

Massachusetts Institute of Technology

5.13: Organic Chemistry II

December 19, 2005

Final Exam

- Question 1 ____/10 points
Question 2 ____/15 points
Question 3 ____/30 points
Question 4 ____/10 points
Question 5 ____/10 points
Question 6 ____/15 points
Question 7 ____/10 points
Question 8 ____/12 points
Question 9 ____/10 points
Question 10 ____/12 points
Question 11 ____/12 points
Question 12 ____/12 points
Question 13 ____/12 points
Question 14 ____/14 points
Question 15 ____/16 points

TOTAL ____/200 points

Name (printed) _____

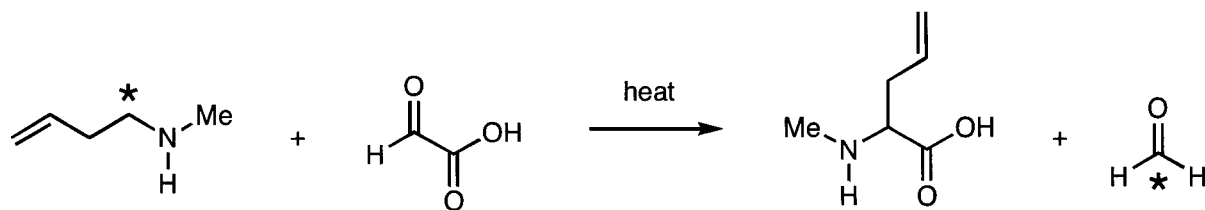
Name (signed) _____

T.A. _____

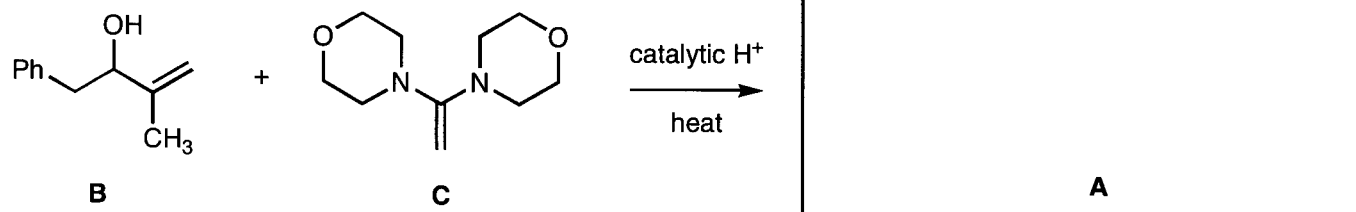
There are 18 pages (2-19) of questions in this exam.

1. (10 points total) Write an **arrow-pushing mechanism** for the reaction below.

Note: Asterisk (*) = ^{13}C .



2. (15 points total) Compound **A** is prepared from **B** and **C** and has the spectroscopic data listed below. **Draw** the structure of **A** in the **box** provided, and write an arrow-pushing **mechanism** for its formation from **B** and **C** in the space below.



