# CH310N
# Spring 2011

## Anslyn

## May 14, 2011

## Final Exam

Please **PRINT** the first three letters of your last name in the three boxes.

| | | |
|---|---|---|
| K | E | Y |

**PRINT Name** _____ **UT-EID** _____

1) _____ ( 8 pts )

2) _____ ( 6 pts )

3) _____ ( 8 pts )

4) _____ ( 7 pts )

5) _____ ( 5 pts )

6) _____ ( 5 pts )

7) _____ ( 8 pts )

8) _____ ( 6 pts )

9) _____ ( 28 pts)

10) _____ ( 6 pts )

11) _____ ( 4 pts )

12) _____ ( 8 pts )

13) _____ ( 6 pts )

14) _____ ( 8 pts )

15) _____ ( 8 pts )

16) _____ ( 8 pts )

17) _____ ( 5 pts )

18) _____ ( 8 pts )

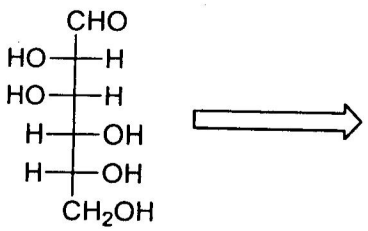
19) _____ ( 8 pts )

Total Score _____ (150 pts)

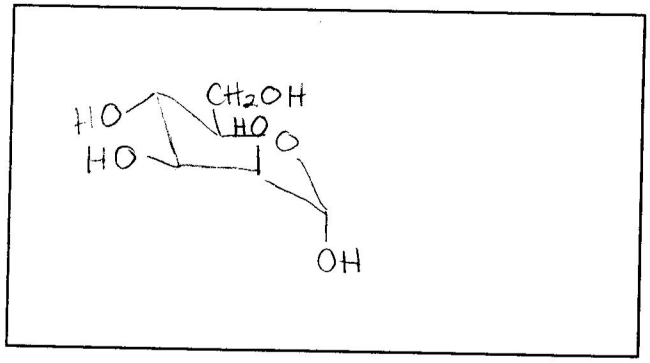
# New Material Covered Since Midterm 3:

1.

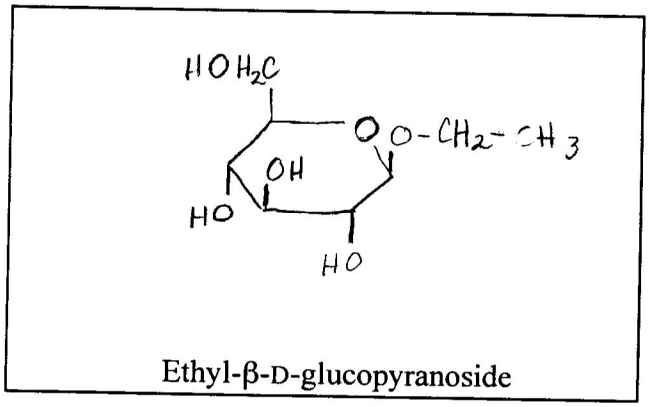
a) Draw the chair conformation of α-D-mannose in its pyranose form. (2 points)




D-Mannose

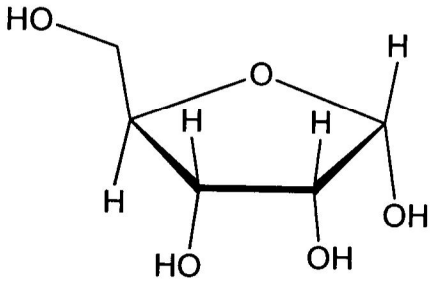



b) Please provide the Haworth projection for the following molecule. (2 points)



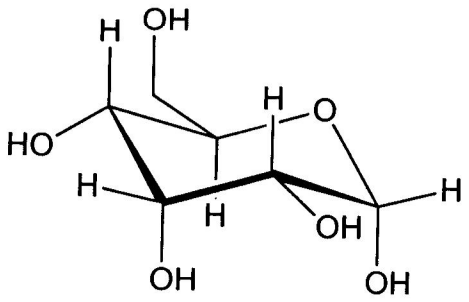

Ethyl-β-D-glucopyranoside

c) Please give the name of the following sugar, as drawn. (2 points)




α-D-Ribofuranose

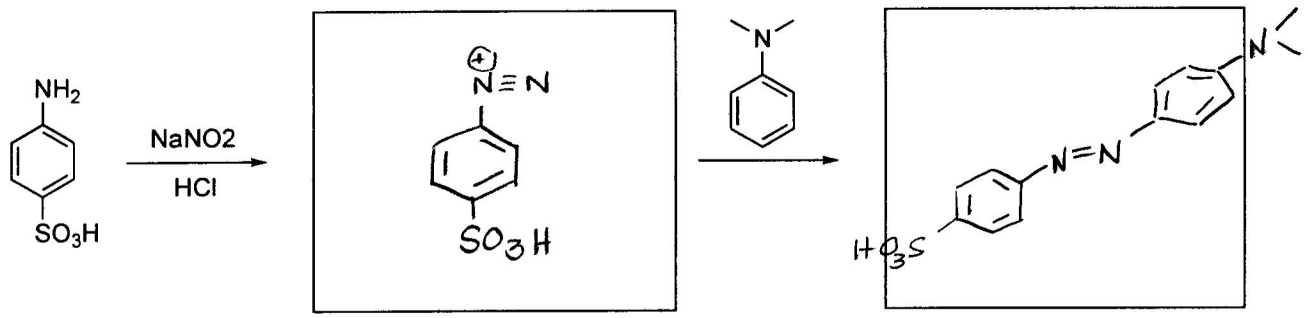
d) The following six carbon aldose is the diastereomer called allose. Give the full name of this representation of allose. (2 points)



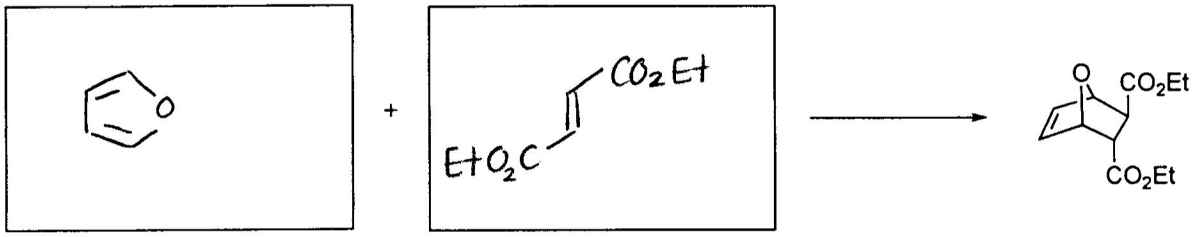

α-D-Allopyranose

2. Fill in the box with the appropriate reactant, reagent, or product. Some boxes require more than one step. (6 points)

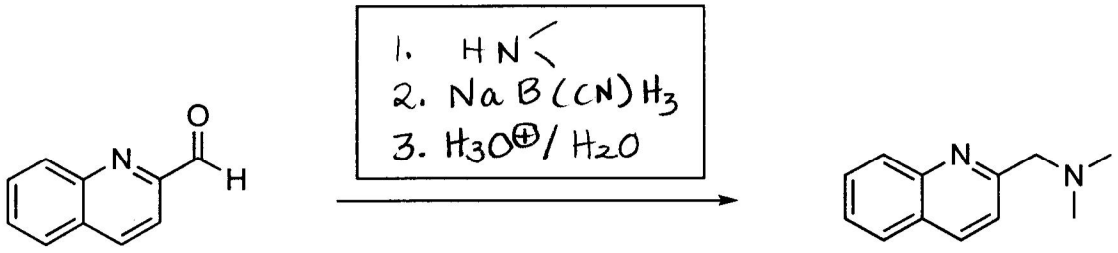
a)



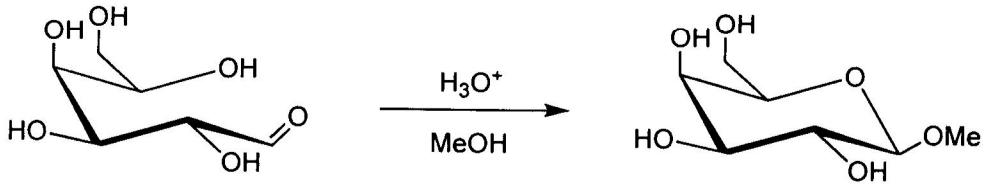

b) From class notes

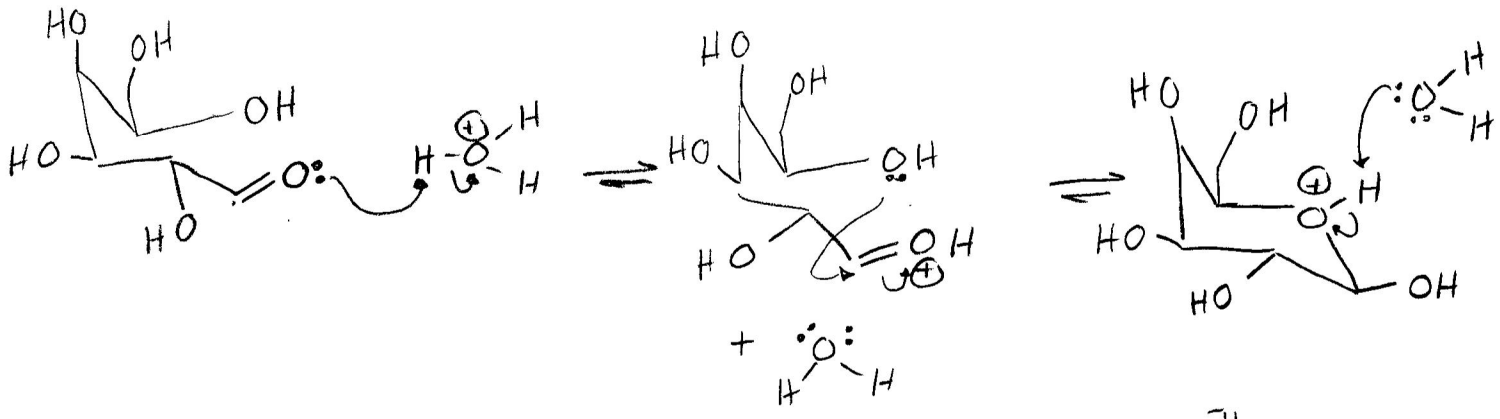



c)

