KEY

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) ________________________________

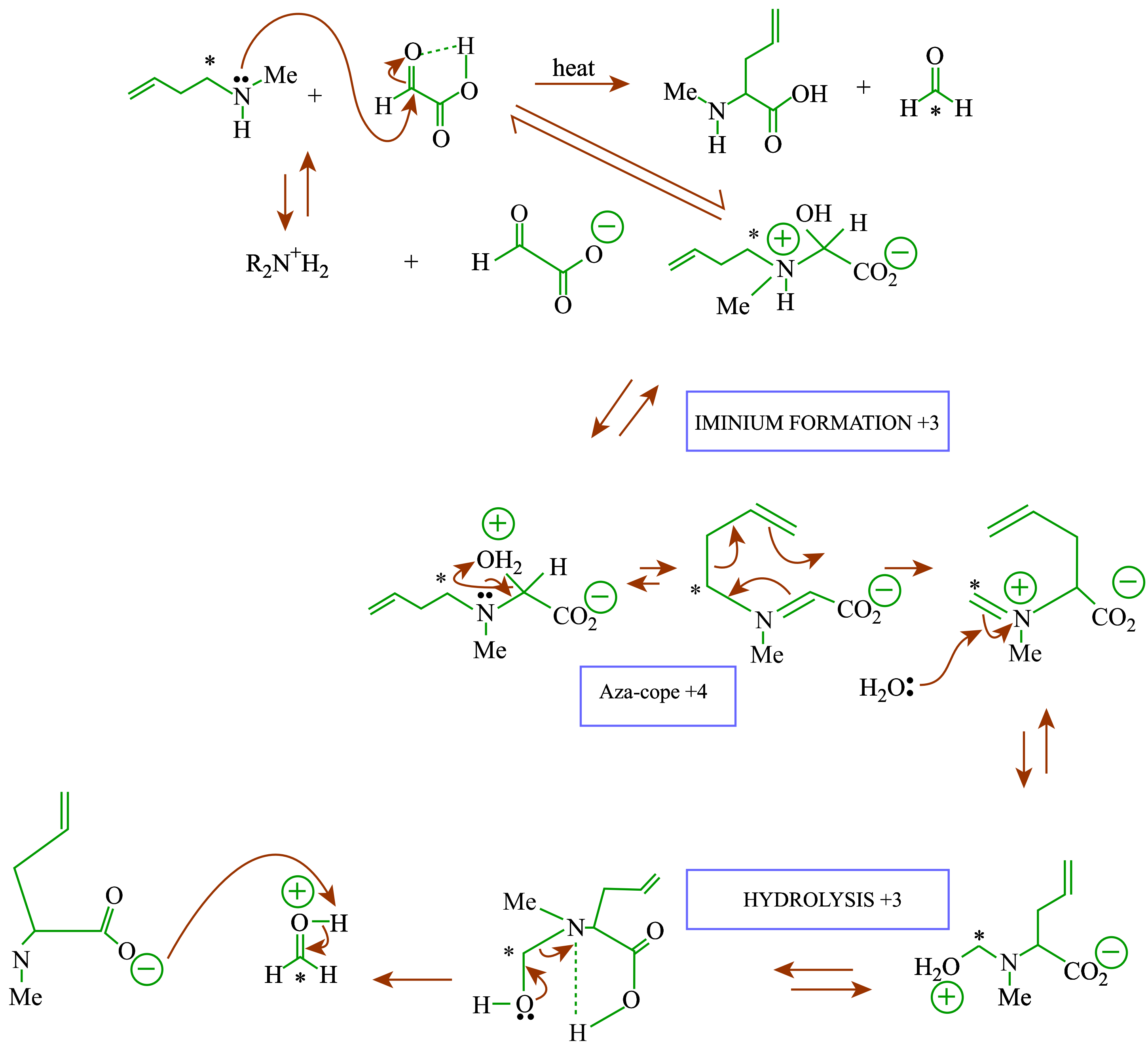
Name (signed) ________________________________

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.

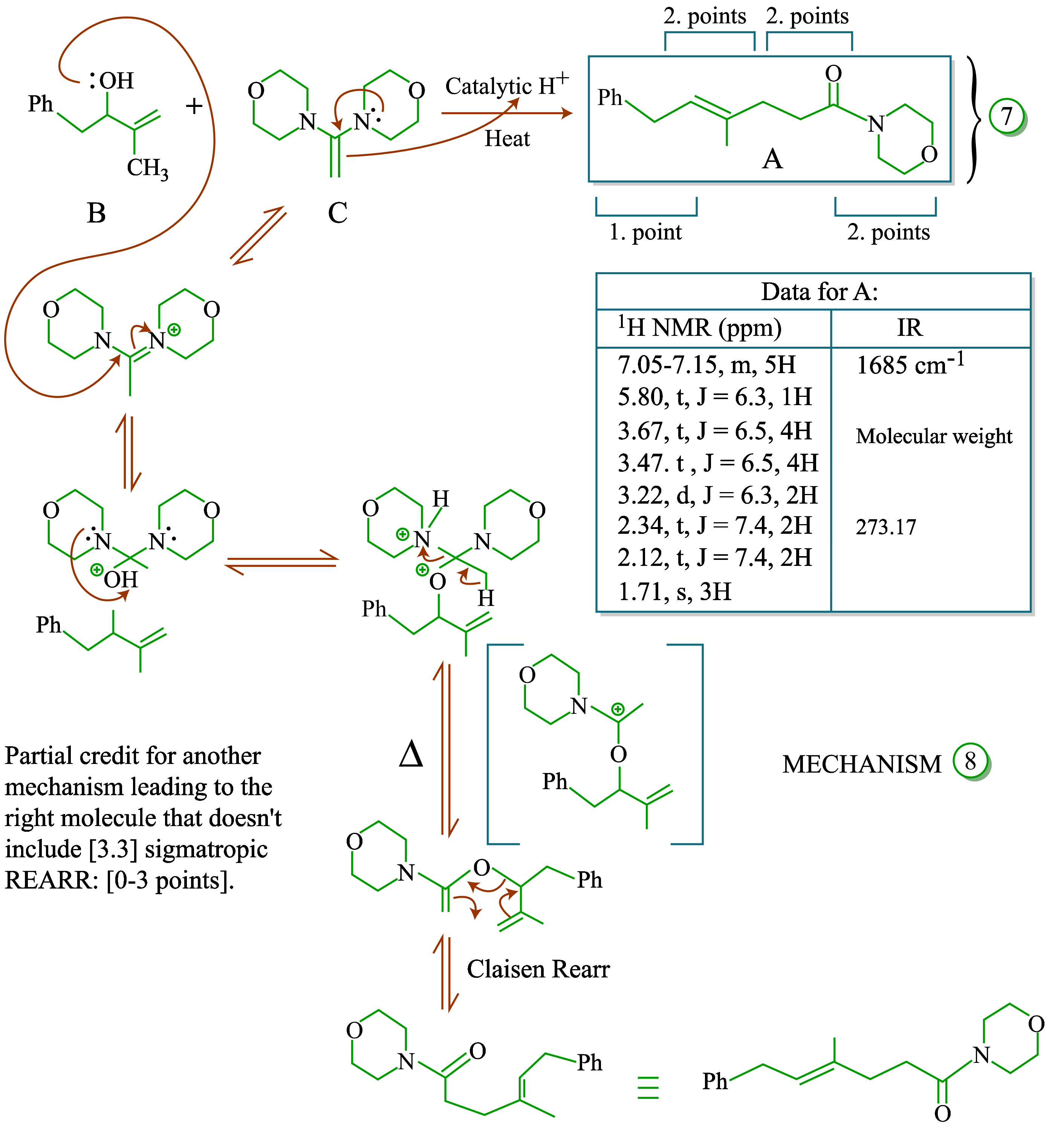
Note: Aste risk(*)=^{13}C.



