Hour Exam #2
Chemistry 345
Professor Gellman
18 March 2015

Last Name Answer

First Name Key

General Instructions:

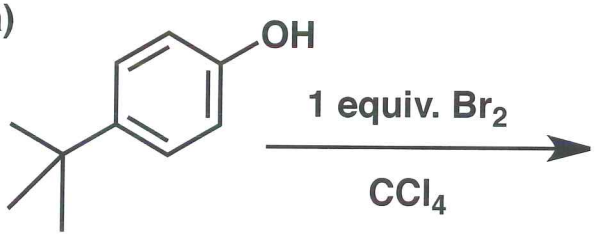
(i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit. Models are allowed.

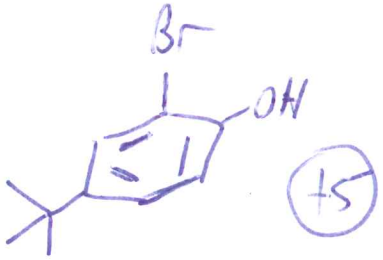
(ii) Print your name on each page.

(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. (17 points) Show the product(s) expected from the reactions indicated below.

(a)

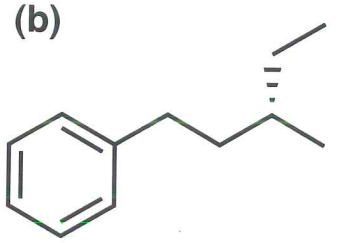


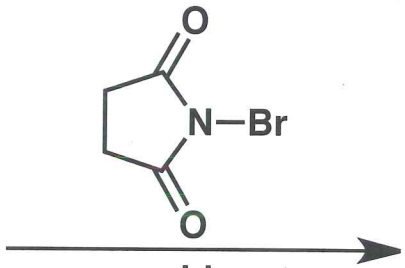


Not required

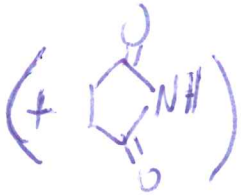
(+ HBr)

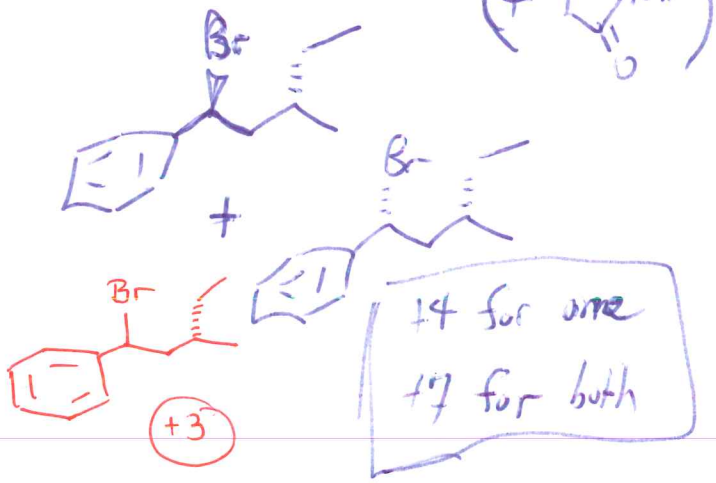
(b)



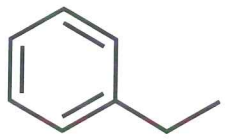


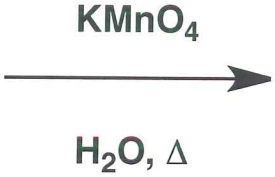
(The starting material is a single enantiomer.)

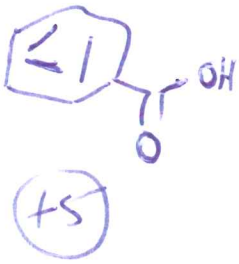




(c)



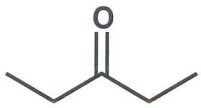




Name _____

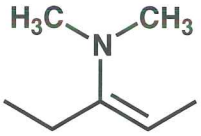
2. (23 points) Show the reagents and other organic molecules required to convert the starting material to the indicated product. Be sure to differentiate clearly between distinct steps, by using "1)", "2)", etc. over or under the arrow.

(a)



(+4) $(CH_3)_2NH$, cat. H_2SO_4 (+2)

CH_3OH

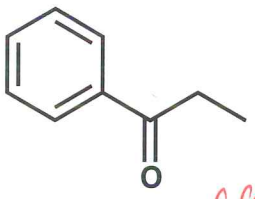


(-2 for H_2O)

4 pts.

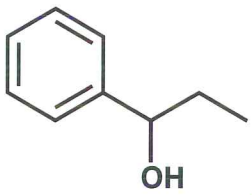
ok if don't have +

(b)



(+3) 1) $LiAlH_4$, Et_2O (don't need) | $NaBH_4$ (+3)

2) H_3O^+ (+2) | CH_3OH (+2)

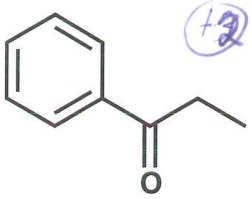


take off 2 pts. if no #s

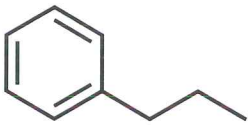
if label ① & ② take off point *

5 pts.

(c)



(+4) (+2) H_2NNH_2, KOH, $HO\sim\sim\sim OH$, Δ | Zn/Hg (+4) | HCl (+2)



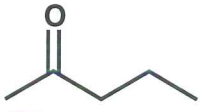
Clemmensen 3 pts.

4 pts.

(d)

(+3) $Hg(OAc)_2$

H_2SO_4, H_2O (+3) for acid



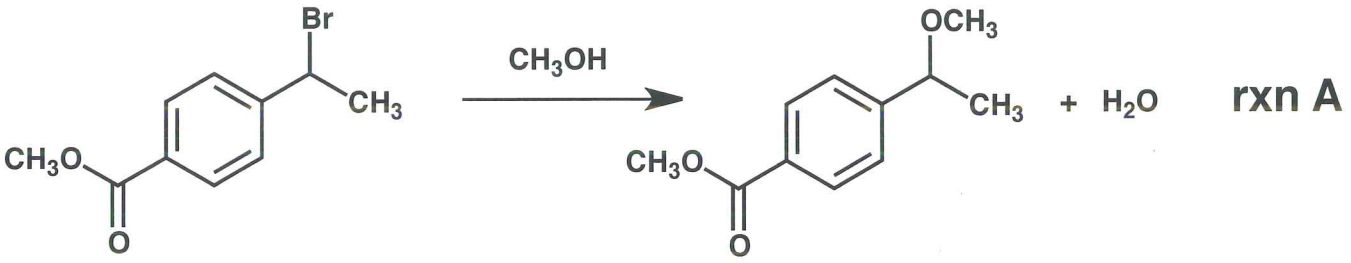
[Any source of Hg^{2+} (+2) ok]

Hg^{2+} alone ok, but must show 2+

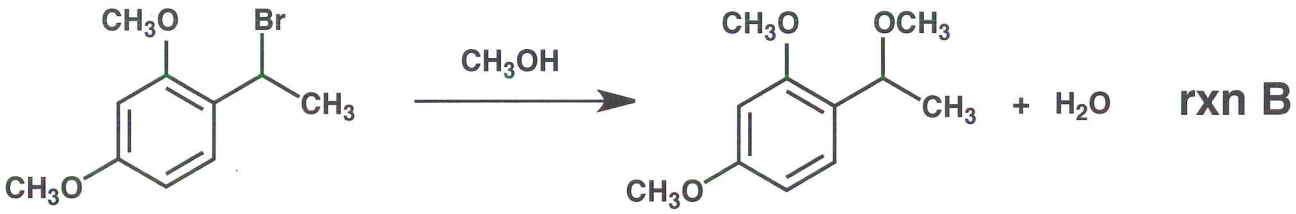
- If add too many things on top of that +0 pts.

Name _____

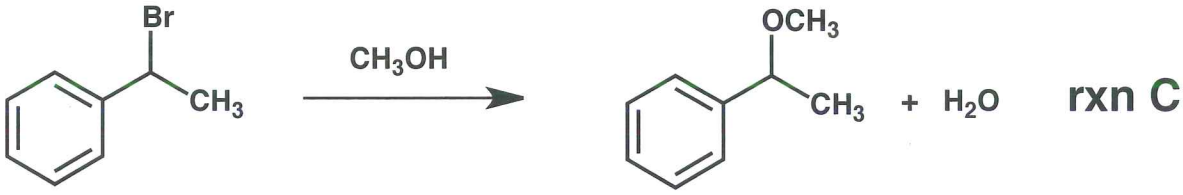
3. (7 points) Rank the four reactions below (A, B, C and D) in terms of the expected relative rates, from SLOWEST (on the left) to FASTEST (on the right). All starting materials and products are racemic.



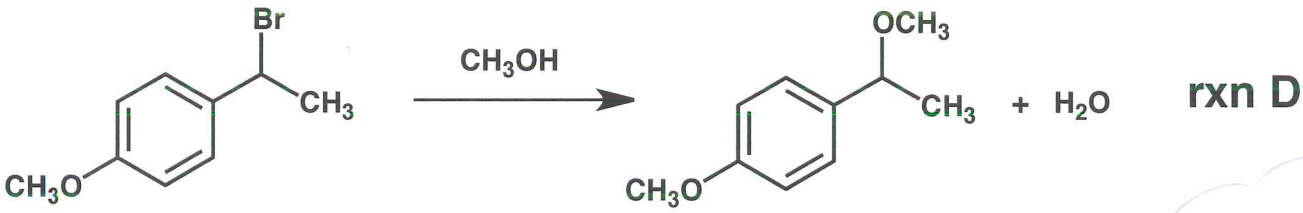
rxn A



rxn B



rxn C



rxn D

+7 total

Relative rate (slowest on the left, fastest on the right):

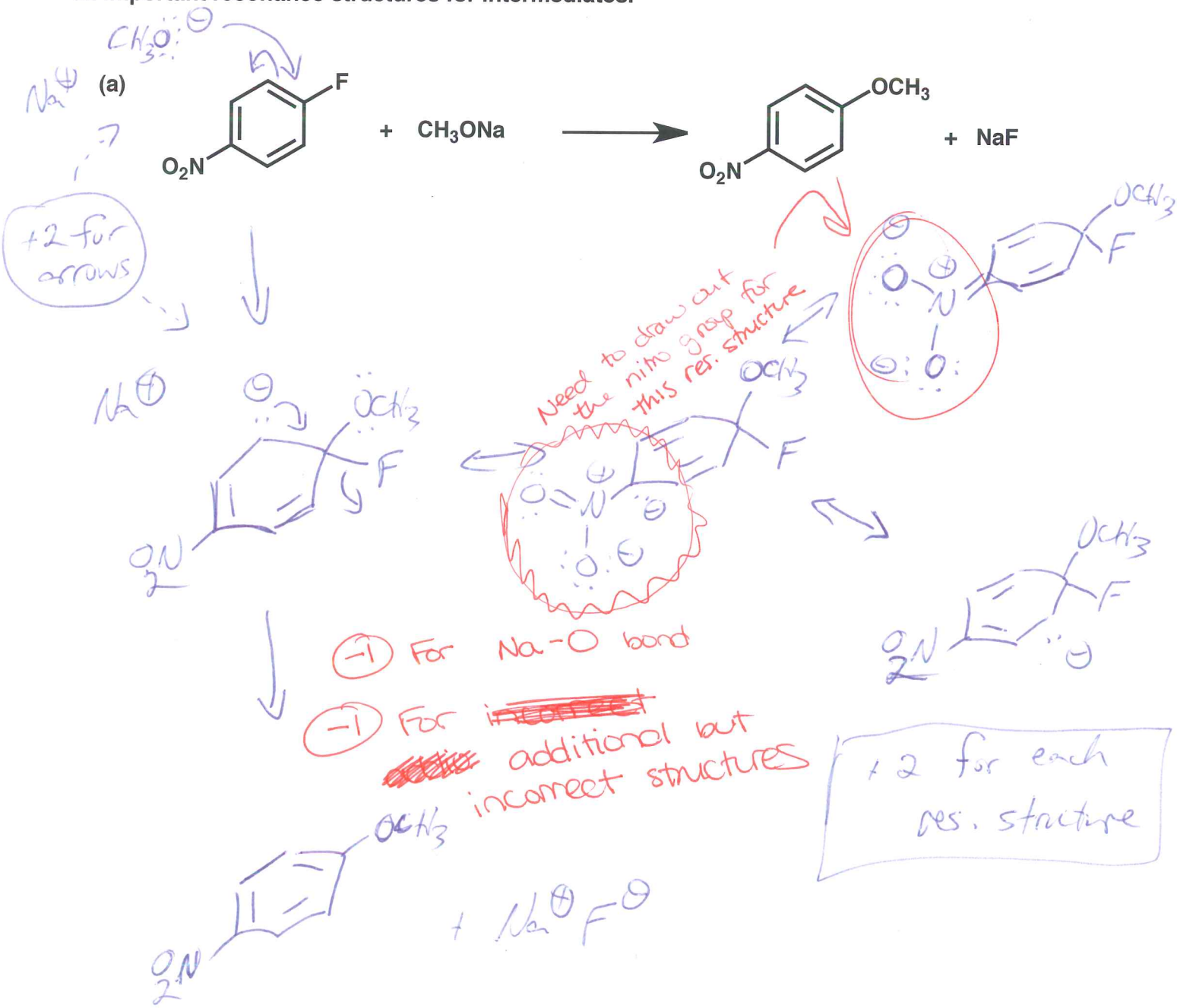
A < C < D < B

+2

+2

Name _____

4. (26 points) Provide a mechanism (curved arrows) for each reaction shown below. Draw all important resonance structures for intermediates.



(-1) Any formal charge error

(max. of (-1))

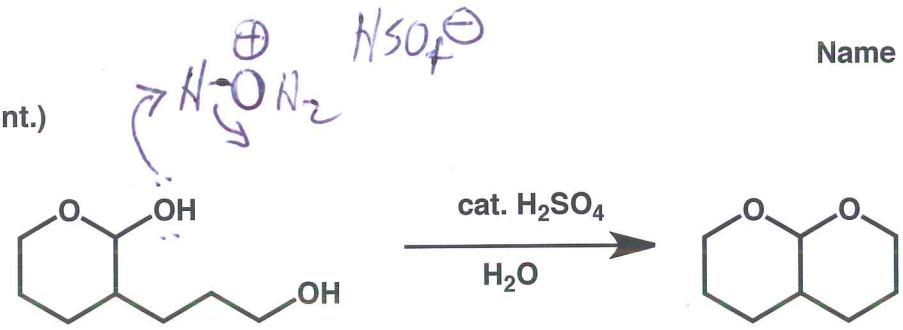
+12 total

(cont. on next page)

Name _____

4. (cont.)

(b)



Note: Do not be concerned about stereochemistry of starting material or product.

+2 for intermediate

+1 for each res. structure

+2 for each set of mechanistic arrows (+8 total)

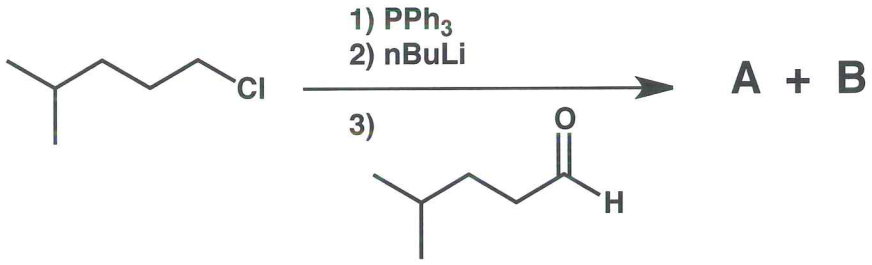
- H^+ as acid ok
- +1 pt for no ⊕ on intermediate
- S_N2 attack of $\ddot{O}H_2$ 8 pts max

- protonate 1° alcohol → points for correct arrows
- deprotonate 1° alcohol before attack (+6 points max)

+14 total

Name _____

5. (12 points) The reaction scheme below gives rise to two products, A and B. If either A or B is allowed to react with H_2 in the presence of Pd/C, both reactions yield the same product. Based on this information, and the ^{13}C NMR information below, provide structures for A and B in the indicated boxes.

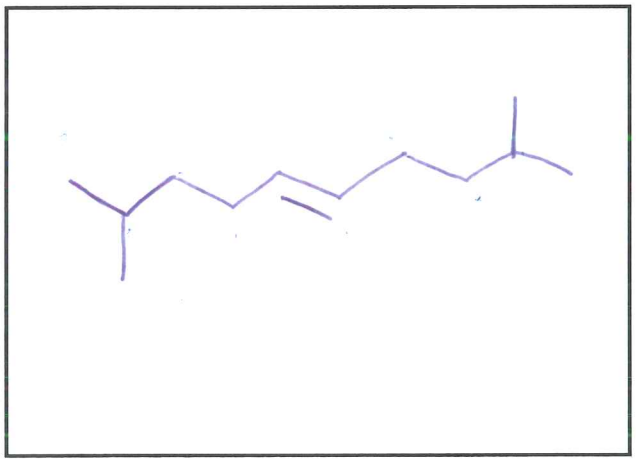


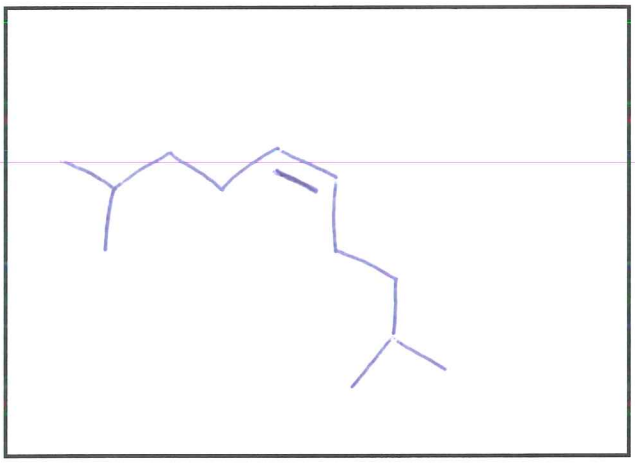
^{13}C NMR data:

Compound A and compound B have different ^{13}C NMR spectra, but these two spectra are similar in that both have four ^{13}C resonances below 50 ppm, and one ^{13}C resonance in the range 130-135 ppm.

missing C
3pts

+6





Draw structures for A & B (don't worry about which is which)

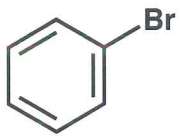
missing C
3pts

+6

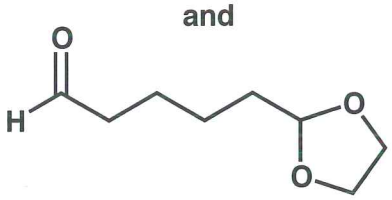
Name _____

7. (15 points) Propose an efficient synthetic route from the indicated starting material to the target. You may use any other starting materials and reagents.

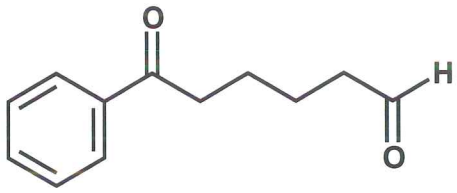
Starting materials =



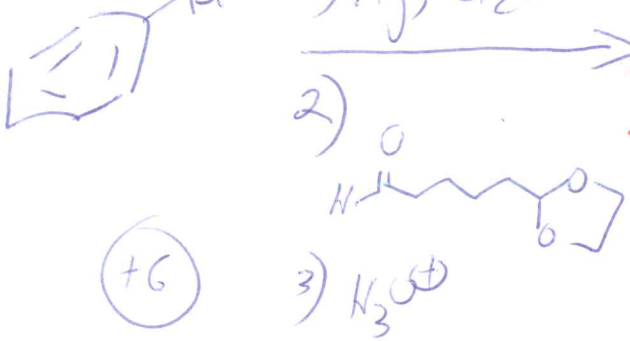
and



Target =

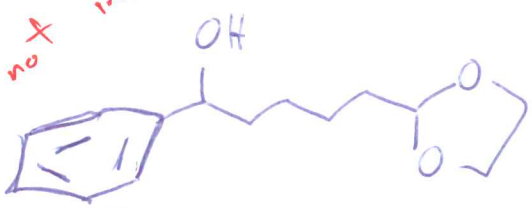


[or Li^0]



+6

-2 for no ✝ indicating wkup separately



-2 for improper step ordering.

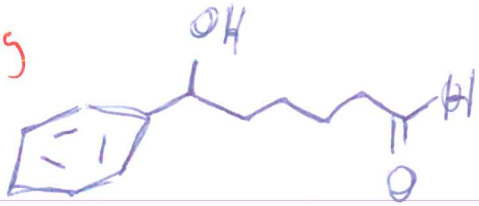
+4

H_2O
cat. H_2SO_4
-2 if no acid.

8/15 for Grignard forming ketone, then deprotection. rxn

Give points for correct individual steps.

12/15 for early deprotection.



[+2 for "$Na_2Cr_2O_7$, H_2SO_4)" etc.]

+5

MnO_2 or PCC