

Answer Key Correct structures are marked with an asterisk *

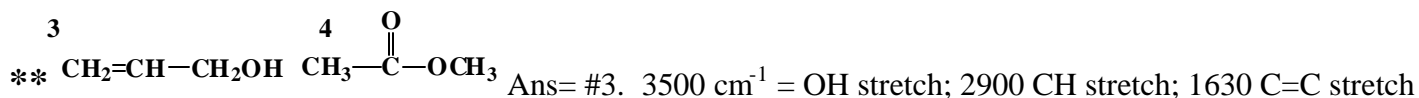
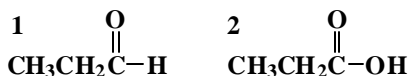
Name: _____

Grade: _____

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. Points appear in () and/or margins. **Good Luck!**

Question	Max Pts	Points	Question	Max Pts	Points
1. 5+6+4	= 15		4. 4+5+ 3+4+3	= 19	
2. 2+4+3+2+2+3	= 16		5. 4+4+3+4	= 15	
3. 5+3+5+4+3	= 20		6. 4+3+4+(2 x 2)	= 15	
Total				100	

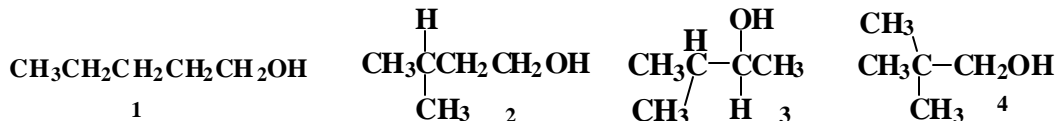
1. (15) a. A compound C_3H_6O has IR peaks at 3500 (broad), 2900, 1630 and nothing in the 1700-1800 cm^{-1} range. . Circle the correct structure below and explain your choice:



The spectrum shows hydroxyl and C=C double bonds, thus #3

5pt (2pt for structure, 3 pt for explanation)

1b. A compound $C_5H_{12}O$ has the following 1H NMR spectrum. Circle the correct structure by explaining every peak including areas and splitting. : δ = 1.0 ppm (d, 6H), 1.2 (d, 3), 1.5 (mult, 1), 3.6 (mult, 1)), 4.4 (s, 1).



Ans= #3

Twin methyls at δ 1.0 ppm give a doublet split by CH. CH_3 (C 4) =doublet at δ 1.2 (d,3), deshielded by OH
 CH (carbon 2) at δ 1.5 is a multiplet since it is split by 6H of the two methyls and also by CH of Carbon 3
 CH of carbon 3 is deshielded to δ 3.6 because of the OH group; it is a multiplet since split by C2 H and C4 methyl (counts as 1 H).

The OH is at δ 4.4 and UNSPLIT because protons on oxygen exchange ca 1000 times faster than the normal NMR "resonance" occurs (thus not enough time to interact with neighbors)

6pt (2 pt for correct structure; 4 pt for explanation)

1c. Explain how the NMR data excludes two of the wrong structures. BE SPECIFIC. Give real (approximate) numbers. **DO 2 OUT OF 3 ONLY**

4pt

No. 1 is excluded since it has only 1 CH_3 (δ =1) and 4 CH_2 groups which are deshielded to ca δ 1.7 and ca δ 3.6 for CH_2 next to OH (counts as 2 H here).

No.2 excluded ; has two CH_2 's: one at δ 1.7 and one at δ 3.6 (next to OH).

No. 4 excluded: has 3 CH_3 groups all together at δ 1.0 and **unsplit**; one CH_2 at δ 3.6 ppm.

2. (16) a. Using a 60 MHz NMR instrument, the ^1H NMR spectrum of a compound had two peaks separated by 50 Hz. Circle the correct separation of these two peaks if a 300 MHz instrument was used?

- 2 (1) 50 Hz (2) 100 Hz (3) 500 Hz *(4) 250 Hz (5) 3 ppm
correct answer (50 x 5)

2b. Using completely proton decoupled ^{13}C NMR, give 2 differences between $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ (A) and $\text{CH}_3\text{CH}_2\text{-O-CH=CH}_2$ (B). Consider chemical shifts and the number of different peaks.

Compound A has 3 different peaks (carbons) : CH_3 ~10 ppm, CH_2 deshielded to 30-40 ppm, C=O above 200 ppm

Compound B has 4 different carbons: CH_3 10 ppm, CH_2O deshielded by oxygen to 40-50 ppm, $=\text{CH}_2$ regular alkene 100-110 ppm, OCH= deshielded by oxygen to ~ 150 ppm.