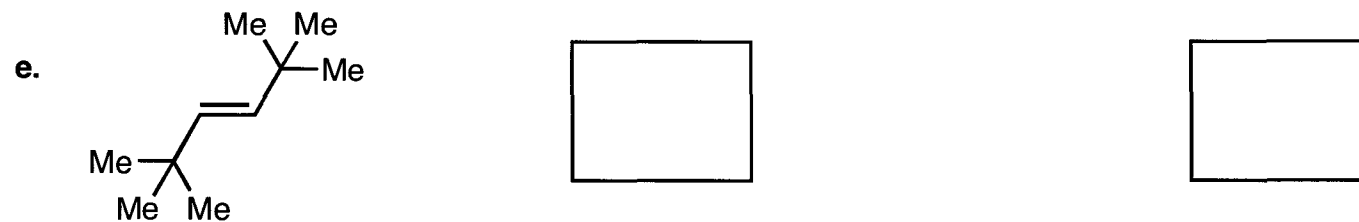
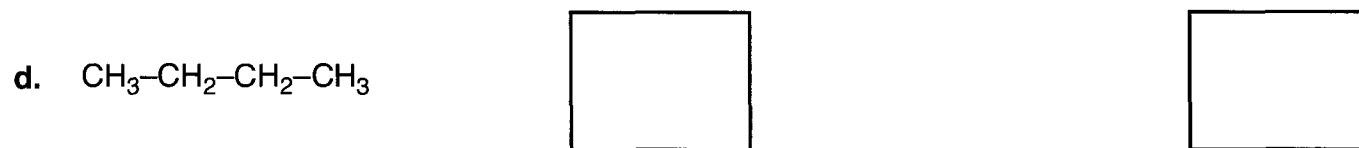
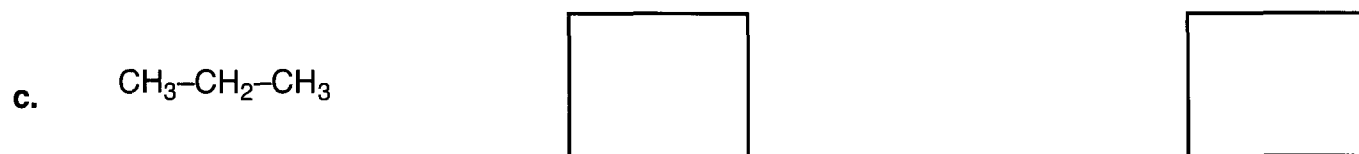
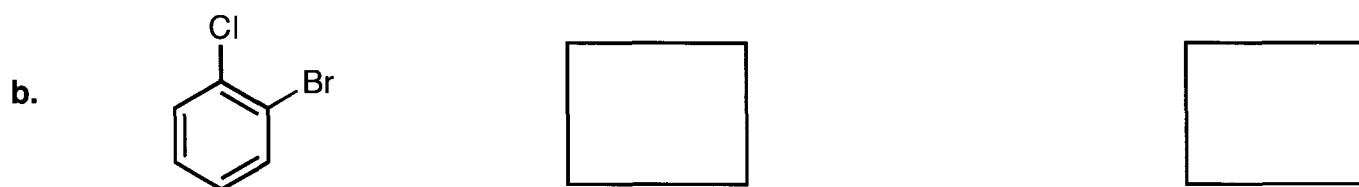
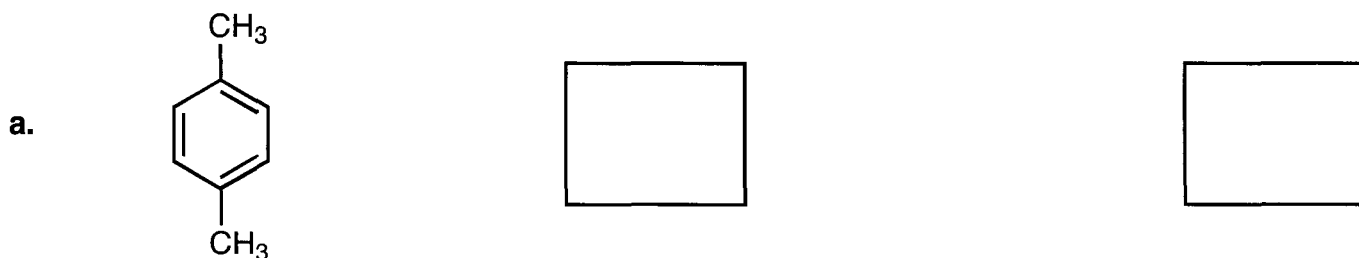
Data for **A**:

^1H NMR (ppm)	IR
7.05-7.15, m, 5H	1685 cm^{-1}
5.80, t, $J = 6.3$, 1H	
3.67, t, $J = 6.5$, 4H	
3.47, t, $J = 6.5$, 4H	Molecular weight
3.22, d, $J = 6.3$, 2H	
2.34, t, $J = 7.4$, 2H	273.17
2.12, t, $J = 7.4$, 2H	
1.71, s, 3H	

3. (30 points total, 1 point per box) For the following 15 structures, write the number of **chemically non-equivalent** (number of "different types") of **hydrogens and carbons** in the **appropriate** boxes below. (Be careful to put the numbers in the correct boxes – we can't read your mind, i.e. wrong numbers will receive no credit – no exceptions.)