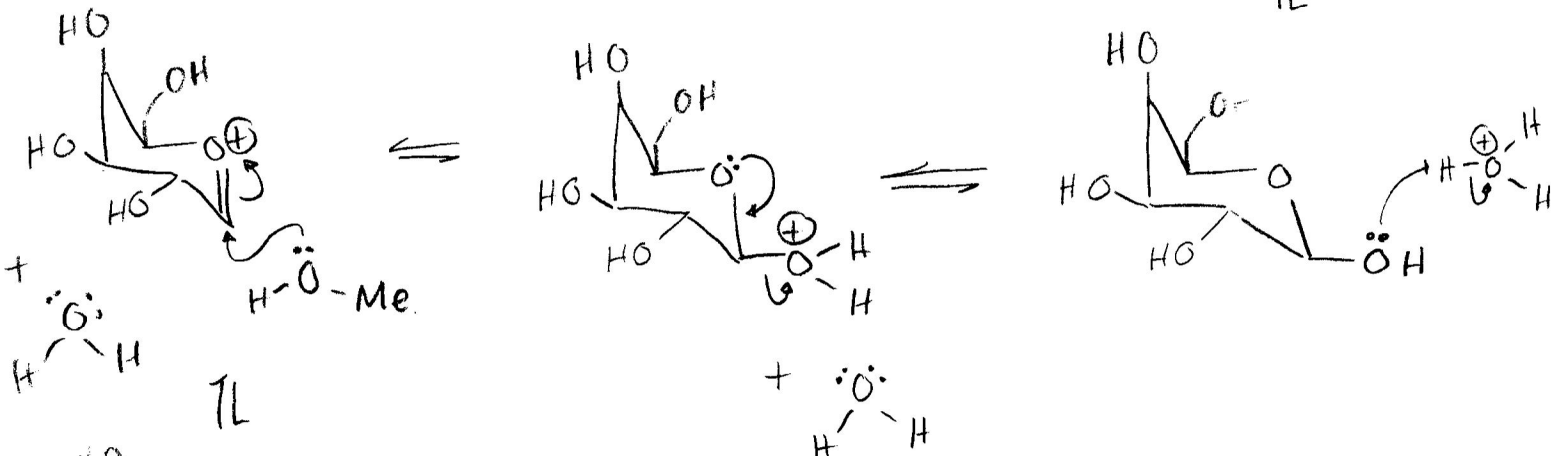


3. Draw the mechanism for the following reaction, making sure to show all participating lone pairs, applicable formal charges, and required arrow pushing to indicate flow of electrons. (8 points)

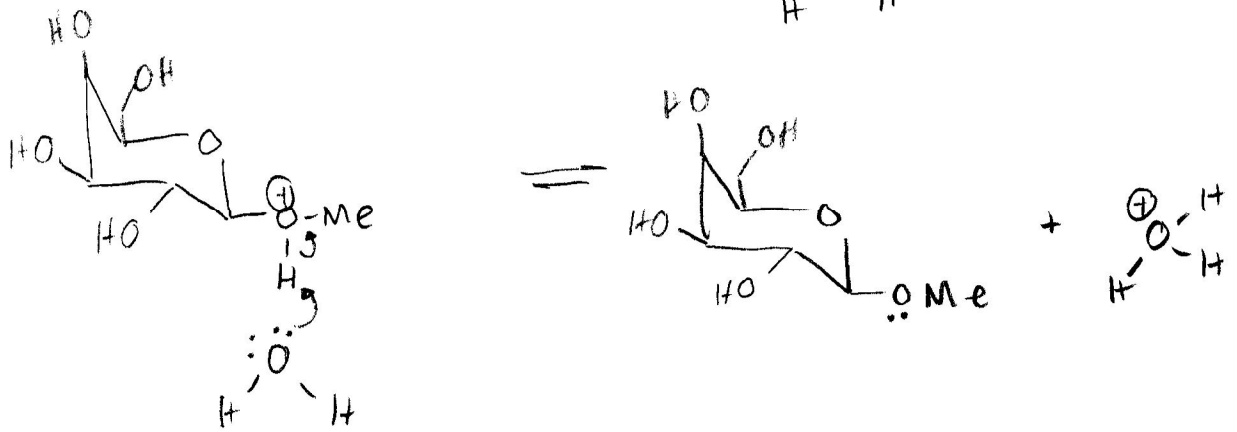



TL



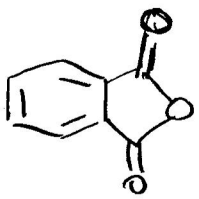

TL



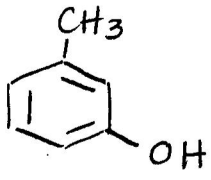

* Also, could have MeOH attack protonated carbonyl to form hemi-acetal, followed by -OH attack to form acetal.

## Cumulative Course Material:

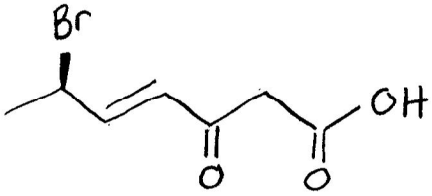
4. a) Please provide the structures of the following compounds from the given names. (7 points)



Phthalic anhydride

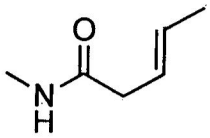



*m*-cresol




(*R*)-*E*-6-bromo-3-oxo-4-heptenoic acid

b) Please name the following molecules, based on the standard listed in parentheses.




(IUPAC)

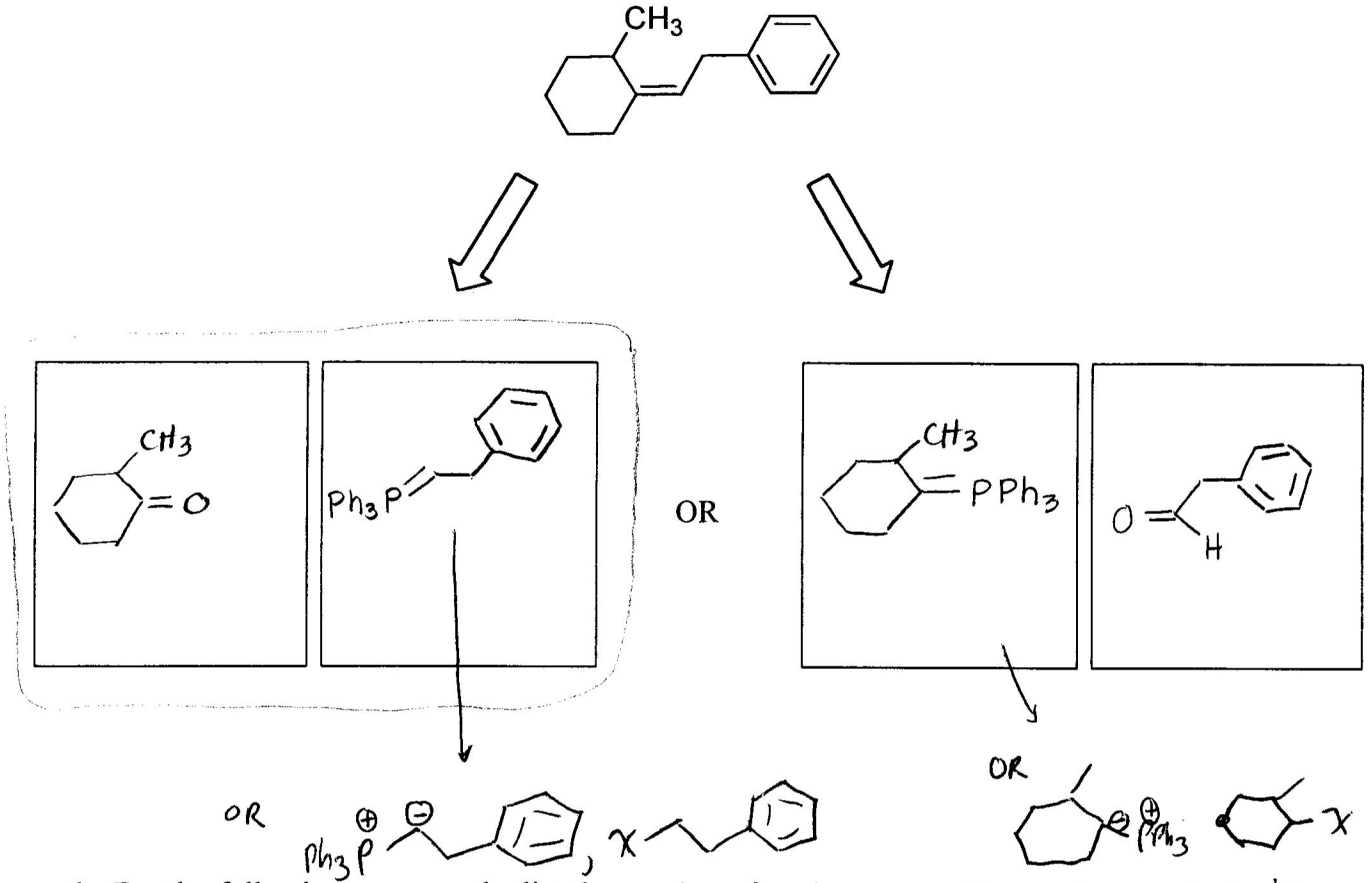
N-methyl-(3E)-pentenamide

$H_3C-C\equiv N$

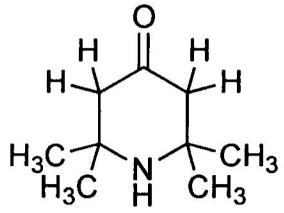
(Common)

Acetonitrile

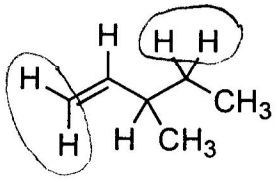
5. In class, we talked about performing retrosynthetic analyses of various compounds. The following compound can be made by a Wittig reaction in two different ways. Fill in the boxes with the two different sets of possible starting reagents for this transformation. Then, circle the set of molecules you have drawn that would give the best yield (Hint: consider how the phosphorous ylide must be prepared). (5 points)



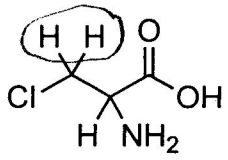

6. For the following compounds, list the number of peaks you would expect to see in the $^1$H-NMR spectrum. Then, circle any protons that are diastereotopic. (5 points)




Number of peaks expected: 3

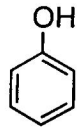
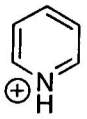
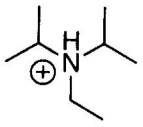
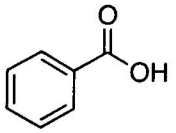



Number of peaks expected: 8

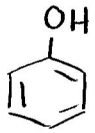
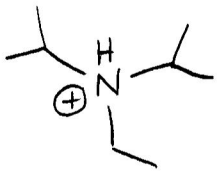
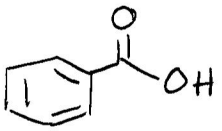



