

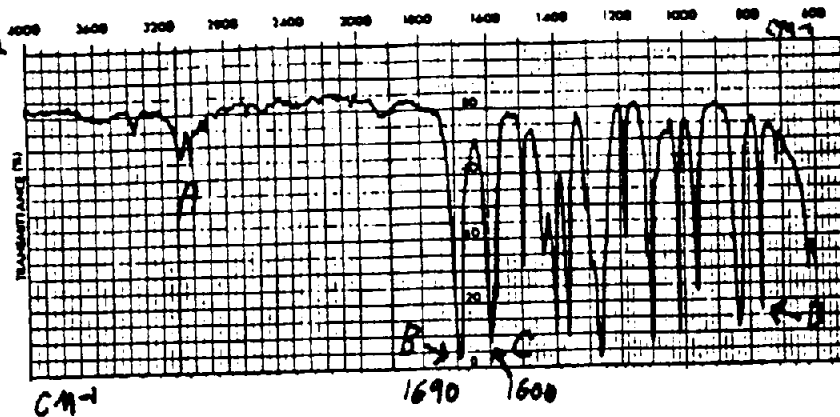
NAME: MAG NETIK & BEN ZEEN

Please use a non-red pen. Answer questions in the provided space. If you write any answers on the back of the page, indicate this on the front of that page. **Good Luck!**

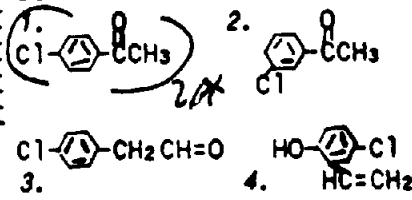
Note: Points appear in parentheses and in margin. USE IR AND NMR TABLES WHICH ARE AT THE END OF THE EXAM.

Question	max. pts.	points
1. $6+3(2)+3$	= 15	
2. $7+3(2)+2$	= 15	
3. $3+3+3+4+4+2$	= 20	
4. $7+4+3+6$	= 20	
5. $6+7+2$	= 15	
6. $6+5+2(2)$	= 15	
<b>total</b>	<b>100</b>	

(15)  
6pt



A compound A  $C_8H_7OCl$  has the IR spectrum at the left. Label peaks a-d by their functional group. Using that information, circle the structure that fits best:



A: AROMATIC C-H (& ALIPHATIC C-H) STRETCH  
 B. C=O KETONE CONJUGATED WITH   
 C. DOUBLE BOND  
 D. PARA-DISUBSTITUTED BENZENE

1b. Write one IR fact that eliminates each of the other three wrong structures (try to use a different piece of IR evidence for each case).

3x2pt=6 } #2: ~~META~~-SUBSTITUTED BENZENE - SHOULD HAVE 2 PEAKS BELOW 3000  $cm^{-1}$   
 #3: NOT A KETONE, AN ALDEHYDE - SHOULD BE AT  $\sim 1725 cm^{-1}$  NOT 1690  
 #4: A PHENOL - SHOULD HAVE OH ( $\sim 3200$  BROAD PEAK)  $cm^{-1}$  & NO C=O

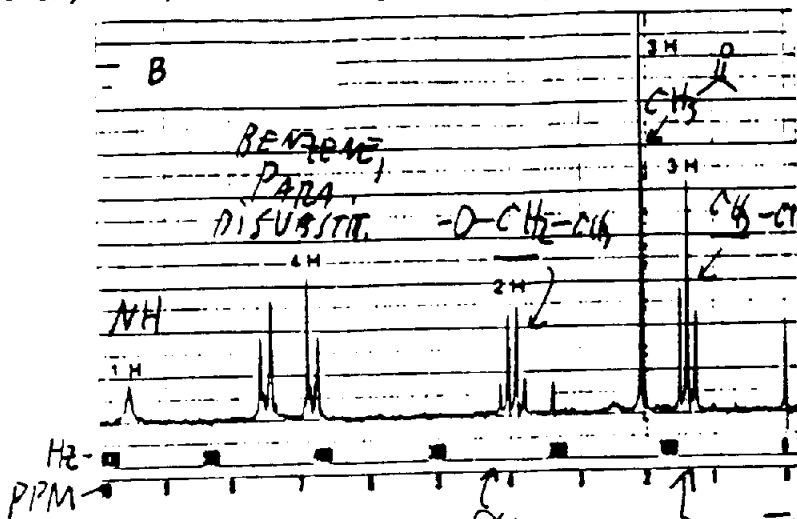
1c. Increased conjugation in a polyene shifts its UV absorption to longer shorter (circle one) wavelength. Explain your answer, relating to the energies involved.

3pt  
 INCREASED CONJUGATION BRINGS ENERGY LEVELS CLOSER TOGETHER SO LESS ENERGY (LONGER  $\lambda$ ) IS NEEDED FOR EXCITATION OF AN ELECTRON FROM HOMO  $\rightarrow$  LUMO

(15)

2a. An analgesic B,  $C_{10}H_{13}NO_2$  has the following proton NMR spectrum. Circle the correct structure for B. Explain your answer by assigning every NMR peak including splitting.

7 pt



1. CC(=O)Nc1ccc(OCC)cc1
2. CC(=O)Nc1ccccc1COC
3. CC(=O)Nc1ccc(OCC)cc1
4. CC(=O)Nc1ccc(OCC)cc1
5. CCOC(=O)Nc1ccc(CCC)cc1

QUARTET IS  $\underline{CH_2-CH_3}$  (DESHIELDED) SO  $\underline{O-CH_2-}$   
 TRIPLET IS  $\underline{CH_2-CH_2-}$

2b. Explain how the NMR data excludes 3 out of the 4 wrong structures. Clearly indicate which structures are discussed.

2 pt = 6

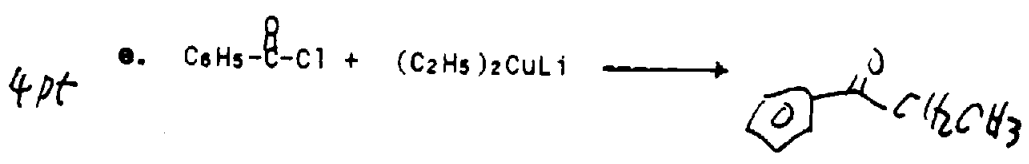
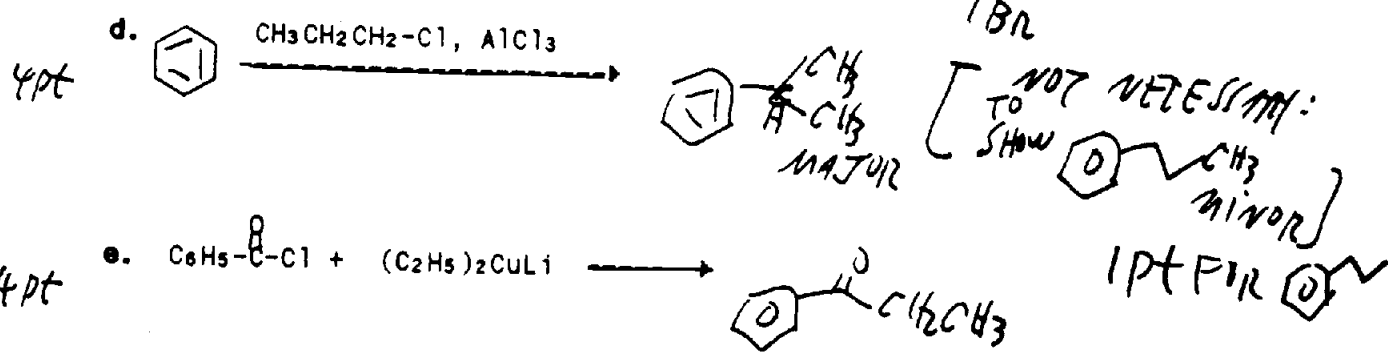
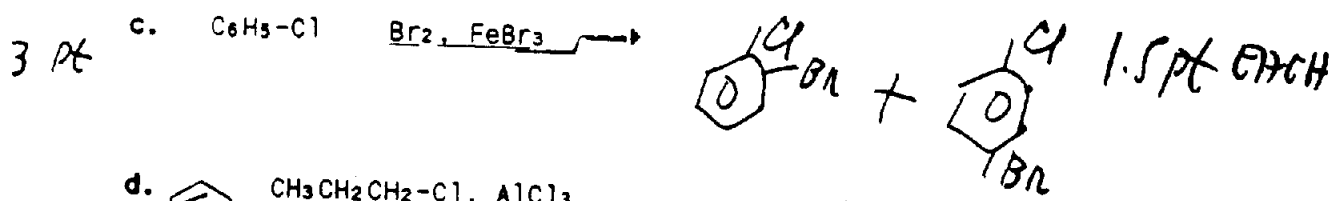
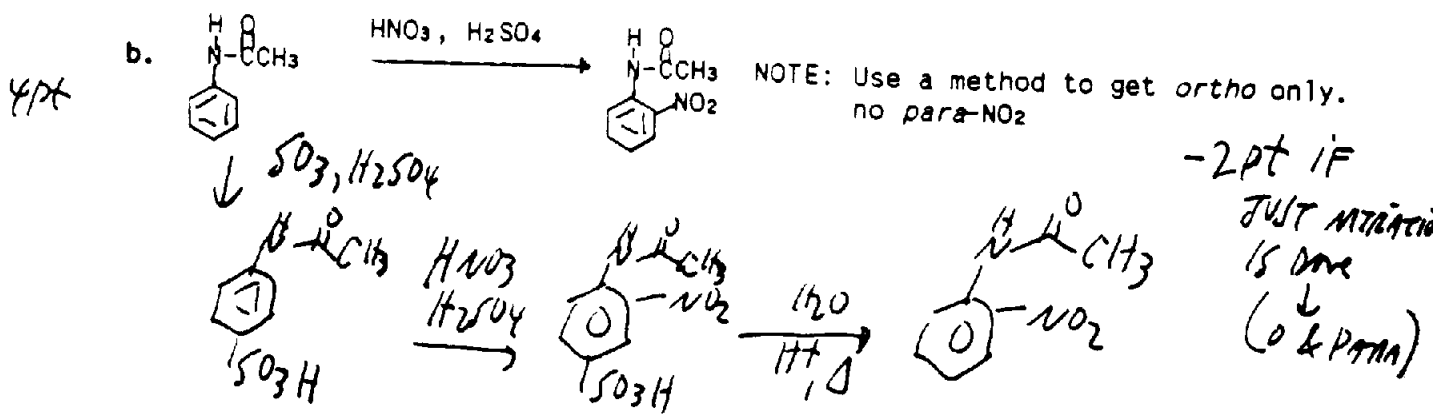
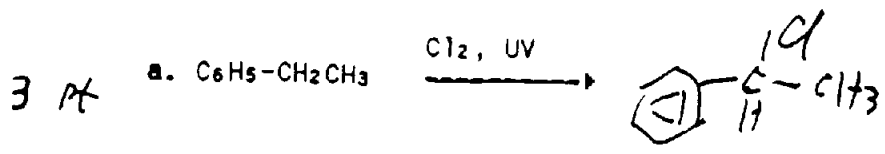
- #1 WOULD HAVE A SPLIT  $CH_3$  (DOUBLET) SINCE IT HAS  $-N-CH_3$  ALSO THIS  $CH_3$  DOUBLET IS ON NITROBEN SO <sup>WOULD BE</sup> BELOW 2.00
- #2 META, NOT PARA-DISUBSTIT, BENZENE SO AROMATIC IT WOULD NOT BE A "QUARTET", BUT A "BROAD SINGLET" (MULTIPLY)
- #4:  $\underline{CH_2-CH_3}$  QUARTET WOULD NOT BE AT 4.00 BUT AT  $\sim 1.80$  (NOT  $O-CH_2-CH_3$  HERE)
- #5 = AS FOR #4; ALSO HERE  $O-CH_3$  WOULD BE AT 3.50, NOT 2.0

2c. What energy levels are involved in IR spectroscopy (circle correct answer)

2 pt

1. electron energy levels (molecular orbitals)
2. vibrational energy levels
3. nuclear energy levels
4. rotational energy levels
5. none of the above

(20) 3. Write the expected **major** organic product(s) for each of the following reactions.