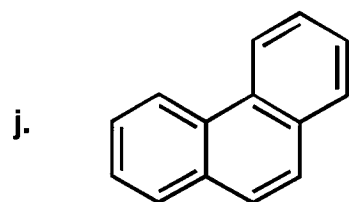
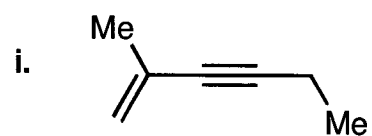
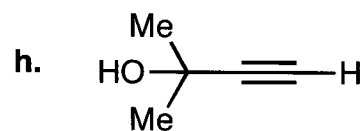
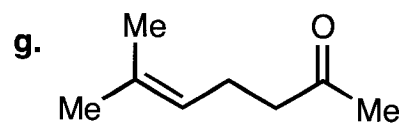
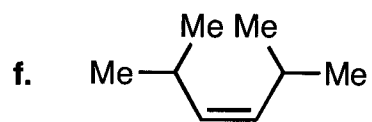
non-equivalent H

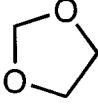
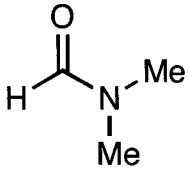
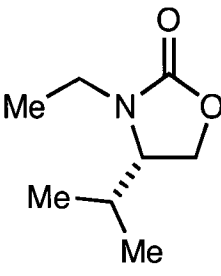
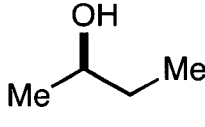
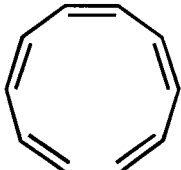
non-equivalent C



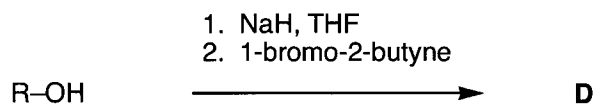
non-equivalent H

non-equivalent C



		# non-equivalent H	# non-equivalent C
k.		<input type="text"/>	<input type="text"/>
l.		<input type="text"/>	<input type="text"/>
m.		<input type="text"/>	<input type="text"/>
n.		<input type="text"/>	<input type="text"/>
o.		<input type="text"/>	<input type="text"/>

4. (10 points) An alcohol (R-OH) was treated with sodium hydride and 1-bromo-2-butyne to give compound **D** (molecular weight = 166.10). Using the ^1H NMR data listed below, determine the structure of the **product** and the **starting alcohol**. Draw the structures in the boxes provided.



^1H NMR data for **D** (ppm)

5.68, ddd, $J = 17.0, 10.5, 8.5$, 1H

5.27, dd, $J = 10.5, 1.5$, 1H

5.19, dd, $J = 17.0, 1.5$, 1H

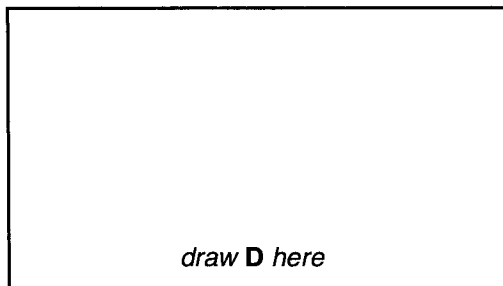
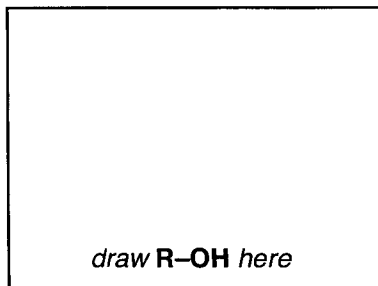
4.14, d, $J = 15.0$, 1H

3.94, d, $J = 15.0$, 1H

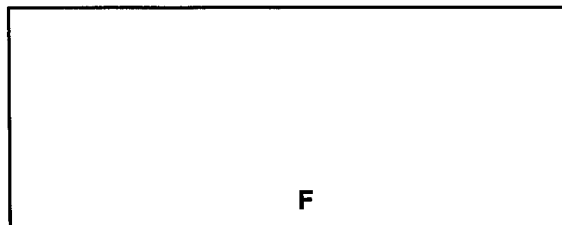
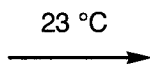
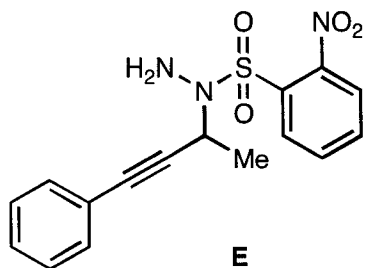
3.42, d, $J = 8.5$, 1H

1.86, s, 3H

0.91, s, 9H



5. (10 points) At room temperature, compound **E** is converted to compound **F** in high yield. Using the data provided, determine the **structure** of **F** (and **draw** the structure in the **box** provided), and **write** an arrow-pushing **mechanism** for its formation from **E**.