Solution must account for ^{13}C in formaldyde, otherwise no more than 5 pts should be awarded.

Figure by MIT OCW.

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:	
^{1}H 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	Molecular weight
3.47. t , J = 6.5, 4H	
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	

Partial credit for another mechanism leading to the right molecule that doesn't include [3.3] sigmatropic REARR: [0-3 points].

Figure by MIT OCW.

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.)

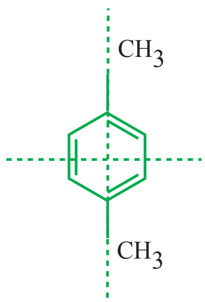
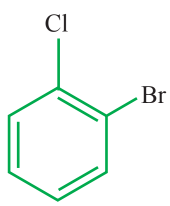
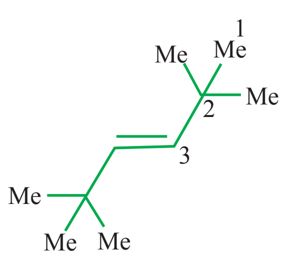
		# non-equivalent H		# non-equivalent C
a.		2	All or nothing	3
b.		4		6
c.	CH_3 — CH_2 — CH_3	2		2
d.	CH_3 — CH_2 — CH_2 — CH_3	2		2
e.		2		3

Figure by MIT OCW.

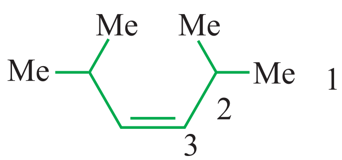
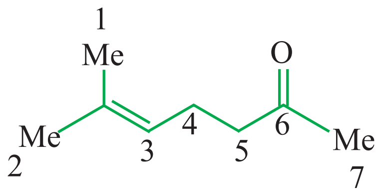
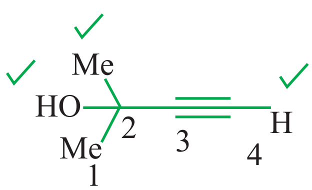
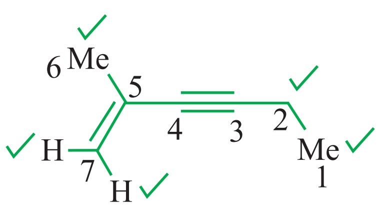
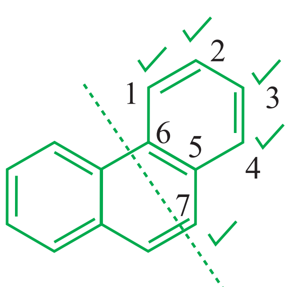
		# non-equivalent H	# non-equivalent C
f.		3	3
g.		6	7
h.		3	4
i.		5	7
j.		5	7

Figure by MIT OCW.

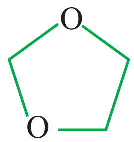
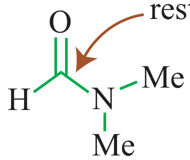
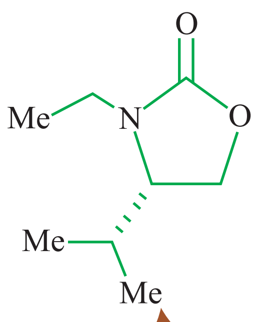
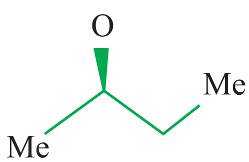
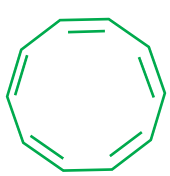
		# non-equivalent H	# non-equivalent C
k.		2 (3 was accepted)	2
i.	restricted rotation 	3	3
m.	(DIASTEREOTOPICITY)  (Me's are diastereotopic)	9	8
n.		6	4
o.	 ($10e^-$, aromatic)	1	1

Figure by MIT OCW.

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 [1]H NMR data listed below, determine the structure of the **product** and the **starting alcohol**. Draw the structures in the boxes provided.