4pt

2c. Write 3 reasons for using tetramethylsilane (TMS) as the proton NMR calibration standard?

3pts

ANSWERS: (DO 3 ONLY)

1. TMS is very volatile; easy to remove from solution
2. TMS is inert; doesn't react with organic molecules
3. TMS has a singlet of very shielded protons ($\delta = 0$) ; no splitting
4. It is at or near the right end of the usual range of proton absorption.

2d. In electrophilic aromatic substitution, the attacking electrophilic species is necessarily a (choose one):

- (1) neutral species (2) positively charged species *(3) Lewis Acid

2Pt (4) proton (5) carbocation

2e. Circle the group whose IR stretch occurs at the LOWEST frequency:

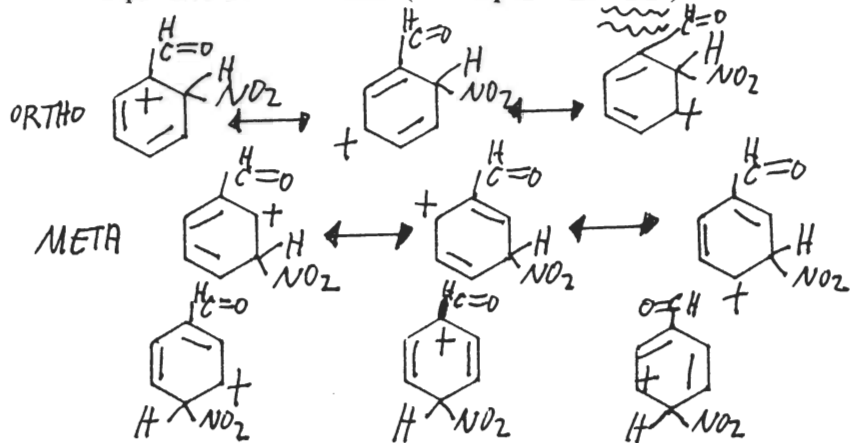
- 2 (1) C-H (2) C-O *(3) C-Br (4) C-N (5) C=O
correct

2f. Does the above circled group's stretch involve the MOST or the LEAST amount of energy? Explain your answer briefly, *i.e.* relate frequency and energy.

3pt

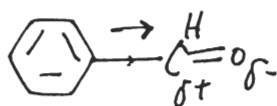
C-Br's stretch involves the LEAST amount of energy. Larger frequency number = greater energy

3 (20) a. By writing and using **all of the resonance structures of the disubstituted intermediates involved**, predict the preferred orientation (*ortho/para* or *meta*) for the mononitration of $C_6H_5-CH=O$:



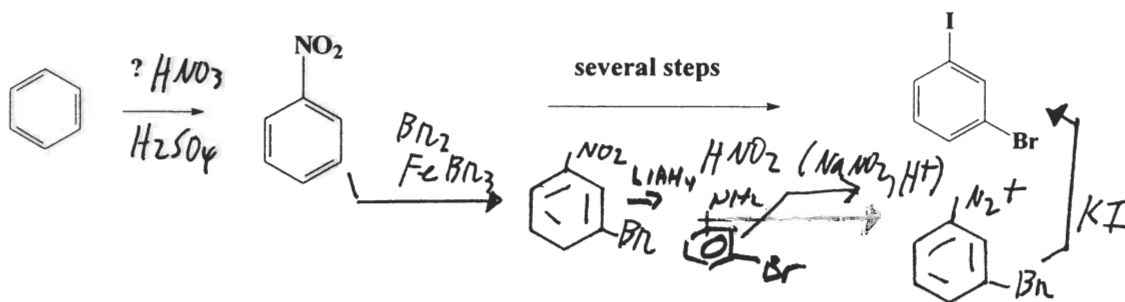
META PREFERRED
⊕ NO₂ NEXT TO
-C=O δ⁻
δ⁺

3b. Does $C_6H_5CH=O$ nitrate faster or slower than does benzene? Explain using resonance or inductive effects.
ANS. = SLOWER because of electron withdrawal by the aldehyde group (inductive effect)



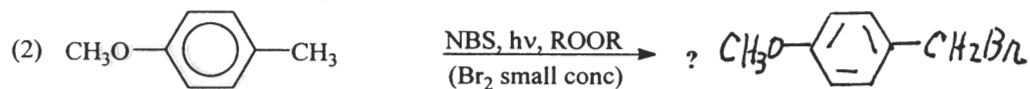
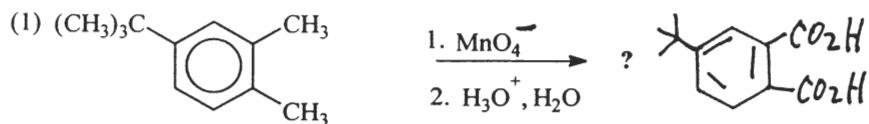
3

3c. Complete the following synthesis using any organic or inorganic reagents as needed. Show all important intermediates (not mechanisms).



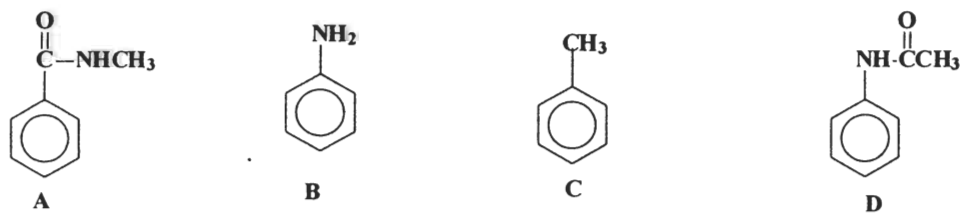
5

3d. Fill in the missing products in the following reactions.



4

3e. Choose the correct order of reactivity toward further electrophilic aromatic substitution (**MOST REACTIVE FIRST**)



(1) B, A, D, C

(2) A, C, D, B

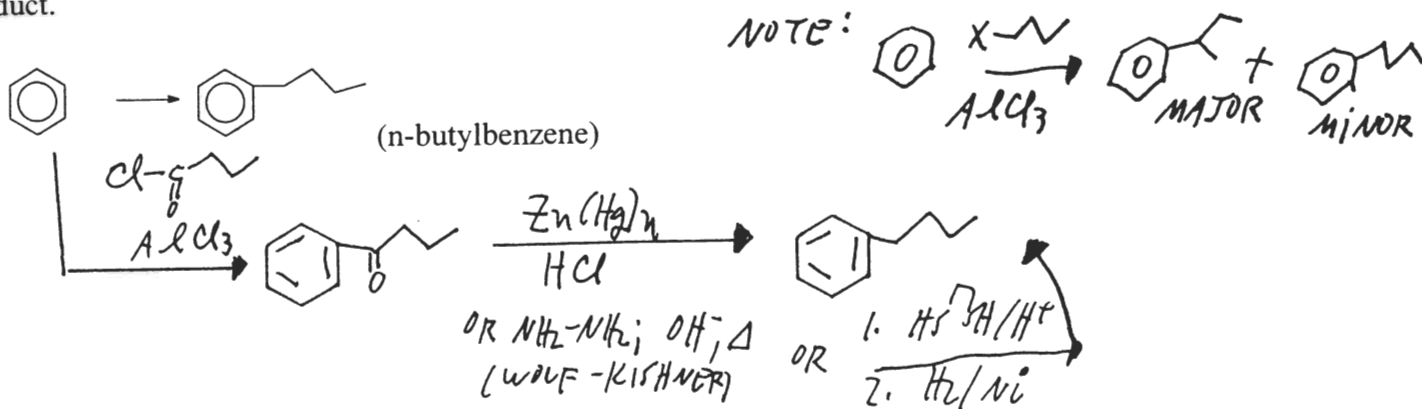
(3) C, D, A, B

(4) B, D, C, A

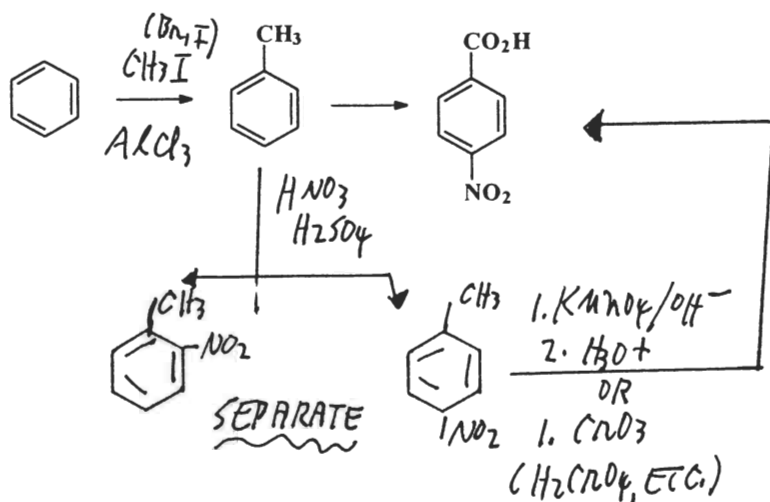
(5) D, C, B, A

correct answer

4. (19) Do the following conversions using the indicated starting compound and any necessary organic/inorganic reagents. Indicate where ortho, para mixtures occur and write "separate" to obtain the desired product.



4
b.



5

- c. Write the structures of the following molecules below their names. Then circle the one that has the highest UV λ_{max} value:
 Ans= #4, a conjugated diene

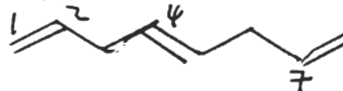
(1) 1,5-octadiene



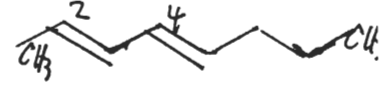
(2) 2-octene



(3) 1,4,7-octatriene



(4) 2,4-octadiene*



3 pt

- d. The *tert*-butyl group can be used as a blocking group in certain syntheses of aromatic compounds. How would you introduce a *tert*-butyl group on a benzene ring? How would you remove it?

The *tert*-butyl group is introduced by any one of several Friedl-Crafts reactions ($t\text{-BuOH} + H^+$; isobutene + H^+

$t\text{-Bu-halide} + AlCl_3$)

The *tert*-butyl group is removed with aqueous acid (and heat).

4pt (2pt x 2)

- e. Circle the two molecules below that cannot participate as a reactant in a Friedl-Crafts reaction:

(1) benzene

(2) chlorobenzene

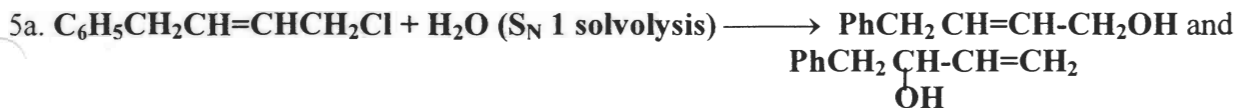
(3) nitrobenzene*

(4) *tert*-butylbenzene

(5) aniline*

3pt (1.5 pt x 2)

5. (15) Write the structure of the expected major organic product(s) in each of the following transformations:



4pt (2pt x 2)

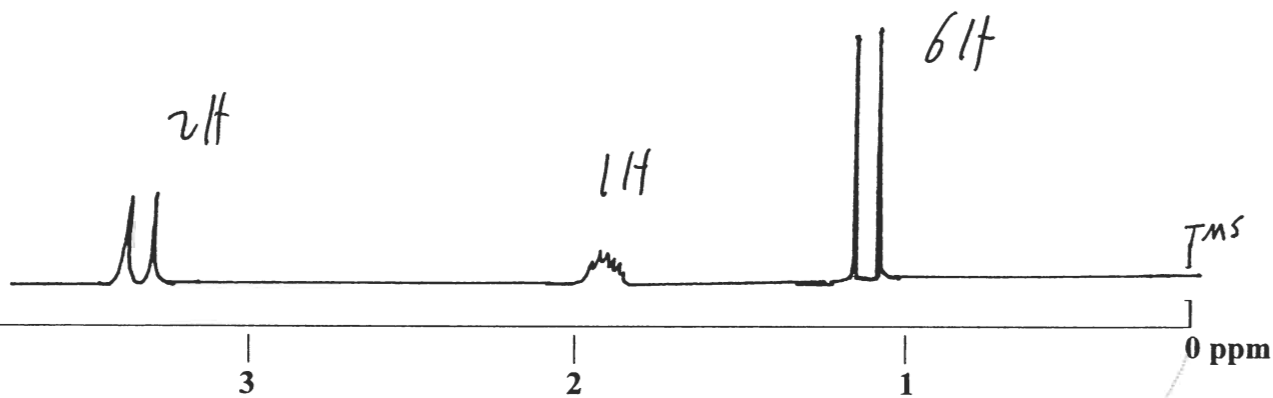
5b. The above chloride reacts many thousand times faster with water than does $Ph(CH_2)_3CH_2Cl$. Explain why, referring to the mechanism of the reaction(s) in 5a.

$C_6H_5CH_2CH=CHCH_2Cl$ gives a carbonium ion which is allylic and resonance stabilized:



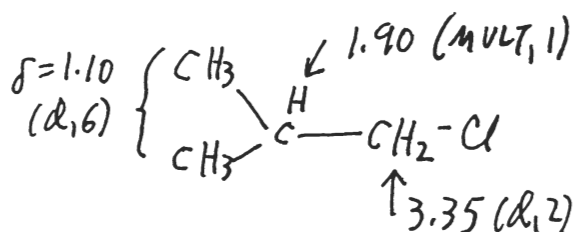
3pt

5c. Draw the proton NMR spectrum for the following data for C_4H_9Cl : $\delta = 1.10$ (d, 6), 1.90 (mult, 1), 3.35 (d, 2) including the expected intensities of the indicated groups of protons.



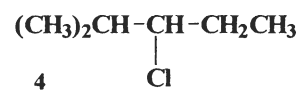
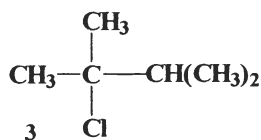
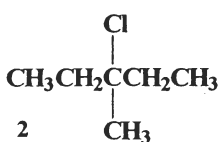
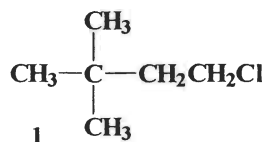
3pt

5d. Write a structure for the compound in 5c which satisfies the proton NMR spectrum. Assign the peaks.



4pt

6 (15) a. The broad band proton-decoupled ^{13}C NMR spectrum of a chlorohexane exhibits four **signals**. Only one signal is in the 10-15 ppm range. Circle the one structure that could be the correct one for this compound? Briefly explain your choice. Hint: start by labeling the different carbons in each structure.



Correct answer = No. 1. It has 3 CH_3 groups which absorb as one unit in δ 10-15 ppm range. The 3 other carbons absorb at higher δ values

No. 2 has 4 different carbons but 2 different CH_3 groups ($\text{CH}_3\text{C}-\text{Cl}$ is different, deshielded, vs the two other CH_3 groups).

No. 3 has 4 different carbons including two sets of CH_3 groups : the ones near $\text{C}-\text{Cl}$ are deshielded.

No. 4 has 5 different carbon signals

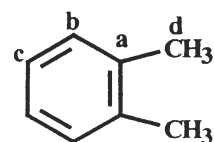
4pt

6b. Which of the following compounds has an off-resonance decoupled ^{13}C NMR spectrum that shows two doublets and one singlet in the 120-140 ppm region?

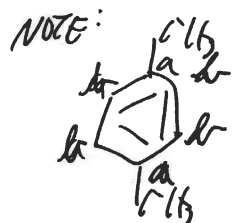
- (1) 1,2-dimethylbenzene* (2) 1,3-dimethylbenzene (3) 1,4-dimethylbenzene (4) ethylbenzene

3

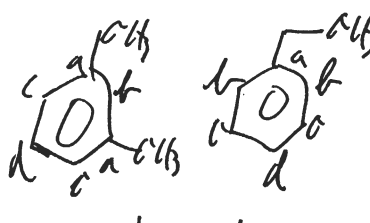
c. Explain your answer to 6b by drawing the correct structure of the answer and labeling the different carbons as a,b,c..



a = singlet
b, c = doublets



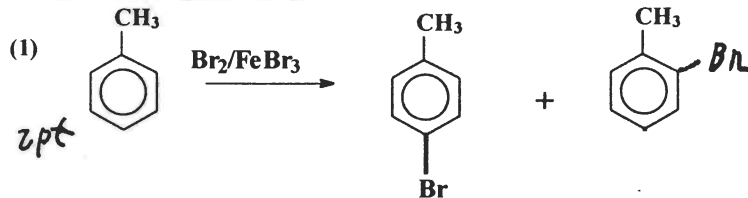
1 DOUBLET



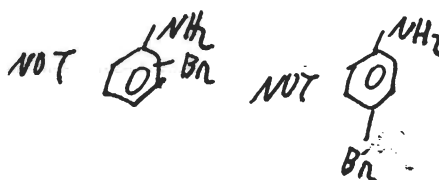
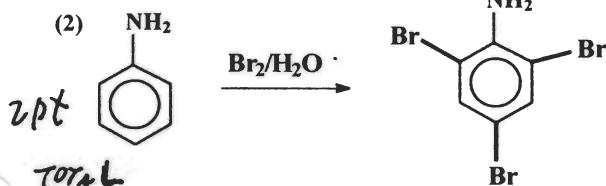
3 DOUBLETS

4pt

6d Show the product(s) of the reaction of toluene with $\text{Br}_2/\text{FeBr}_3$ and aniline with $\text{Br}_2/\text{H}_2\text{O}$.



1 pt each



7074L
4pt (2x2)