Data for **F**:

¹H NMR (ppm)

7.15-7.30, m, 5H

5.99, d, *J* = 2.0, 1H

5.25, dq, *J* = 7.0, 2.0, 1H

1.59, d, *J* = 7.0, 3H

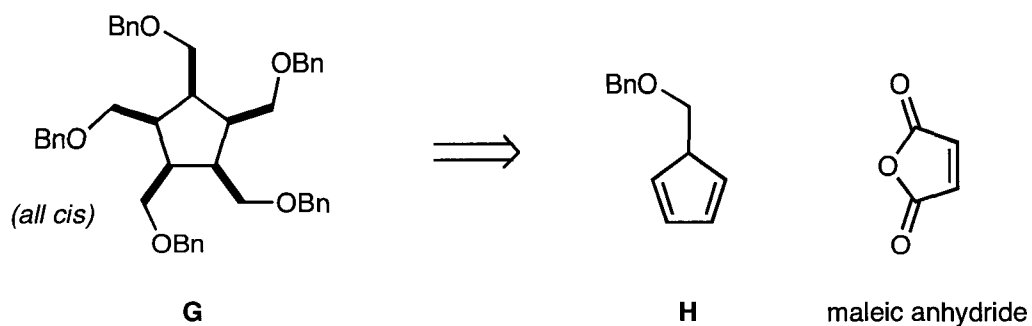
IR

1955 cm⁻¹

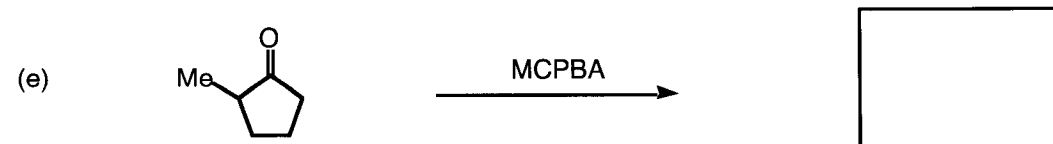
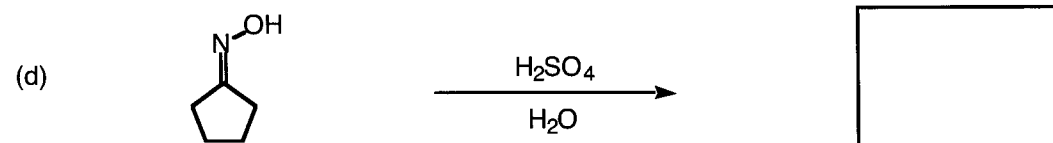
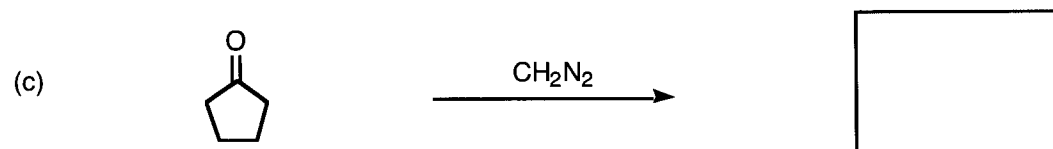
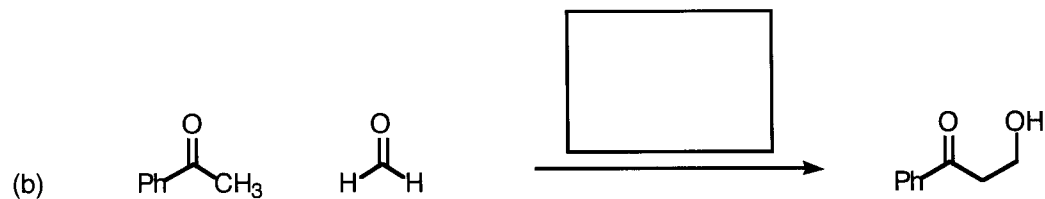
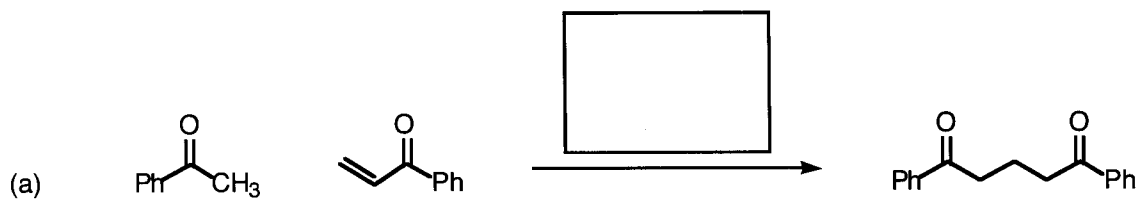
Molecular weight

