Chem 331
Exam 3
December 6, 2002
Prof. Fox
50 minutes

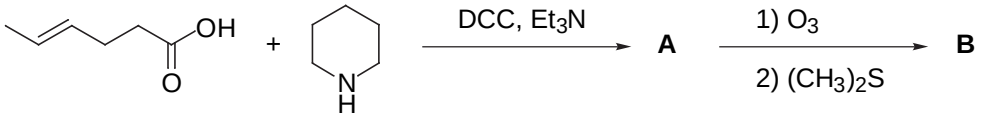
The exam is open book,
Open notes. Models are permitted
Show your work in detail

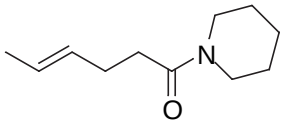
WRITE YOUR NAME ON EVERY PAGE

NAME KEY _____

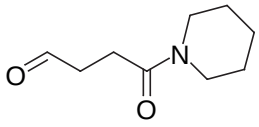
Chem 331, Exam 3. December 6, 2002 **NAME** _____

1. Draw the structures of **A** and **B**. You do not need to provide mechanisms (25 pts)



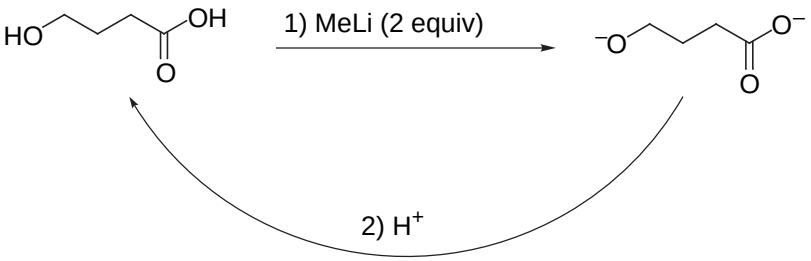


A



B

2. The reactions below would not proceed as shown. Explain why (be concise), and indicate which product would be formed instead.

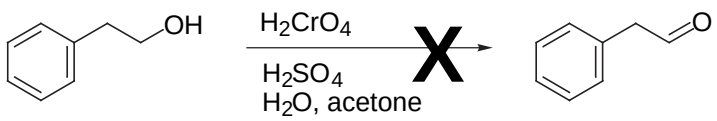


(20 pts)

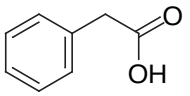
This substrate has 2 hydroxyls, so the MeLi is completely comsumed by deprotonating the two hydroxyls. Addition of acid regenerates the starting material.

2 (continued). The reactions below would not proceed as shown. Explain why (be concise), and indicate which product would be formed instead.

b.

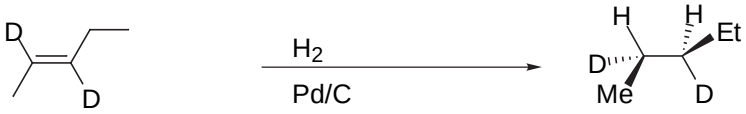


(20 pts)



overoxidizes to the acid

c.

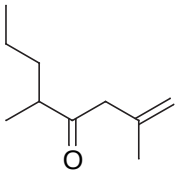


(25 pts)

Pd catalyzed hydrogenation occurs by cis-addition across the double bond. The product above is that of trans addition.

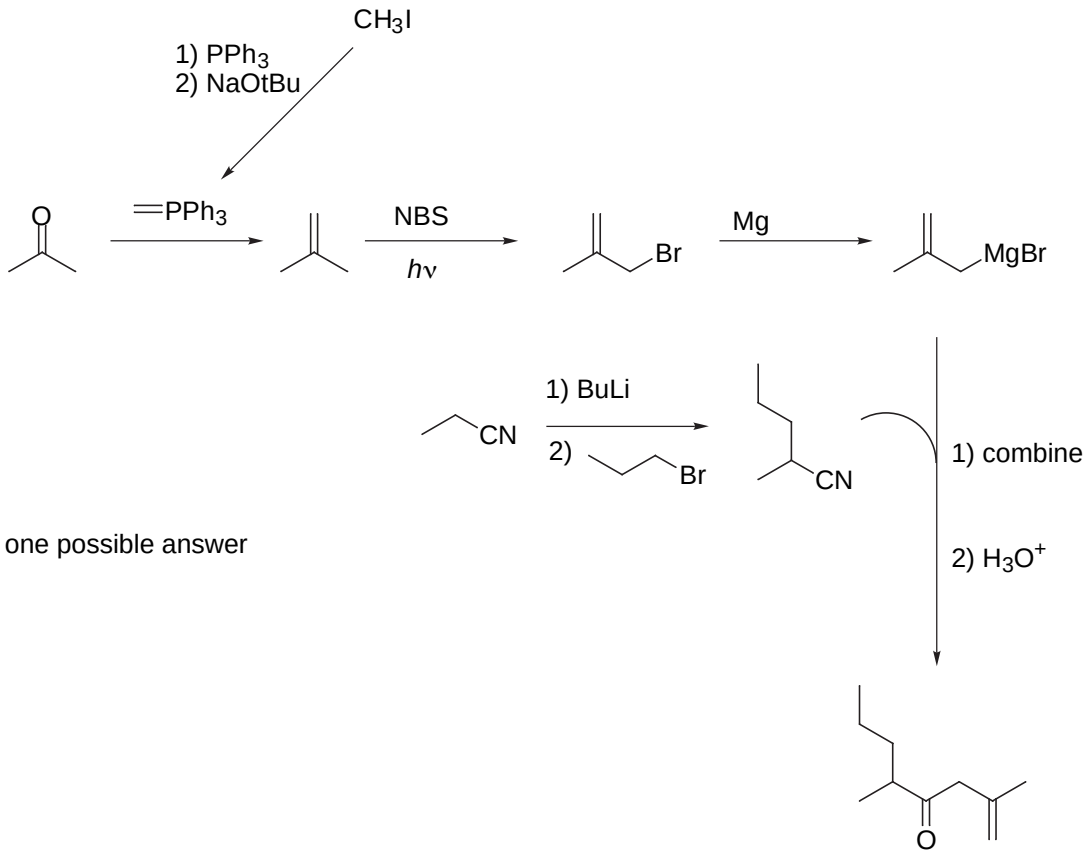
either of the enantiomers below were accepted

3. Propose a synthesis for **1** starting with any materials that contain 3 carbons or less. You may also use *reagents* that contain more than 3 carbons (e.g. BuLi, Ph_3P, LDA, MCPBA, DIBAL, DCC, pyridine, TsCl, NaOtBu, Et_3N). However, *Grignard and Wittig reagents must be prepared.*



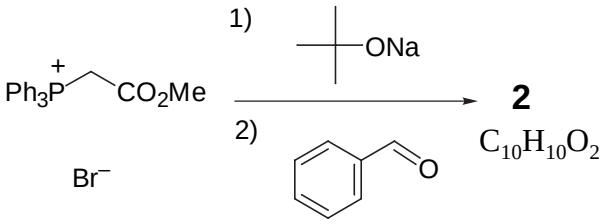
(40 pts)

1



one possible answer

4. Propose the structure of **2** (10 points). Explain how the spectroscopic data helped you make your *stereochemical* assignment. (25 points).



^{13}C NMR

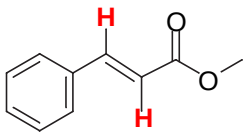
167.3, s
144.8, d
134.5, s
130.2, d
128.9, d, 2 carbons
128.8, d, 2 carbons
117.9, d
51.5, q

^{1}H NMR

7.67 (1H, d, ***J*= 15.8 Hz**)
7.6–7.2 (m, 5H)
6.40 (d, 1H, ***J*=15.8 Hz**)
3.80 (s, 3H)

10 points for connectivity

25 points:



15.8 Hz coupling constant indicates that this is a trans alkene

(35 total pts)

5. Propose a detailed mechanism for the rearrangment below (35 pts)