CHEM 3331, Professor Zhang, Spring 2012
Second hour exam, Mar 13, 2012

Printed Name: Key Student ID: _____

Recitation TA Name: _____ Recitation day and time: _____

Scores:

1)

2)

3)

4)

5)

_____

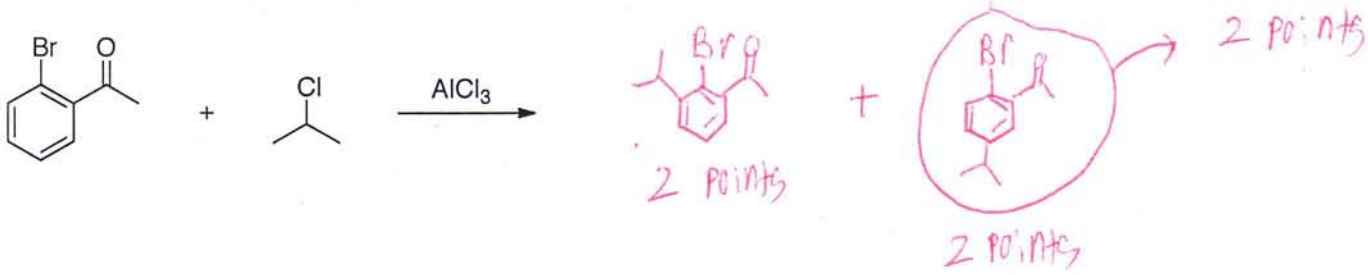
CU Honor Code Pledge: On my honor, as a University of Colorado at Boulder Student, I have neither given nor received unauthorized assistance.

This is a closed-book exam. The use of notes, models, calculators, scratch paper will not be allowed during the exam. Please put all your answers on the test. Use the backs of the pages for scratch.

Partial Periodic Table

1A							8A
1 H	2A	3A	4A	5A	6A	7A	2 He
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
						35 Br	
						53 I	

1) (22pts) a) 2-Bromonitrobenzene (1) reacts with isopropyl chloride and aluminum trichloride to give two major products. Give the structures of the two major products (4pts)

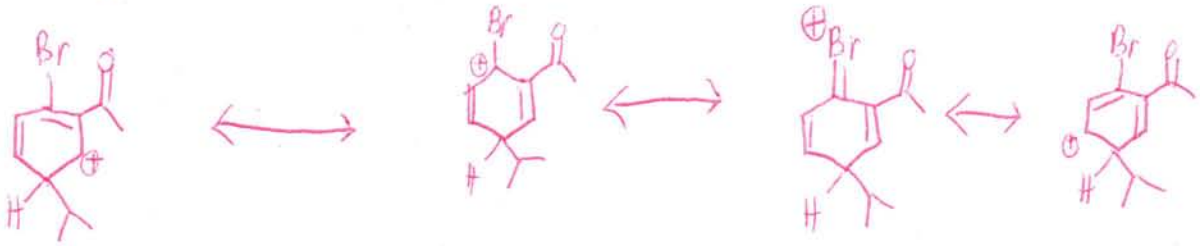


b) Which of these two major products is more favored? Give **brief** explanation. (4 pts)

Less Sterics
2 pts

c) The reactions above involve formation of reactive intermediate cations. For the more favored product, draw all the important resonance contributors to the structure of the cation intermediate. (6pts)