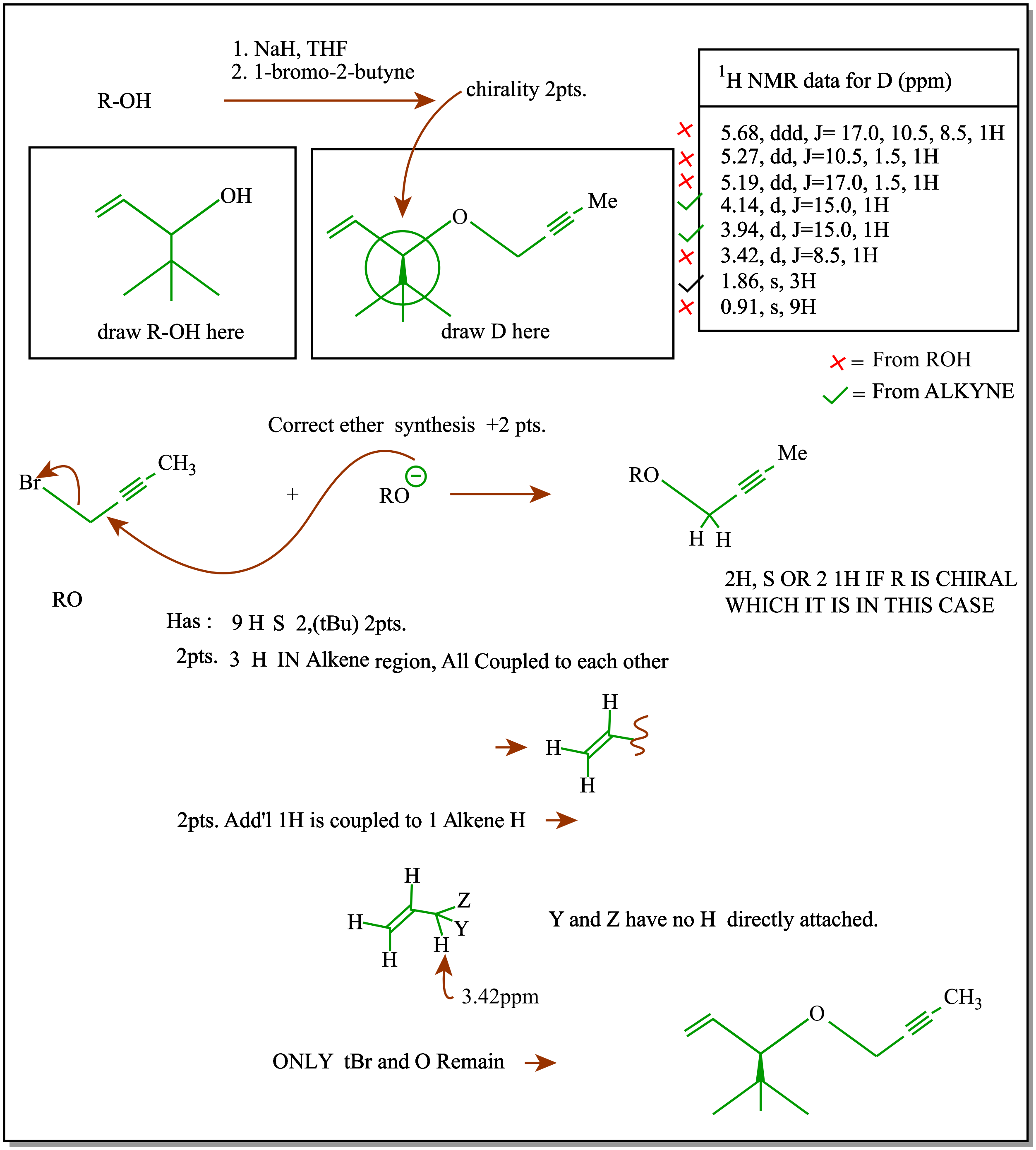
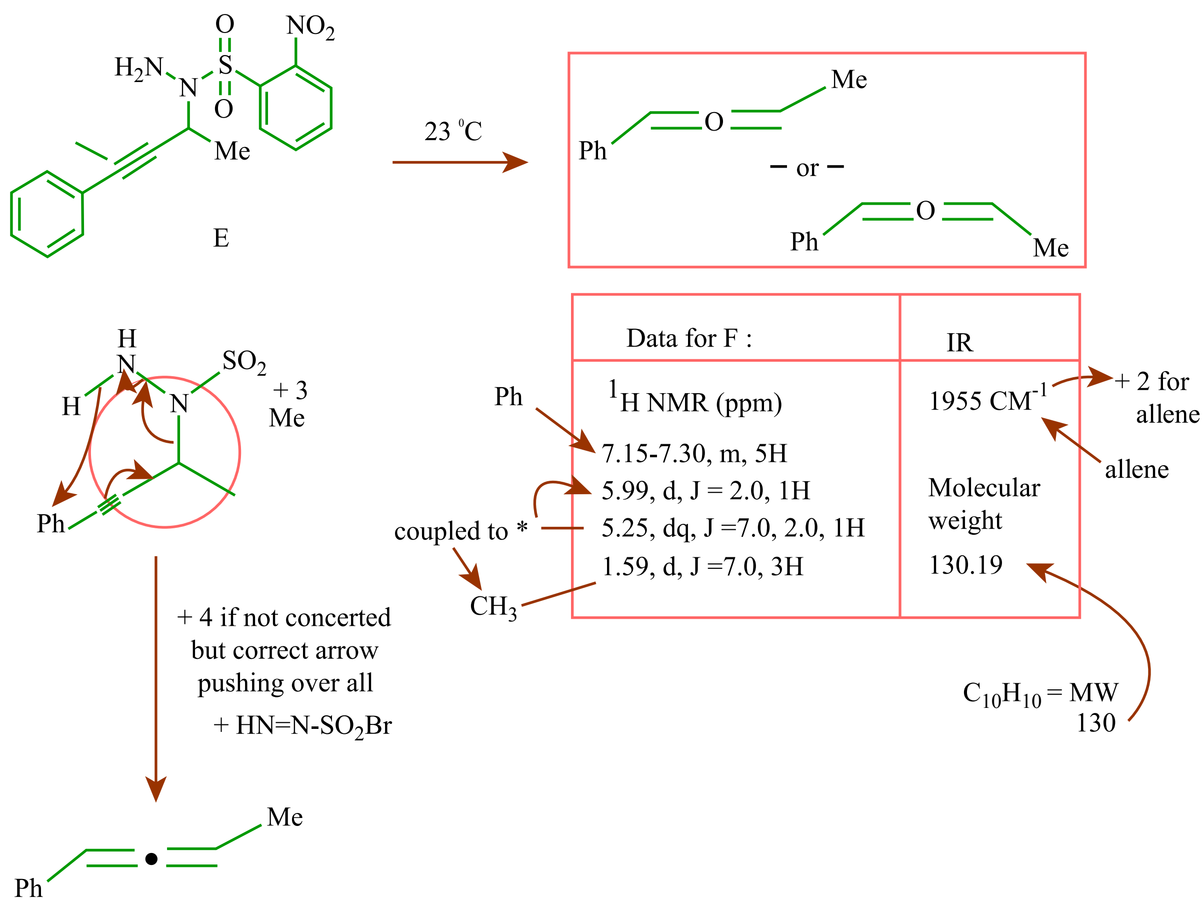


Figure by MIT OCW.

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**.



CORRECT
ARROW PUSHING AND STRUCTURE =10 pts

1 OF ABOVE CORRECT: 5pts

PARTIAL CREDIT FOR PARTIALLY CORRECT MECH AND/OR STRUCTURE BOTH OK.

Figure by MIT OCW.

6. (15 points) Propose a synthesis of **G** from **H**, maleic anhydride, and benzyl bromide (BnBr = $PhCH_2Br$). (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.

