

Chem 41c Final Exam

Stoltz, Spring 2006, June 5, 2006

The exam begins when you turn to page 2. You have 4 hours to complete the exam. This is a closed note and closed book exam with no collaboration. You may use the periodic table on the last page of this packet. You may not use any other materials. The exam has a total of 180 points and counts for 40% of your course grade. Good luck.

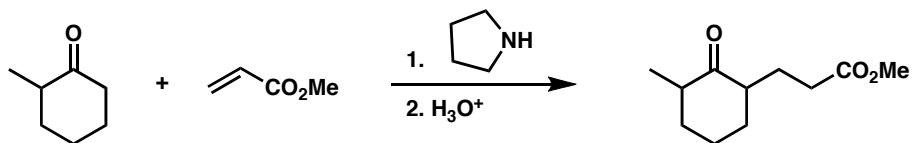
There are 17 pages in this exam packet.

The Exam is due by Friday June 9, 2006 by 5 PM.

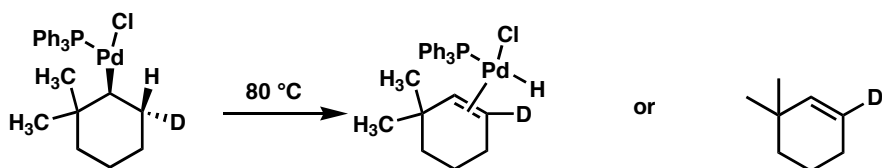
Name: _____

1. Predict the major non-volatile products (if any) of the following reactions or sequences. Clearly mark your answers by placing a **box** around the compound that you believe to be the major product. (5 points each).

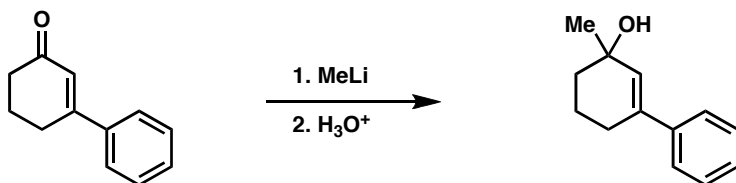
a.



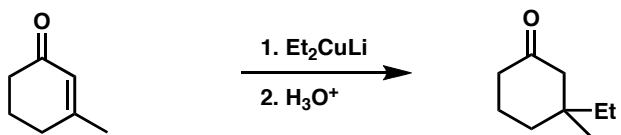
b.



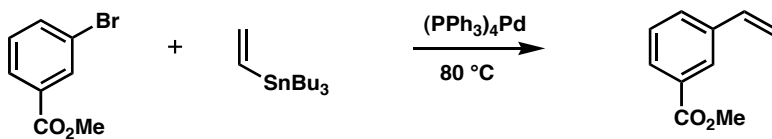
c.



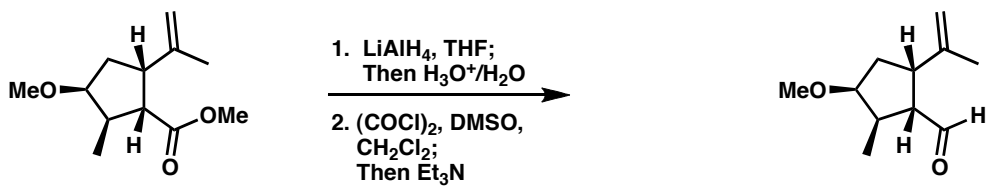
d.



e.

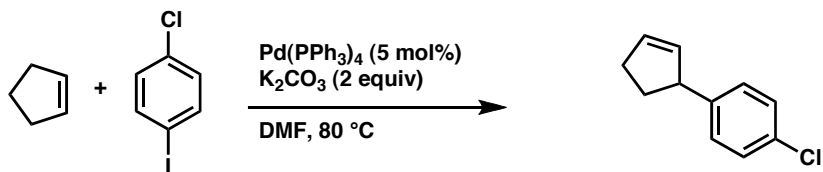


f.

