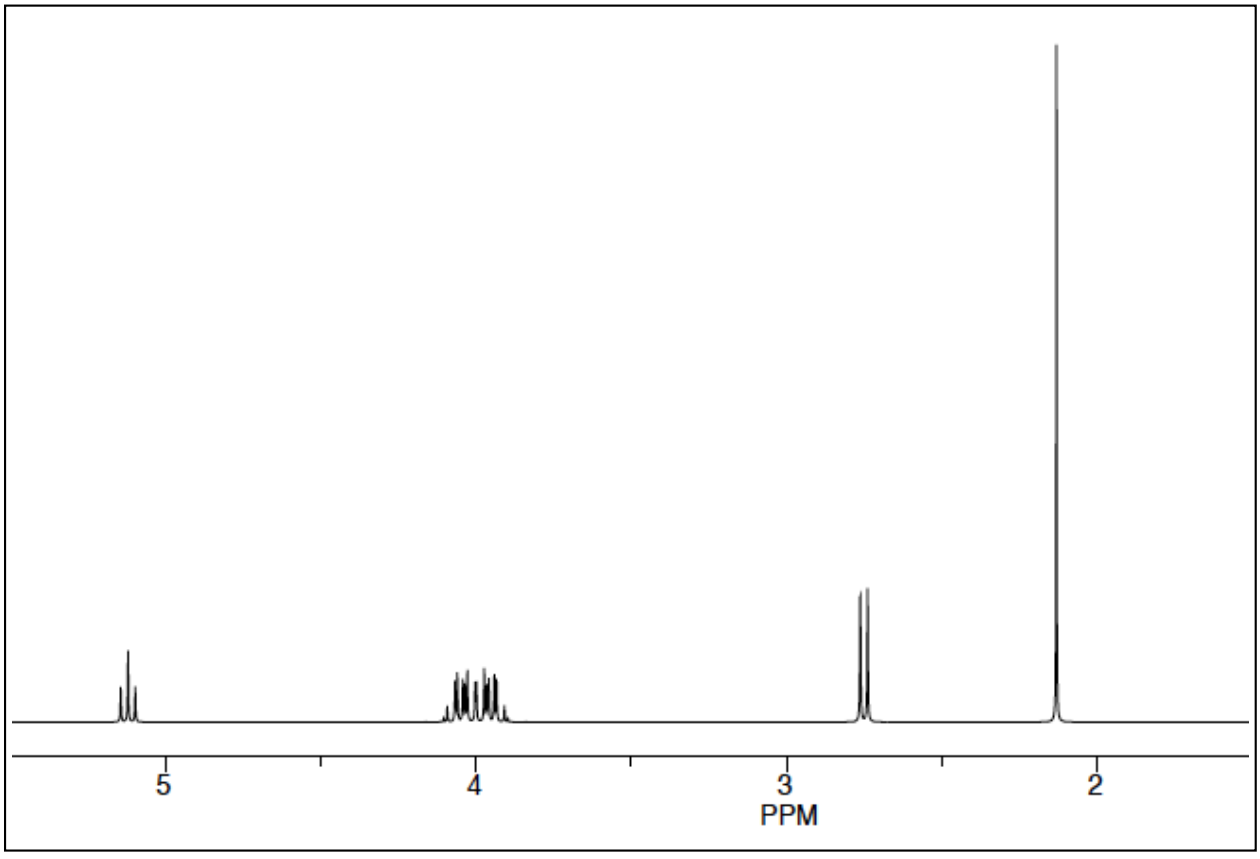
Chemistry 41c
MIDTERM EXAM KEY
May 6, 2013

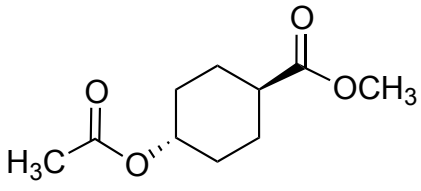
Name (print)_____Answer Key_____

Note: You have 55 minutes to take the exam. This exercise is to be worked alone and is closed book and closed notes. No electronic devices are allowed.



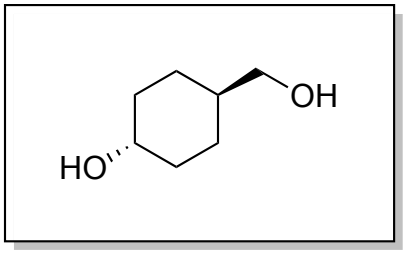
1. Predict the principal products or intermediates expected (if any) for the following reaction sequences. For each, draw the structure you want to be evaluated in the box provided. (6 pts each)

a)

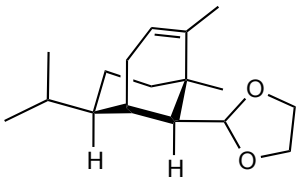


1. $LiAlH_4$, THF

2. H_3O^+ (work-up)

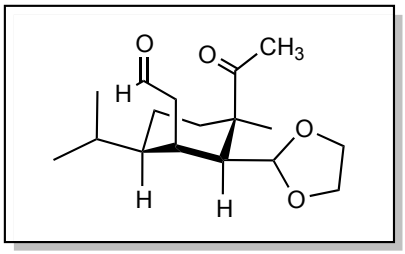


b)



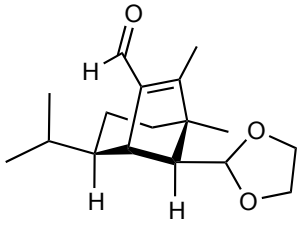
1. OsO_4, Py

2. H_5IO_6, HOAc

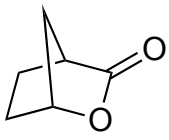


NaOH

EtOH, Δ

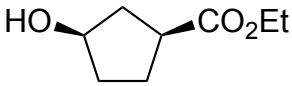


c)



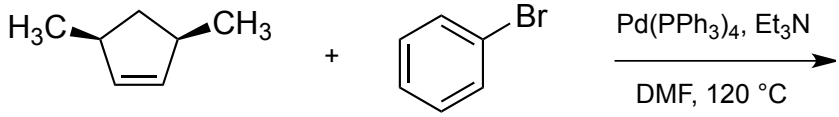
1. NaH, EtOH

2. H_2O (work-up)



1. Predict the principal products or intermediates expected (if any) for the following reaction sequences. For each, draw the structure you want to be evaluated in the box provided. (6 pts each)

d)

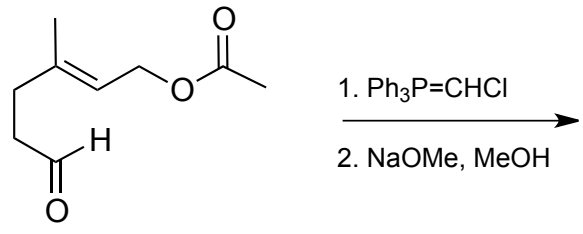


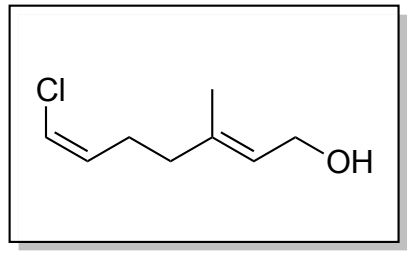
racemic

Bonus: Provide the following for Pd in the catalyst for this reaction. (3 pts)

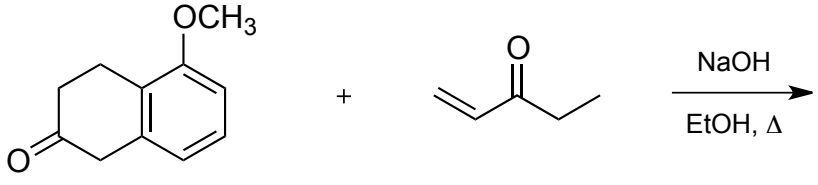
d^n count: d^{10}
oxidation state: Pd^0
valence e^- count: **18 e^-**

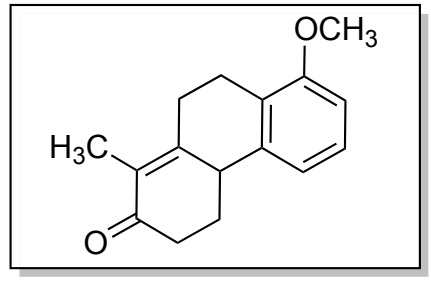
e)





f)

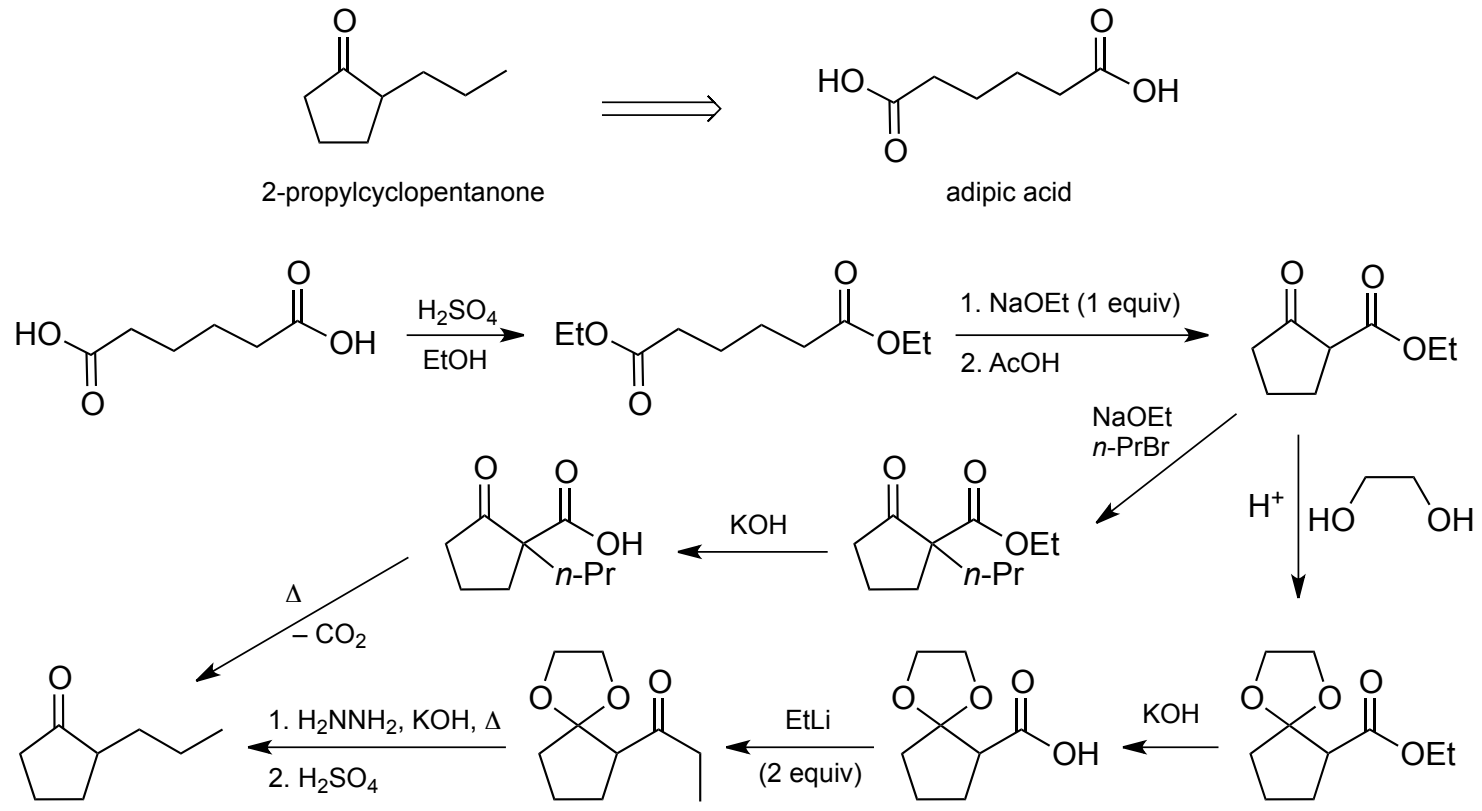




Bonus: What is the name of this reaction? (1 pt)

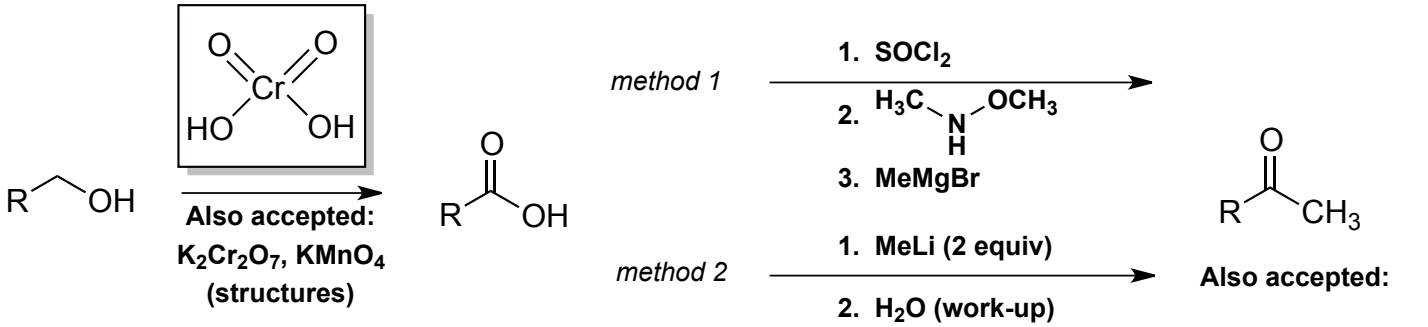
Robinson Annulation

2. Propose a synthesis of 2-propylcyclopentanone from adipic acid, using any other reagents containing 3 carbons or fewer. Show the structures of key intermediates. Mechanisms are not required. (15 pts)

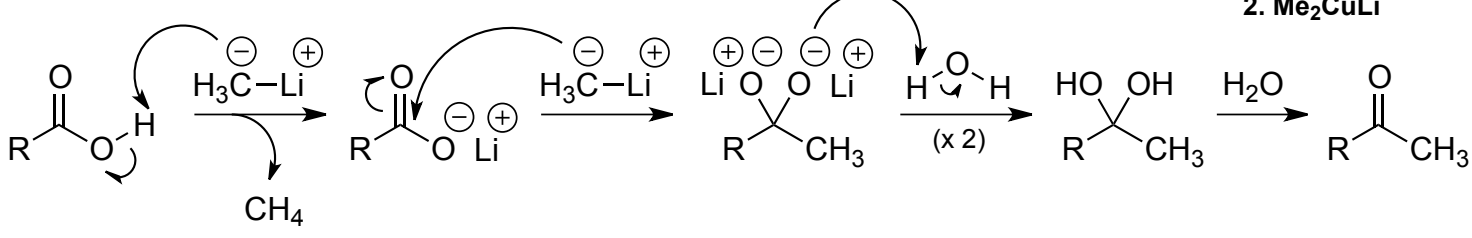


3. Describe two methods for preparing a methyl ketone from the corresponding carboxylic acid. Over the arrows below, provide the structure(s) of reagent(s) used for your proposed transformations. For your second method, write the mechanism of the reaction in which the C–C bond is formed. (15 pts)

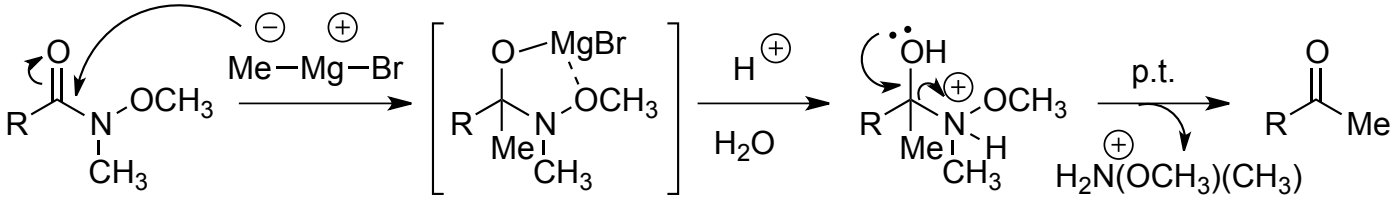
Bonus: In the box provided, draw the structure of a reagent for the oxidation of the alcohol to the carboxylic acid. (2 pts)



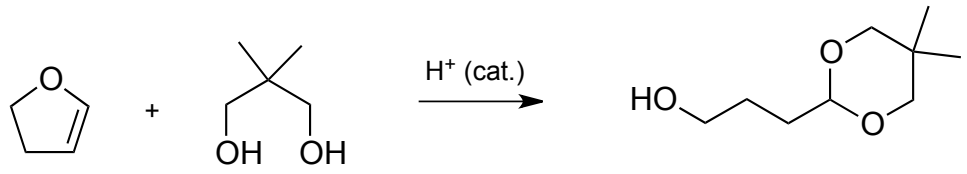
Mechanism for Method 2:



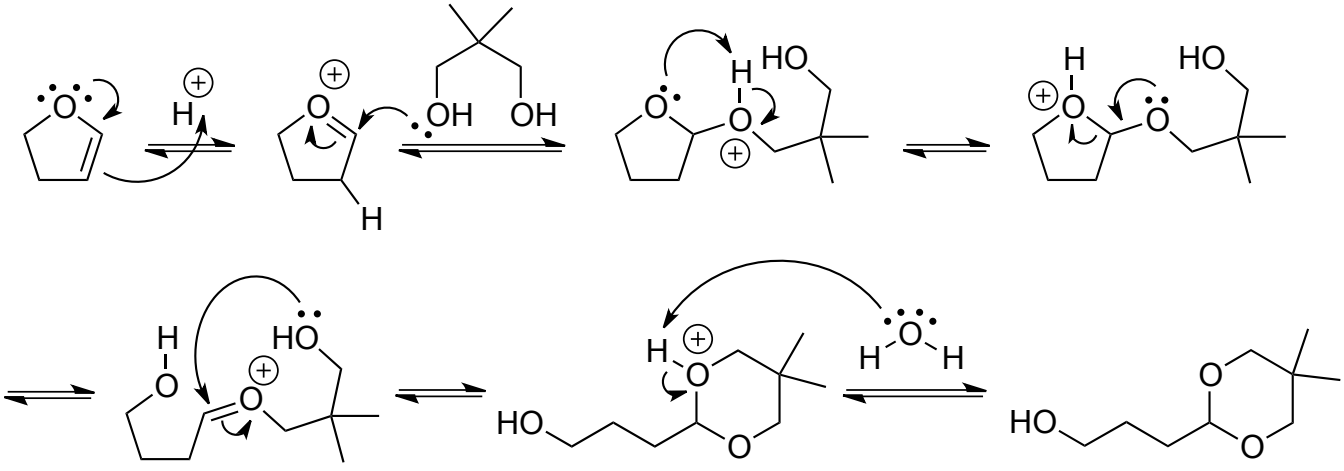
[Mechanism for Method 1]:



4. Propose a mechanism for the following transformation. (15 pts)

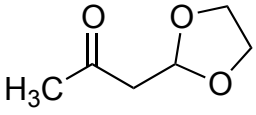


Bonus: Using a Dean-Stark apparatus would ensure a high yield for this reaction. (2 pts) **TRUE** / **FALSE**



5. Compound **A** has the molecular formula $C_6H_{10}O_3$ and shows a strong IR absorption peak near 1710 cm^{-1}. When treated with I_2 in aqueous sodium hydroxide, **A** gives a yellow precipitate. When **A** is treated with Tollen's reagent (Ag^+), no reaction occurs. However, if **A** is treated first with water containing a drop of sulfuric acid a new compound is isolated and is found to have a ^1H NMR spectrum which includes a downfield triplet at 9.5 ppm.

Compound **A** shows the following ^1H NMR spectrum (see cover page): singlet (2.13 ppm, 3H), doublet (2.75 ppm, 2H), multiplet (3.95 ppm, 2H), multiplet (4.05 ppm, 2H), triplet (5.12 ppm, 1H). ^{13}C signals for **A**: 205.1, 108.4, 64.4 (2C), 48.2, 30.1 ppm. Deduce the structure of **A**, and write annotated reactions to explain the outcome of each chemical test. (15 pts)



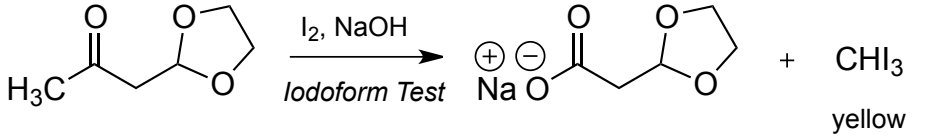
compound **A**

Bonus: Calculate the degree of unsaturation for **A**. (2 pts)

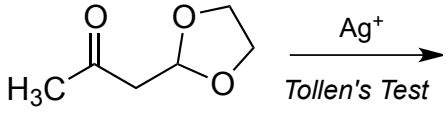
U = 0.5(2C – H + 2)

U = 0.5(12 – 10 + 2) = 2

test 1:

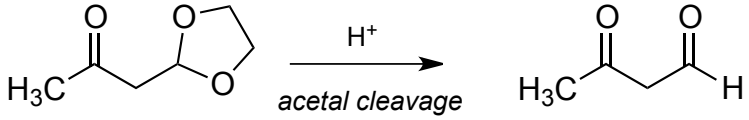


test 2:



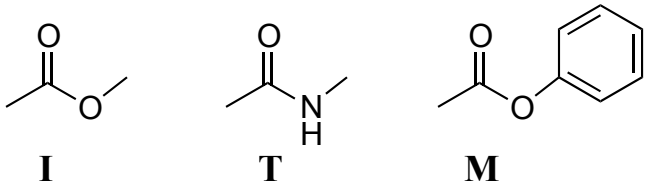
(no aldehyde present for oxidation)

test 3:



aldehyde seen in ^1H NMR at 9.5 ppm

6. Rank the following functional groups in order of decreasing reactivity in addition-elimination reactions by putting the letter corresponding to each structure in the boxes at right. (4 pts)



I **T** **M**

M > **I** > **T**

most reactive *least reactive*

Problem 1 (36 pts) _____

Problem 2 (15 pts) _____

Problem 3 (15 pts) _____

Problem 4 (15 pts) _____

Problem 5 (15 pts) _____

Problem 6 (4 pts) _____

TOTAL (100 pts) _____