5

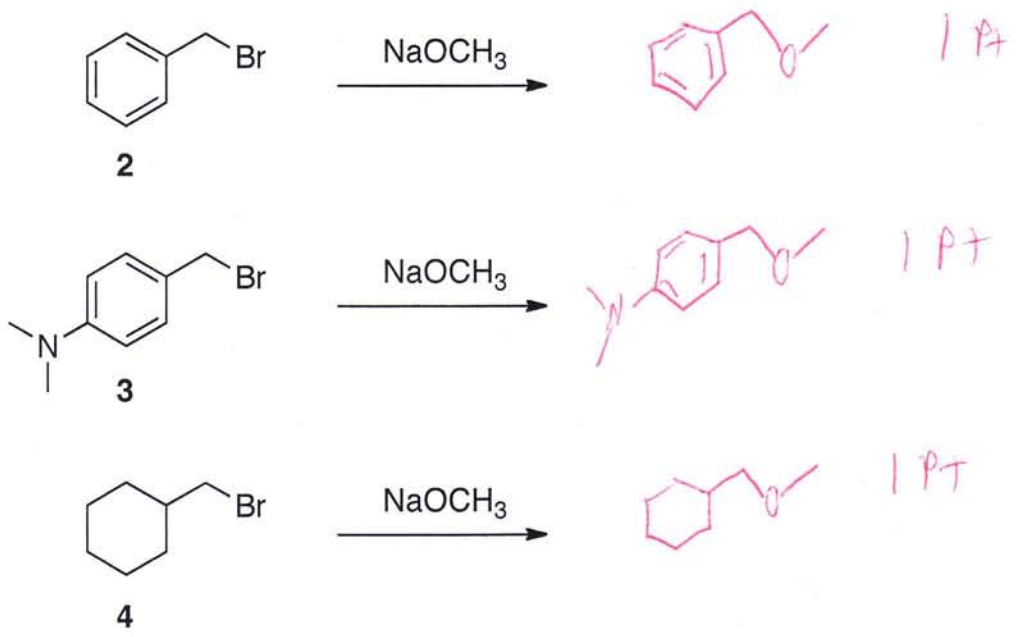


d) Are the reactions in part 1b FASTER or SLOWER than the alkylation of benzene? (2 pts).

3

Total points for this page 16

e) Give the structures of the products obtained when bromide **2**, **3** and **4** are reacted with sodium methoxide, respectively. (3pts)



1 Pt

1 Pt

1 Pt

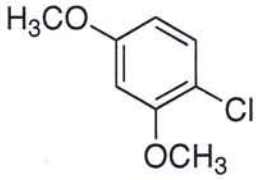
f) Under the same conditions, which reaction in 1e proceeds much FASTER than the other two? **Briefly** explain the reasoning. (3pts)

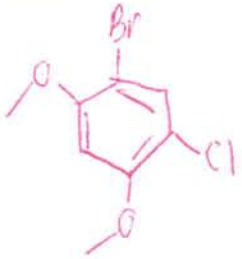
3, the electron donating group stabilizes the SN2 transition state

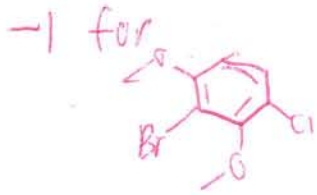
2 pts for picking 3, 1 Pt for explanation

Total points for this page 6

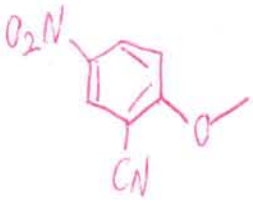
2) (20 pts) Give the single major product of each of the following reactions, carefully showing stereochemistry if appropriate. If a racemate is formed, show only one enantiomer, and label it "rac". All reactions have an appropriate aqueous work up. (4 pts each)

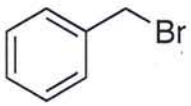
a) 

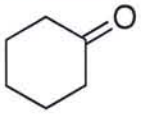
Br_2, $FeBr_3$ → 

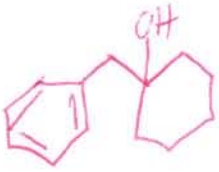


b) 

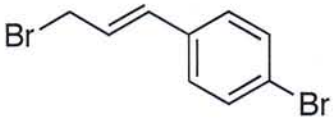
CH_3ONa → 

c) 

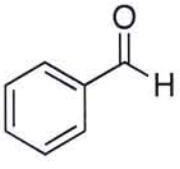
a) Mg, ether
b) 

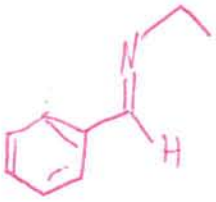


~~OH~~

d) 

CH_3ONa → 

e) 

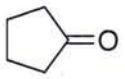
$CH_3CH_2NH_2$
cat. TsOH
molecular sieves → 

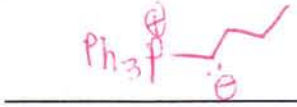
Total points for this page 20

3) (20 pts) Propose reagents for accomplishing the following transformations. NOTE: more than one step may be required! Try to make your synthesis efficient (i.e. the desired product should be the major product, and generally a shorter synthesis is better than a longer one). You must use the starting material given; you may use any other reagents you need.

