

Chem 41c Midterm Exam

Stoltz, Spring 2005, May 2, 2005

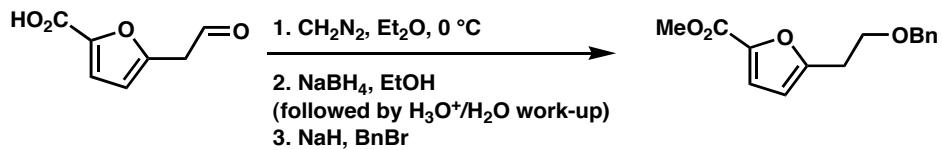
The exam begins when you turn to page 2. You have 55 minutes to complete the exam. This is a closed note and closed book exam with no collaboration. You may use the periodic table at the front of the room or the one on the last page of this packet. You may not use any other materials. The exam has a total of 135 points. Your grade will be calculated based on 120 points (i.e., you have 15 bonus points built-in). (Also, remember that your midterm counts 60 points toward your final grade, e.g., 5 quiz points = 10 points here). Good luck.

There are 9 pages in this exam packet.

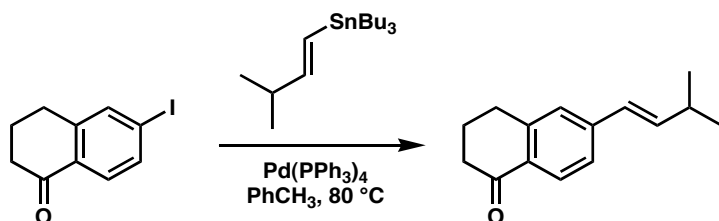
Name: _____

1. Predict the major non-volatile products (if any) of the following reactions or sequences. (5 points each)

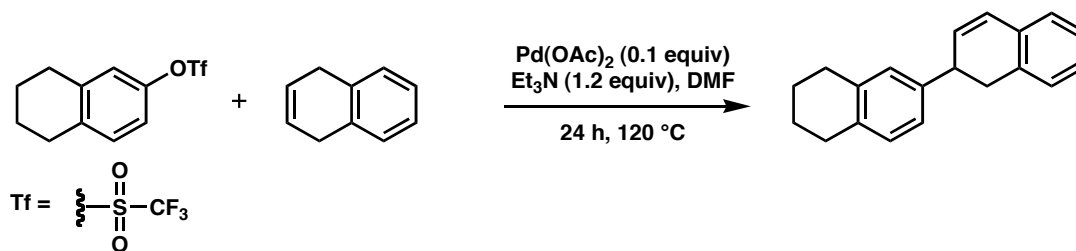
a.



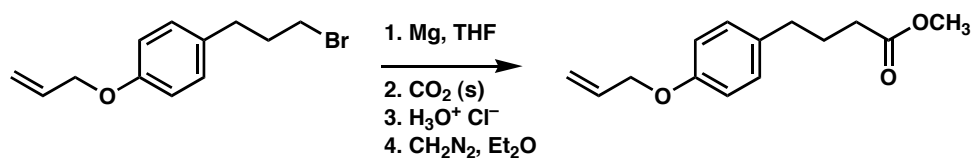
b.



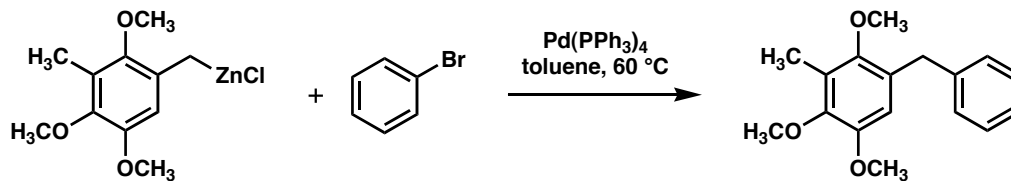
c.



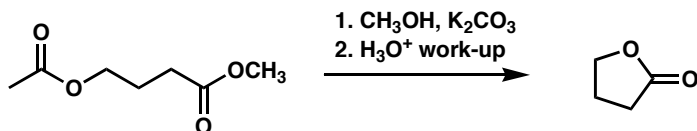
d.



e.

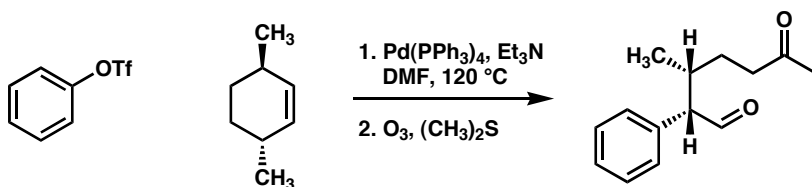


f.