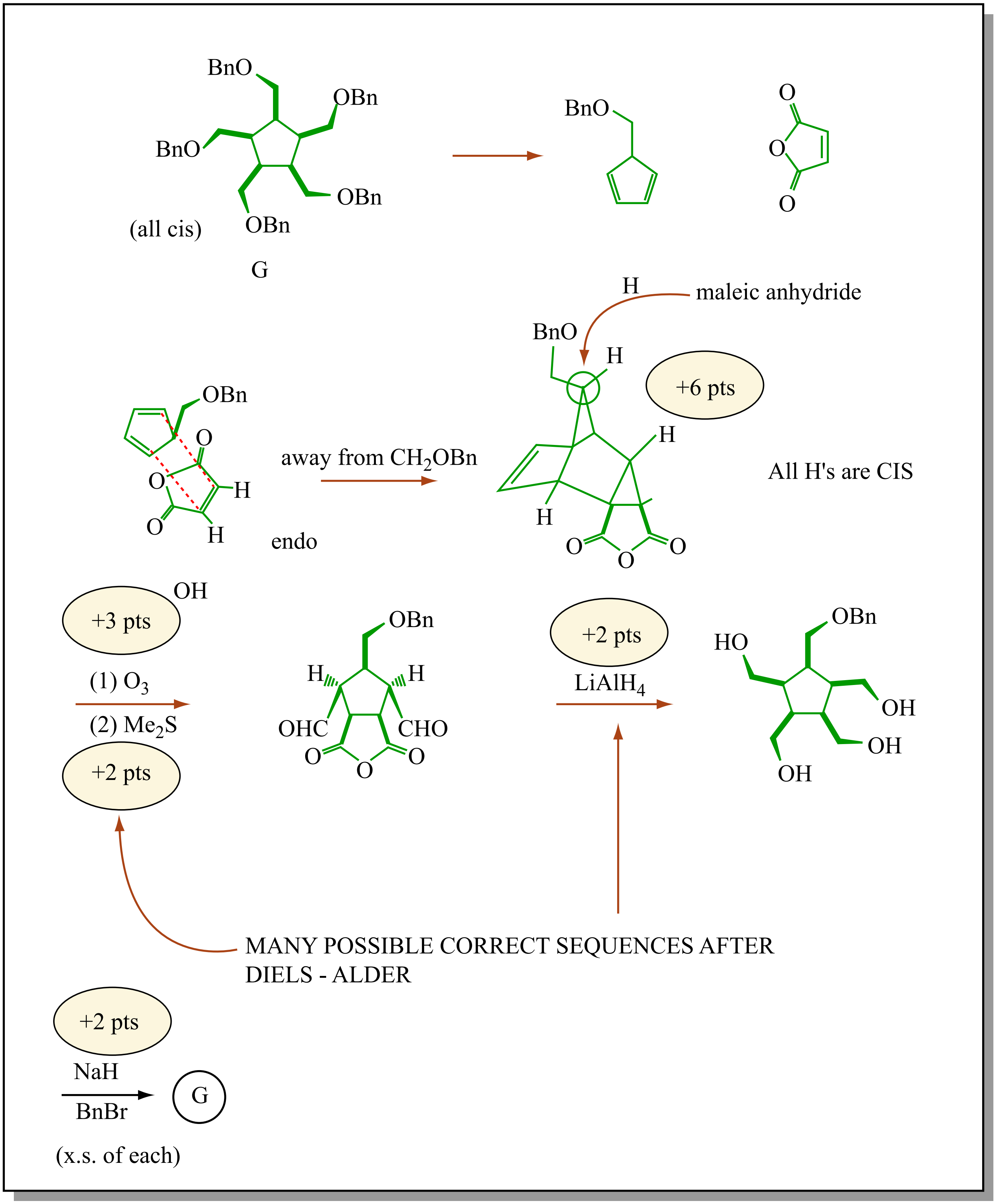


Figure by MIT OCW.

(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.

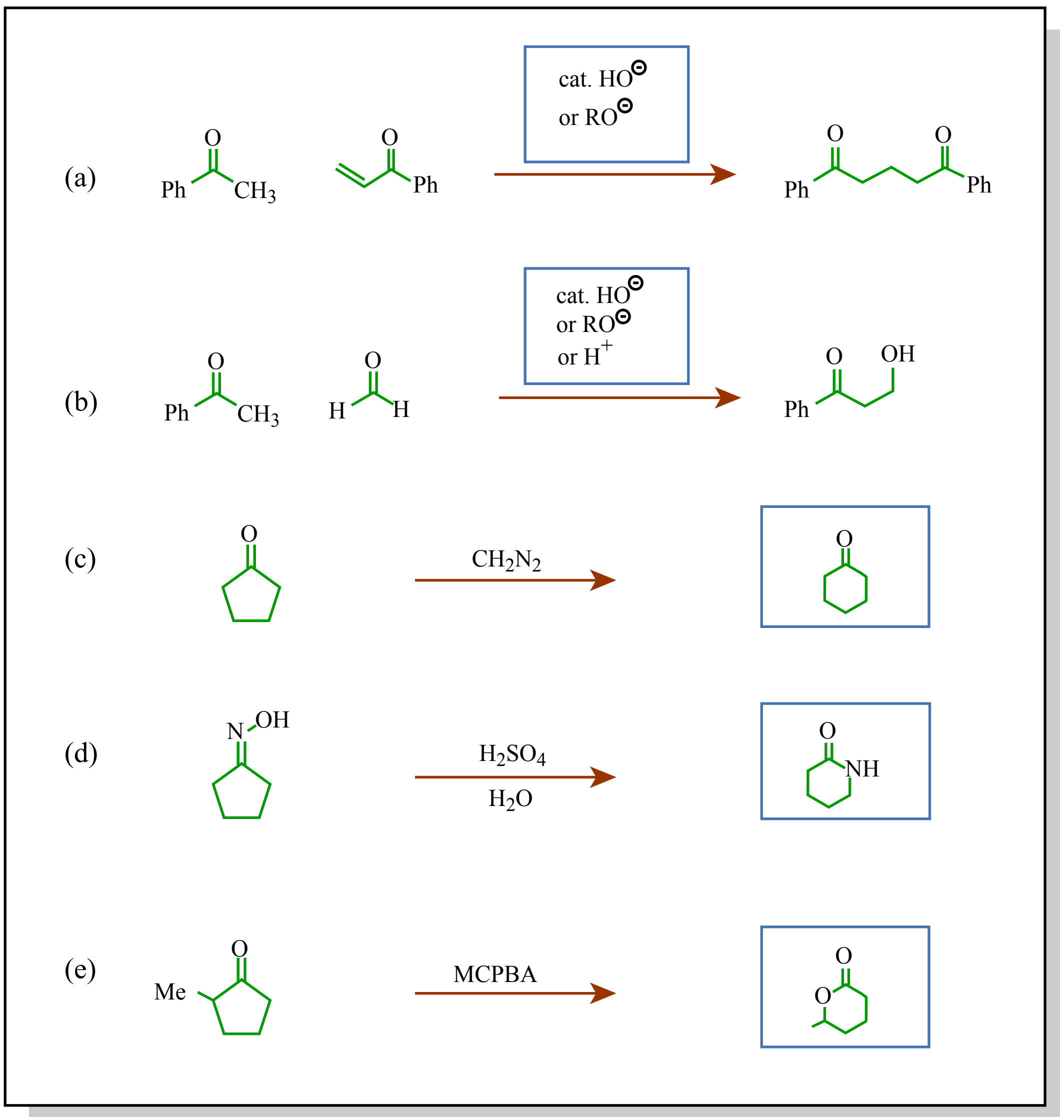
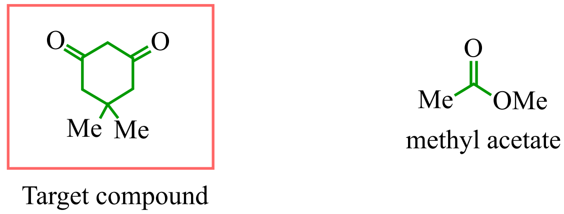


Figure by MIT OCW.

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



Various routes were possible and partial credit was given depending on efficiency.
Below are the most common:

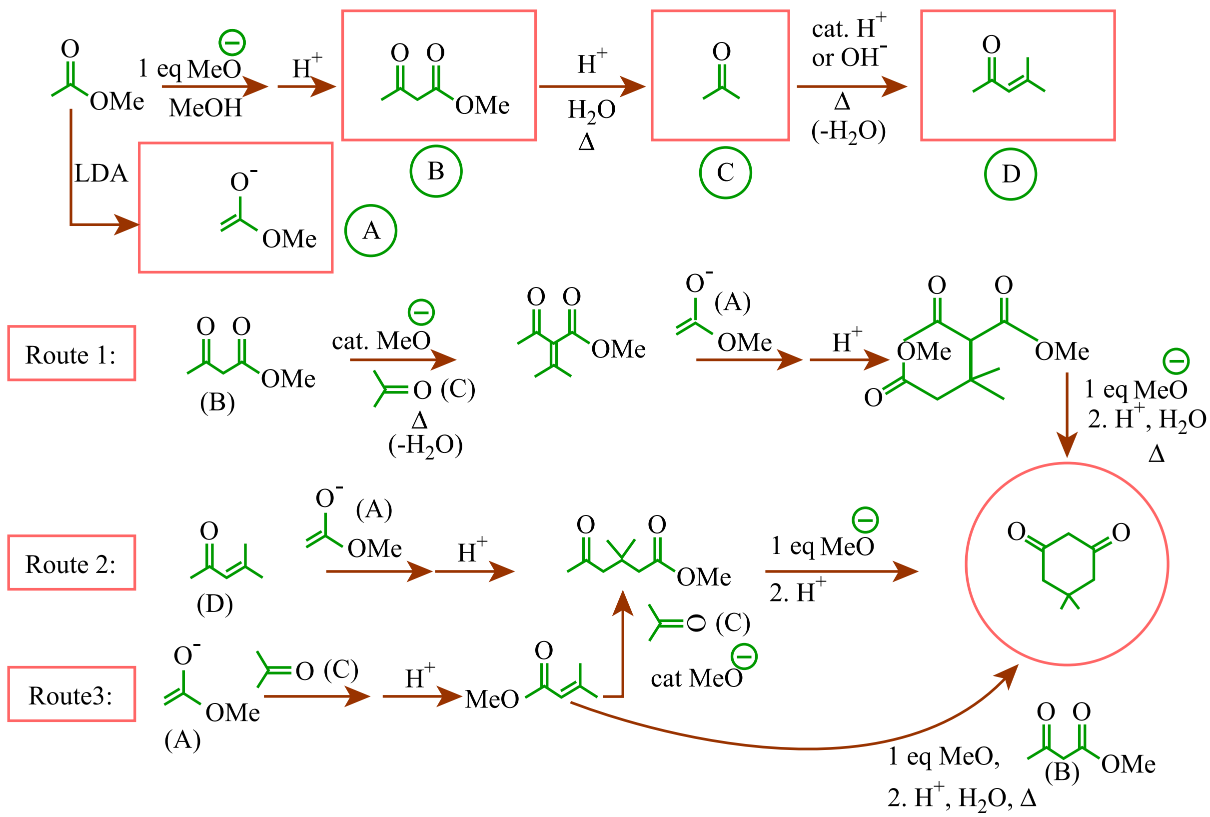


Figure by MIT OCW.

(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.

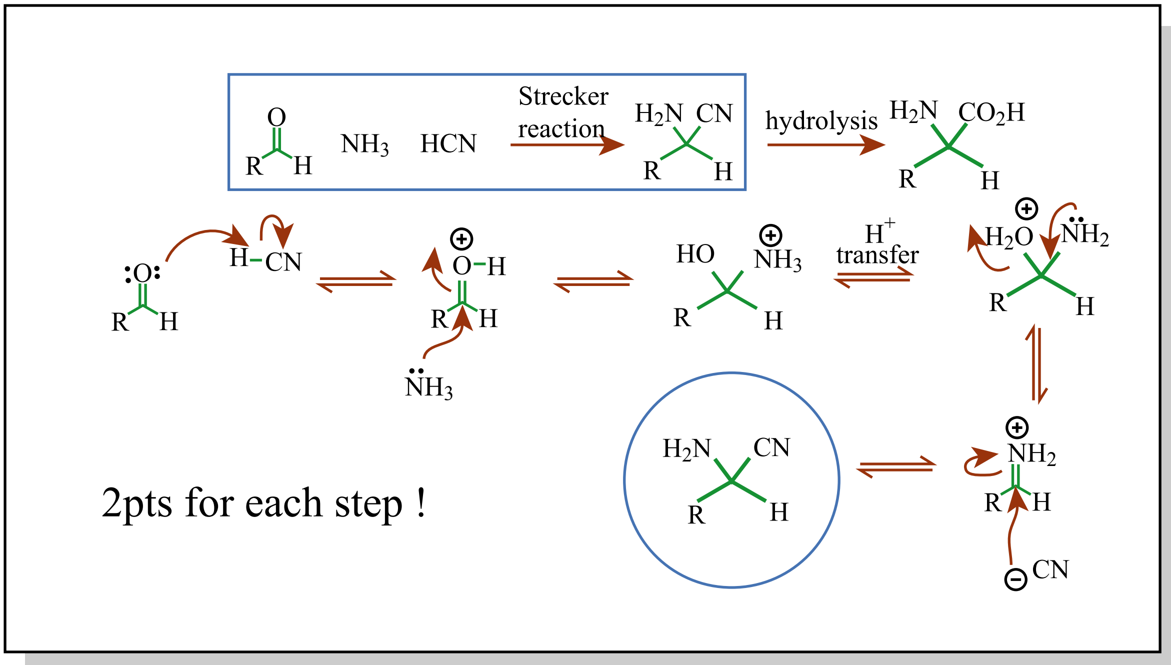


Figure by MIT OCW.

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

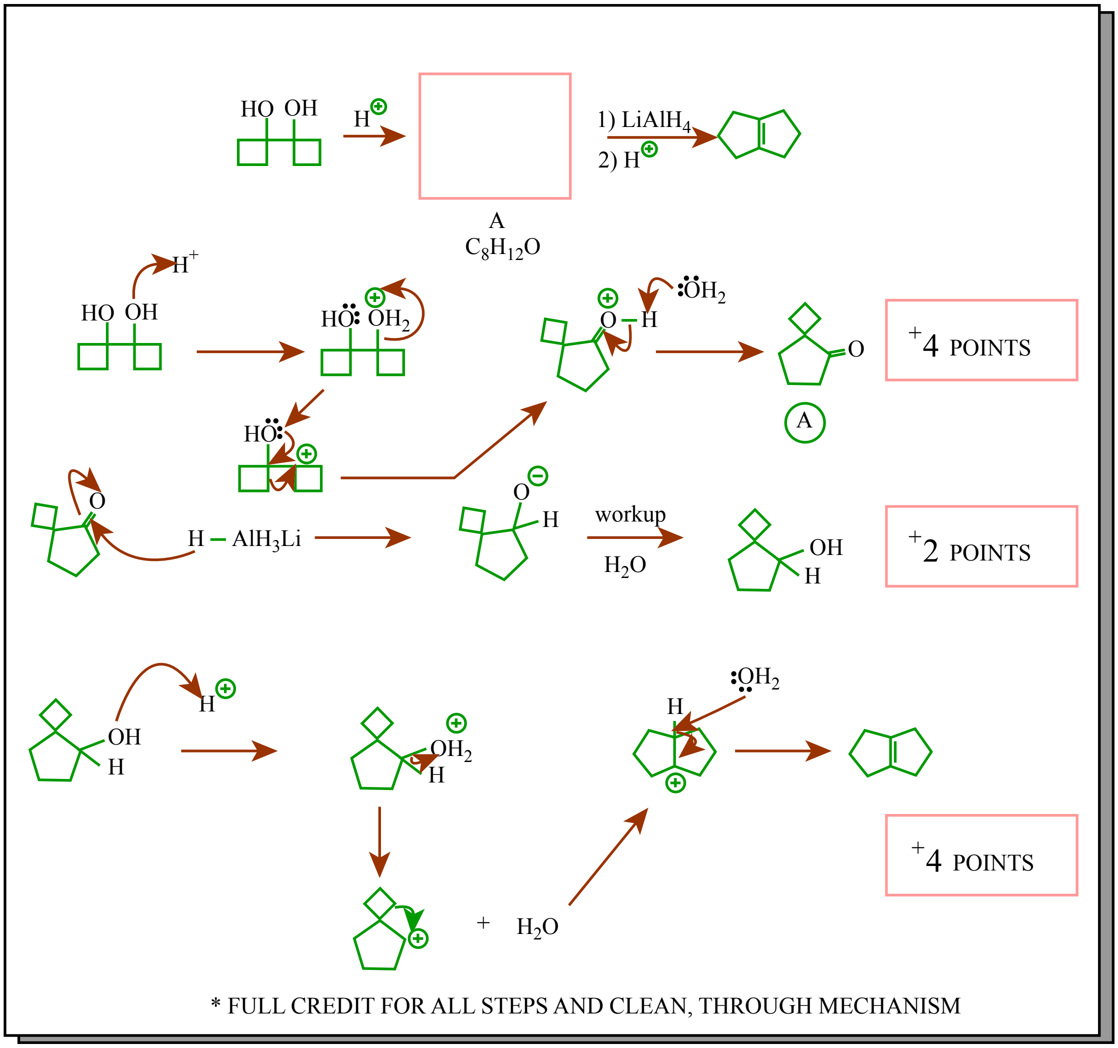
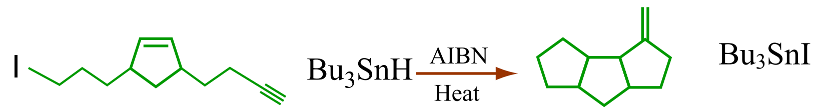
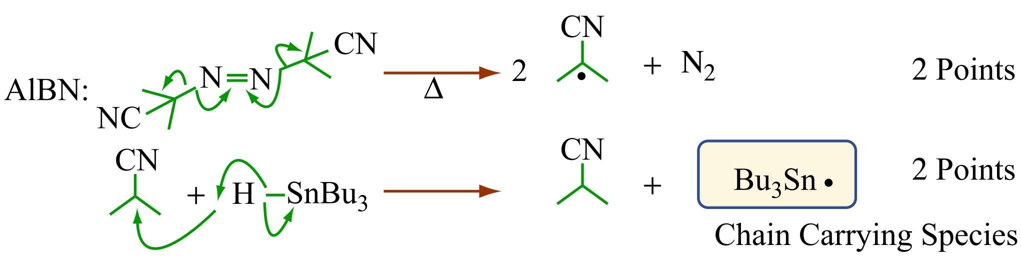