4 pts each

3/4 wrong order
Missing carbon
3/4 weak base

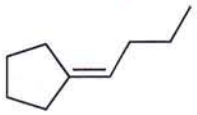
a) 



← wrong ylide 1/4

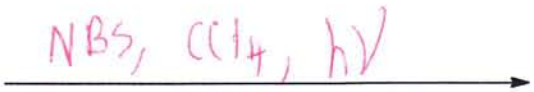
PPh_3, BuLi (0/4)

PPh_3 + RBr (1/4)



BuLi then H^+ (2/4)

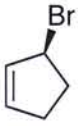
b) 



NBS, CCl_4, hv

NBS + Δ full credit

NBS + HBr (1/4)

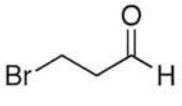


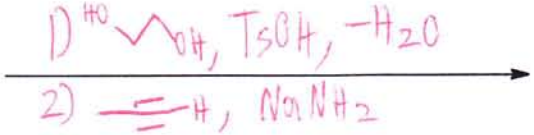
rac

3/4 No Δ or hv

Br_2 (0/4)

NBS

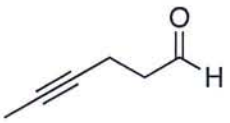
c) 



1) , TsOH, $-H_2O$

2) , $NaNH_2$

3) H_3O^+

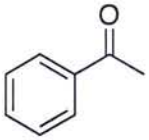


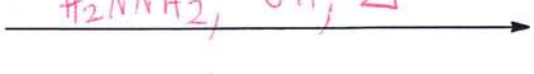
Missing deprotection 3/4
Just alkyne + 2

Protection/deprotection = 2 pts
Alkyn addition = 2 pts

No $-H_2O$ 3/4

MgBr + Alkyne 0

d) 



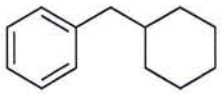
H_2NNH_2, $^{\ominus}OH$, Δ

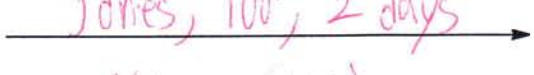
Zn/Hg HCl Full credit

Missing Δ (3/4)

No base (0/4)

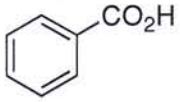
H_2NNH_2 + H^+ (0/4)

e) 



Jones, 100°, 2 days

$KMnO_4$ (4/4)



O_3 then Jones 3/4

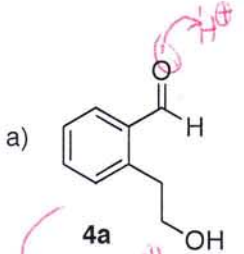
No duration 3/4

No Δ, duration 2/4

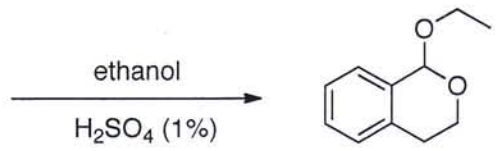
Total points for this page: 20

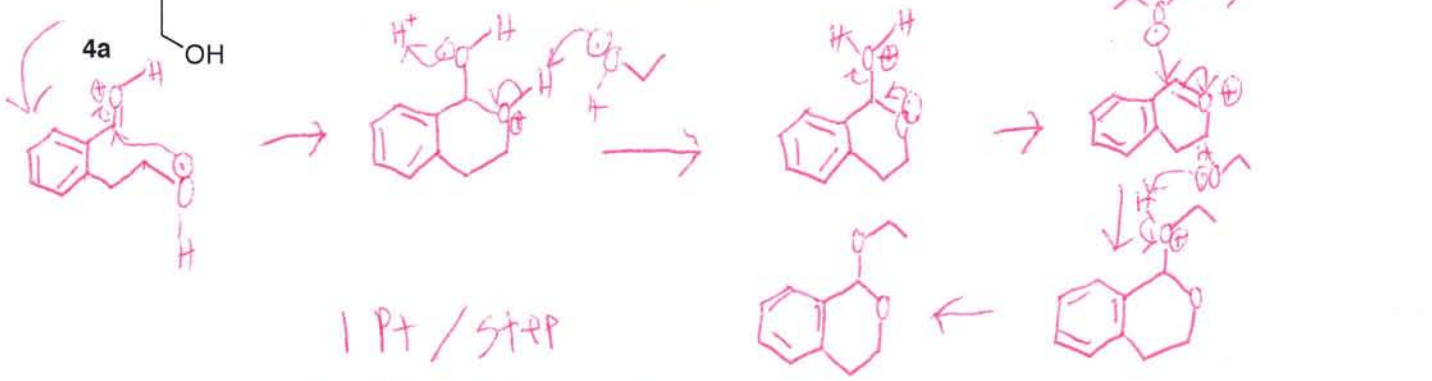
4) (20 pts) Propose arrow-pushing mechanism for the reactions of **4a** and **4b**. (6pts each)

a)



4a



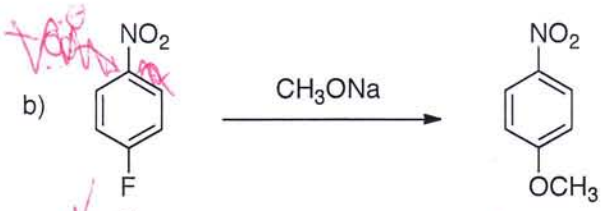


1 Pt / step

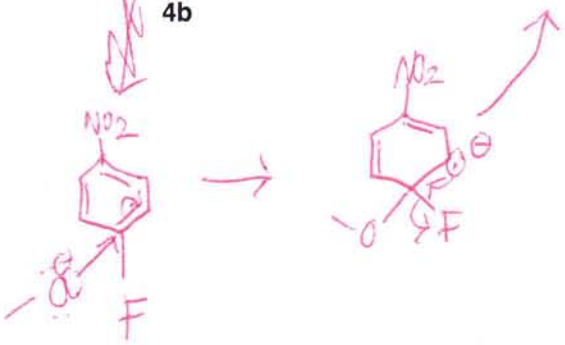
-2 if ethanol before internal

-1 pt if

b)



4b

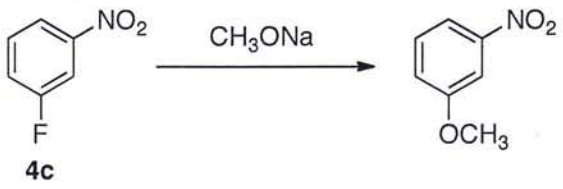


3pts / step

1 point off for missed charges

Total points for this page 12

c) m-Fluoronitrobenzene (**4c**) can also react with sodium methoxide. Which reaction is FASTER, **4b** or **4c**? Briefly explain the reasoning. (4pts)



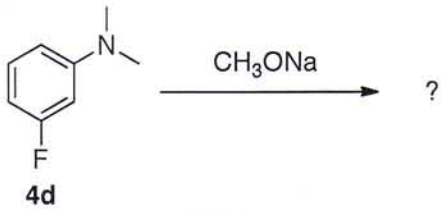
4c

4b, negative charge can resonate onto NO_2

↓ 2pts

↘ 2pts

d) Can m-fluorodimethylaminobenzene (**4d**) also react with sodium methoxide? Briefly explain the reasoning. (4pts)



4d

No, an electron withdrawing group is required

↙ 2pt

↘ 2pts

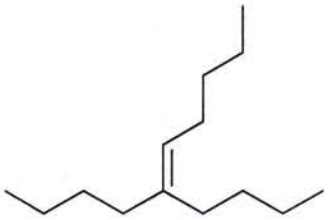
1 Point for yes but very slow

8

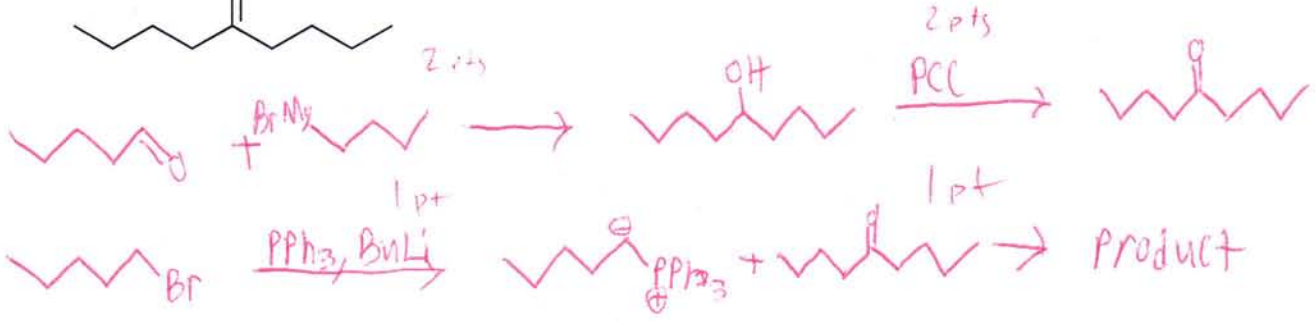
Total points for this page

5) (18 pts) Propose a synthesis of each of the following **three (3)** targets. Allowed starting materials include benzene, triphenylphosphine, and/or any other organic molecules containing **five (5)** carbons or less. You may use any necessary inorganic reagents. Try to make your synthesis efficient (i.e. the desired product should be the major product, and generally a shorter synthesis is better than a longer one). More than one step may be required.

a)

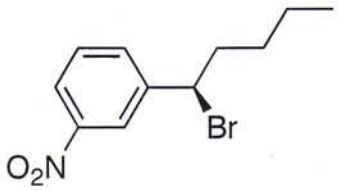


- 1 wrong # C's
- 1 for typo



6 pts

b)

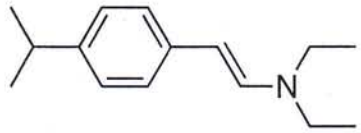


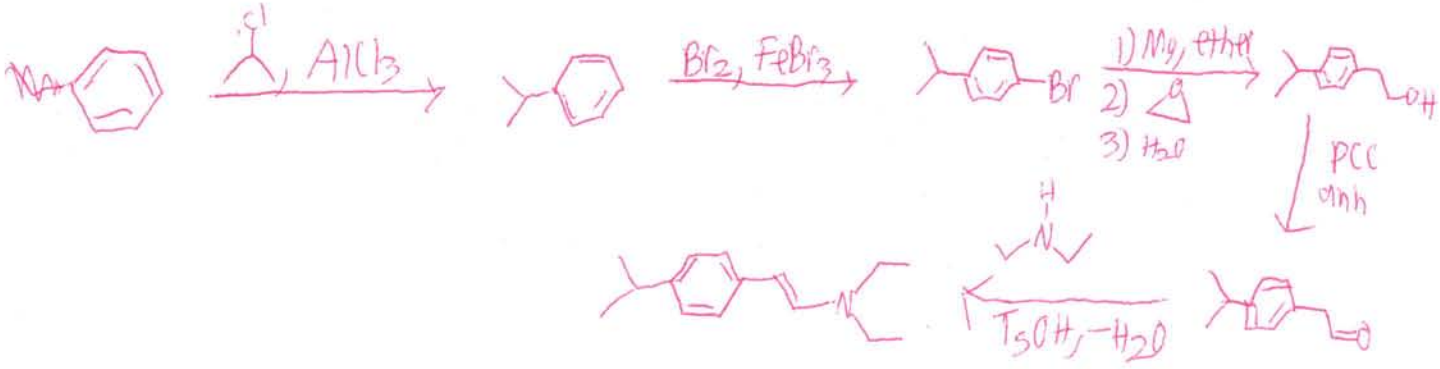
rac

6 pts

Total points for this page: 12

c)





-3

Total points for this page 6