

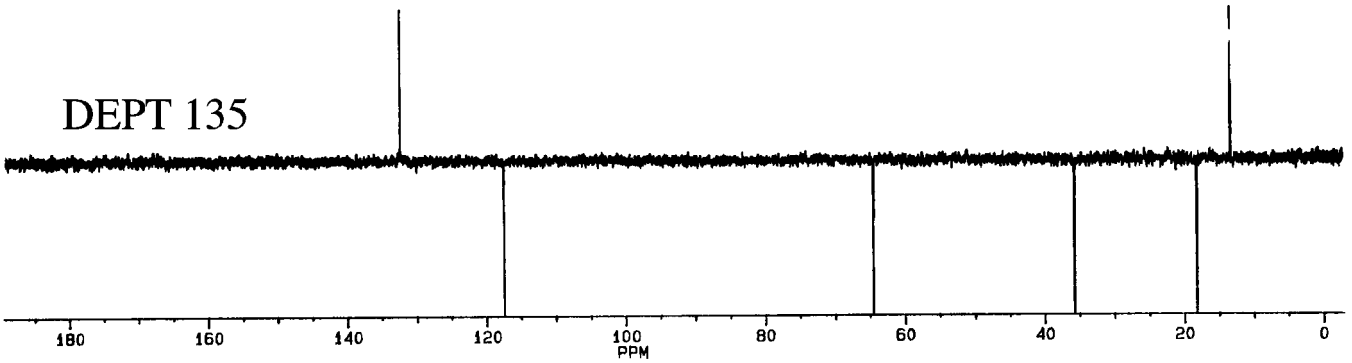


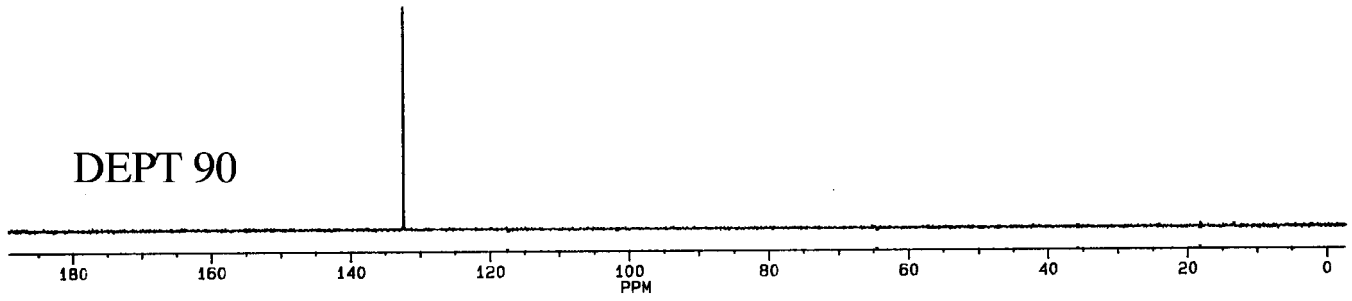
^{13}C NMR (SUPPLY below)

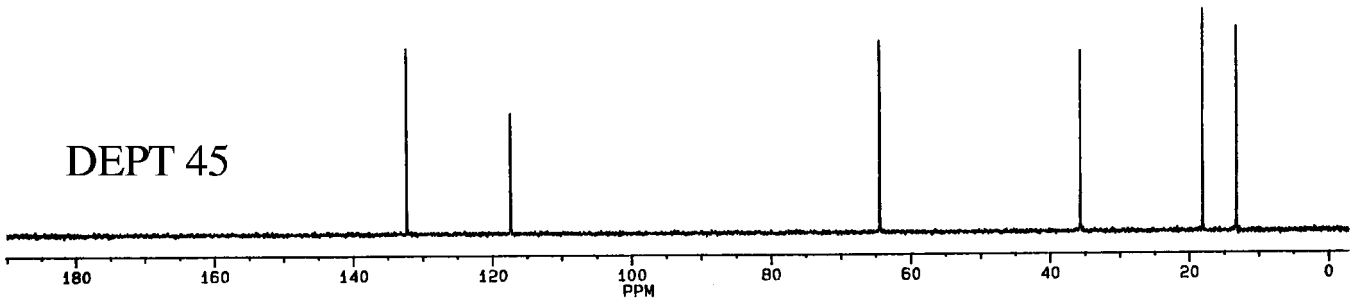


DEPT Logic Table

	# of attached hydrogens			
	0	**1**	**2**	**3**
DEPT 135	0	up	down	up
DEPT 90	0	up	0	0
DEPT 45	0	up	up	up

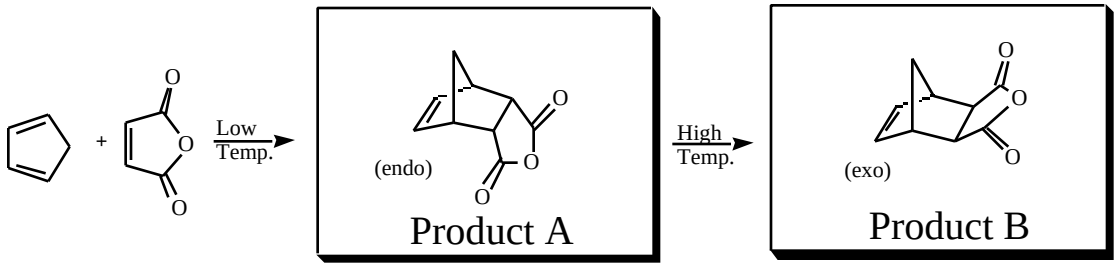


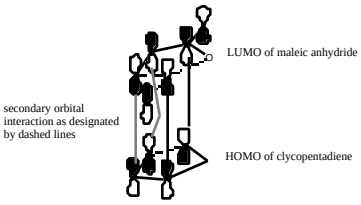




Condensed Answer Key
FINAL EXAMINATION
Organic Chemistry 130AL
Instructor: Mouser

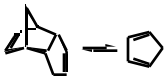
1.





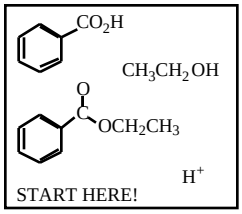
The endo product is the kinetic product. The secondary orbital overlap stabilizes the transition state (thus lowering the energy of the transition state).

2. exo diacid

3.  heating of the dimer results in thermal decomposition to the monomer cyclopentadiene

4. Refer to the below melting point–composition curve and answer the following questions.
   a. 158 (±1)
   b. 58 X: 42 Y
   c. 144-128
   d. No, cause at the Eutectic composition the melting point is sharp!
      [if Yes is given, then full credit if it is mentioned that the compound melts at 146°C]

5.



1. disolve in diethyl ether or methylene chloride
2. extract with aqueous 5-10% $NaHCO_3$
3. isolate organic layer
4. dry over Na_2SO_4
5. evaporate off ether (or methylene chloride)

6. 0.075 moles **W** distills with every mole of water

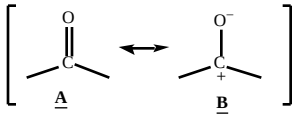
7. Work must be shown for full credit.
   K = 120 mg/mL÷ 120 mg/mL = 1.00

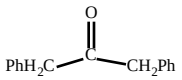
   a. 300 mg was isolated.
   b.

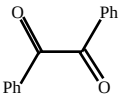
$$\text{Amount of solute extracted} = 600 - 600\left(\frac{6}{1\left(\frac{6}{3}\right) + 6}\right)^3 = 27 \div 64 = 600 - 253 \text{ mg} = 347 \text{ mg (or 350 mg)}$$

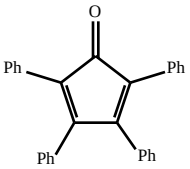
8. R_f #1 = 0.95 (or 19/20)
   R_f #2 = 0.48 (or 12/25)

9. dibenzyl ketone, benzil, tetraphenylcyclopentadieone









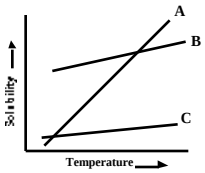
most polar least polar

Dibenzyl ketone has the largest dipole.

The dibenzyl ketone carbonyl dipole's oppose each other (however they don't completely cancel out.).

Resonance Structure **A** for the tetraphenylcyclopentadieone carbonyl group is not that strong of a contributor since it is antiaromatic. Also, a sterics argument could be used

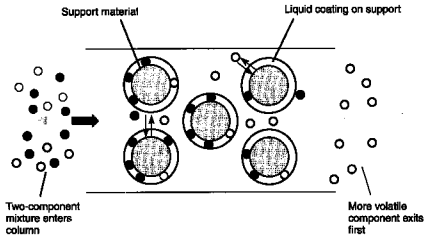
10. In the aldol experiment, the final product was recrystallized in a 1:1 mixture of toluene and ethanol.



Solubility vs. Temperature

A = 1:1 mixture; a steep solubility curve is optimal for recrystallization
B = toluene; soluble at all temperatures
C = ethanol; poor solubility at all temperatures.

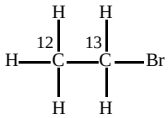
11.



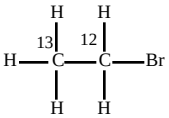
(**4 points**)

a. see above
b. Helium, Nitrogen.
c. poor resolution
d. methylene chloride, diethyl ether, *ortho*-xylene, anisole,
e. diethyl ether, methylene chloride, anisole, *ortho*-xylene

12. 2 signals

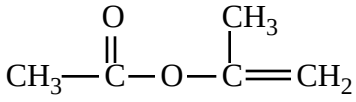


C



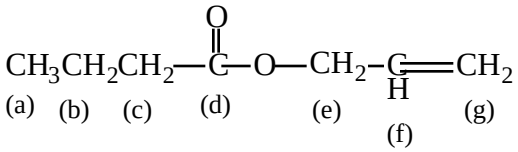
D

13.



assign IR signals for full credit

14.



a. $=CH_2$ stretch, C–H stretch, C=O stretch, C=C stretch, C–O stretch
b. (d), (f), (g), (e), (c), (b), (a) [in decreasing order of chemical shift]
c. (d) is a **singlet**
   (b), (c), (e) and (g) are **triplets** with splitting intensity of 1:2:1
   (a) is a **quartet** with splitting intensity of 1:3:3:1