Figure by MIT OCW.

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



Initiation (4 points):



Total 4 Points

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

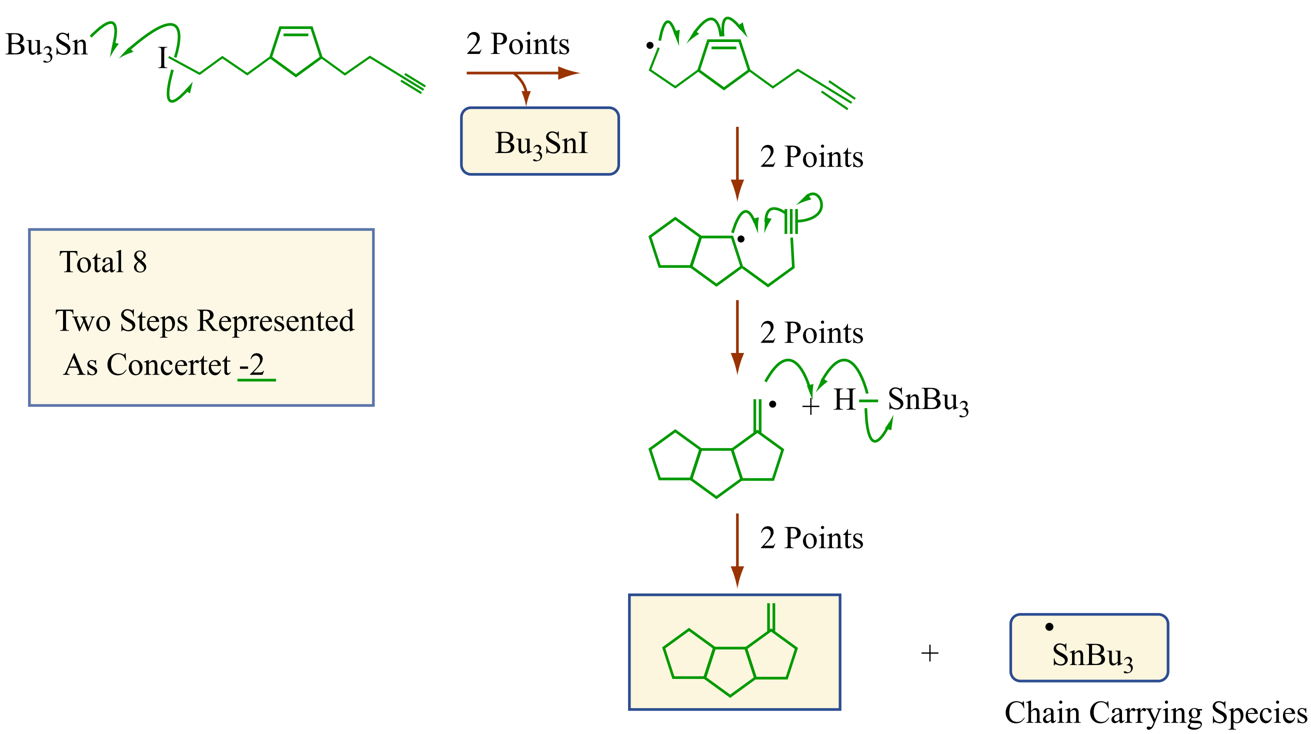


Figure by MIT OCW.

(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.

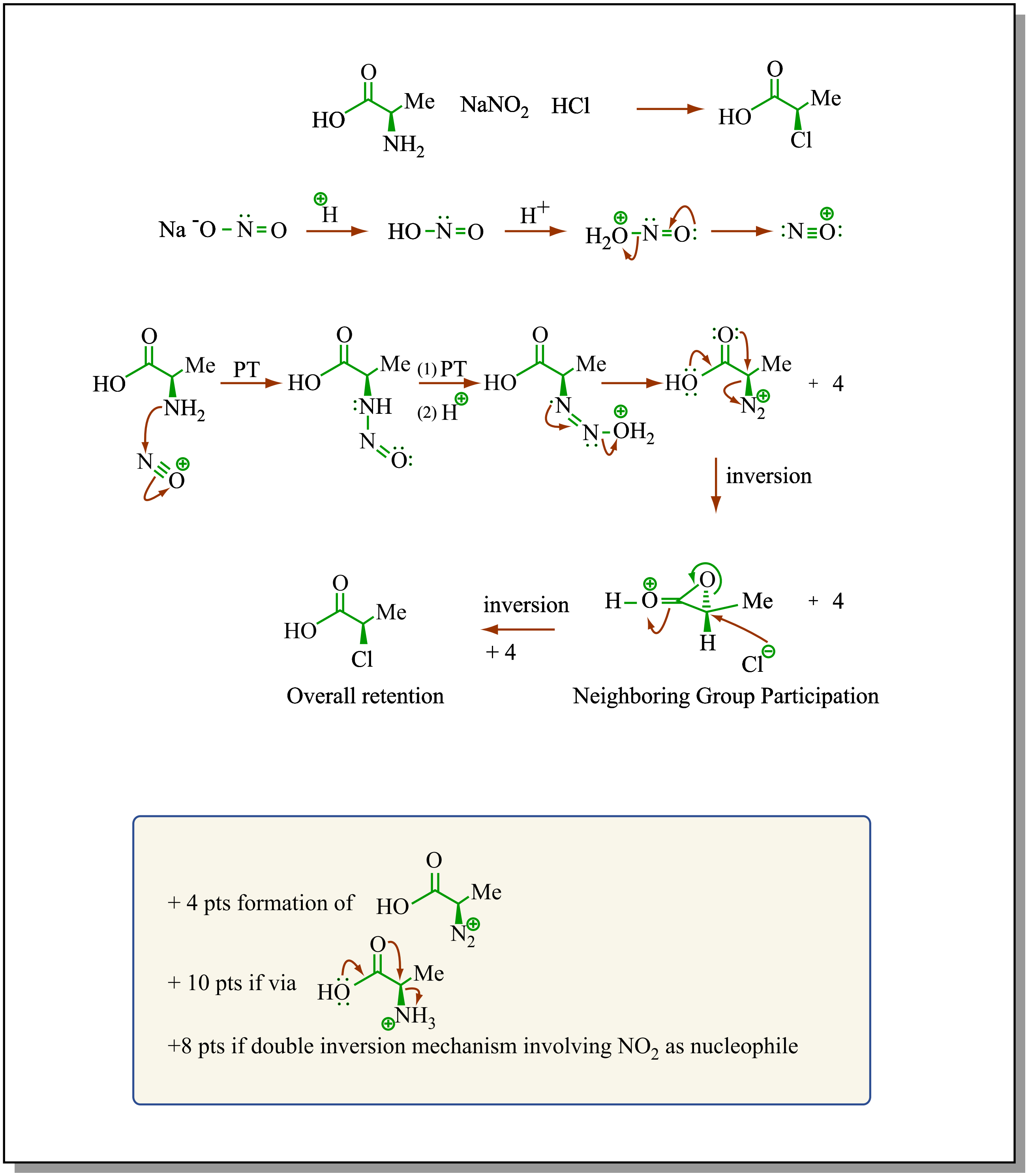


Figure by MIT OCW.

(13) (10 points) Please provide a detailed mechanism for the illustrated transformation. Show all arrow pushing. (Bn = CH_2Ph)
Hint #1: Number your carbons! **Hint #2:** PhSH is catalystic!

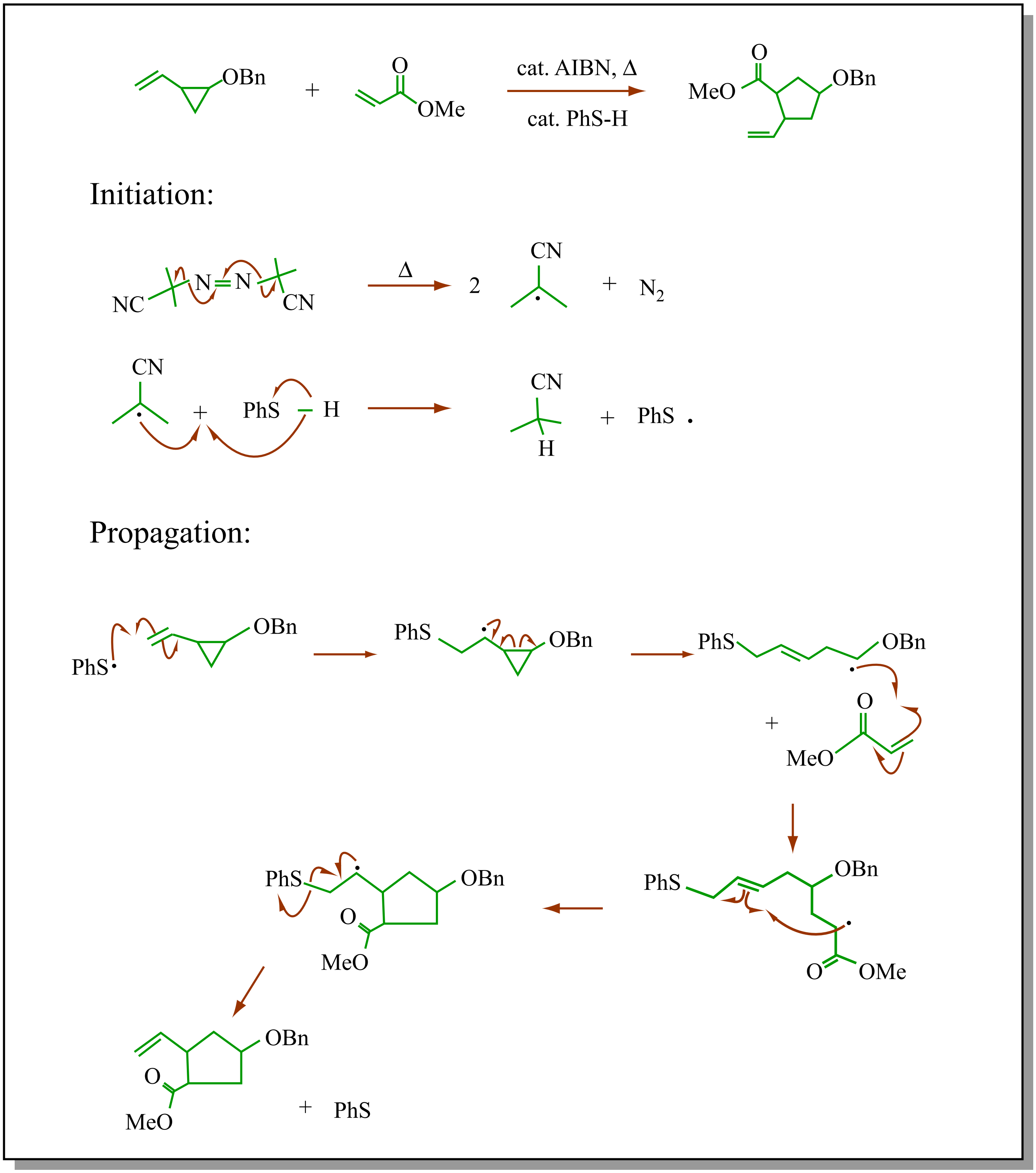


Figure by MIT OCW.

(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).

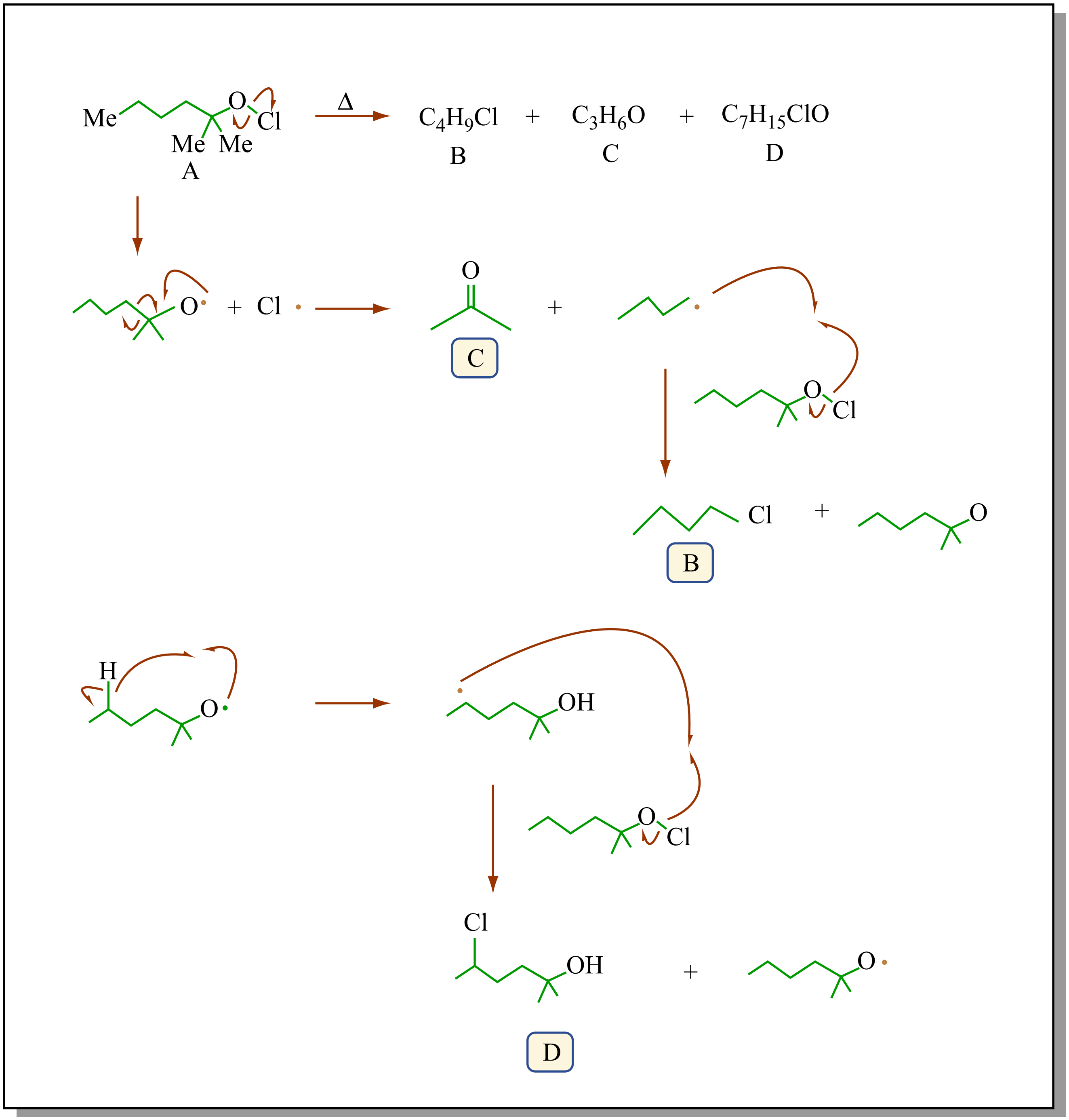
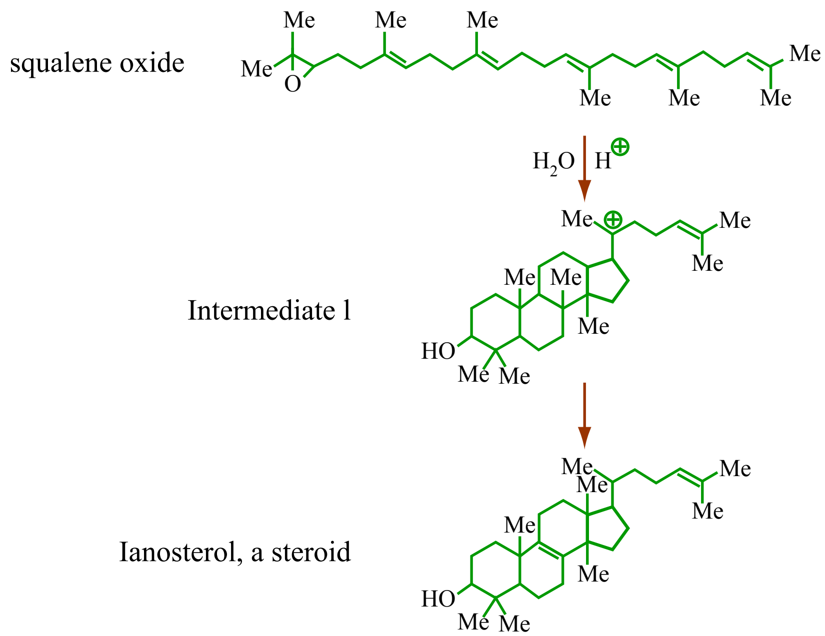
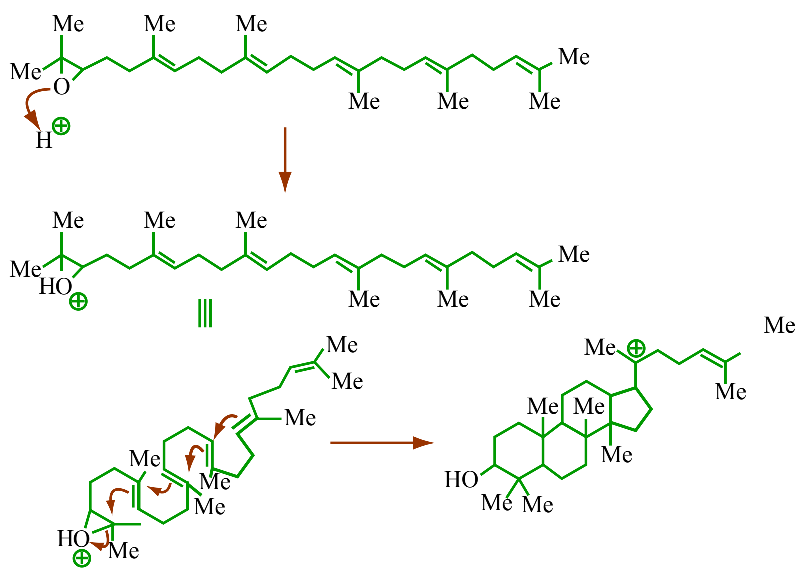


Figure by MIT OCW.

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



(a). (10 points) Squalene oxide into intermediate l:



* or Show Stepwise $\bar{C}$⊕ Charges

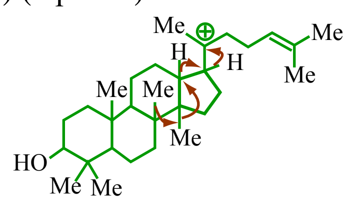
Figure by MIT OCW.

+2 for each step: Protonation opening of epoxide each cation π – Cyclization

* if no errors

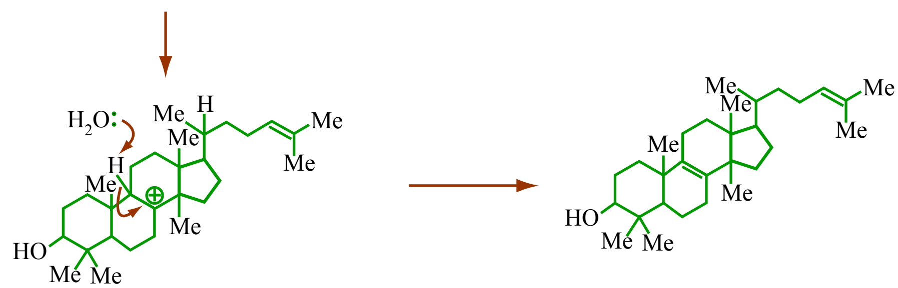
-2 if show wrong connectivity after cation π – Cyclic.

(b) (6 points) Intermediate 1 into lanosterol:



+2 for deprotonation

+1 for every 1,2-shift



* or show stepwise $\bar{C}$ ⊕ charges !

-1 if show deprotonation in same step at alkyl shift.

-1 if show formation of double bond $\bar{s}$ deprotonation, but show arrow

-2 for every 1,3 shift

-1 for every 2 missing mech. arrows

Figure by MIT OCW.