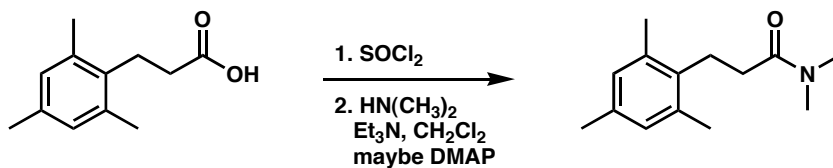


2. Provide reagents for the following transformations. They may be multistep processes (none are longer than 5 steps). (5 points each)

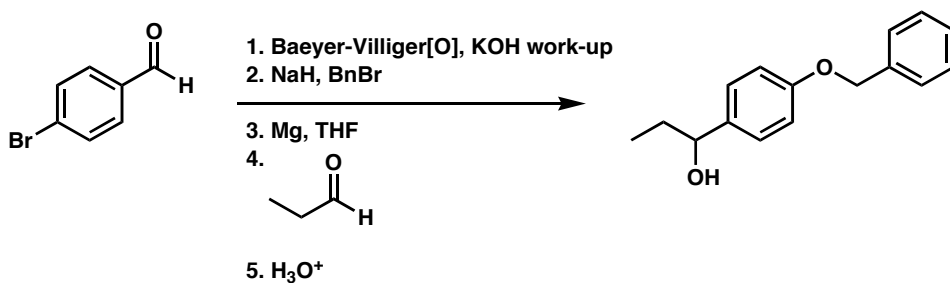
a.



b.

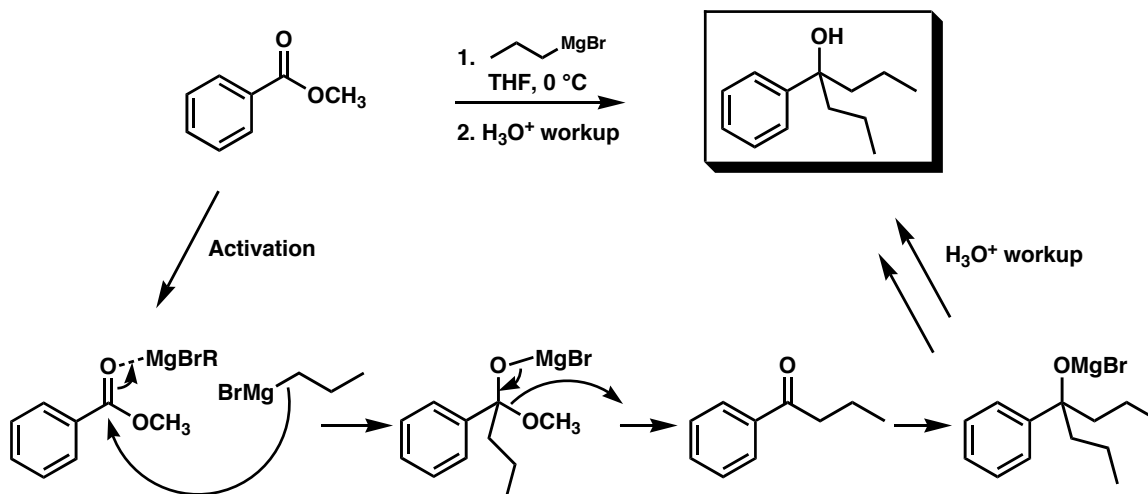


c.

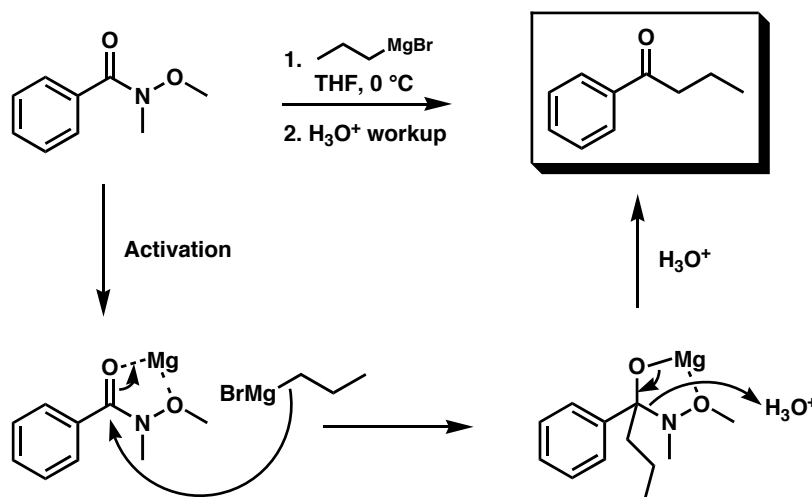


3. Provide the product of the following reactions and give a mechanistic rationale complete with curved arrows for the formation of two different products. Be sure to clearly indicate at which stage the work-up begins. (20 points)

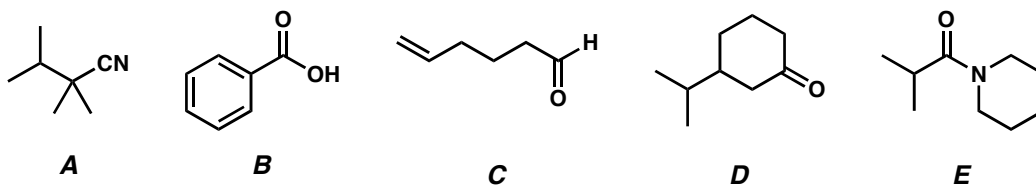
a)



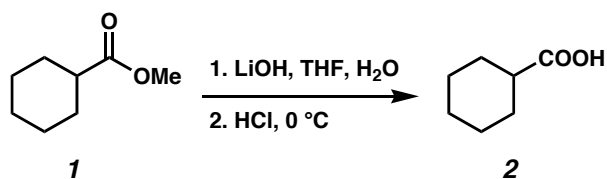
b)



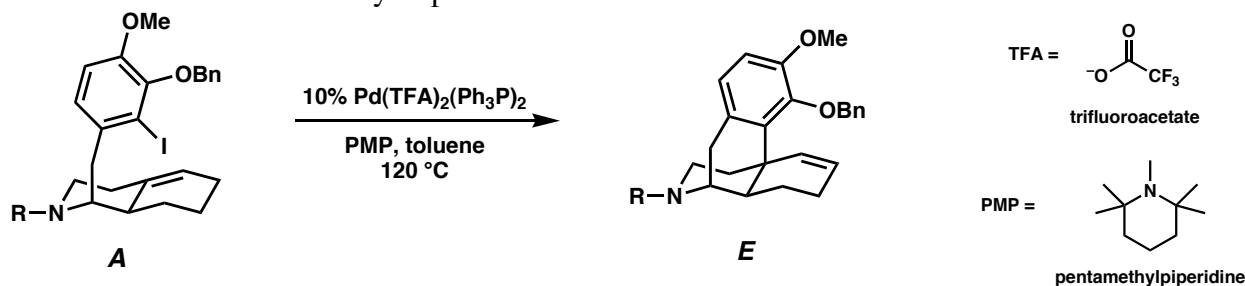
4. Rank the following compounds in order of reactivity with MeMgBr. (5 points)



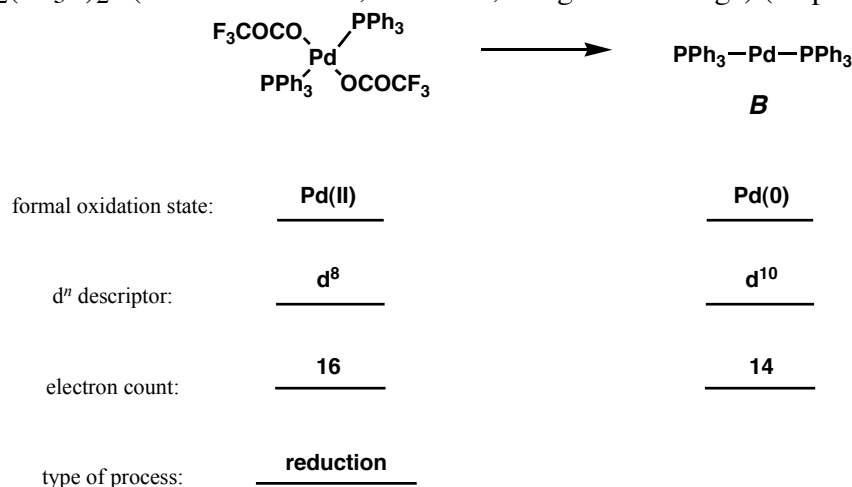
5. Provide a detailed curved arrow mechanism for the following reaction. What drives the equilibrium to the product side? (10 points)



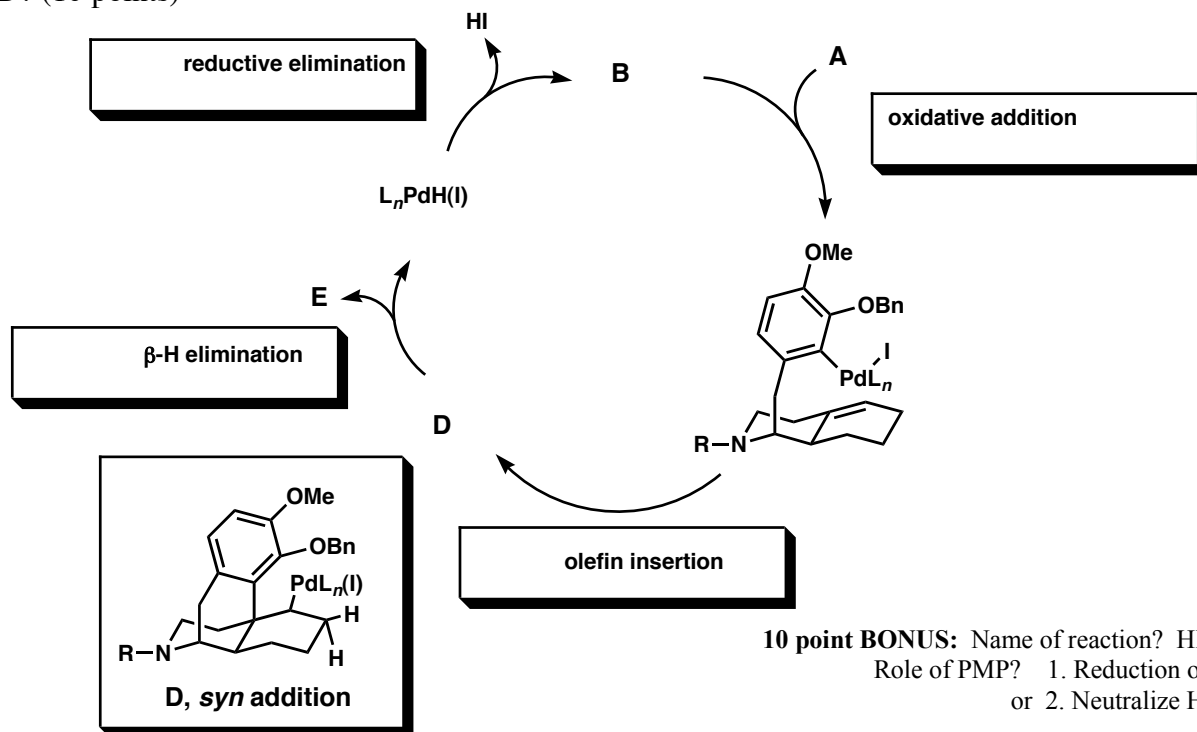
6. Recently, an asymmetric synthesis of (–)-Morphine was reported utilizing the Palladium-catalyzed reaction described below as the key step.



a) The active catalyst for the reaction is believed to be **B**, not $\text{Pd(TFA)}_2(\text{Ph}_3\text{P})_2$. Give the formal oxidation state, d^n descriptor, and electron count for each complex. Also, what is a general name for the process to get to **B** from $\text{Pd(TFA)}_2(\text{Ph}_3\text{P})_2$? (HINT: oxidation, reduction, or ligand exchange) (10 points)



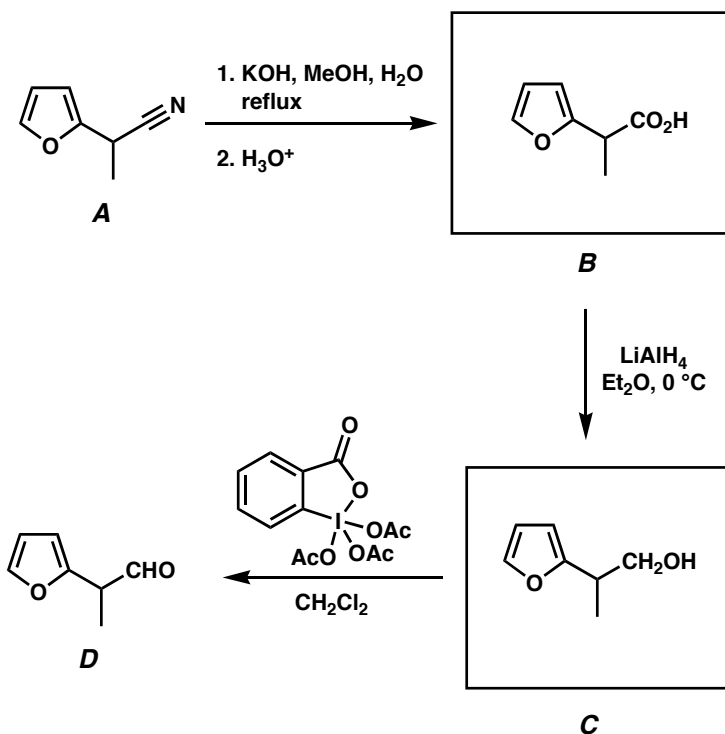
b) Label each of the boxes below describing the key steps in the catalytic cycle. Also, what is the structure of **D**? (10 points)



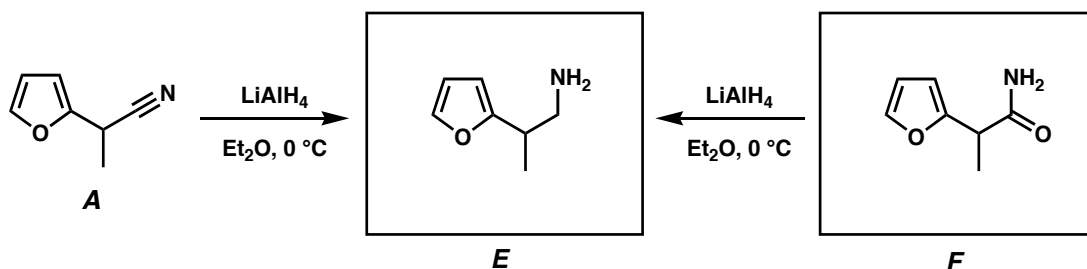
7. Imagine yourself as a graduate student in a famous laboratory working on a complex synthetic problem. After a long day of frustrating chemistry at the "cutting edge", you decide to rattle off some easy chemistry for the synthesis of compounds needed for simpler work (i.e., **A**→**B**→**C**→**D**). After a few hours of this "sophomore" organic chemistry, you return to your desk to realize that you have not labeled your IR spectra for compounds **B** through **D**.

(a) Draw compounds **B** and **C** into the boxes below

(b) Looking at your three IR spectra, you take note of a key peak in each. These key peaks fall at 3200 (broad), 1725 and 1710 cm^{-1} . (hint: the spectrum that has a strong peak at 1710 cm^{-1} also has a large, broad peak from 2400-3600 cm^{-1}). Assign your spectra to compounds **B**-**E** below by writing the key frequency below the corresponding compound.(25 points total)



b) Since the chemistry was so simple, you decide to scale up the process. Unfortunately, as a result of this somewhat rushed series of experiments and your general sleepiness, you completely forget the first step and mistakenly treat compound **A** with LiAlH₄. What is the structure of your product **E**? Fortunately, your labmate happens to need this compound, but usually synthesizes it from an alternative carboxylic acid derivative. Please provide the structure of **E** from your mistake and predict the compound that your lab-mate uses as starting material (i.e., **F**).



hint: this is a carboxylic acid derivative but is different than **A** or **B**

PERIODIC TABLE OF THE ELEMENTS

<http://www.ktf-split.hr/periodni/en/>

[illegible]

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)

Relative atomic mass is shown with five significant figures. For elements having no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@netlinx.com)

LANTHANIDE														Copyright © 1998-2002 ENIG. (enig@kf-split.hr)															
57	138.91	58	140.12	59	140.91	60	144.24	61	(145)	62	150.36	63	151.96	64	157.25	65	158.93	66	162.50	67	164.93	68	167.26	69	168.93	70	173.04	71	174.97
La		Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu	
LANTHANUM		CERIUM		PRASEODYMIUM		NEODYMIUM		PROMETHIUM		SAMARIUM		EUROPIUM		GADOLINIUM		TERBIUM		DYSPROSIUM		HOLMIUM		ERBIUM		THULIUM		YTTERBIUM		LUTETIUM	

ACTINIDE																													
89	(227)	90	232.04	91	231.04	92	238.03	93	(237)	94	(244)	95	(243)	96	(247)	97	(247)	98	(251)	99	(252)	100	(257)	101	(258)	102	(259)	103	(262)
Ac		Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md		No		Lr	
ACTINIUM		THORIUM		PROTACTINIUM		URANIUM		NEPTUNIUM		PLUTONIUM		AMERICIUM		CURIUM		BERKELIUM		CALIFORNIUM		ENSTEINIUM		FERMIUM		MENDELEVIUM		NOBELIUM		LAWRENCIUM	

The End