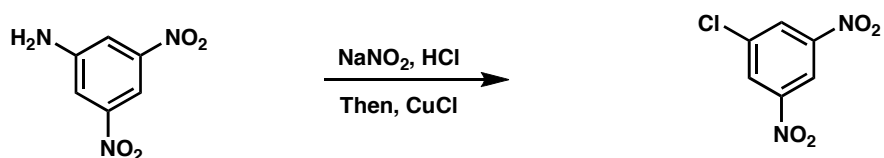


PNAS, 2004, 101, 12073-12078

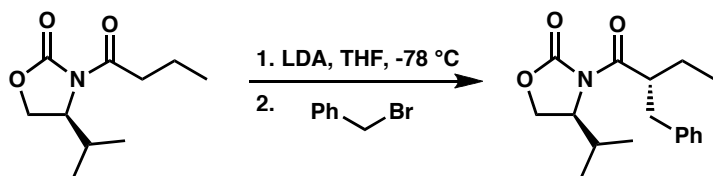
g.



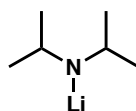
h.

*Can. J. Chem.* **2005**, *83*, 213-219

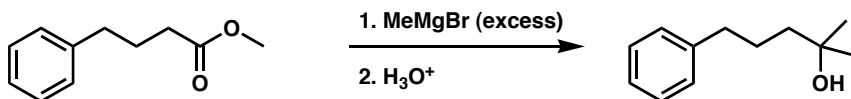
i.



5 point bonus: what is the structure of LDA?

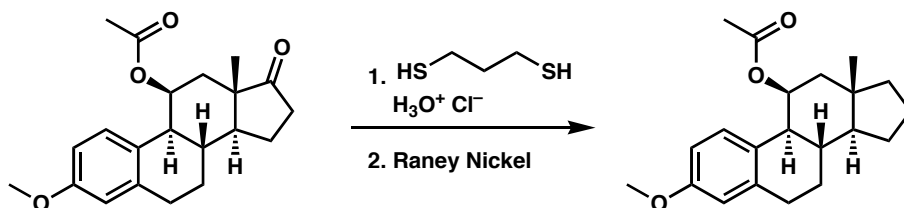


j.



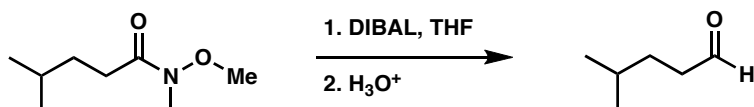
2. Provide reagents for the following transformations. They may be multistep processes, but should not be longer than 5 steps. (5 points each)

a.

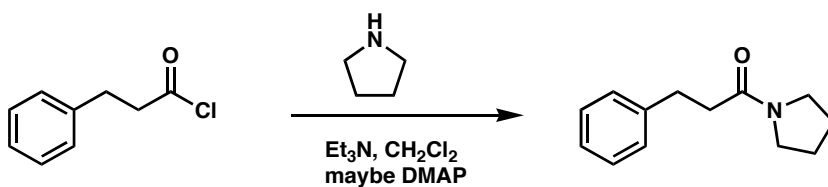


(maybe Clemmenson...not Wolf Kischner)

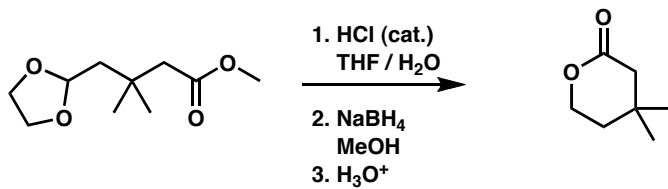
b.



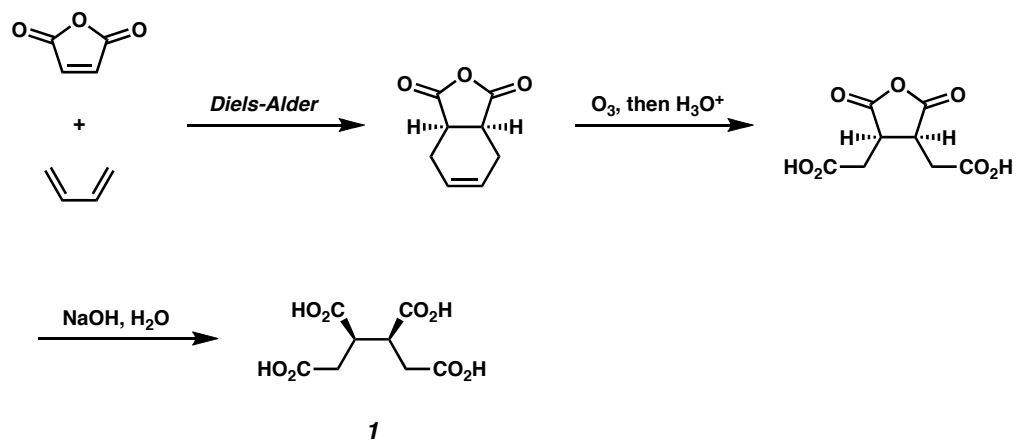
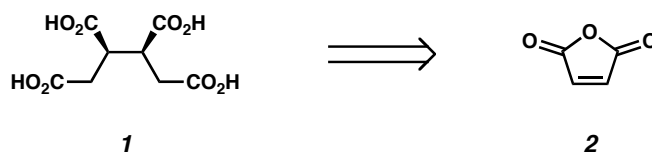
c.



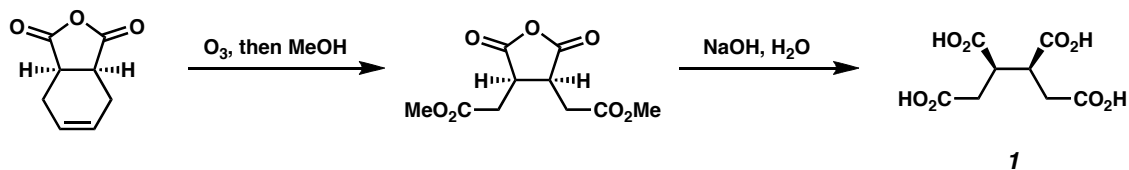
d.



3. Design a synthesis of tetracarboxylic acid **1** starting from maleic anhydride (**2**) and any other materials containing 4 carbons or less. (15 points)

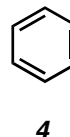
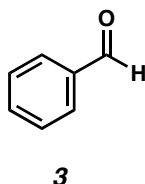
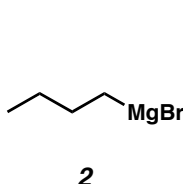
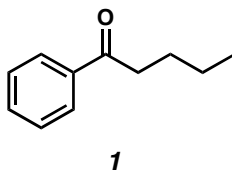


Alternative:

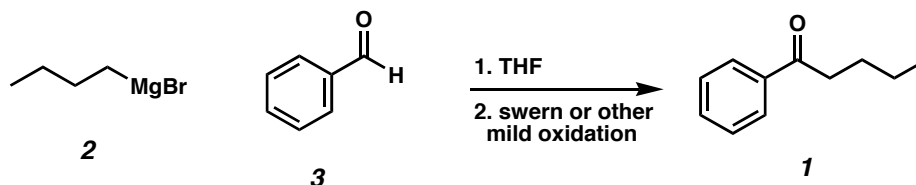


Warren p. 113

4. a) In the lab on an unusually hot and humid Sunday afternoon, you set out to prepare ketone **1**. The door to the stockroom is unfortunately locked, and you have left your keys at your friends home in Newport Beach. Due to a big game between the Los Angeles Angels of Anaheim and the Boston Red Sox, the freeways are too clogged to drive and pick them up in time to complete the synthesis of **1**. Your boss is counting on the your preparation of **1** for a big project grant that is due on the following day. Luckily, you happen to find some butyl magnesium bromide (**2**), benzaldehyde (**3**), benzene (**4**), and you have access to the inorganic stockroom full of common reagents and plenty of dry-ice (solid CO₂), solvents, and N₂ gas. Design a synthesis of **1** from any of these simple starting materials. (15 points total)



Possible Route a:



b) Unfortunately, the keys to the NMR lab were on the same key ring and are lost at the beach as well. Provide two analytical tools that you can use other than NMR that will allow you to elucidate the structure of your synthetic **1**. Explain your answer and specifically how you will know that your synthesis was a success.

We learned three...

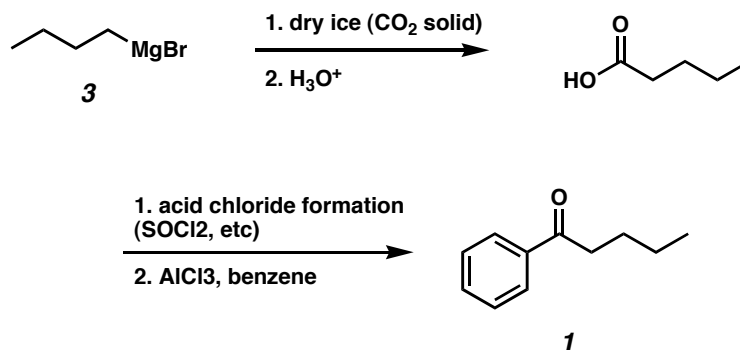
Mass Spec: for Mass and McLafferty rearrangement fragmentation

IR: for a peak at 1690 cm⁻¹

Uv-Vis: strong lambda max at 246 nm with a ε > 10,000

c) Because you are so industrious, you realize that from the given resources, a second independent route is possible to generate **1**. If successful, this independent route will provide you with additional evidence that you have successfully prepared the key molecule **1**. Provide this synthesis for final confirmation of your ketone **1**.

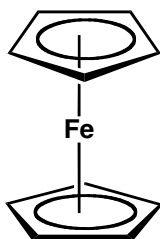
Possible Route b:



d) All the while as you sweat through the day you wish you had some pentanoic acid. Why? Which reagent would you want to avoid on a very humid day **2**, **3**, or **4** and why?

5. In the following complexes, what is the formal oxidation state of the metal, the d^n description, and the electron count? Feel free to use the periodic table in the room (5 points each-no partial credit)

a.

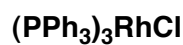


Fe(II)
or
Fe²⁺

d^6

18 electron complex

b.



Rh(I)

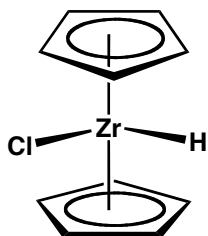
or

Rh¹⁺

d^8

16 electron complex

c.

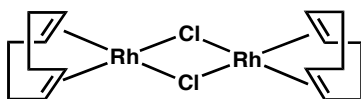


Zr(IV)
or
Zr⁴⁺

d^0

16 electron complex

d.

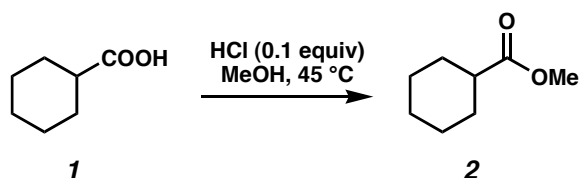


Rh(I)
or
Rh⁺¹

d^8

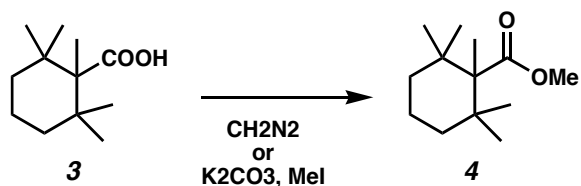
16 electron each Rh

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

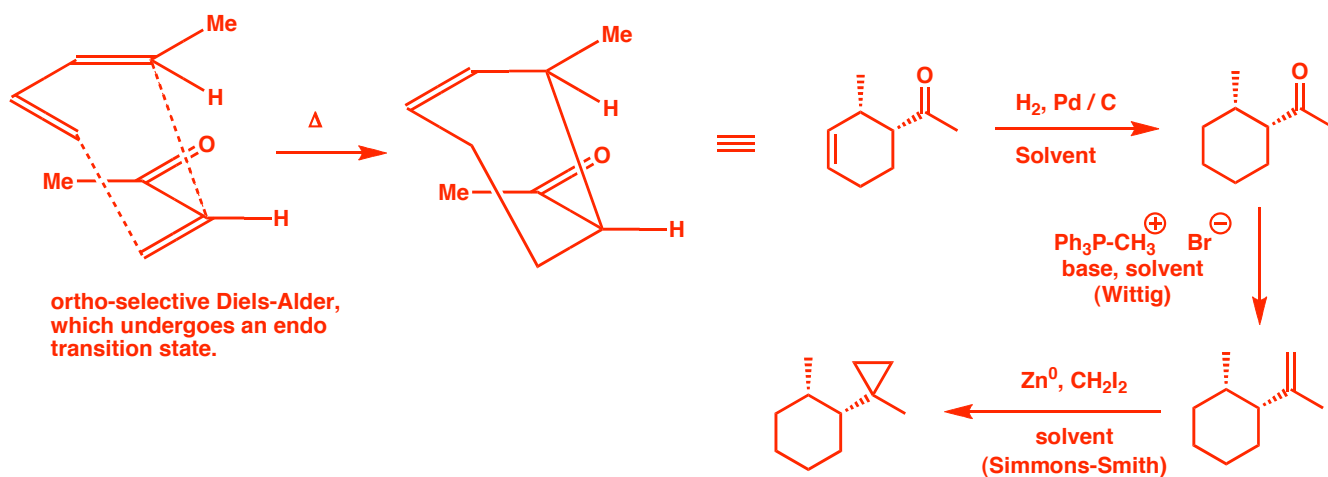
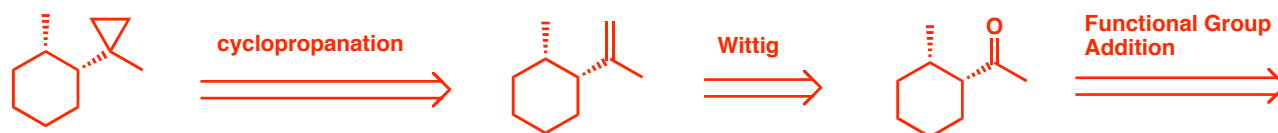
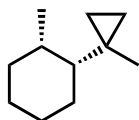


Fisher esterification

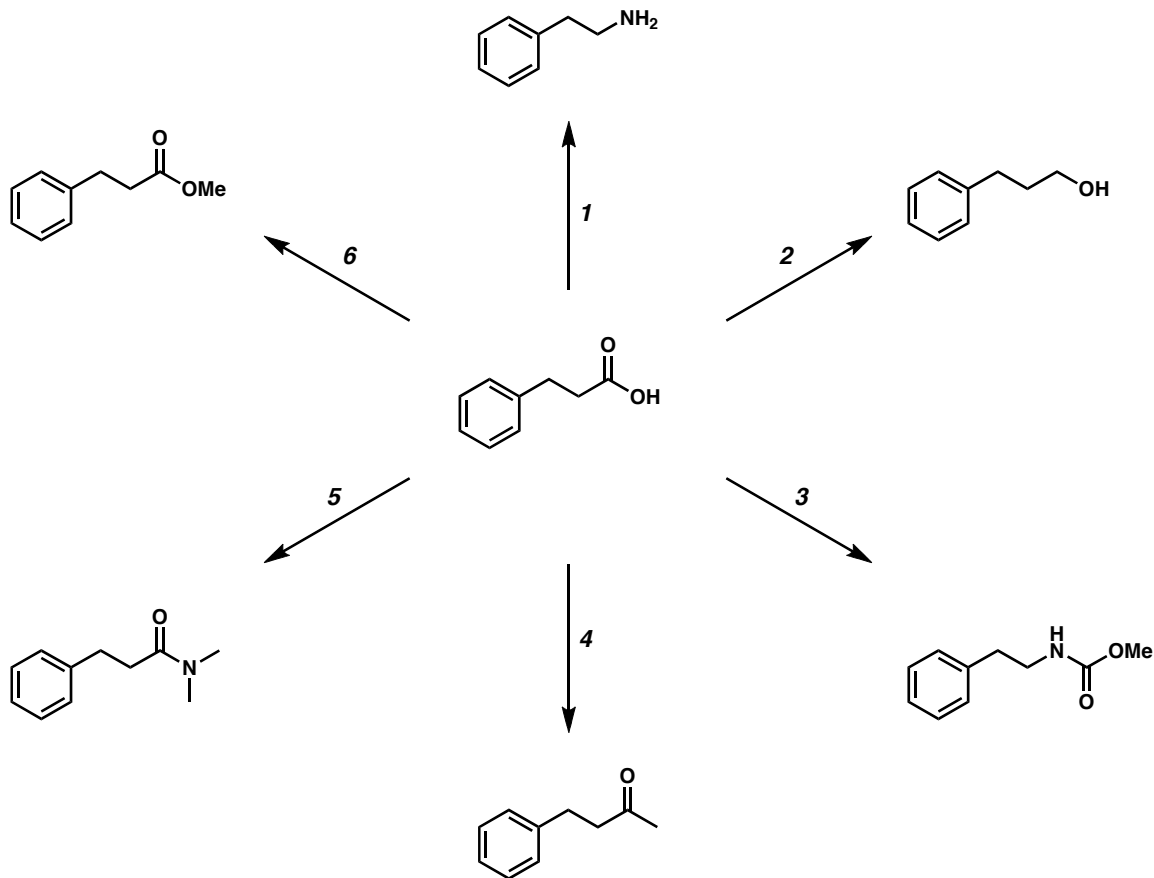
b) In contrast to part a of this problem, under the same conditions the following reaction (**3**→**4**) is extremely slow. Why do you think this is the case? Provide an alternative method for preparing the methyl ester **4** from carboxylic acid **3** that you believe would be fast and high yielding. Provide a detailed curved arrow mechanism for your new synthesis of **4** from **3** and explain why the new method should be better. (10 points)



7. Design a retrosynthesis and a complete forward process for the synthesis of the following compound as a single diastereomer (in racemic form) starting from fragments of less than 6 carbons (or benzene). (20 points) (hint: disconnect the cyclopropane first!)



8. As you can see, carboxylic acids are valuable synthons in organic chemistry. Provide reagents for each of the following six transformations in the spaces below the figure. Keep in mind that some transformations may require more than one step. (15 points)



1. 1. SOCl₂

2. NaN₃, then Δ

3. H₂O

2. LiAlH₄

3. 1. SOCl₂

2. NaN₃, then Δ

3. MeOH

4. 1. SOCl₂

2. HN(OMe)Me

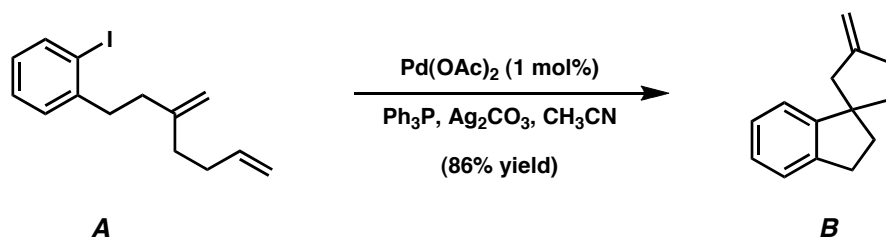
3. MeMgBr

5. 1. SOCl₂

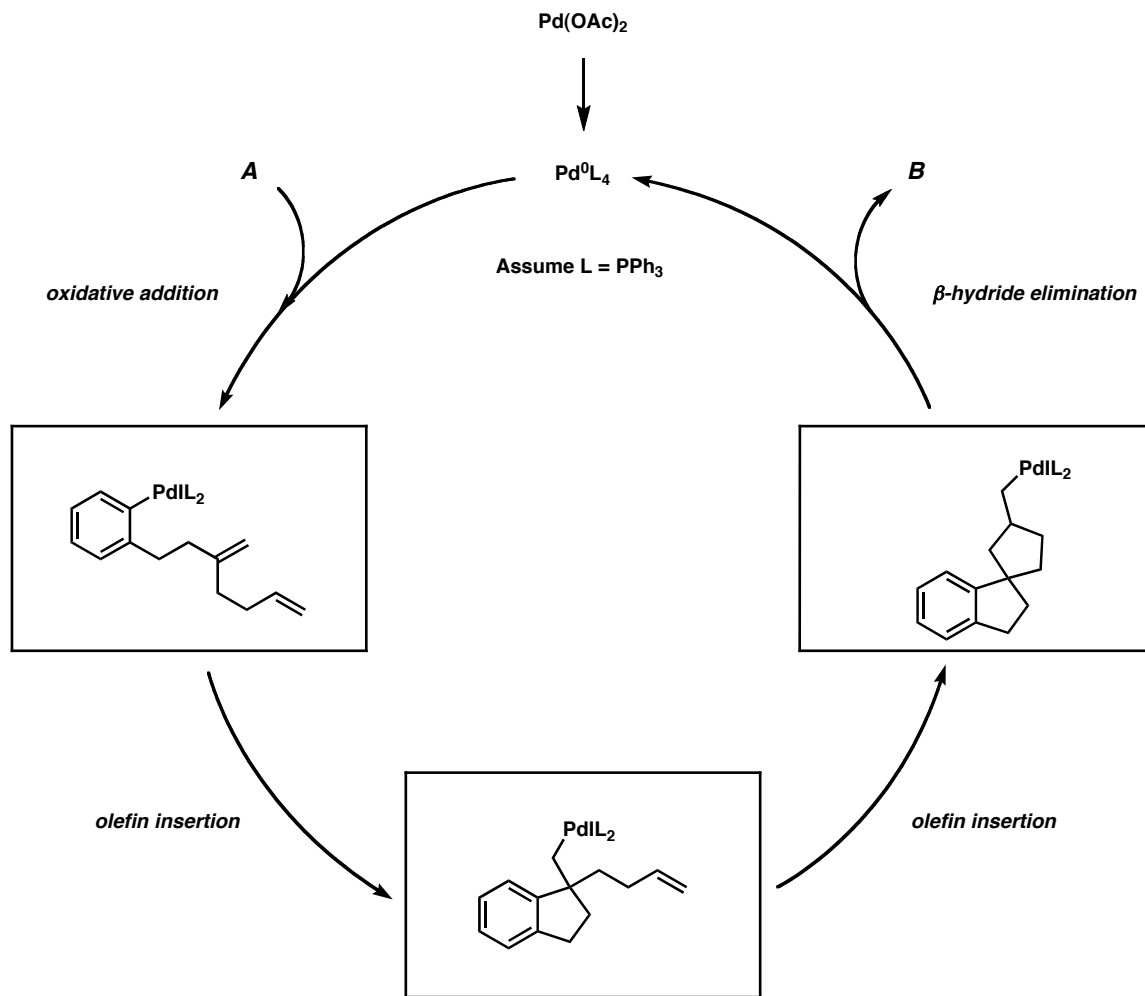
2. Me₂NH

6. MeOH, H⁺ or CH₂N₂

9. In 1988, Larry Overman at the University of California, Irvine, showed that polyenes such as compound **A** could be cyclized to form spiro arenes (e.g., **B**) using palladium-catalyzed “zipper” reaction sequences.

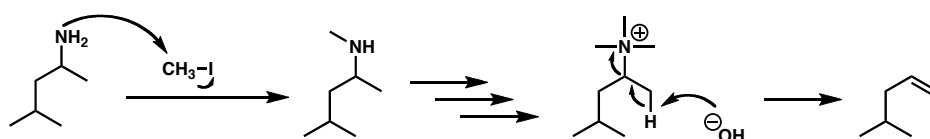
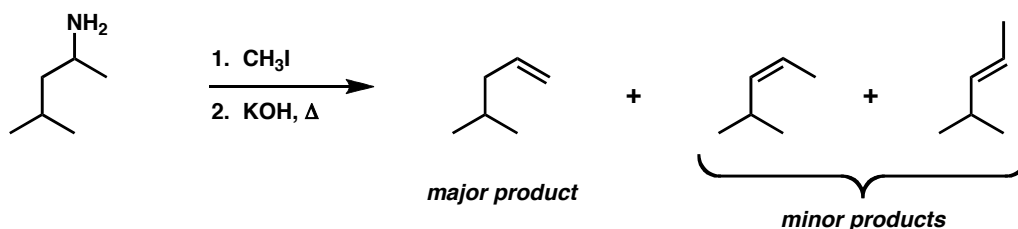


A catalytic cycle for this reaction is shown below. Each of the key steps is labeled next to the arrows. Using these clues, fill in each of the boxes with the structure of intermediates **C**, **D**, and **E**. (10 points)
 (5 point Bonus: What is the name of this reaction?)

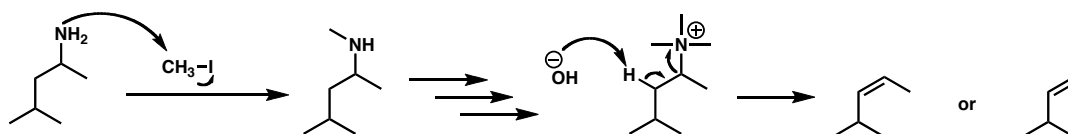
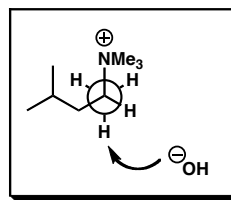


Reaction Name: Heck Reaction (Cascade)
JACS (1988) 110, 2328-2329

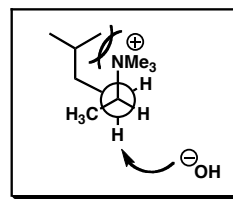
10. The following reaction, known as the Hofmann elimination, generates the product bearing the terminal olefin in much greater yield than the combined internal olefins products. Using arrow pushing conventions, provide a detailed mechanistic explanation of how the product is formed, and *why* the terminal olefin is produced preferentially. (10 points)



Anti-periplanar elimination to give the external olefin does not suffer from bad steric interactions between the ammonium group and the isopropyl.



Anti-periplanar elimination to give the internal olefin does suffer from deleterious steric interactions between the ammonium group and the isopropyl, and thus is produced in a lower yield.



PERIODIC TABLE OF THE ELEMENTS
<http://www.ktf-split.hr/periodni/en/>

GROUP NUMBERS IUPAC RECOMMENDATION (1985) GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)

ATOMIC NUMBER RELATIVE ATOMIC MASS (1)

SYMBOL ELEMENT NAME

1	1	1.0079	1	1A	1	H	1	1A	18	18	4.0026	2	He	18	VIIIA
1	1	1.0079	1	1A	1	H	1	1A	18	18	4.0026	2	He	18	VIIIA
2	2	6.941	4	2A	2	Li	2	2A	10	10	20.180	10	Ne	10	VIIIA
2	2	6.941	4	2A	2	Li	2	2A	10	10	20.180	10	Ne	10	VIIIA
3	3	22.990	12	3A	3	Na	3	3A	16	16	35.453	16	Ar	16	VIIIA
3	3	22.990	12	3A	3	Na	3	3A	16	16	35.453	16	Ar	16	VIIIA
4	4	39.098	20	4A	4	K	4	4A	28	28	78.96	28	Kr	28	VIIIA
4	4	39.098	20	4A	4	K	4	4A	28	28	78.96	28	Kr	28	VIIIA
5	5	85.468	38	5A	5	Rb	5	5A	46	46	126.90	46	Xe	46	VIIIA
5	5	85.468	38	5A	5	Rb	5	5A	46	46	126.90	46	Xe	46	VIIIA
6	6	132.91	56	6A	6	Cs	6	6A	84	84	208.98	84	Rn	84	VIIIA
6	6	132.91	56	6A	6	Cs	6	6A	84	84	208.98	84	Rn	84	VIIIA
7	7	223.018	88	7A	7	Fr	7	7A	118	118	289	118	Uuq	118	VIIIA
7	7	223.018	88	7A	7	Fr	7	7A	118	118	289	118	Uuq	118	VIIIA

(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 (Tl, Pb, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (advan@netnet.com)

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The End