Hour Exam #1 **Chemistry 345** Professor Gellman 18 February 2015

**Last Name** 

**First Name** 

## **General Instructions:**

- (i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit. Models are allowed.
- (ii) Print your name on each page.
- (iii) Please keep your paper covered and your eyes on your own work. No electronic devices may be used. Misconduct will lead to failure in the course.

1. (18 points) Show the product(s) expected from the reactions indicated below. for extra dor

(c) 
$$O$$

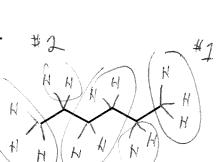
$$SO_3$$

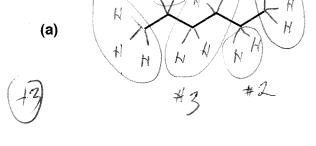
$$H_2SO_4$$

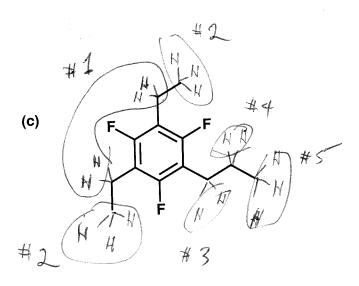
$$+5 \text{ for both}$$

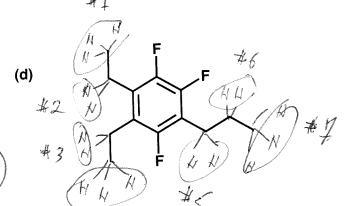
For each molecular drawing below, put a circle around sets of H atoms that you expect to be NMR-equivalent to one another (achiral solvent). In many cases you will have to draw in the H atoms yourself. Designate sets of non-equivalent H atoms as "#1", "#2", etc., as illustrated in the example below (propane). (Note: The numerical order (1, 2, etc.) does not matter.)

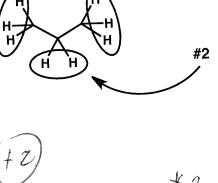
Example: **Answer** 

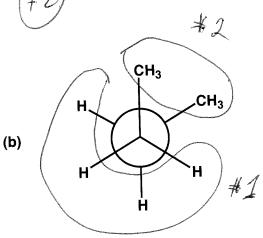












## 3. (14 points)

For each molecule drawn below, with reference to the H indicated by the arrow, label other H's as indicated...

...Put a CIRCLE around any homotopic H's.

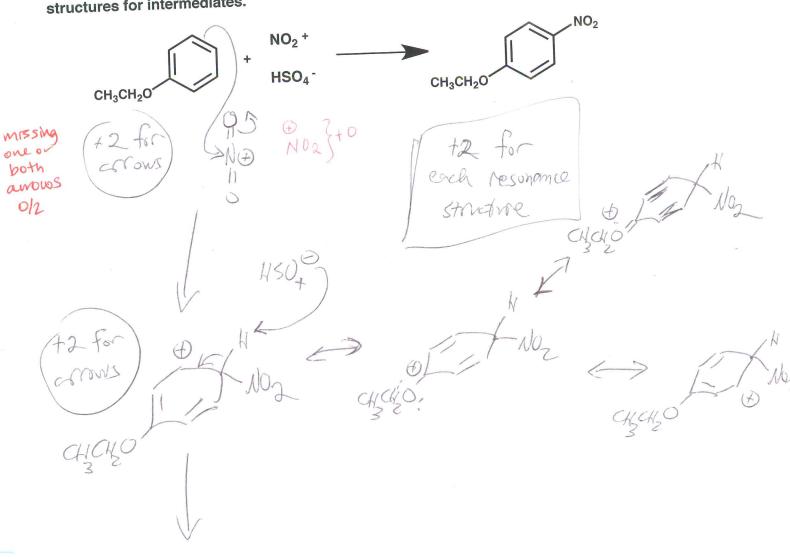
...Put a TRIANGLE around any enantiotopic H's.

...Put a SQUARE around any diastereotopic H's.

(Be sure to label only those H's that are appropriate.)

Name	

4. (12 points) In class we discussed nitration of aromatic rings with a mixture of  $HNO_3$  and  $H_2SO_4$ . Provide a mechanism (curved arrows) for the reaction shown below, which begins <u>after</u> the key electrophile has been generated. Draw all important resonance structures for intermediates.



CH3CH20

. Half for ortho . (-2) for no formal charges when arow out nitro . Half total of for -No on ser

Name	Name	
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5. (12 points) Propose a structure for products A and B formed in the reaction shown below. Your proposal should be consistent with the available data.

A + B

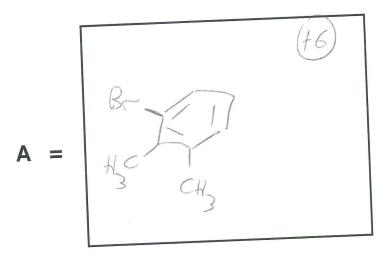
(Note: these products are isomers of one another)

The <sup>1</sup>H NMR spectrum of this molecule has the following features:

A singlet  $\delta$ 2.3

Two doublets in the range  $\delta$ 7-8, coupling constant ~8 Hz.

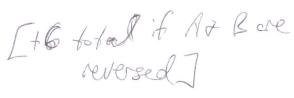
Singlet integration 3x larger than each doublet integration.



<sup>1</sup>H NMR spectrum includes the following:

Two singlets near  $\delta$ 2.3, 1:1 integration

Three resonances in the range  $\delta$ 7-8, each a doublet-of-doublets. For one, both coupling constants are large (~8 Hz); for the other two, one coupling constant is large (~8 Hz) and the other is small (~1 Hz).

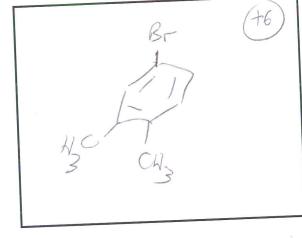


<sup>1</sup>H NMR spectrum includes the following:

Two singlets near  $\delta$ 2.3, 1:1 integration

Three resonances in the range  $\delta$ 7-8. Two are doublets, one with a large coupling constant (~8 Hz) and the other with a small coupling constant (~1 Hz). The third is a doublet-of-doublets, with one large coupling constant (~8 Hz) and one small (~1 Hz).





Name	

6. (15 points) For each of the molecules drawn below, place as many of the indicated numerals as appropriate on the line below the structure Extra #5 = -1

1 = IR spectrum contains a strong signal at 1710 cm<sup>-1</sup>

 $2 = {}^{13}C$  NMR spectrum contains exactly 2 resonances

 $3 = {}^{13}C$  NMR spectrum contains exactly 3 resonances

 $4 = {}^{13}$ C NMR spectrum contains exactly 7 resonances

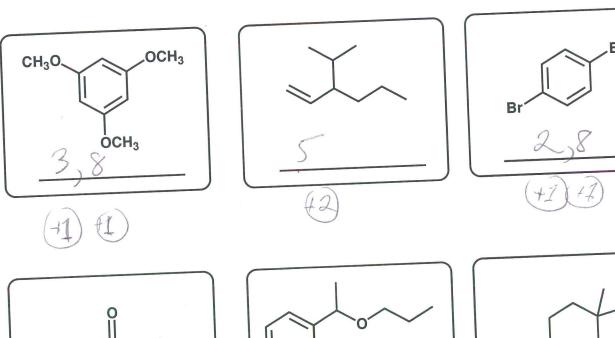
 $5 = {}^{13}$ C NMR spectrum contains exactly 9 resonances

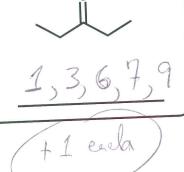
6 =  $^{13}\text{C}$  NMR spectrum contains one and only one resonance at  $\delta$  > 200

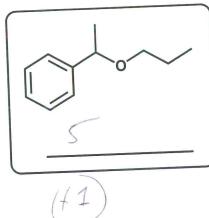
7 = All <sup>1</sup>H resonances at at  $\delta$  < 3.0

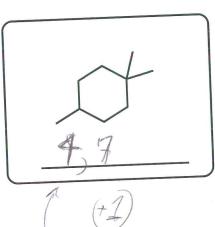
8 = The only kind of resonance in the <sup>1</sup>H NMR spectrum is a singlet

9 = <sup>1</sup>H NMR spectrum contains only one triplet and one quartet









Name	

7. (12 points) For each set of four molecules shown below, rank them in order of INCREASING reactivity for an electrophilic aromatic substitution reaction (e.g., chlorination).

A

B



D

EAS reactivity increases in the order:

(b)

B'

 $NO_2$ 

D'

EAS reactivity increases in the order: \_\_\_\_ < \_\_\_

[+3 for these 2]