Number of peaks expected: 5

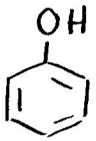
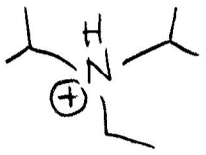
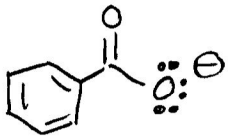
7. For the following compounds **1-6**, draw the compound in the correct protonation state based on the given pH. (8 points)

| | | | |
|---|---|---|---|
|  |  |  |  |
| **1** | **2** | **3** | **4** |

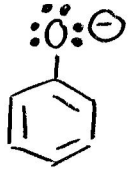
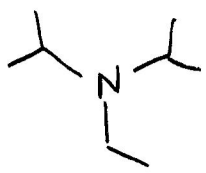
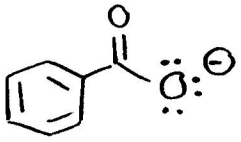
## pH = 3

| | | | |
|---|---|---|---|
|  |  |  |  |
| **1** | **2** | **3** | **4** |

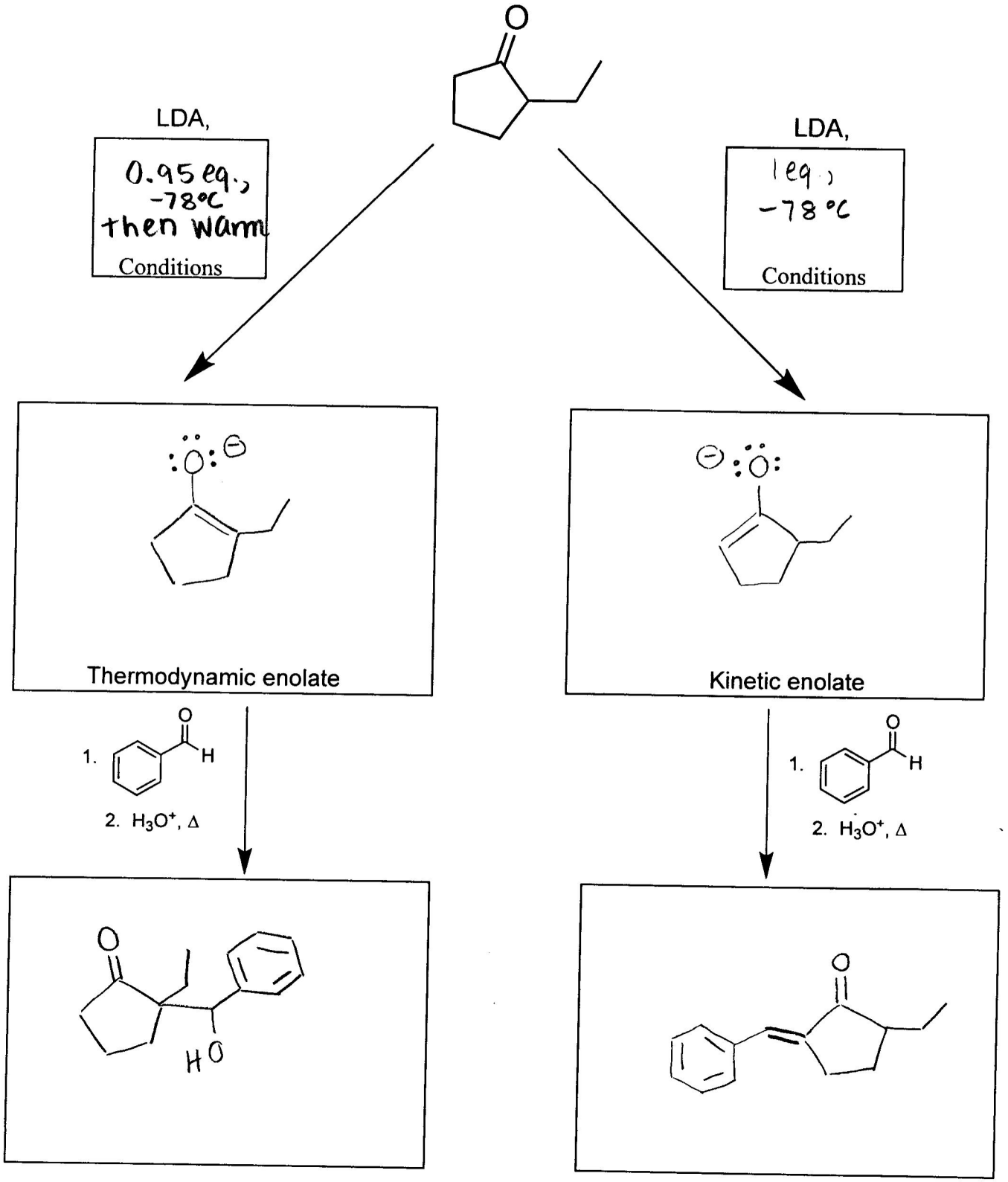
## pH = 7

| | | | |
|---|---|---|---|
|  |  |  |  |
| **1** | **2** | **3** | **4** |

## pH = 11

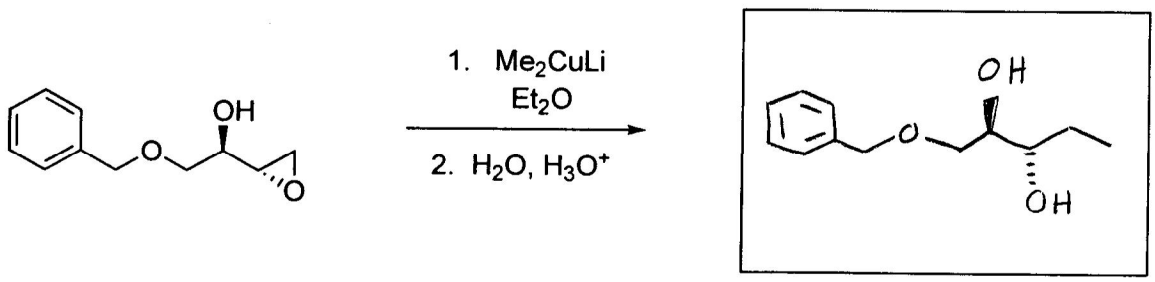
| | | | |
|---|---|---|---|
|  |  |  |  |
| **1** | **2** | **3** | **4** |

8. The following problem refers to enolate formation, which can occur in either a kinetic or thermodynamic fashion. The following ketone is deprotonated by LDA, and forms two different products depending on reaction conditions. First, indicate these conditions by filling in the top boxes. Then, fill in the structure of either the kinetic or thermodynamic enolate. Finally, fill in the product obtained from the reaction of these enolates with benzaldehyde. (6 points)

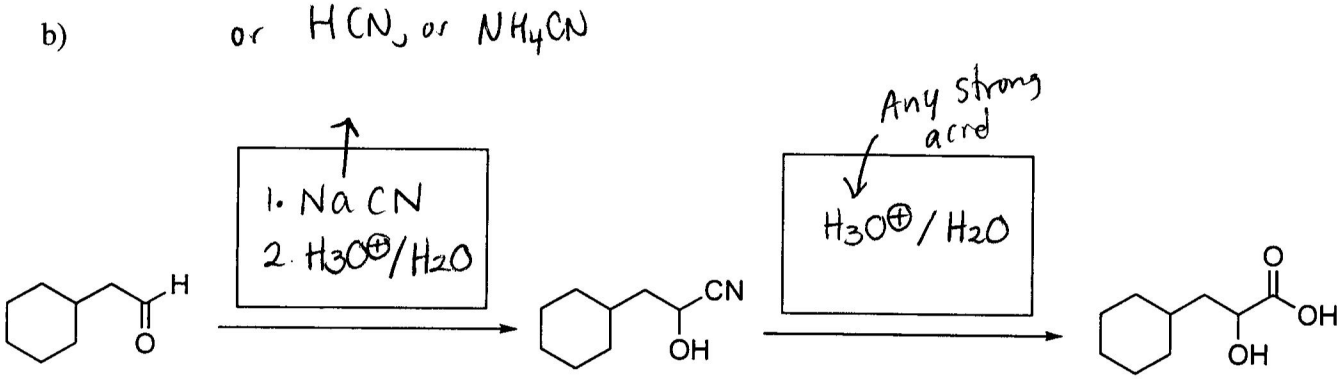


9. Fill in the box with the appropriate reactant, reagent, or product. Some boxes require more than one step. (28 points)

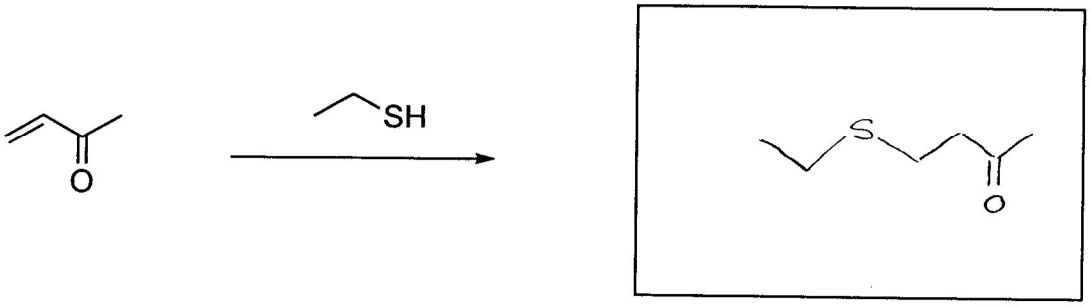
a) From homework, problem 15.23



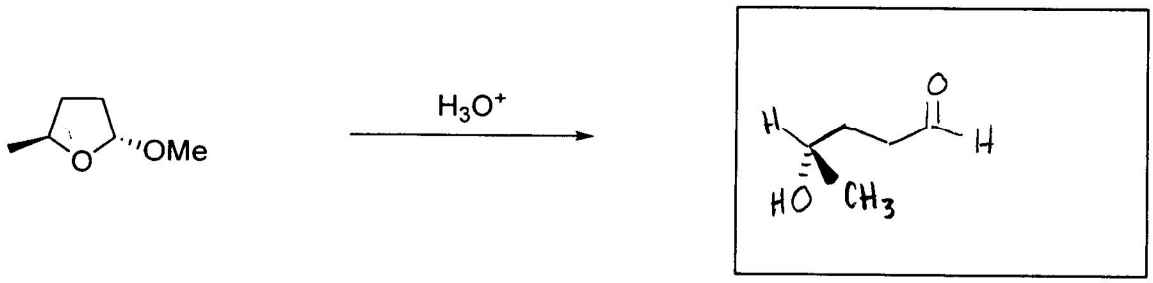

b)



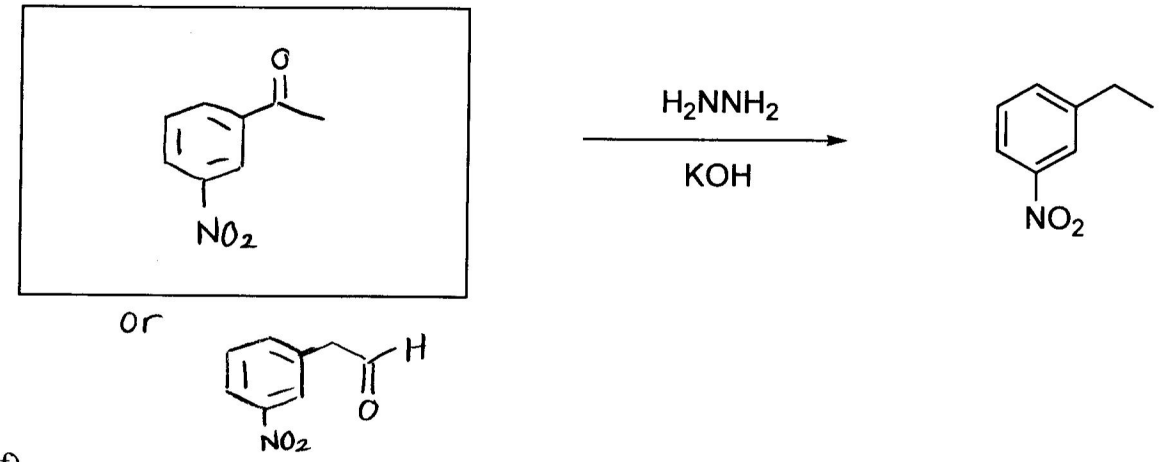

c) From class notes



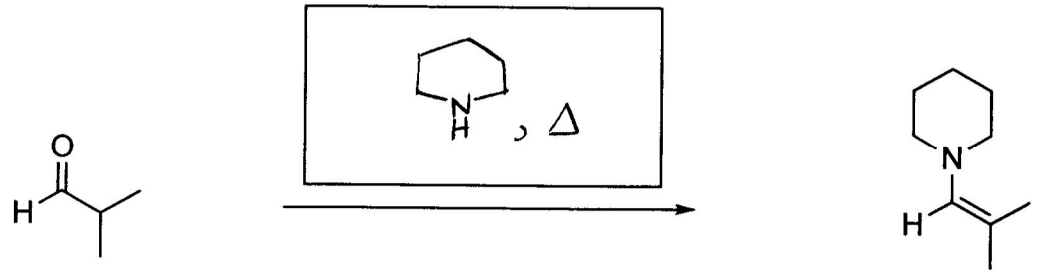
d)



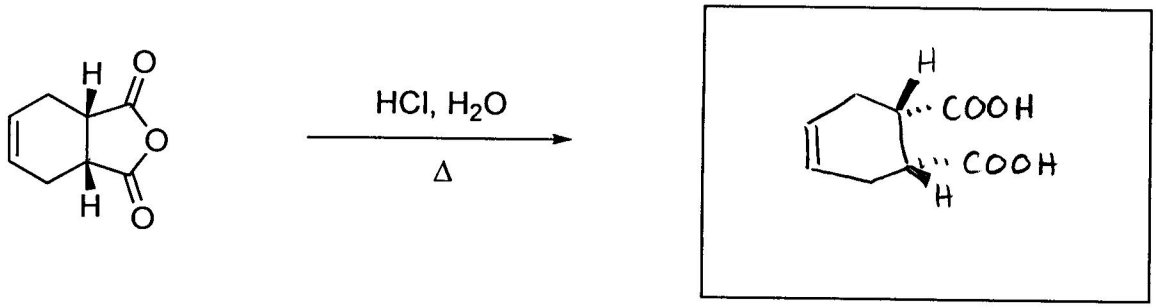

e)



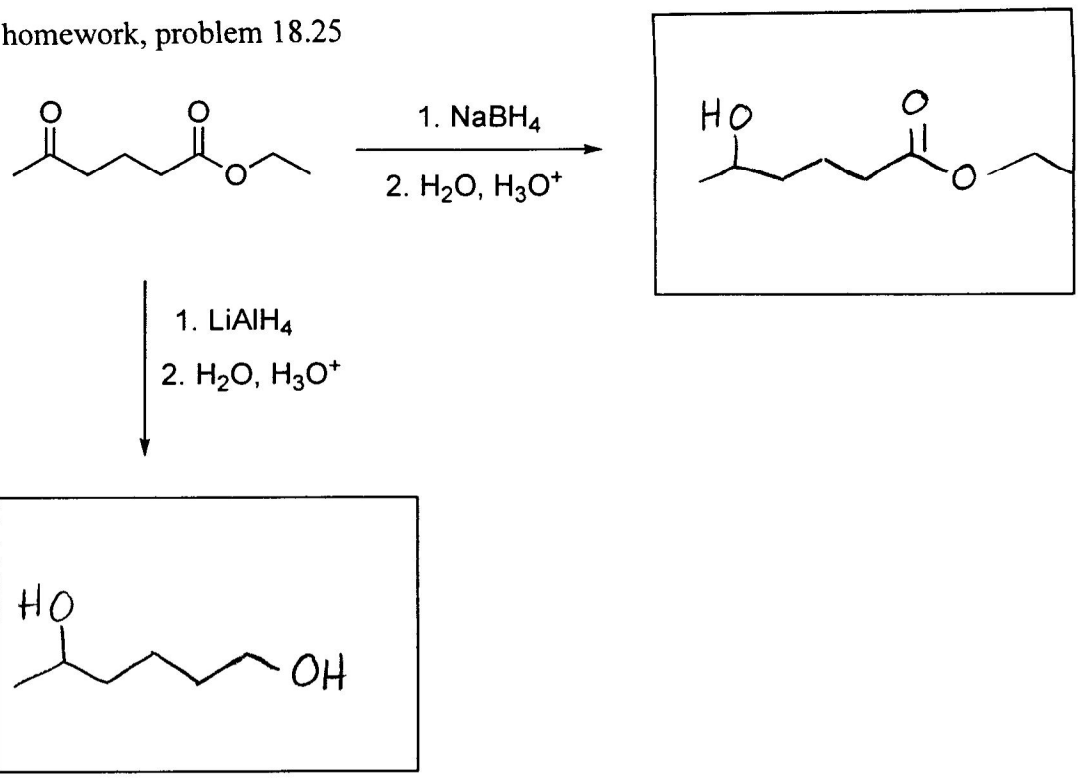

f)




g) From homework, problem 18.27



h) From homework, problem 18.25

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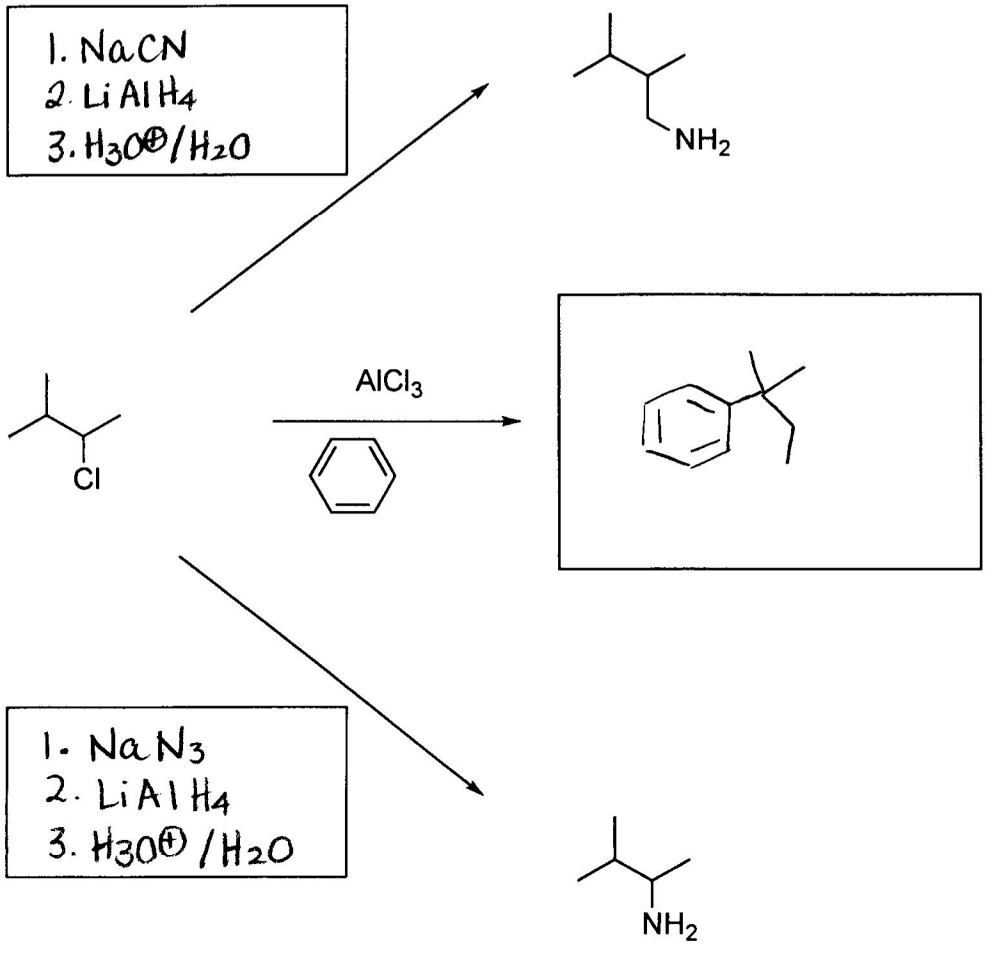
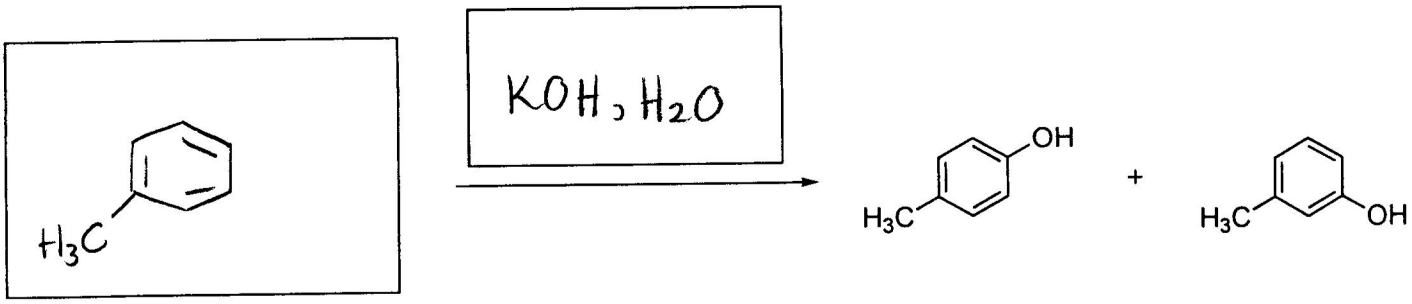
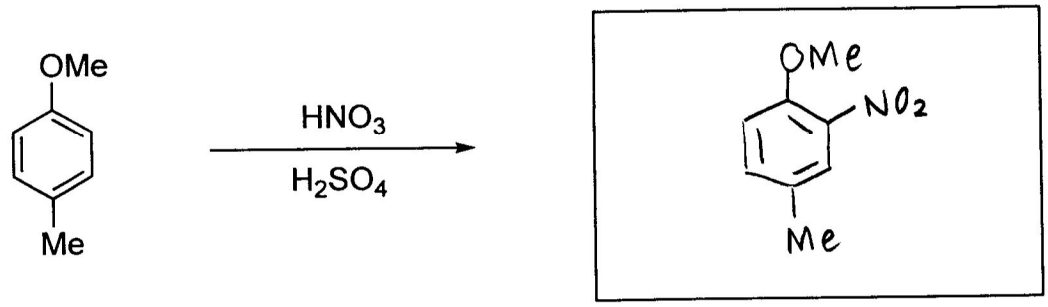
i)



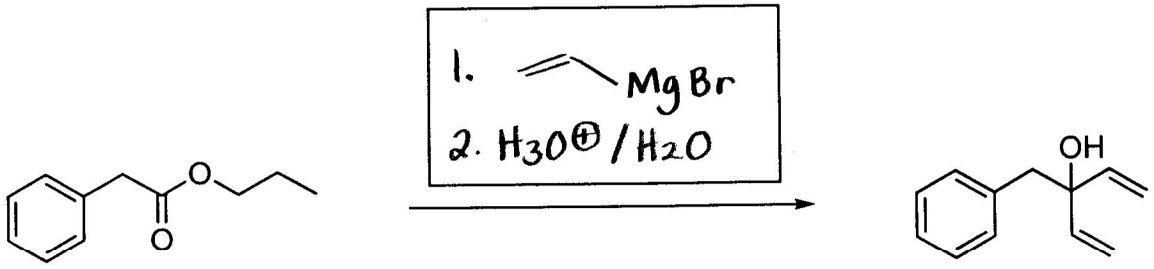
j)




k) From homework, problem 22.20

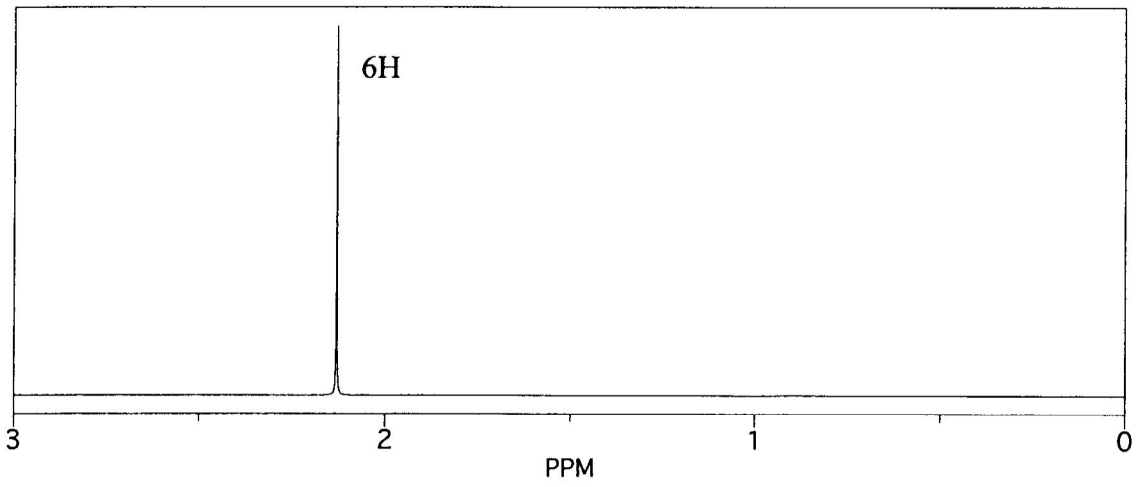



l)

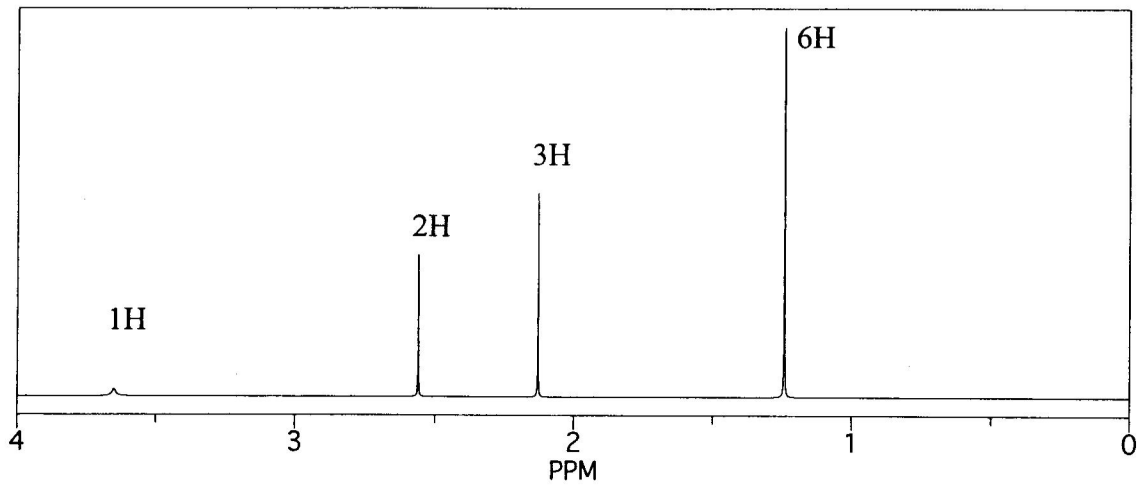


10. Below are shown three $^1$H-NMR spectra for compound A ($C_3H_6O$), compound B ($C_6H_{12}O_2$), and compound C ($C_6H_{10}O$). Upon stirring compound A in sodium ethoxide and ethanol, compound B is formed, and upon further stirring in sodium ethoxide and ethanol, compound C is formed. Deduce the structural formulas for compounds A, B, and C. (Note: the ppm axes on the NMR spectra are not all plotted from 0-10) (6 points)

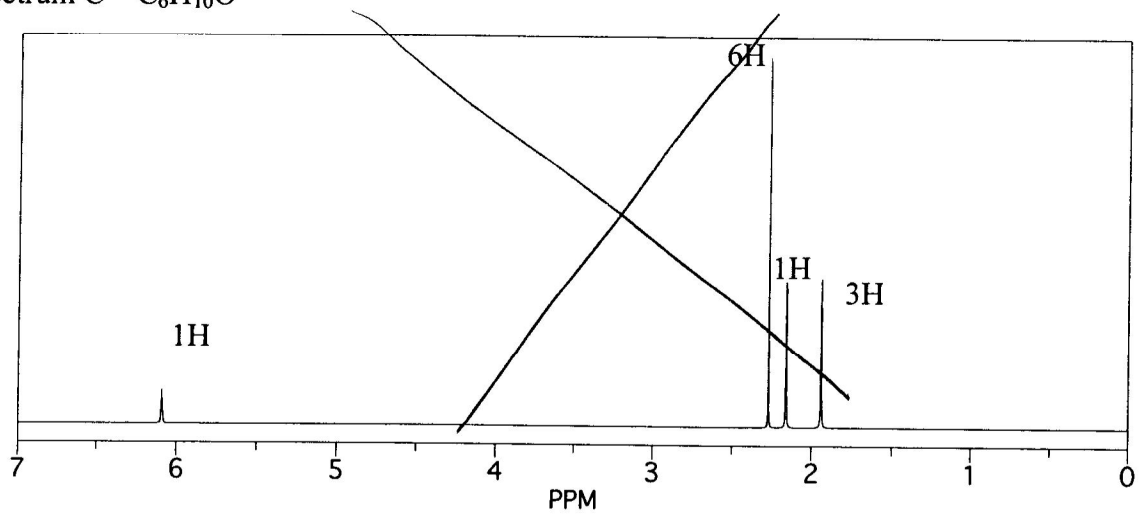
Spectrum A – $C_3H_6O$




Spectrum B – $C_6H_{12}O_2$

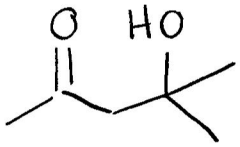


Spectrum C – $C_6H_{10}O$




Compound A ($C_3H_6O$)


Compound B ($C_6H_{12}O_2$)

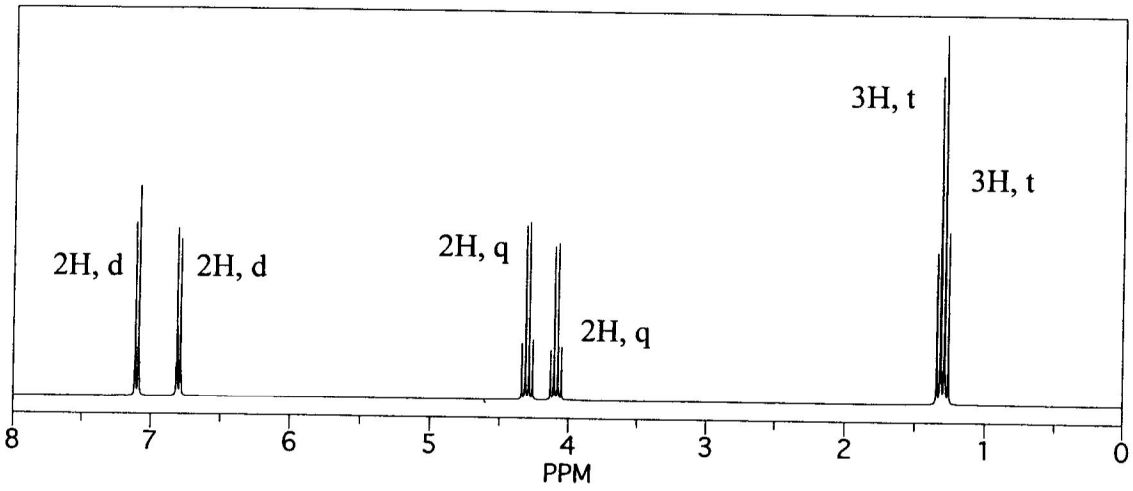



Compound C ($C_6H_{10}O$)

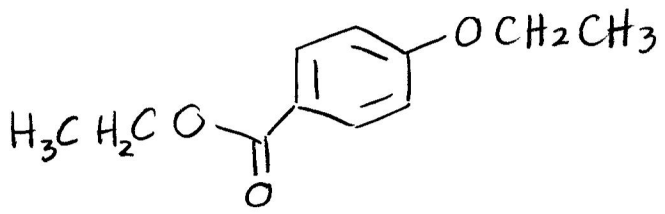
OMIT

11. Propose a structural formula for compound D with a molecular formula of $C_{11}H_{14}O_3$ based on its $^1$H-NMR spectrum. (4 points)

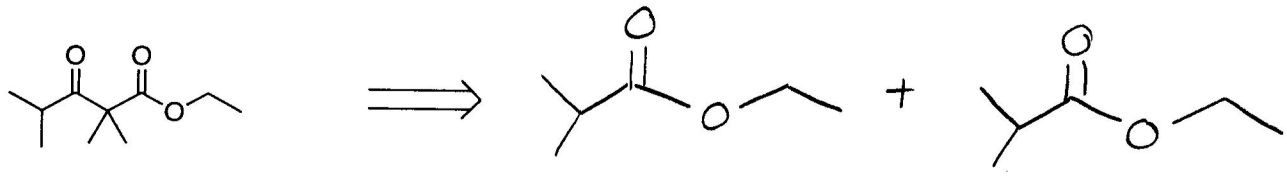
Spectrum for compound D– $C_{11}H_{14}O_3$

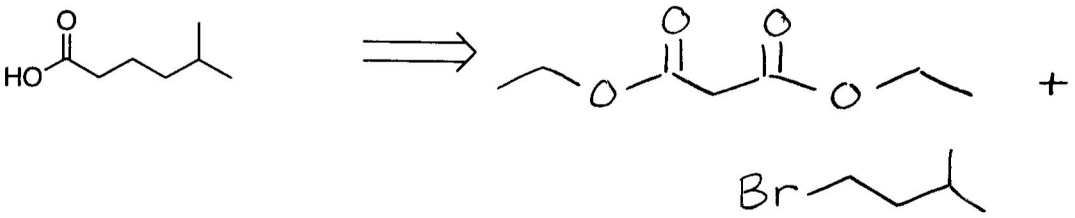


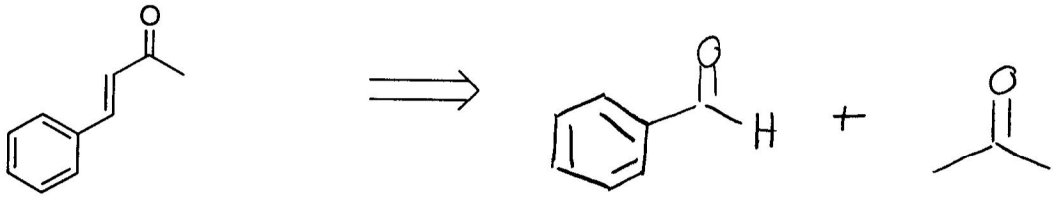

Structure for Compound D

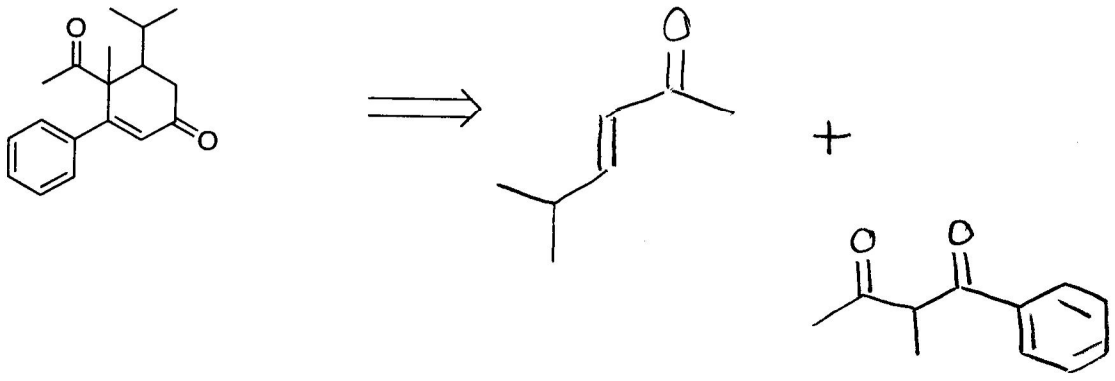


12. Using a retrosynthetic approach, draw the starting materials needed to make each product listed below by one of the reactions from chapter 19 (aldol condensation, Claisen condensation, Michael addition, acetoacetic ester synthesis, malonic ester synthesis, Robinson annulation, etc.) (8 points)

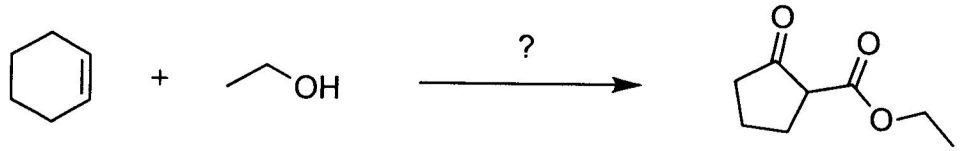
a) 

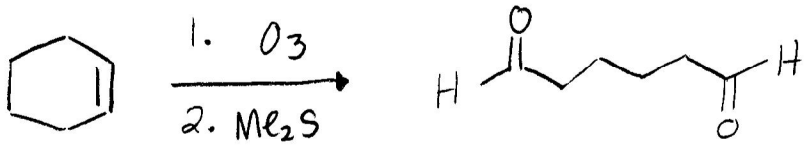
b) 

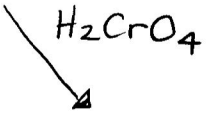
c) 

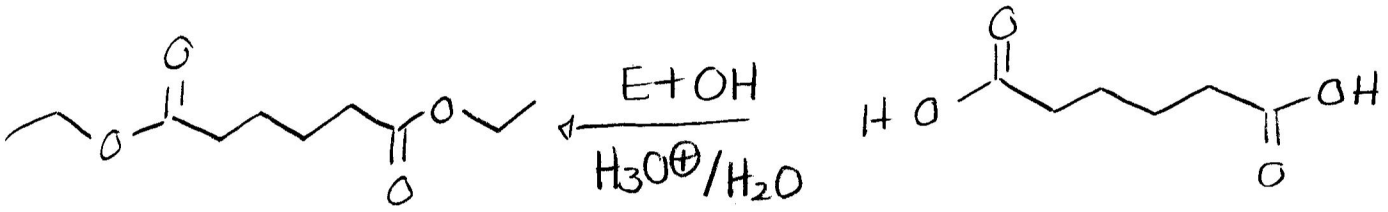
d) 

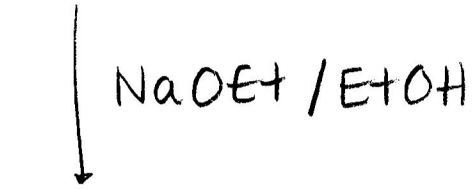
13. From homework, problem 19.75. Show how to convert cyclohexene and ethanol into ethyl-2-oxocyclopentanecarboxylate, as shown below. You may use any reagents you wish, but all carbon atoms in the final product must be from cyclohexene and ethanol. Show all reagents used and synthetic intermediates that are created. You do not need to show a mechanism for the transformations. (6 points)

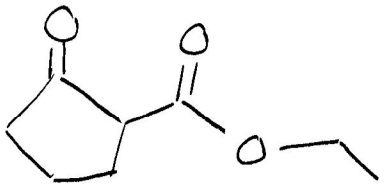


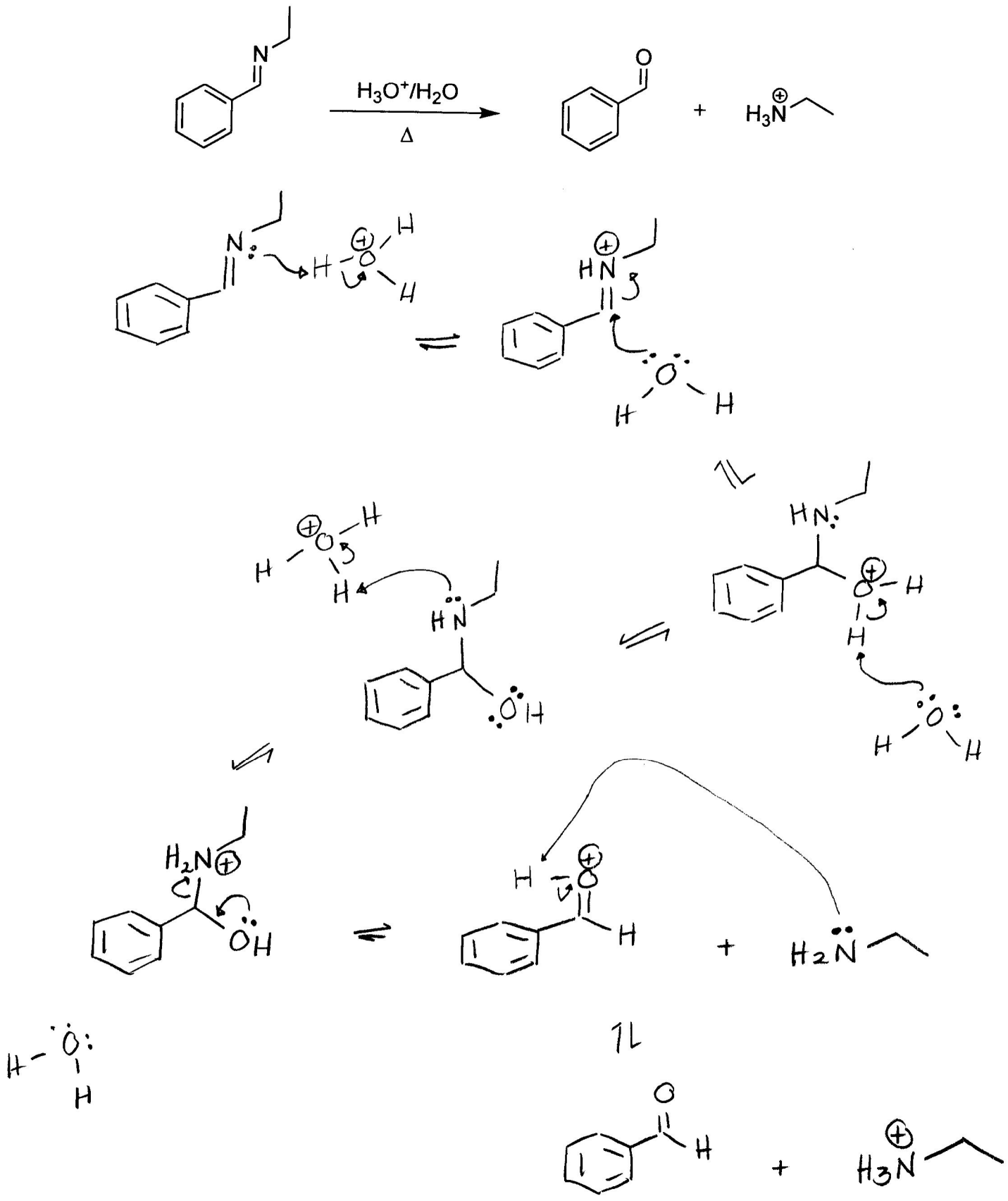



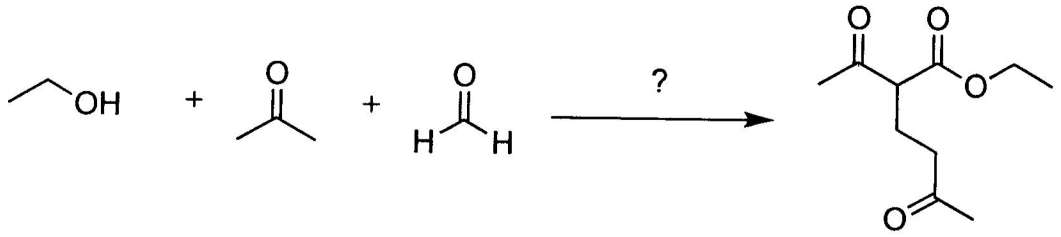



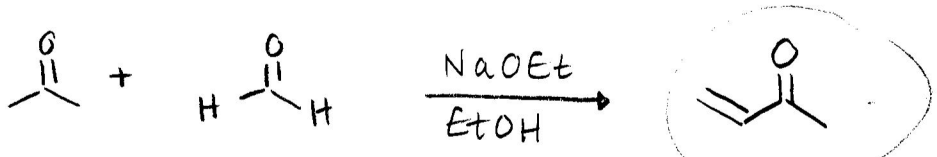



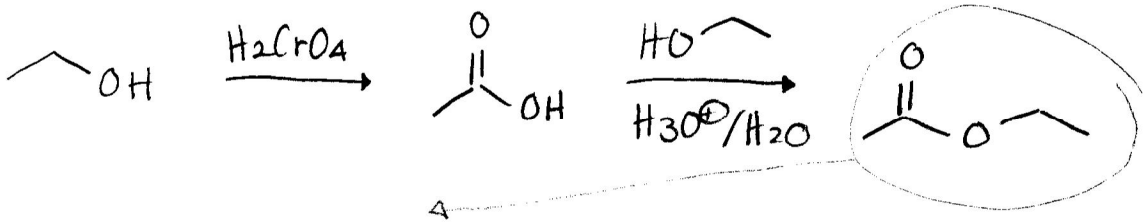
14. Draw the mechanism for the hydrolysis of an imine back to the parent aldehyde. Make sure you show all participating lone pairs, applicable formal charges, and required arrow pushing to indicate flow of electrons. (8 points)

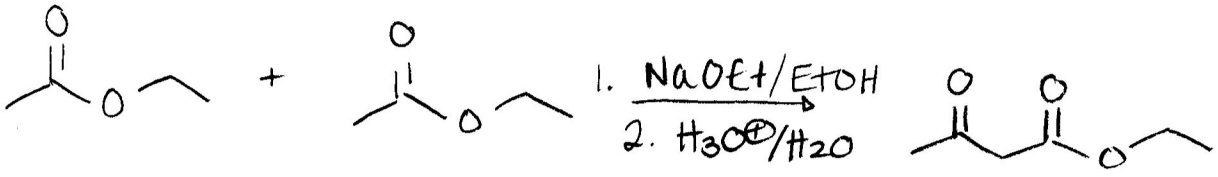


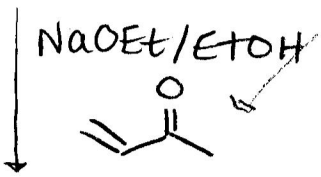
15. From homework, problem 19.74. Show how to convert ethanol, formaldehyde, and acetone into ethyl 2-acetyl-5-oxohexanoate. You may use any reagents you wish, but all carbon atoms in the final product must be from ethanol, formaldehyde, and acetone. Show all reagents used and synthetic intermediates that are created. You do not need to show a mechanism for the transformations. (8 points)

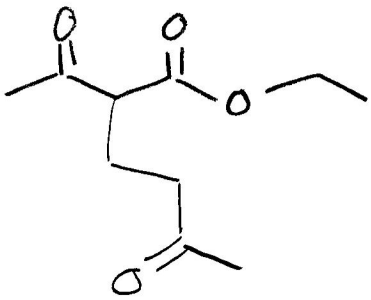


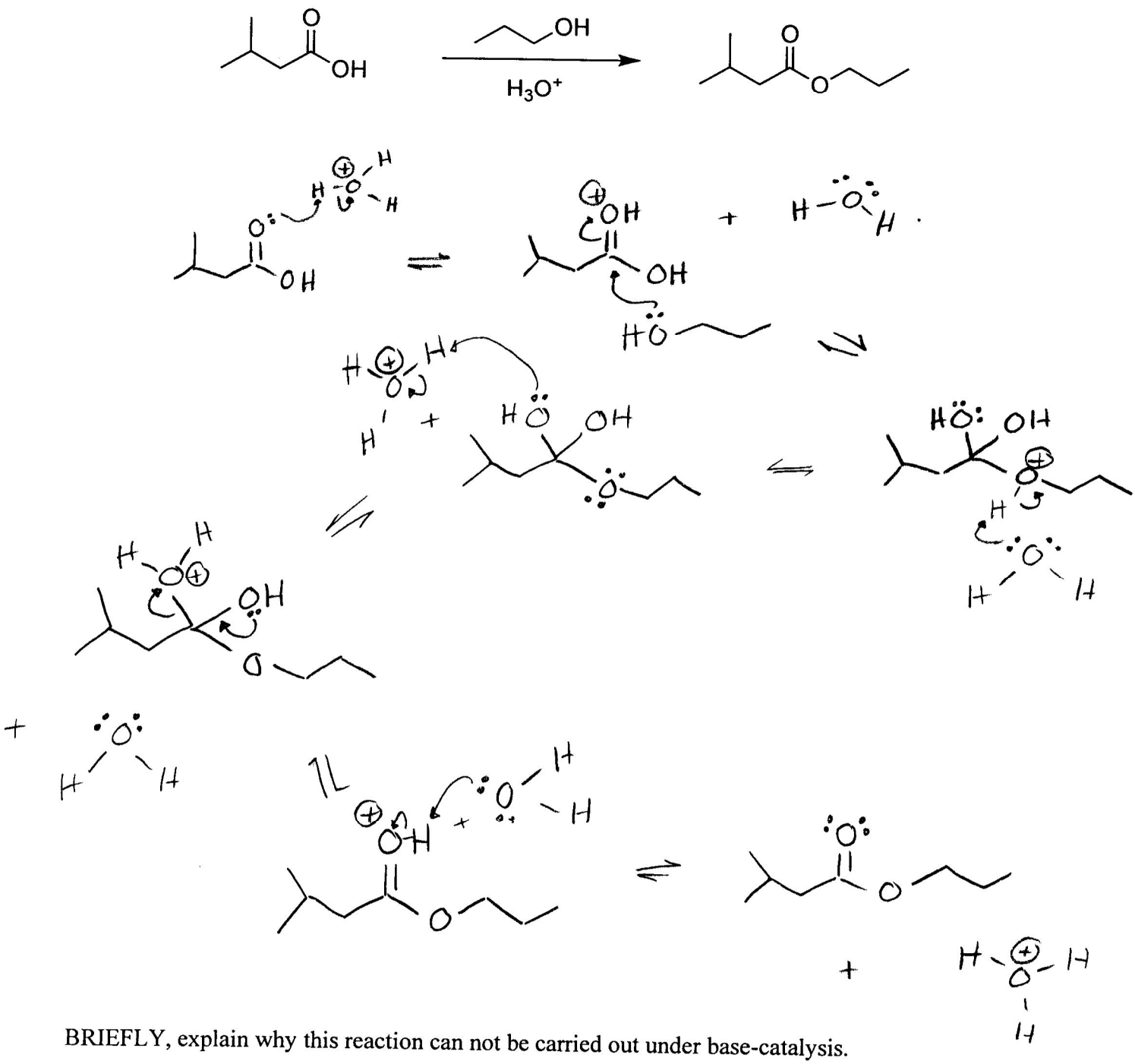



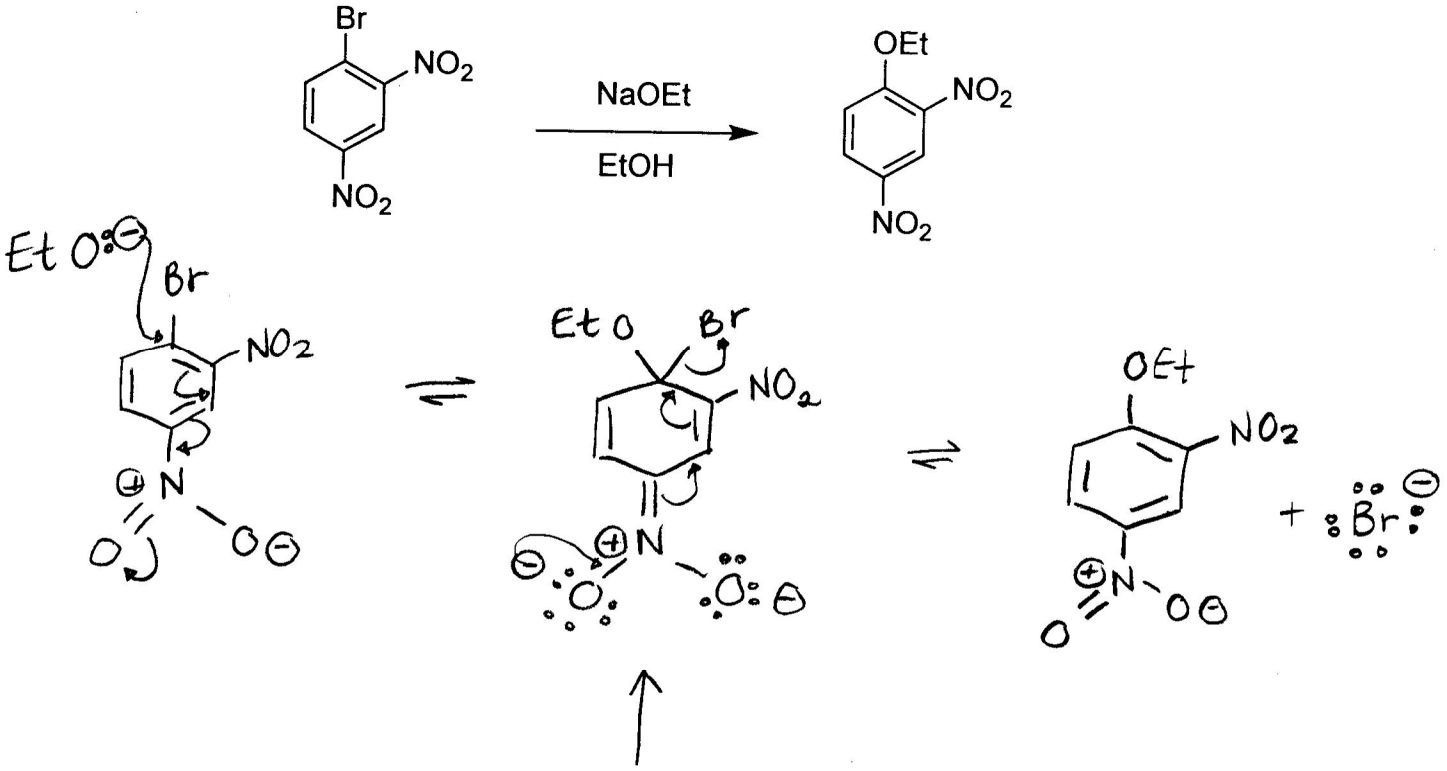
16. Draw the mechanism for the acid-catalyzed Fischer esterification, as shown below. Make sure you show all participating lone pairs, applicable formal charges, and required arrow pushing to indicate flow of electrons. (8 points)




BRIEFLY, explain why this reaction can not be carried out under base-catalysis.

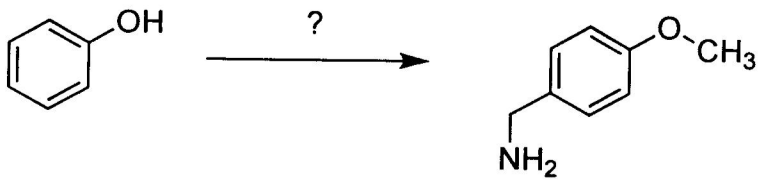
$pK_a$ of -COOH ~4-5, under base deprotonation of -COOH will occur - not esterification

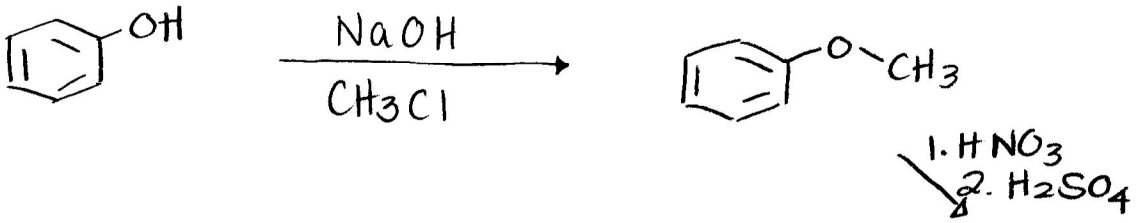
17. Draw the mechanism for the following reaction, making sure to show all participating lone pairs, applicable formal charges, and required arrow pushing to indicate flow of electrons. (5 points)

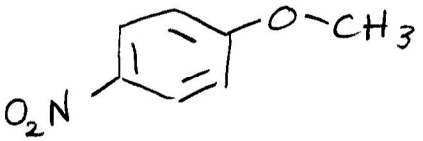


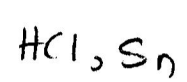

Could put this Charge on other nitro group, or the carbon bearing either nitro.

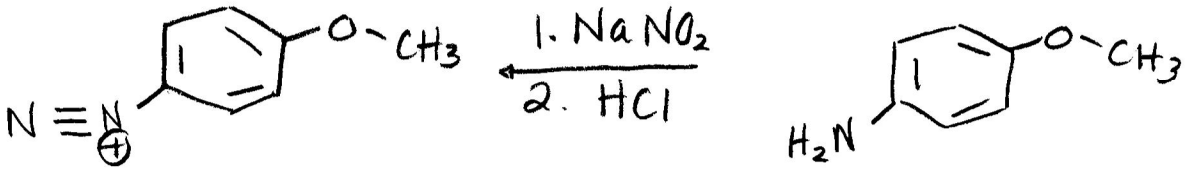
18. From homework, problem 23.47. Show how you would bring about the following transformation. You may use any reagents you wish, making sure to show all reagents used and synthetic intermediates that are created. You do not need to show a mechanism for the transformations. (8 points)

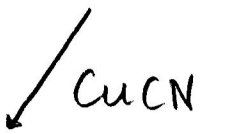


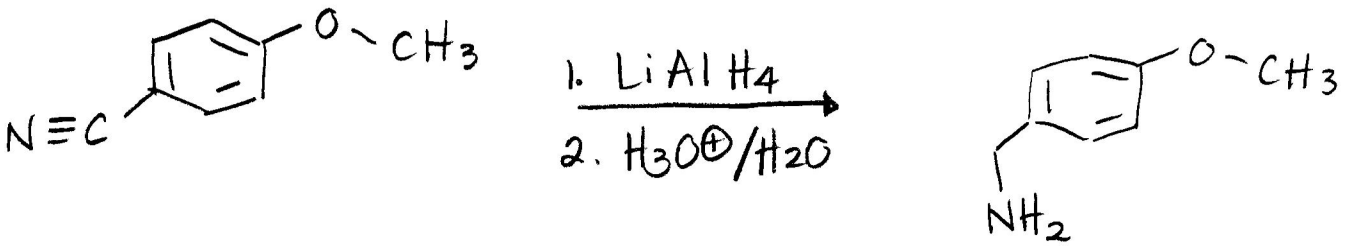



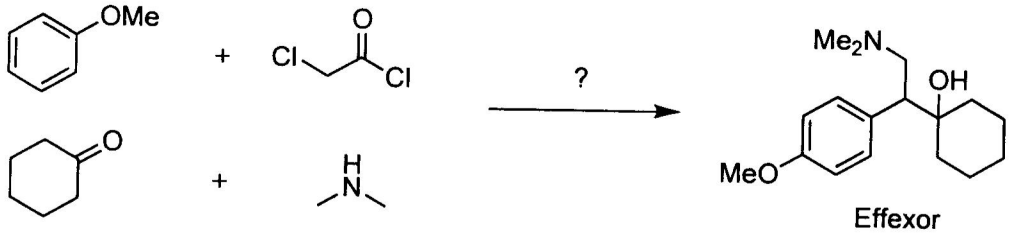



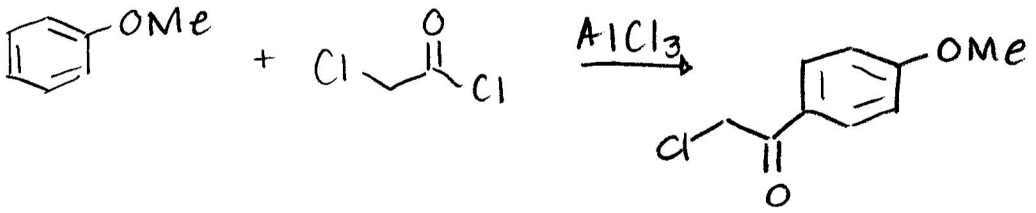



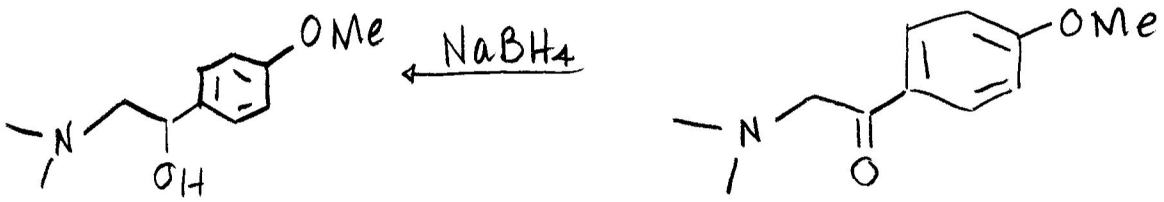
19. From homework, problem 22.52. Using only the indicated starting materials, show how you would synthesize the antidepressant venfalaxine (Effexor). You may use any reagents you wish, making sure to show all reagents used and synthetic intermediates that are created. You do not need to show a mechanism for the transformations. (Hint: Victor Grignard won the 1912 Nobel Prize in chemistry for a transformation you may end up using here.) (8 points)

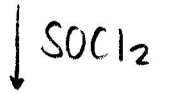


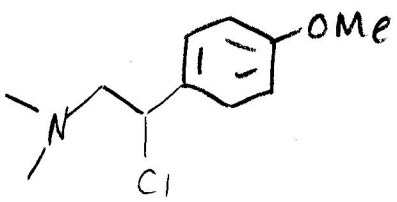

Effexor

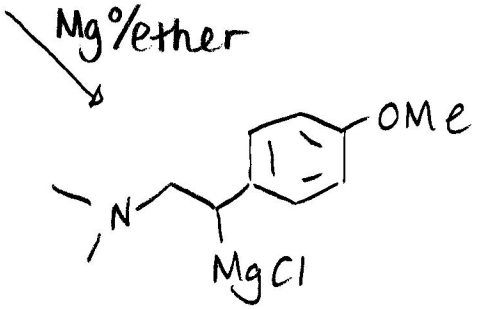


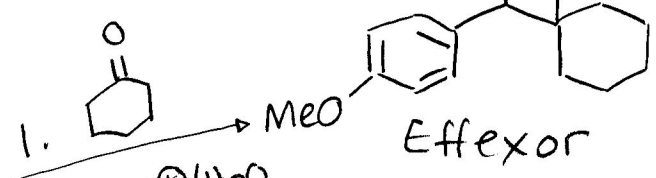





Effexor