

**INTRODUCTORY ORGANIC CHEMISTRY II --- PROBLEM SET #2**DISTRIBUTED: Thurs. Nov. 15<sup>th</sup>. COMPLETION DEADLINE: Thurs. Nov. 29<sup>th</sup> @ 10:15am.

**INSTRUCTIONS:** Work through all problems thoroughly and write your organized final answers in the space provided. Your written answers will be handed in; however, only some questions will be graded. The solutions will be posted after the due date. Keep a photocopy of your assignment (but hand in the original) so you can check your work promptly in preparation for the final exam. You will need to use your textbook for reference - some details may not be explicitly covered in class.

Problem #1 - Consider the following reaction:

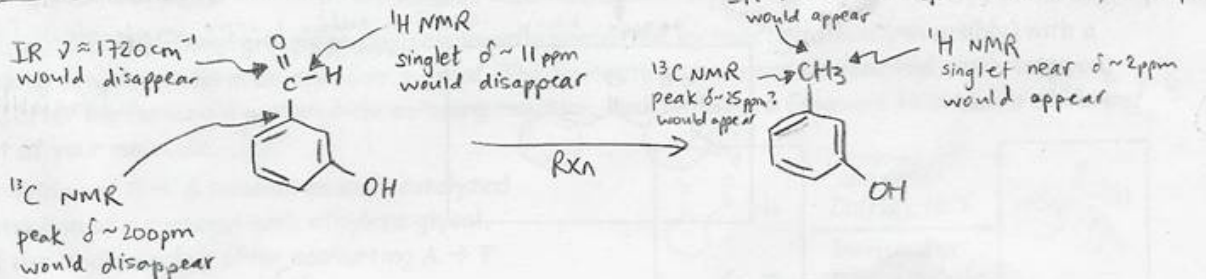
a) What reagents would you use to perform this transformation?

① thioacetal desulfurization: 1) 2RSH, H<sup>+</sup>, -H<sub>2</sub>Oor ② Wolff-Kishner reduction: H<sub>2</sub>NNH<sub>2</sub>, OH<sup>-</sup>, Δ

or ③ Clemmensen reduction: Zn(Hg), HCl

b) Briefly outline how you could use both IR spectroscopy and NMR spectroscopy to determine whether the reaction had occurred.

AS THE REACTION PROCEEDS...



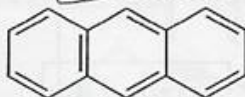
Problem #2 - Which of the following molecules are aromatic? If not aromatic, state which part(s) of Hückel's rules is/are not followed. aromatic if:  $4n+2 \pi e^-$  in uninterrupted cyclic array of p-orbitals

NOT AROMATIC



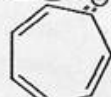
- ✓  $6e^- = 4n+2$   
 ✗ interrupted by  $sp^3 \text{ C}$

AROMATIC



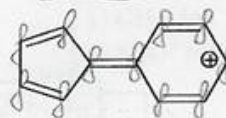
- ✓  $14e^- = 4n+2$   
 ✓ uninterrupted cyclic array