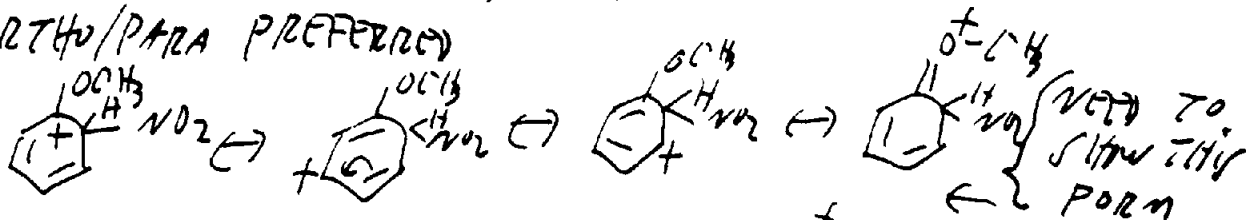


- f. Circle the correct following statement or statements about benzene:
1. Benzene tends to undergo addition rather than substitution reactions
  2. All of the hydrogen atoms are equivalent.
  3. The carbon-carbon bonds of benzene are alternatively short and long around the ring.
  4. The benzene ring is a distorted hexagon.
  5. None of the above.

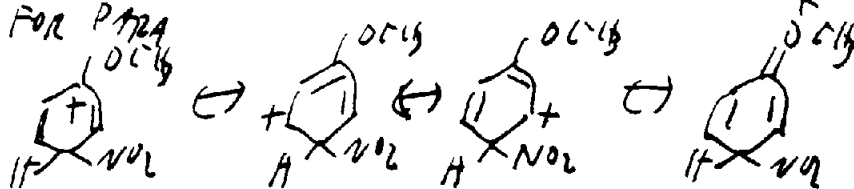
2 pt

4a. Using the resonance structures of the disubstituted intermediates involved predict the preferred orientation (ortho/para or meta) for the mononitration of anisole (methoxybenzene).

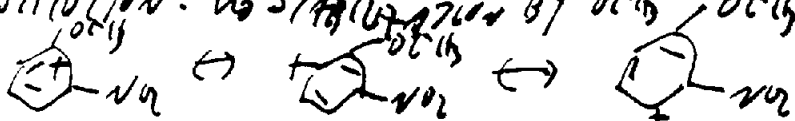
ORTHO/PARA PREFERRED



SAME FOR PARA



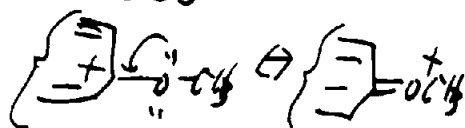
BUT META-SUBSTITUTION: NO STABILIZATION BY OCH<sub>3</sub>



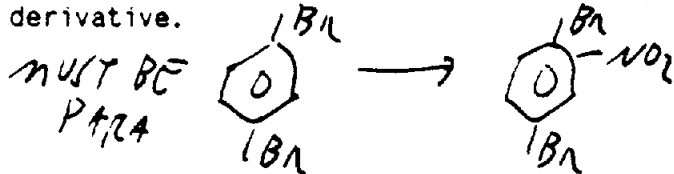
b. Does anisole nitrate faster or slower than does benzene? Explain.

4 pt FASTER, OCH<sub>3</sub> IS ELECTRON DONATING TO ADJACENT C<sup>+</sup>

CH<sub>3</sub> STABILIZES TRANSITION STATE

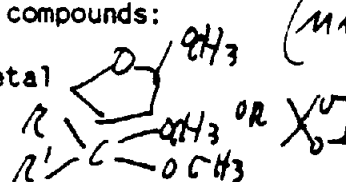


c. Which dibromobenzene can yield only one mononitro derivative? Write the structures of the dibromobenzene and the mononitrodibromobenzene derivative.

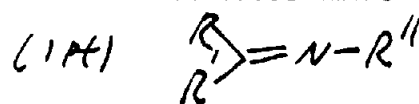


d. Write a structure using real groups (not R, R') for each of the following groups of compounds:

1. An acetal

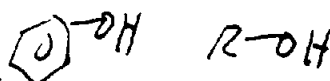


2. An N-substituted imine



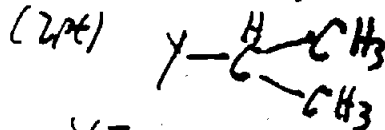
3. A compound which absorbs at 3600 cm<sup>-1</sup> in the IR

ANY OH OF ALCOHOL OR PHENOL



4. A compound's NMR has a doublet at δ 1.0 ppm (6H) and a septet at δ 1.8 (1H).

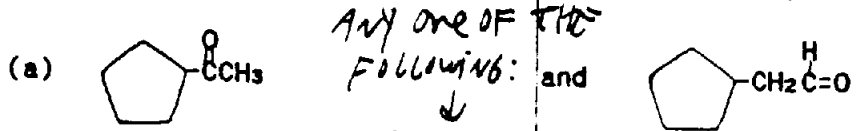
ANY ISO PROPYL CPD



WILL BE ACCEPTED.  
 (REALLY SHOULD BE H<sub>2</sub>O) → OH  
 ALCOHOL: ν<sub>OH</sub> - H BOND (OH)

Y = NO<sub>2</sub>, C<sub>6</sub>H<sub>5</sub> (ACCEPT OH, HALOGEN) ALSO

5. For the following pair of compounds, write a CHEMICAL TEST or REACTION that will distinguish them. Write the structures of major organic and inorganic products. For a TEST, what would you see?



6 pt

- $I_2, NaOH \rightarrow$  C1CCCC1 + CC(=O)I yellow ppt
- no such oxidation
- no such rxn
- a a

- no such rxn
- $H_2CrO_4$  (ORANGE)  $\rightarrow$   $Cr^{3+}$  (GREEN) + C1CCCC1C(=O)O
- $Ag(NH_3)_2^+ OH^- \rightarrow$  Ag mirror + C1CCCC1C(=O)O
- $Cu(NH_3)_2^+ \rightarrow$   $Cu_2O$  (RED PPT) + C1CCCC1C(=O)O

DEEP BLUE

(b) Using IR and proton NMR spectroscopy, distinguish between the following two compounds. Write two differences (one IR, one NMR) using specific values:

7 pt

CC(=O)c1ccccc1

IR AROMATIC BANDS (2) 900-600  $cm^{-1}$  OR OVERTONES 2400-1800 OR  $C=O \sim 1690$  CONT. KETONE

CC(=O)C1=CC=CC=C1

NO AROMATIC BANDS 900-600  $cm^{-1}$  NO OVERTONES KETONE 1715  $cm^{-1}$

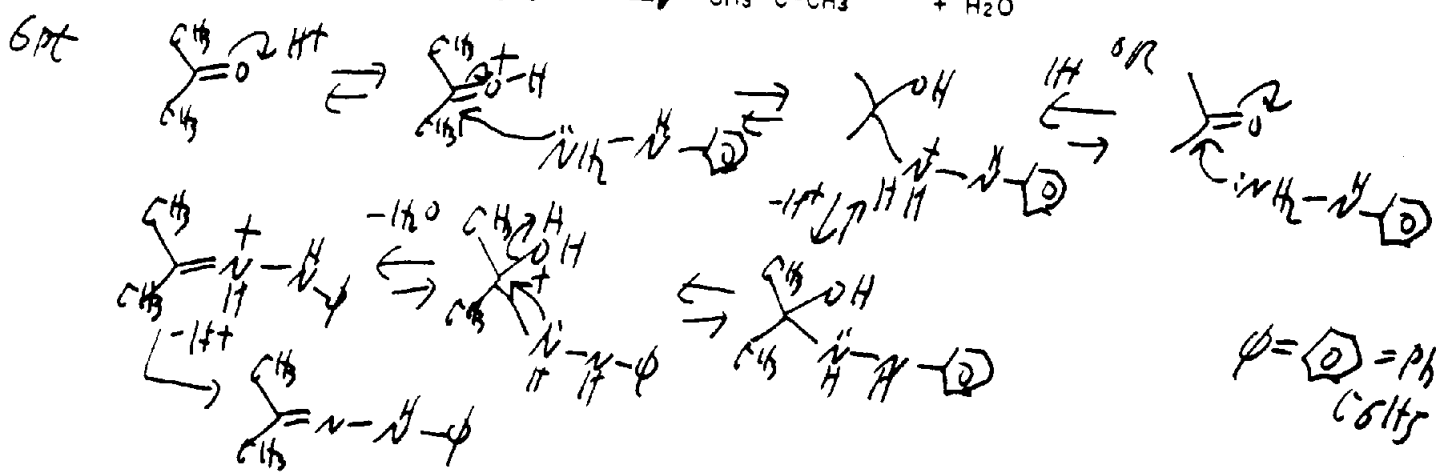
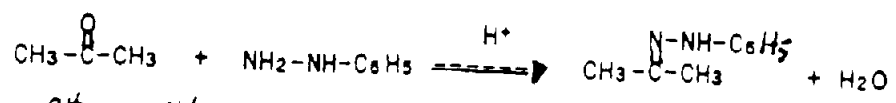
NMR AROMATIC MULTIPLET 7.30 NO  $C=C$  at  $\delta$  5-6  $CH_3$  - 2.05 SINGLET NO TRIPLET  $C_4H_3$   $\delta$  1

NO 7.30 PEAK  $H-C=C-H \sim \delta$  5-6  $CH_2$  QUARTET  $\delta > 2.0$  (~2.2?)  $CH_3$  - TRIPLET  $\delta$  1

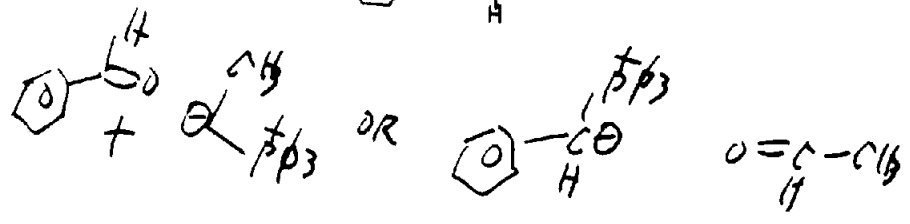
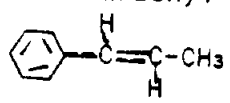
c. Which one of the following is not a synthesis of benzophenone O=C(c1ccccc1)c2ccccc2 : (NOTE: Ph =  $C_6H_5$ )

- 2 pt
- Cc1ccccc1 + CC(=O)Cl  $\xrightarrow{AlCl_3}$
  - OC(c1ccccc1)c2ccccc2  $\xrightarrow{NaBH_4 / CH_3OH}$
  - C=C(c1ccccc1)c2ccccc2  $\xrightarrow[2. Zn, H_2O]{1. O_3}$
  - OC(=O)c1ccccc1 + 2 LiC\_6H\_5  $\xrightarrow[2. H_3O^+]{1. reaction in Et_2O}$

(15) 6a. Write a step-by-step mechanism for the following reaction. Use arrows to show the direction of electron flow.



5pt b. Write two combinations of a carbonyl compound + a phosphorus-containing ylid which will give



c. Name the following compounds using IUPAC nomenclature:

