Hour Exam #1
Chemistry 345
Professor Gellman
17 February 2016

Last Name Answer

First Name Key

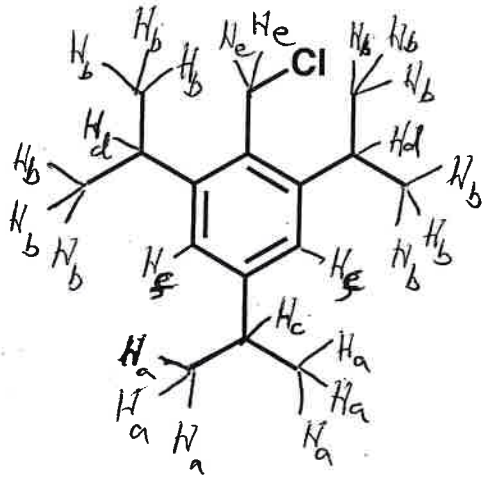
General Instructions:

(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) The resonances observed in the ^{1}H NMR spectrum of the molecule shown below are listed. Draw in all the H atoms on the molecular structure, and indicate which H's give rise to each of the ^{1}H NMR signals in the list (that is, indicate which H's are H_a, which are H_b, etc.).



H_a = Doublet, 6H, δ1.25

H_b = Doublet, 12H, δ1.29

H_c = Septet, 1H, δ2.88

H_d = Septet, 2H, δ3.31

H_e = Singlet, 2H, δ4.75

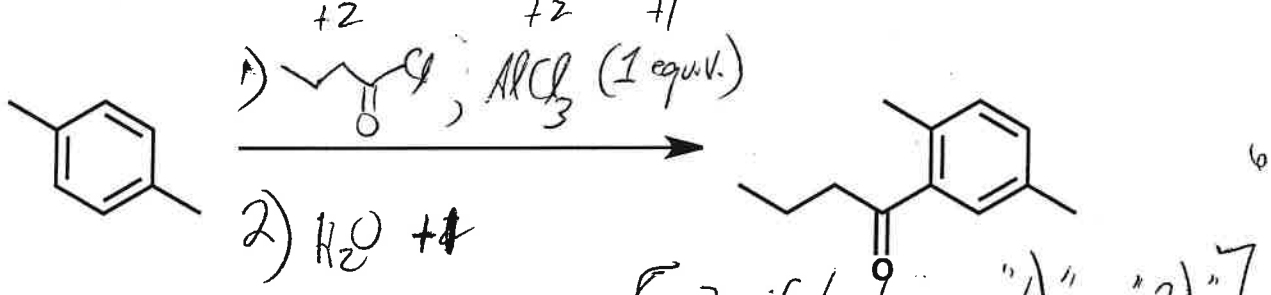
H_f = Singlet, 2H, 7.02

+3 for each correct assignment

Name _____

2. (17 points) Show the reagents and other organic molecules required to convert the starting material to the indicated product. Be sure to differentiate clearly between distinct steps, by using "1)", "2)", etc. over or under the arrow.

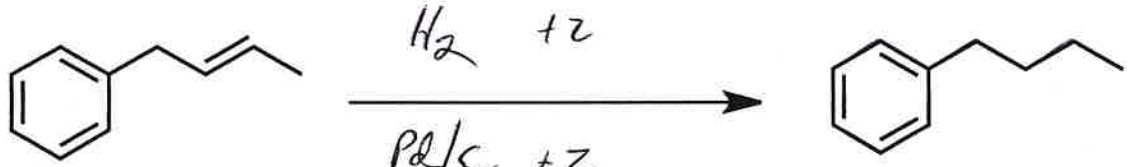
(a)



6

[-2 if lacking "1)" & "2)"]

(b)



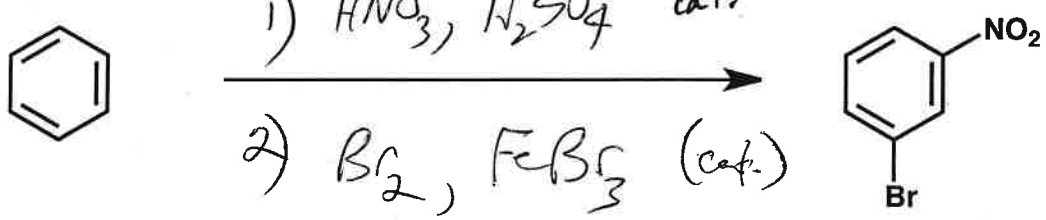
4

-1 if "high pressure"

-1 for Ni

-2 if an extra step

(c)



7

IF 1) Br_2
2) $FeBr_3$
3) HNO_3
4) H_2SO_4
(-5)

[-2 if missing "1)" + "2".]

[-3 if incorrect EAS order.]

Not required

3. (17 points) Name _____

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

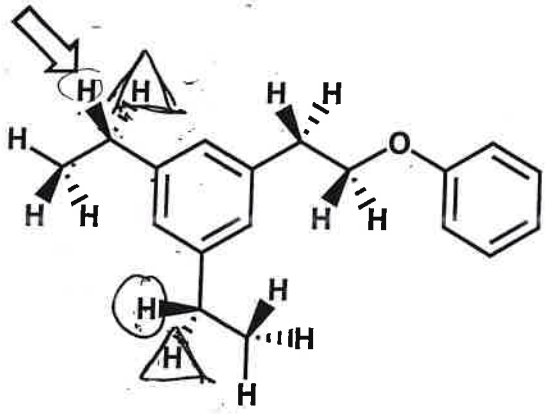
...Put a CIRCLE around any homotopic H's.

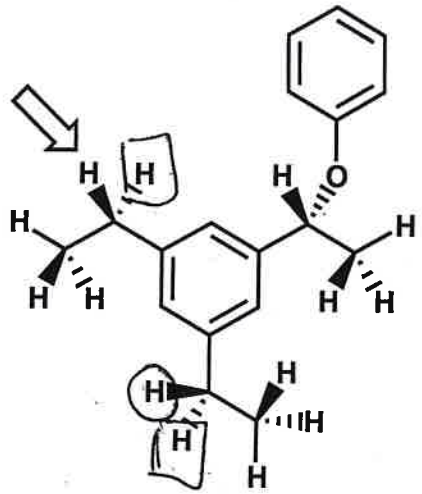
...Put a TRIANGLE around any enantiotopic H's.

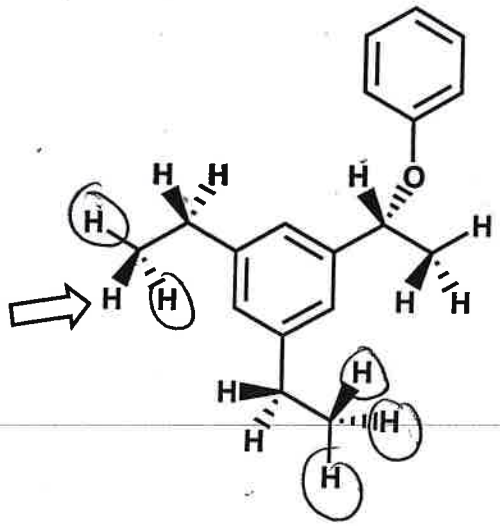
...Put a SQUARE around any diastereotopic H's.

(Be sure to label <u>only</u> those H's that are appropriate.)

+2 for each correct symbol





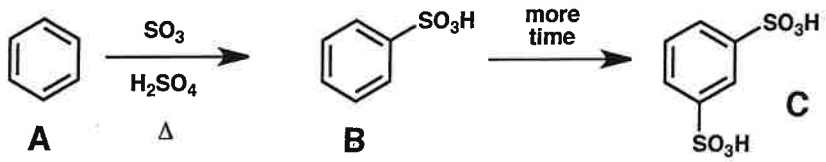


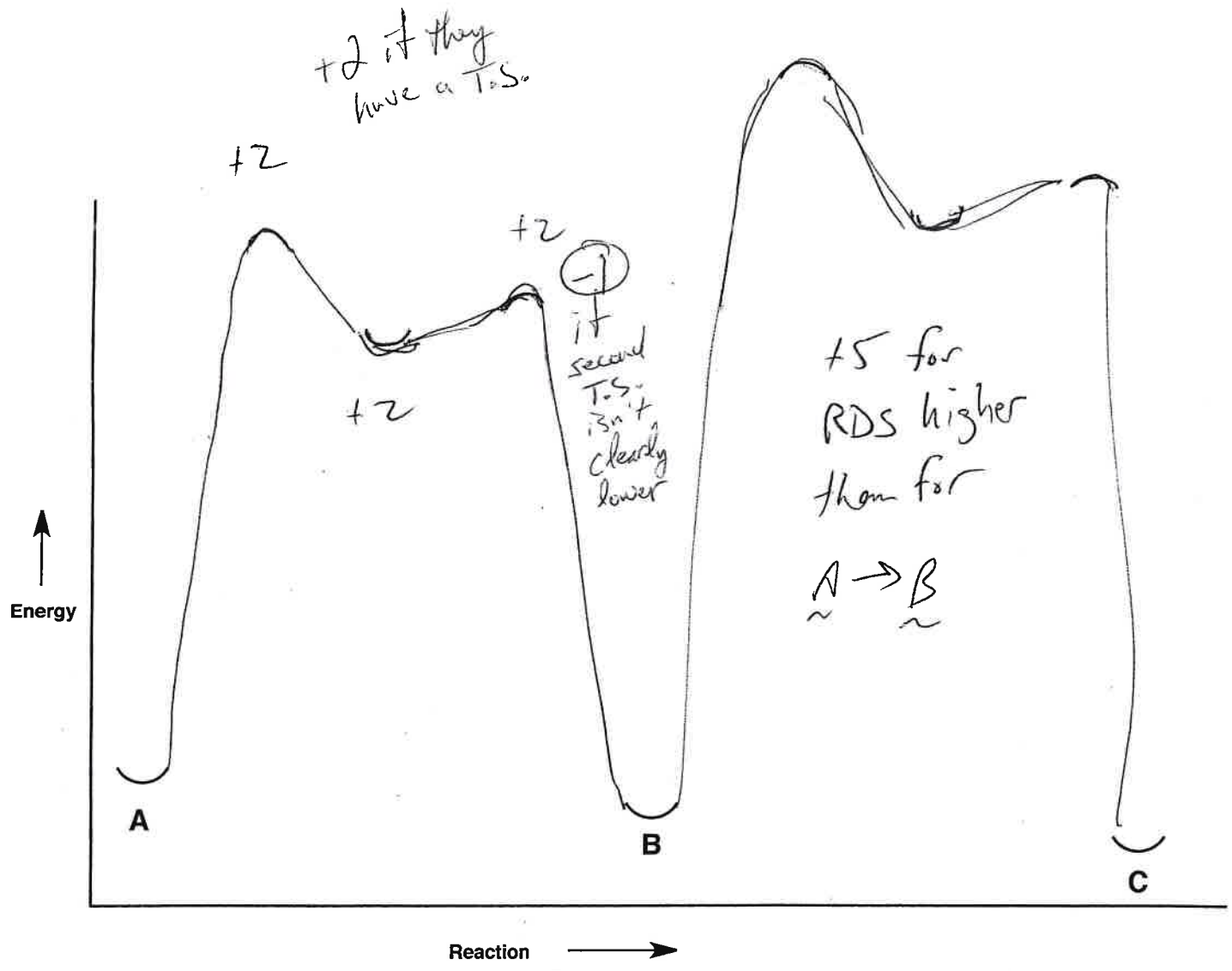
+1 for each correct symbol

-1 for "extra" symbols (each) on other carbons

Name _____

4. (11 points) As shown below, reaction of benzene (A) with the indicated reagents and heating initially generates B, but after more time product C is formed. Fill in the reaction energy diagram, given the positions of A, B and C as indicated.





Name _____

5. (22 points) For each of the molecules drawn below, place as many of the indicated numerals as appropriate on the line below the structure

1 = IR spectrum contains a strong signal at 3300 cm^{-1}

2 = IR spectrum contains a strong signal at 1720 cm^{-1}

3 = ^{13}C NMR spectrum contains a total of 3 resonances

4 = ^{13}C NMR spectrum contains a total of 4 resonances

5 = ^{13}C NMR spectrum contains a total of 5 resonances

6 = ^{13}C NMR spectrum contains a total of 6 resonances

7 = ^{13}C NMR spectrum contains a total of 7 resonances

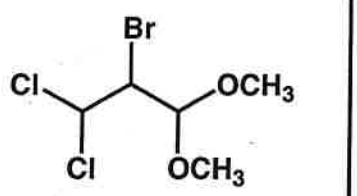
8 = ^{1}H NMR spectrum consists of 2 triplets and 1 singlet

9 = All ^{1}H resonances appear at $\delta > 3.0$

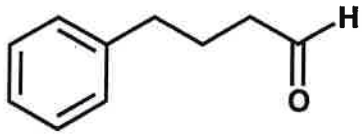
10 = All ^{1}H resonances appear at $\delta < 3.0$

+2 for each correct assignment

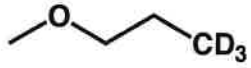
-1 for each incorrect assignment



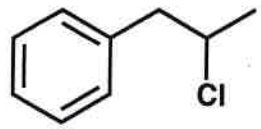
5, 9



2



4, 8



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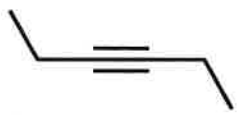
1, 7, 10



3, 10

6. (15 points)

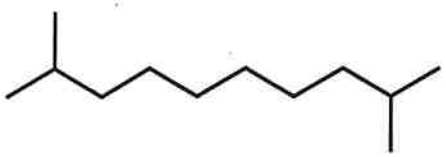
Name _____

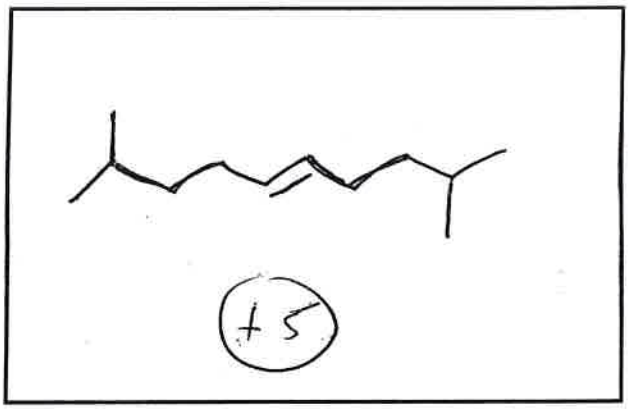
(a) When molecule X is allowed to react with H_2 in the presence of Pd/C, 1 mole of H_2 is consumed per mole of X, and the product is alkane AA, shown below.

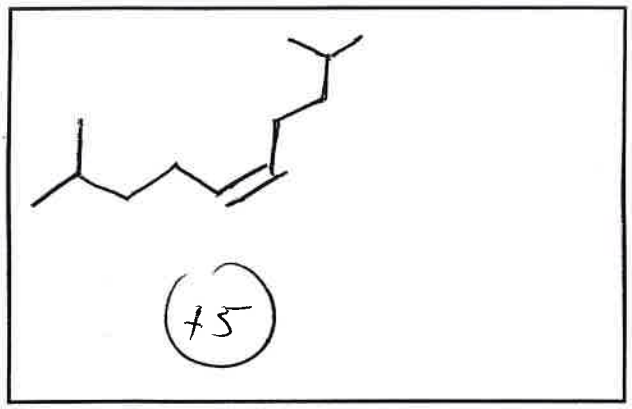
The ^{13}C NMR spectrum of molecule X contains a total of 5 resonances; only 1 of these resonances is found above 100 ppm, and the remainder occur below 50 ppm.

The ^{1}H NMR spectrum of molecule X contains a total of 5 resonances (don't worry about the splitting of these resonances), with only 1 resonance above 4 ppm; the remainder are below 2.5 ppm.

Propose two possible structures for molecule X (in the boxes).

AA = 





(b) When molecule Z is allowed to react with H_2 in the presence of Pd/C, 1 mole of H_2 is consumed per mole of Z, and the product is alkane AA, shown above.

The ^{13}C NMR spectrum of molecule Z contains a total of 10 resonances; only 2 of these resonances are found above 100 ppm, and the remainder occur below 50 ppm.

The ^{1}H NMR spectrum of molecule Z contains a total of 10 resonances (don't worry about the splitting of these resonances), with only 1 resonance above 4 ppm; the remainder are below 2.5 ppm.

Propose a structure for molecule Z (in the box).

+3 if correct, except additional/missing carbon