ANTI-AROMATIC



- ✗  $8e^- \neq 4n+2$   
 $8 = 4n$   
 ✗ uninterrupted cyclic array

AROMATIC



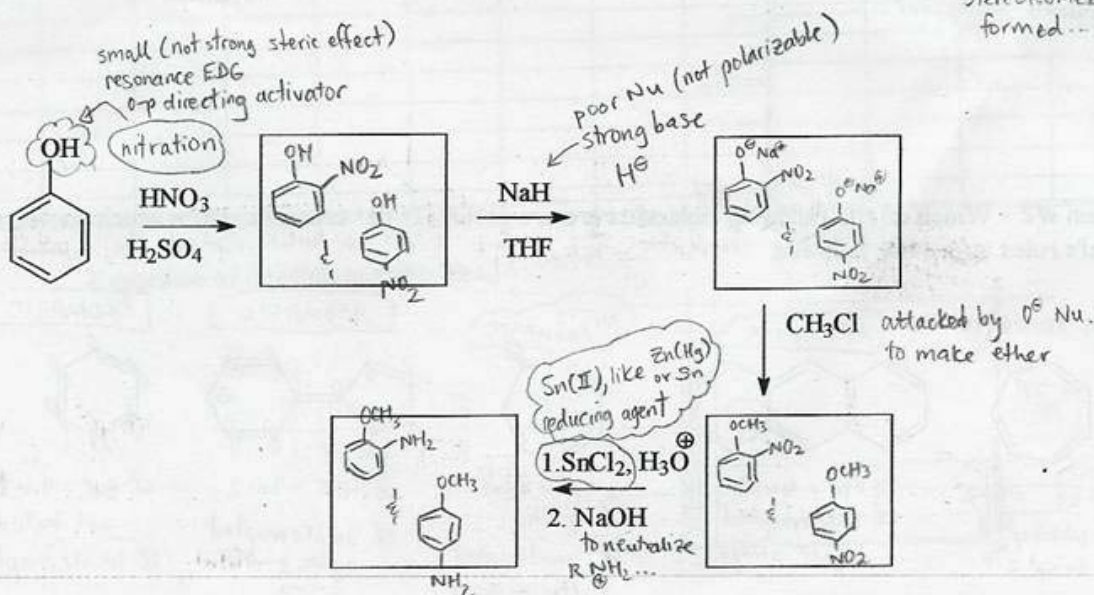
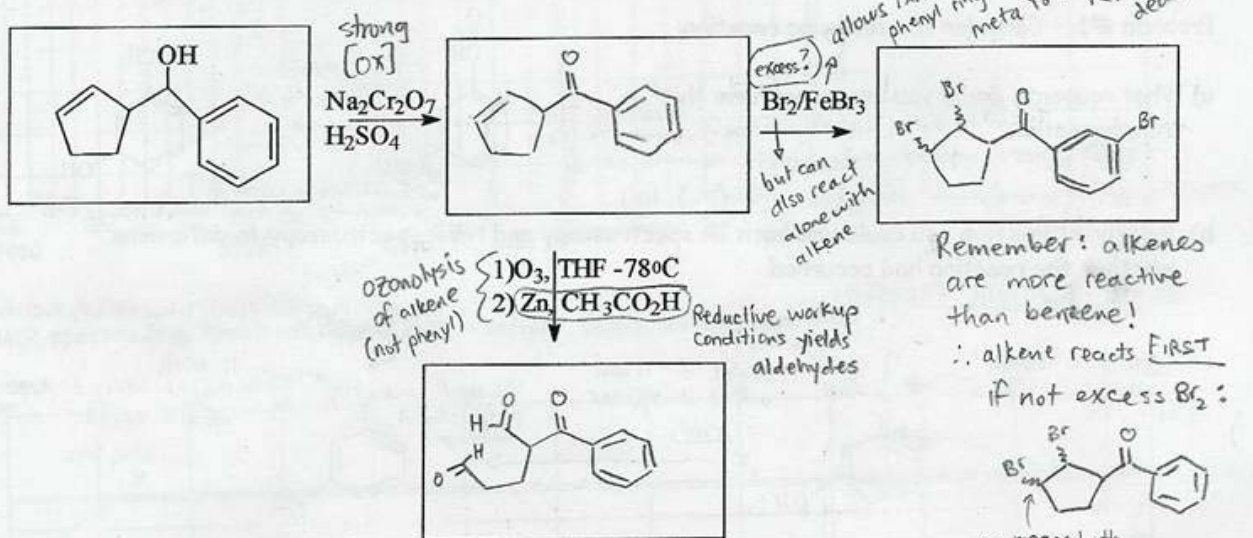
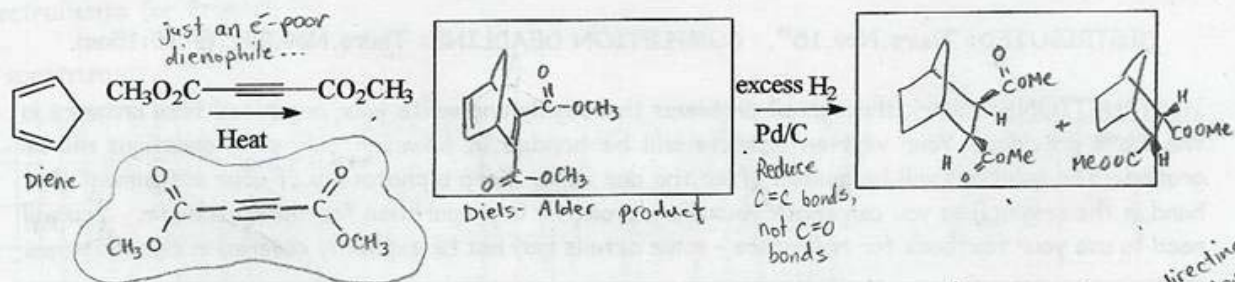
- ✓  $10e^- = 4n+2$   
 ✓ uninterrupted cyclic p-orbital array

AROMATIC

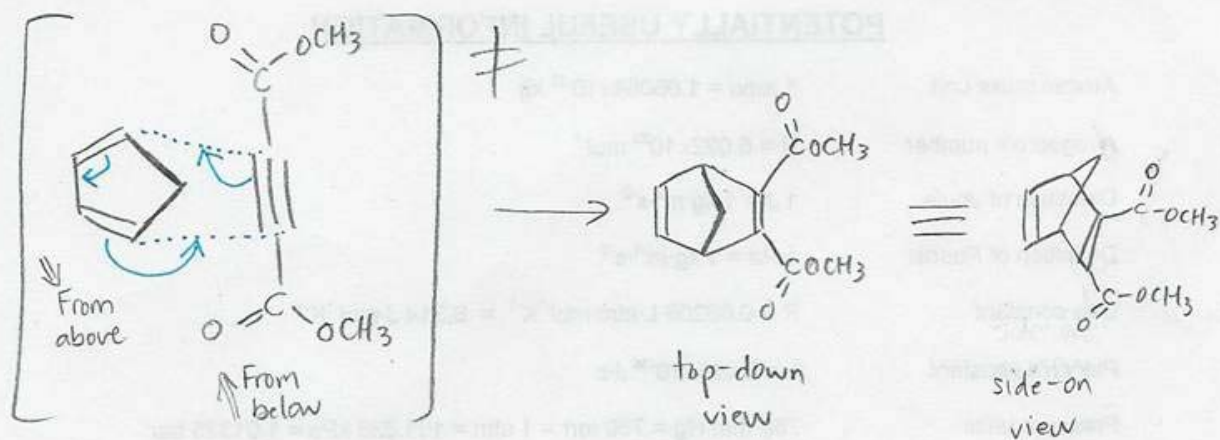


- ✓  $6e^- = 4n+2$  not including lone pair  
 ✓ uninterrupted...

Rogers

Problem #3 - Draw structures of the organic products expected in each of the following reactions.

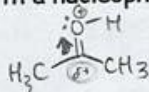
Problem #3 : Diels-Alder rxn





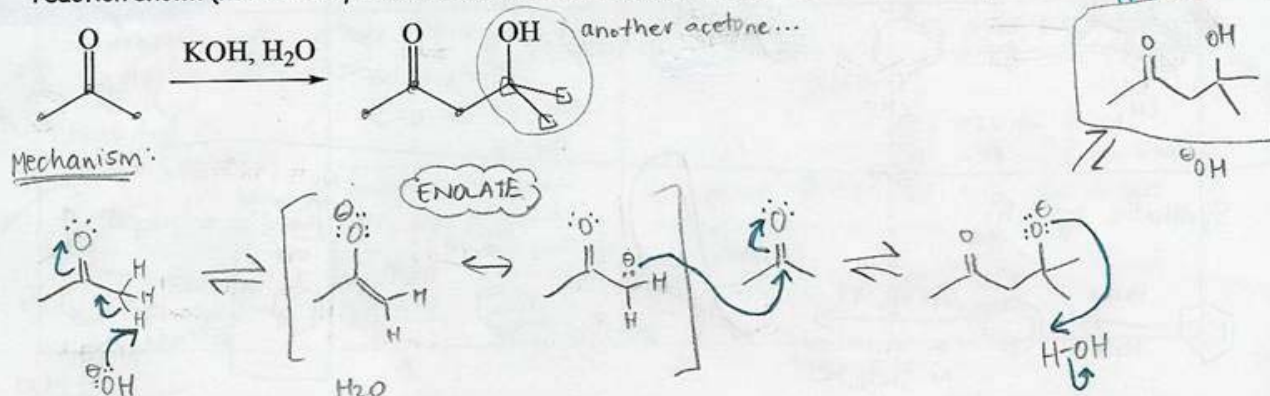
Rogers

**Problem #4 - a)** Consider acetone under acidic conditions: the O is protonated. Why does reaction with a nucleophile always occur at carbon rather than at the positive oxygen? (1-2 sentences max!).



A nucleophile is attracted to an electron-deficient centre such as the carbonyl carbon. Protonation of the oxygen makes it an even stronger EWG, amplifying the C=O polarity & the C's electrophilic nature.

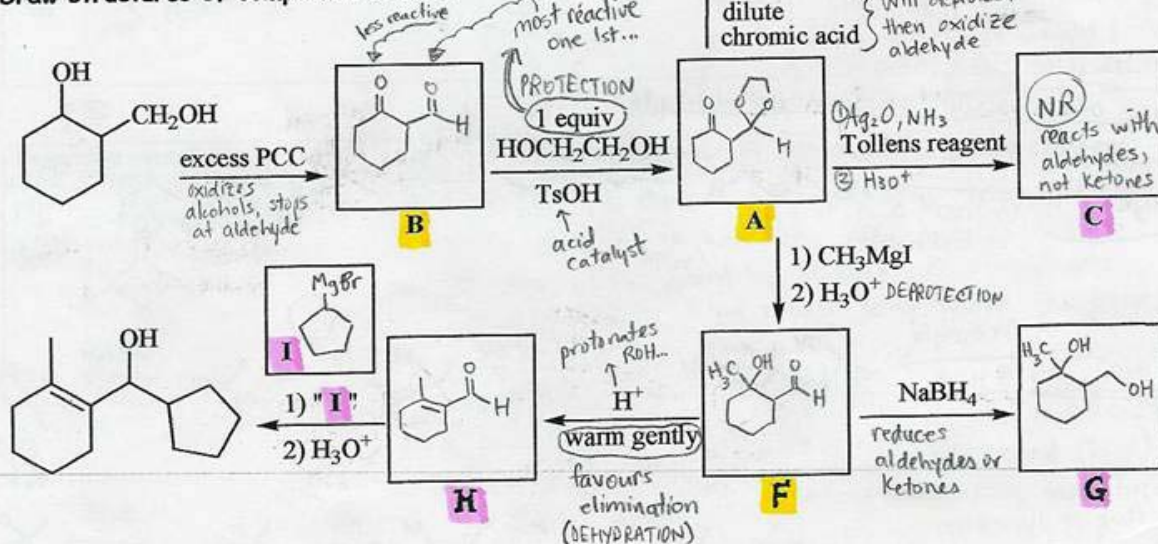
**b)** Consider acetone again, but this time under basic conditions. Write a full mechanism for the reaction shown (not the only reaction acetone can undergo under these conditions...).



**Problem #5 -** Carbonyl groups can be temporarily protected by reacting them (reversibly) with a masking reagent to form an *acetal* or a *ketal*. The protecting group can be removed easily later on; e.g., after performing a carbonyl-threatening reaction, such as using a Grignard to attack a *different* part of your molecule.

Conversion of **B**  $\rightarrow$  **A** involves an acid-catalyzed protection of a carbonyl with ethylene glycol, and the acidic workup after converting **A**  $\rightarrow$  **F** will cause deprotection.

Draw structures of compounds **A** to **I**.



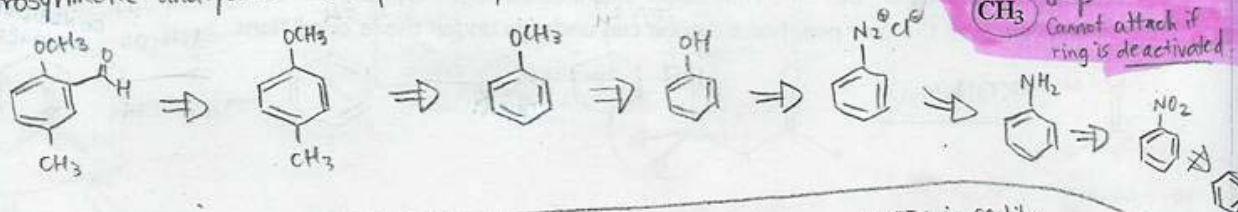


NOTE: Cannot do normal  $S_N1/2$  at  $sp^2$  C's (i.e. can't use Ph-Br to make Ph-OH)

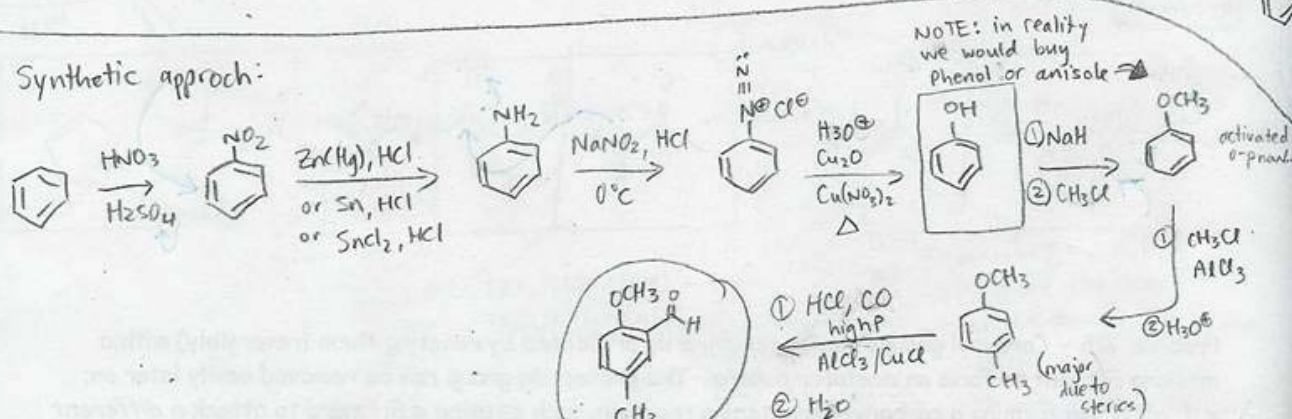
**Problem #6a** - Outline a sequence of reactions to synthesize the compound shown. Indicate the reagents and reaction conditions for each step. You can use benzene and any reagent with a maximum of 1 carbon atom and 1 functional group.

Hint: look in the textbook for conditions required for making benzaldehyde

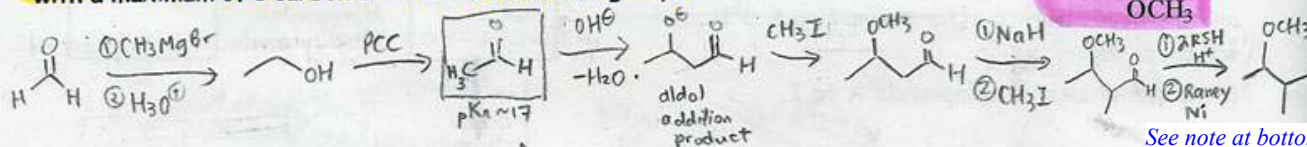
Retrosynthetic analysis: one possibility...



Synthetic approach:

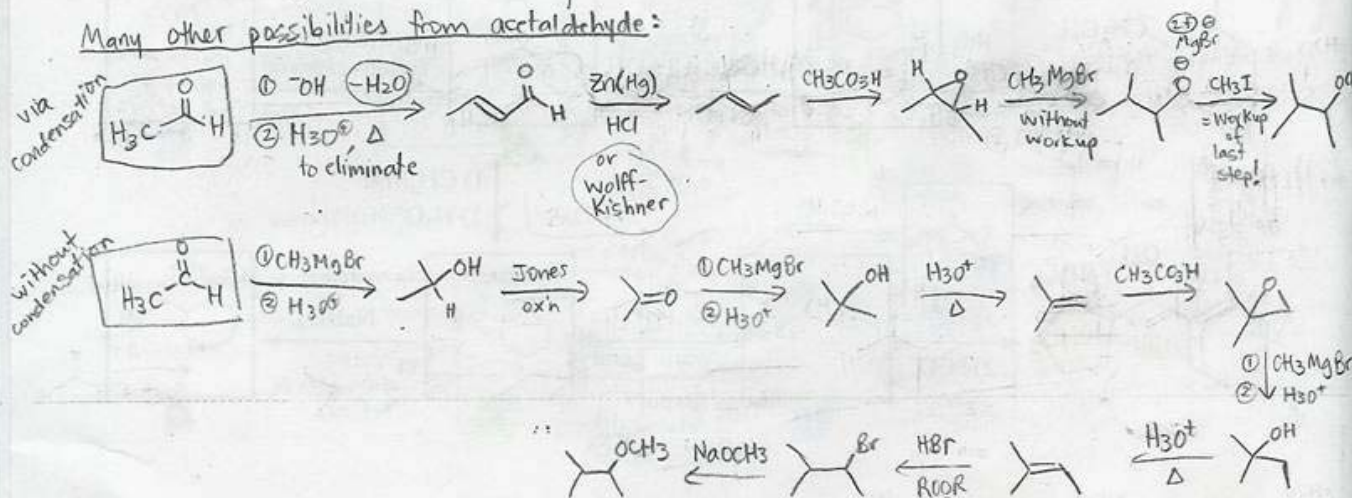


**Problem #6b** - Outline a sequence of reactions to synthesize the compound shown. Indicate the reagents and reaction conditions for each step. You can use any reagent with a maximum of 1 carbon atom and 1 functional group.



See note at bottom

Many other possibilities from acetaldehyde:



Last step of first strategy: deoxygenation of carbonyl...

- Clemmensen reduction: would likely not work fine  $\Rightarrow$   $OCH_3$  would be protonated in acid, so  $Cl^-$  would displace  $HOCH_3$
- Wolff-Kishner reduction: would likely work fine (basicity  $OR > ^-OH$ , so would not harm ether substituent)
  - Perhaps even a better choice than desulfurization of thioacetal (RSH may displace protonated  $OCH_3$ ...)

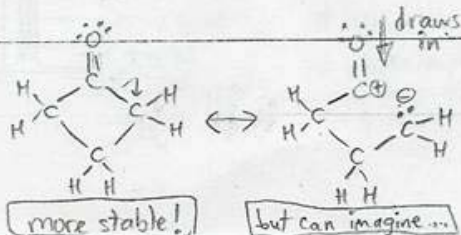


**Problem #7** - An unknown compound gives a molecular ion of  $m/z$  70 in the mass spectrum. It reacts with semicarbazide hydrochloride ( $\text{PhNHNH}_3\text{Cl}$ ) to give a crystalline derivative, but it gives a negative Tollens test. The NMR and IR spectra follow. Propose a structure for this compound, and summarize the information learned from each piece of data in the table provided. Briefly explain why the signal at  $1790\text{ cm}^{-1}$  appears at an unusual frequency.

Reactivity data	Mass spectral data	IR data	$^{13}\text{C}$ NMR data
Semicarbazide test $\Rightarrow$ aldehyde / ketone	$m/z$ 70 $\Rightarrow$ 70 g/mol not very large... $\text{C}=\text{O} \Rightarrow$ 28 g/mol... $\therefore$ 42 left...	absence: OH NH $\text{C}\equiv\text{C}$ , $\text{C}\equiv\text{N}$ $\text{C}=\text{C}$ , $\text{C}\equiv\text{N}$	3 peaks $\Rightarrow$ 3 carbon environments
Tollens test $\ominus$ $\Rightarrow$ NOT aldehyde	Combine with NMR: $^{13}\text{C}$ tells 3 types of C (210) $\text{C}=\text{O}$ = 28 g/mol so far (48) C + 12 + 2H? (10) C + 12 + 2H? 14 left another $\text{CH}_2$ ?	presence: $2900\text{--}3000\text{ cm}^{-1}$ $\text{sp}^3\text{C-H}$ $1790\text{ cm}^{-1}$ $\text{C}=\text{O}$ $< 400\text{ cm}^{-1}$ $\text{CH}_3$ ?	① $\delta \sim 210\text{ ppm}$ $\text{C}=\text{O}$ ② $\sim 48$ $\text{sp}^3\text{C}$ near EWG ③ $\sim 10$ shielded $\text{sp}^3\text{C}$
$\therefore$ KETONE 			

$^1\text{H}$ NMR data
2 signals $\Rightarrow$ 2 hydrogen environments only...
<p>① <math>\delta</math> 3.15 ppm, triplet, (4H)  <math>\uparrow</math> near EWG (carbonyl)          coupled to 2 adjacent H's must be </p> <p>② <math>\delta</math> 2.05 ppm, quintet, (2H)  <math>\uparrow</math> farther from EWG.          coupled to 4 adjacent H's must be </p> <p>relative 2:1 ratio from integration</p>
 $\text{C}_4\text{H}_6\text{O}$ only way to explain low molecular weight (70 g/mol) + symmetry (3C types, 2H types)

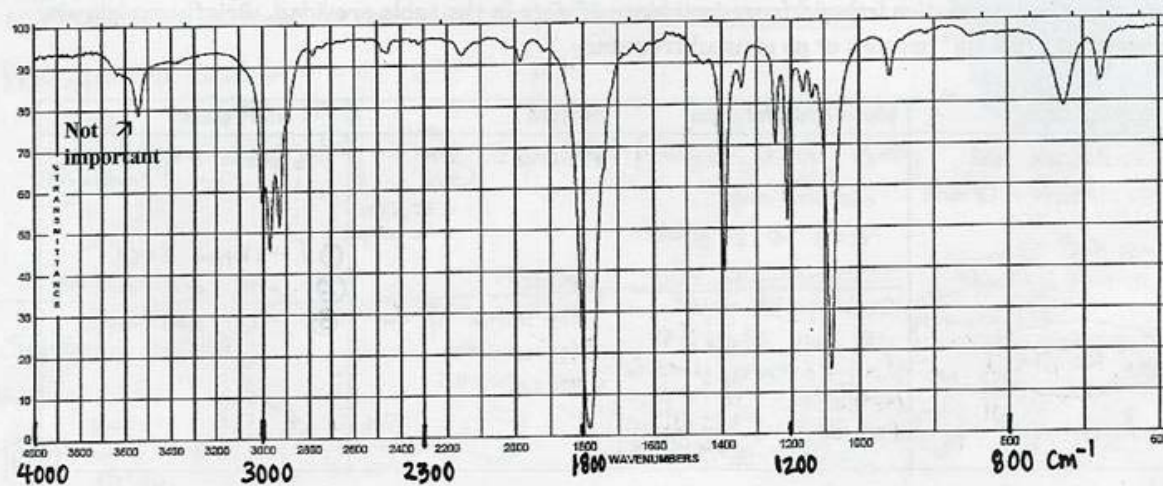
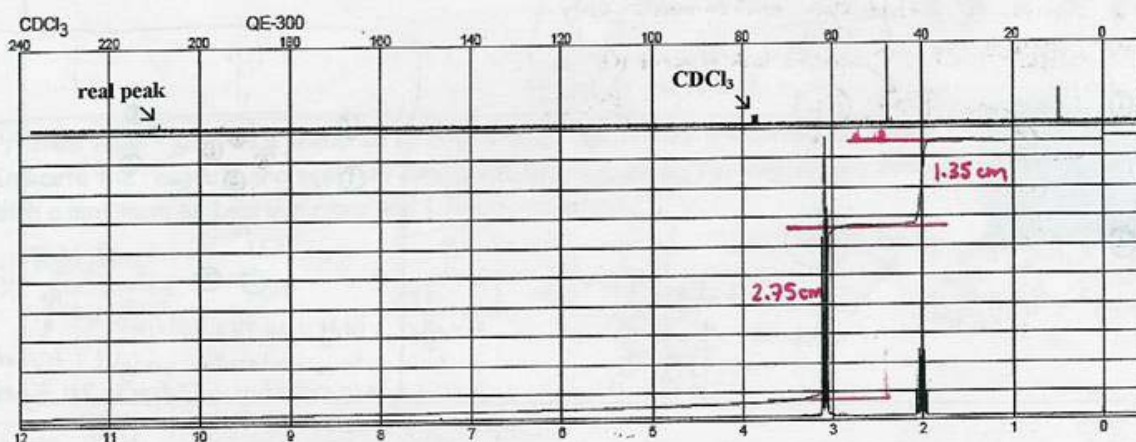
Proposed structure	& Explanation for unusual frequency of IR peak at $1790\text{ cm}^{-1}$
	$1790\text{ cm}^{-1}$ is higher frequency than ketone $\text{C}=\text{O}$ . This is seen normally for esters/acids, where electron-withdrawal by adjacent O strengthens the $\text{C}=\text{O}$ bond. Ring strain may cause this here:



i.e. this represents:  
weakened (bent)  $\sigma$ -bonds  
in ring must force  $\text{C}=\text{O}$   
carbonyl to pull more  
strongly on its unstrained  
 $\text{C}=\text{O}$  bond!

## Spectral data for Problem #7

IR spectrum:

NMR spectra (top spectrum  $^{13}\text{C}$ :  $\delta$  77ppm = solvent,  $\text{CDCl}_3$ ; bottom spectrum  $^1\text{H}$ ):Expansion of  $^1\text{H}$  NMR multiplets:

Ratio:

$$\frac{2.75 \text{ cm}}{1.35 \text{ cm}} \approx \frac{2}{1} = \frac{4}{2} \dots$$