130.19

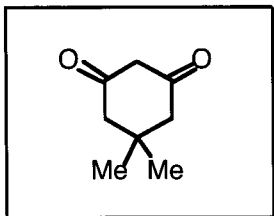
6. (15 points) Propose a synthesis of **G** from **H**, maleic anhydride, and benzyl bromide (BnBr = PhCH₂Br). (All of the substituents on the five-membered ring in **G** are cis to one another, and your synthesis must establish this relative configuration.) Your synthesis must use **H**, maleic anhydride, and BnBr. You may use any other reagents in addition to these. Write your synthesis **neatly** in the forward direction, and for each transformation, write the **reagents** necessary over the arrow.



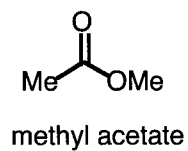
(7) (2 points for each box; 10 points total) Please provide the indicated information. If you use a base or an acid, please specify whether a "catalytic amount", "1 equivalent", etc. is required.



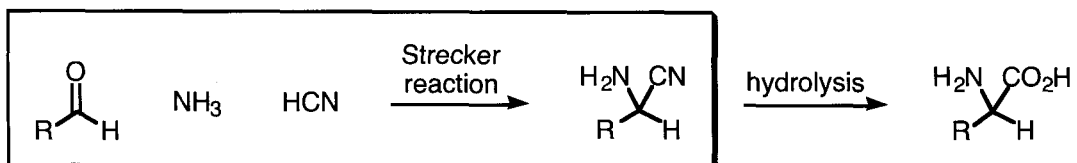
(8) (12 points) Please provide an efficient synthesis of the indicated target compound. All of the carbons of the target compound must come from methyl acetate.



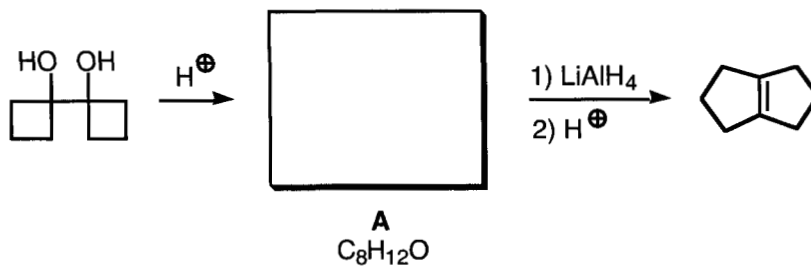
target compound



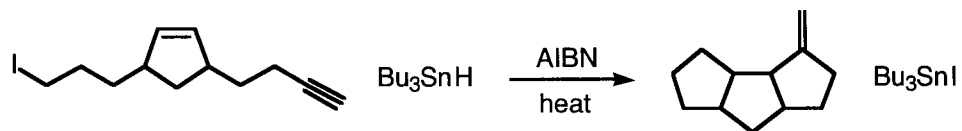
(9) (10 points) The Strecker reaction, followed by a hydrolysis reaction, is an excellent method for synthesizing amino acids, which are the building blocks of proteins. Provide the best mechanism for this process. Please show all arrow pushing. Note: You do NOT have to draw the mechanism for the hydrolysis reaction.



(10) (12 points) Provide the structure of **A** and the best mechanism for both of the illustrated transformations. Please show all arrow pushing.



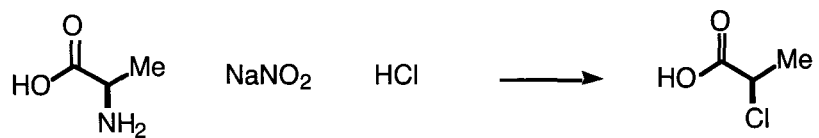
(11) (12 points) Provide the best mechanism for the illustrated process. Please show all arrow pushing.



Initiation (4 points):

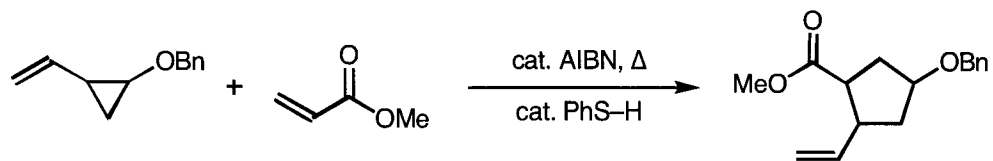
Propagation (8 points; please draw this in standard mechanism form, not as a sum/series of equations):

(12) (12 points) Provide the best mechanism for the illustrated process. Please show all arrow pushing. Your mechanism should rationalize why the reaction proceeds with complete retention of stereochemistry.



13. (10 points) Please provide a detailed mechanism for the illustrated transformation. Show all arrow pushing. (Bn = CH₂Ph)

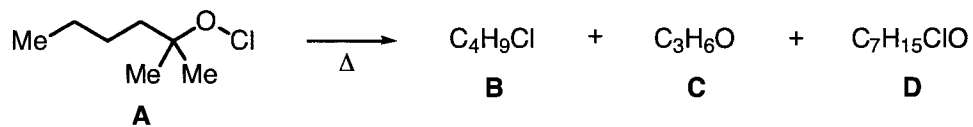
Hint #1: Number your carbons! **Hint #2:** PhSH is catalytic!



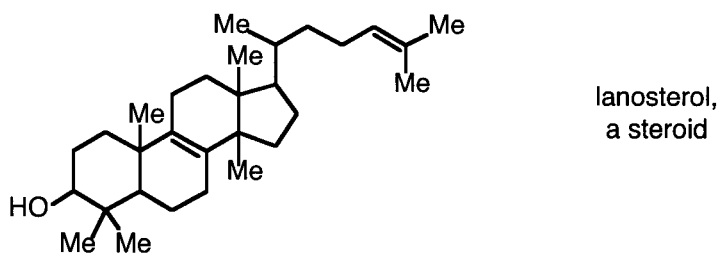
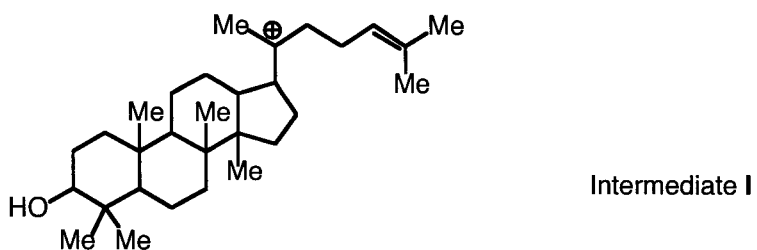
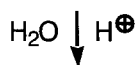
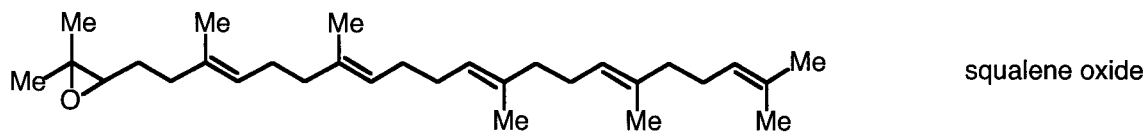
Initiation:

Propagation:

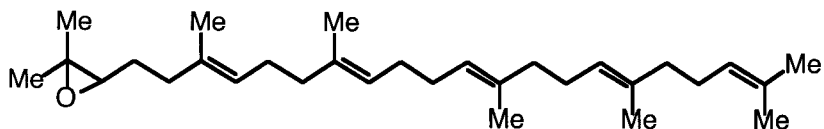
14. (10 points) Compound **A** is converted to **B**, **C**, and **D** upon heating. The reaction is accelerated by irradiation. Provide the structures of **B**, **C**, and **D**, and provide the mechanisms by which they are formed (please show all arrow pushing).



(15) (16 points total) In an amazing process, Nature transforms squalene oxide into steroids (as a single stereoisomer!). For both of the processes illustrated below, provide the best mechanism. Please show all arrow pushing.



(a) (10 points) Squalene oxide into intermediate I:



(b) (6 points) Intermediate I into lanosterol:

