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) _____

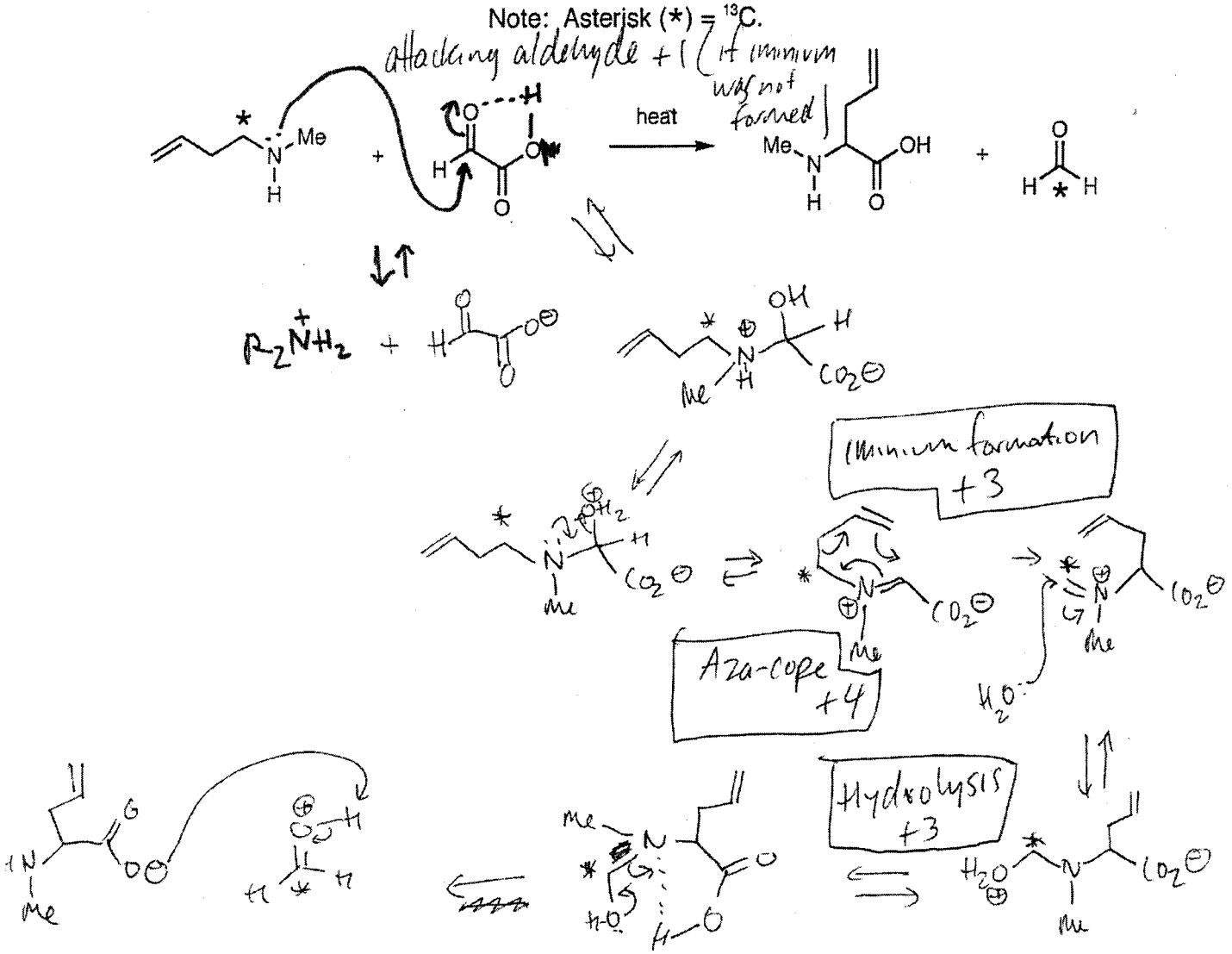
Name (signed) _____

T.A. Key

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

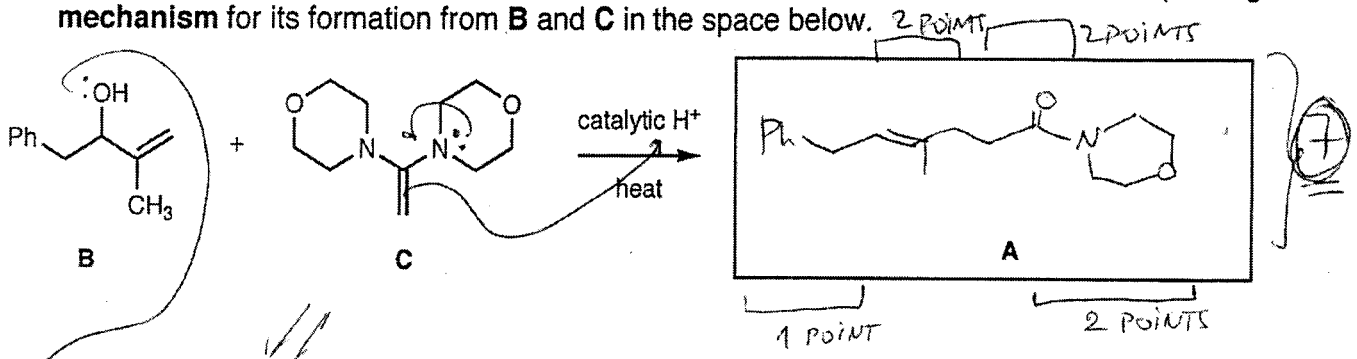
1. **(10 points total)** Write an **arrow-pushing mechanism** for the reaction below.

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



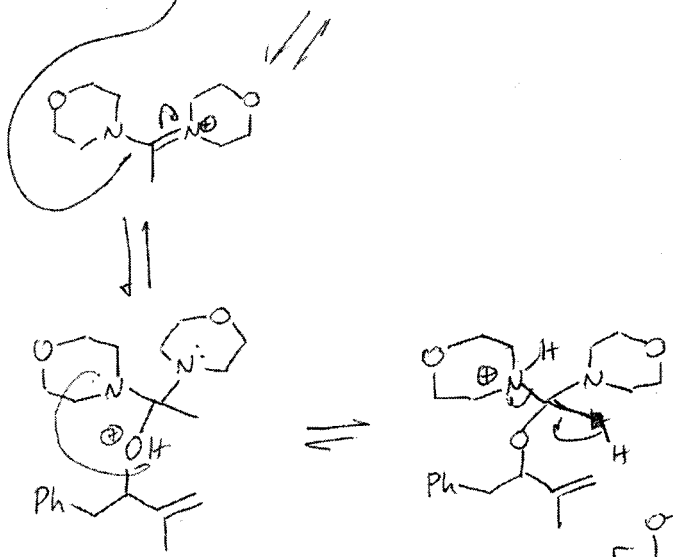
Solution must account for ^{13}C in formaldehyde, otherwise no more than 5 pts should be awarded.

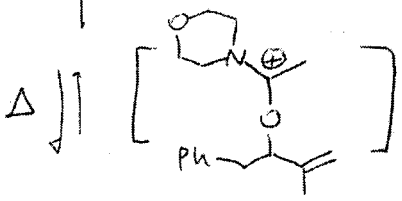
2. **(15 points total)** Compound **A** is prepared from **B** and **C** and has the spectroscopic data listed below. **Draw** the structure of **A** in the **box** provided, ***and*** **write** an arrow-pushing **mechanism** for its formation from **B** and **C** in the space below.



Data for **A**:

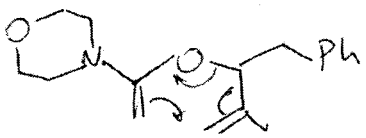
^{1}H NMR (ppm)	IR
7.05-7.15, m, 5H	1685 cm^{-1}
5.80, t, J = 6.3, 1H	
3.67, t, J = 6.5, 4H	
3.47, t, J = 6.5, 4H	Molecular weight
3.22, d, J = 6.3, 2H	
2.34, t, J = 7.4, 2H	273.17
2.12, t, J = 7.4, 2H	
1.71, s, 3H	



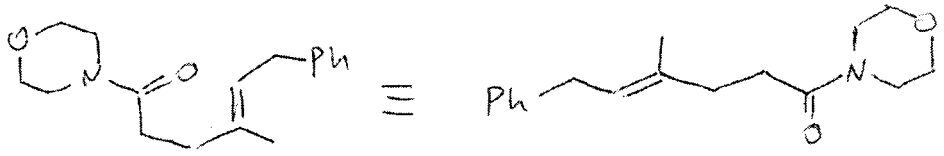


MECHANISM (8)

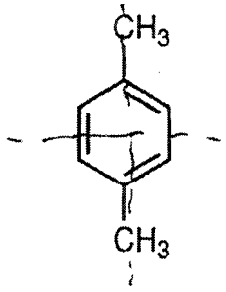
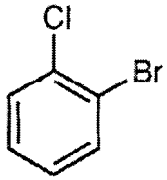
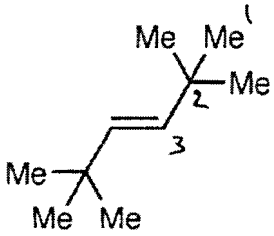
PARTIAL CREDIT FOR ANOTHER MECHANISM LEADING TO THE RIGHT MOLECULE THAT DOESN'T INCLUDE [3,3] SIGMATROPIC REARR. [0-3 POINTS]



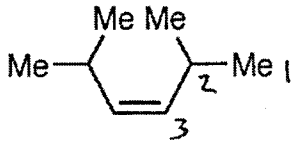
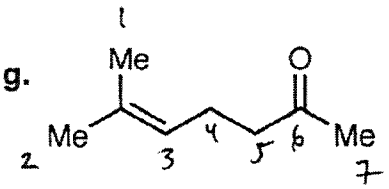
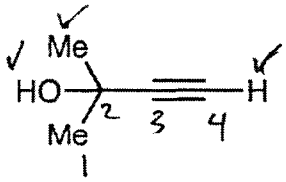
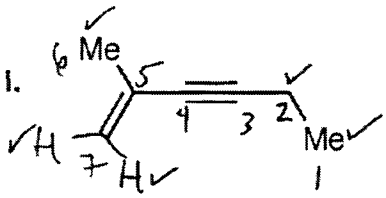
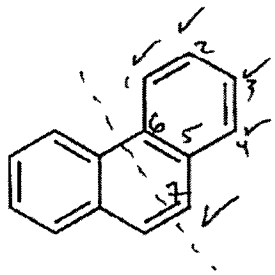
Claisen Rearr.

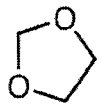
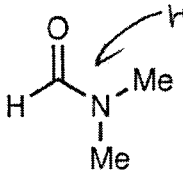
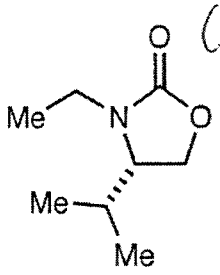
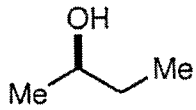
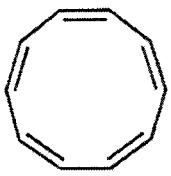


3. **(30 points total, 1 point per box)** For the following 15 structures, write the number of **chemically non-equivalent** (number of "different types") of **hydrogens and carbons** in the **appropriate** boxes below. (Be careful to put the numbers in the correct boxes – we can't read your mind, i.e.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

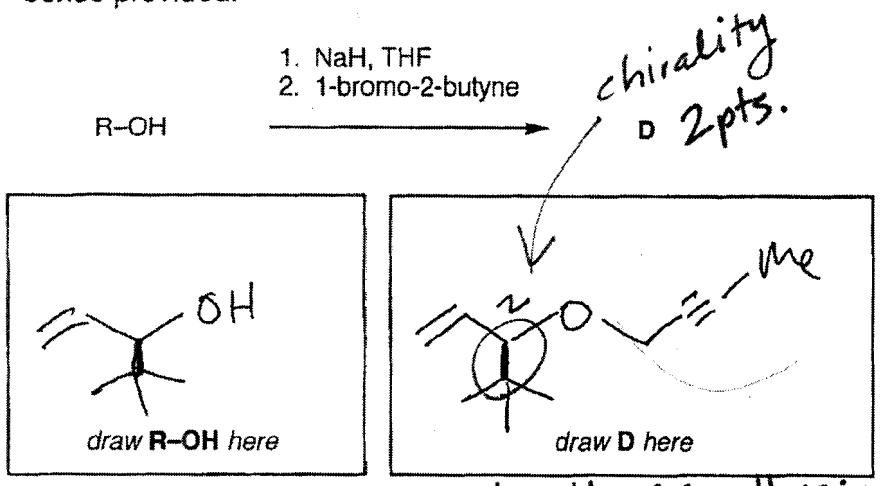
		# non-equivalent H	# non-equivalent C
a.		2	3
b.		4	6
c.	$CH_3–CH_2–CH_3$	2	2
d.	$CH_3–CH_2–CH_2–CH_3$	2	2
e.		2	3

ALL OR NOTHING

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

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

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.



chirality D 2pts.

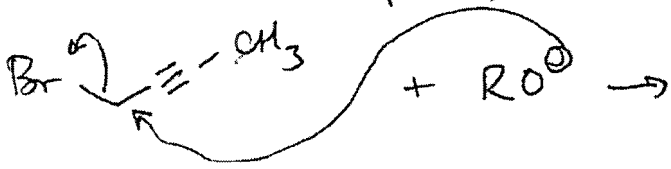
^{1}H NMR data for **D** (ppm)

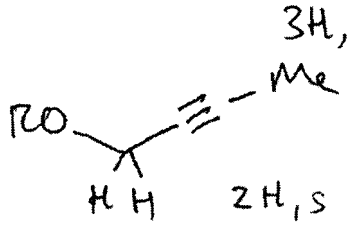
- ✓5.68, ddd, J = 17.0, 10.5, 8.5, 1H
- ✓5.27, dd, J = 10.5, 1.5, 1H
- ✓5.19, dd, J = 17.0, 1.5, 1H
- ✓4.14, d, J = 15.0, 1H
- ✓3.94, d, J = 15.0, 1H
- ✗3.42, d, J = 8.5, 1H
- ✓1.86, s, 3H
- ✗0.91, s, 9H

✓ = FROM ALKYNE

✗ = FROM ROH

correct ether synthesis +2 pts.



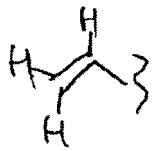


CH–B QUARTET

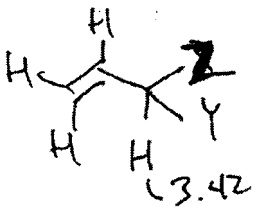
2H, s OR 2 1H IF R IS CHIRAL, WHICH IT IS IN THIS CASE.

RO HAS: • 9H s 2→ (tBu) 2 pts.

2 pts. • 3 H IN ALKENE REGION, ALL COUPLED TO EACH OTHER 2→

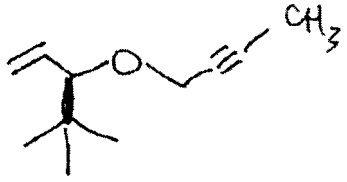


2 pts. XS. ADD'L • 1 H IS COUPLED TO 1 ALKENE H 2→

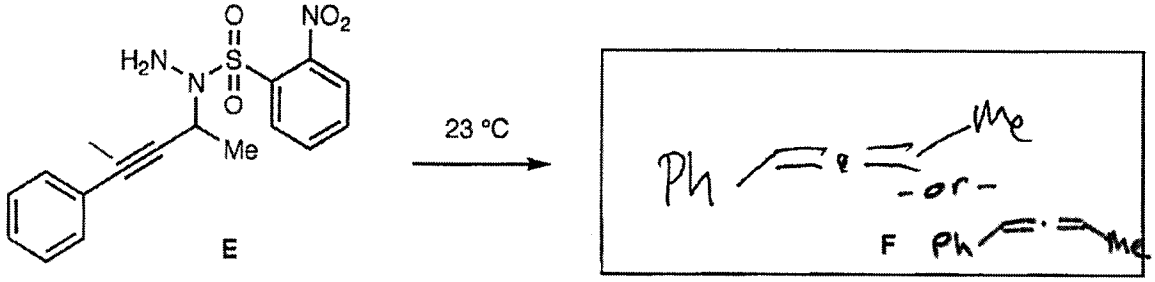


Y & Z HAVE NO H DIRECTLY ATTACHED.

• ONLY tBu & O REMAIN 2→



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**.



E

Data for F:

IR

1955 cm^{-1} → +2 for allene

ALLENE

^{1}H NMR (ppm)

Ph — 7.15-7.30, m, 5H

5.99, d, J = 2.0, 1H

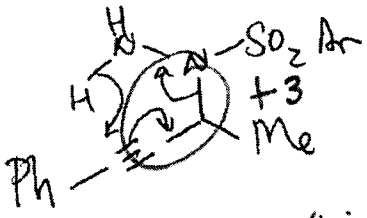
5.25, dq, J = 7.0, 2.0, 1H

1.59, d, J = 7.0, 3H

Molecular weight

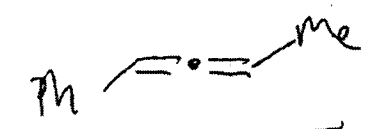
130.19

$C_{10}H_{10}$ = MW 130



+4 if not concerted (CH_3 COUPLED TO 4)

but correct arrow pushing overall + $HN{=}N{-}SO_2Ar$



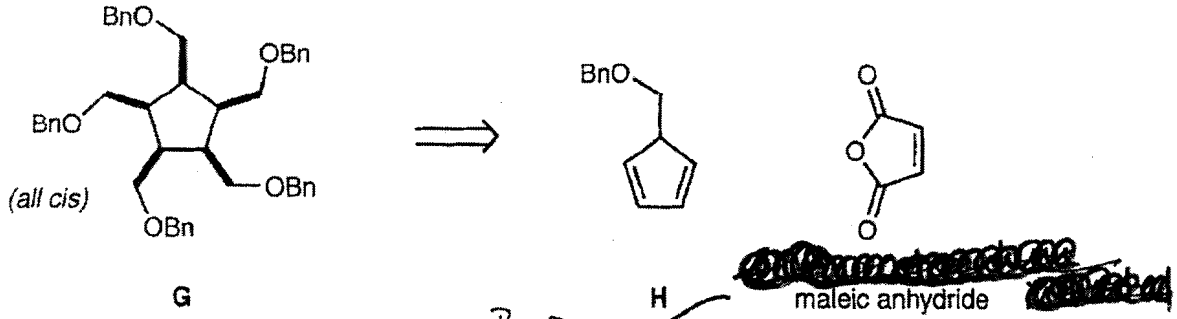
CORRECT

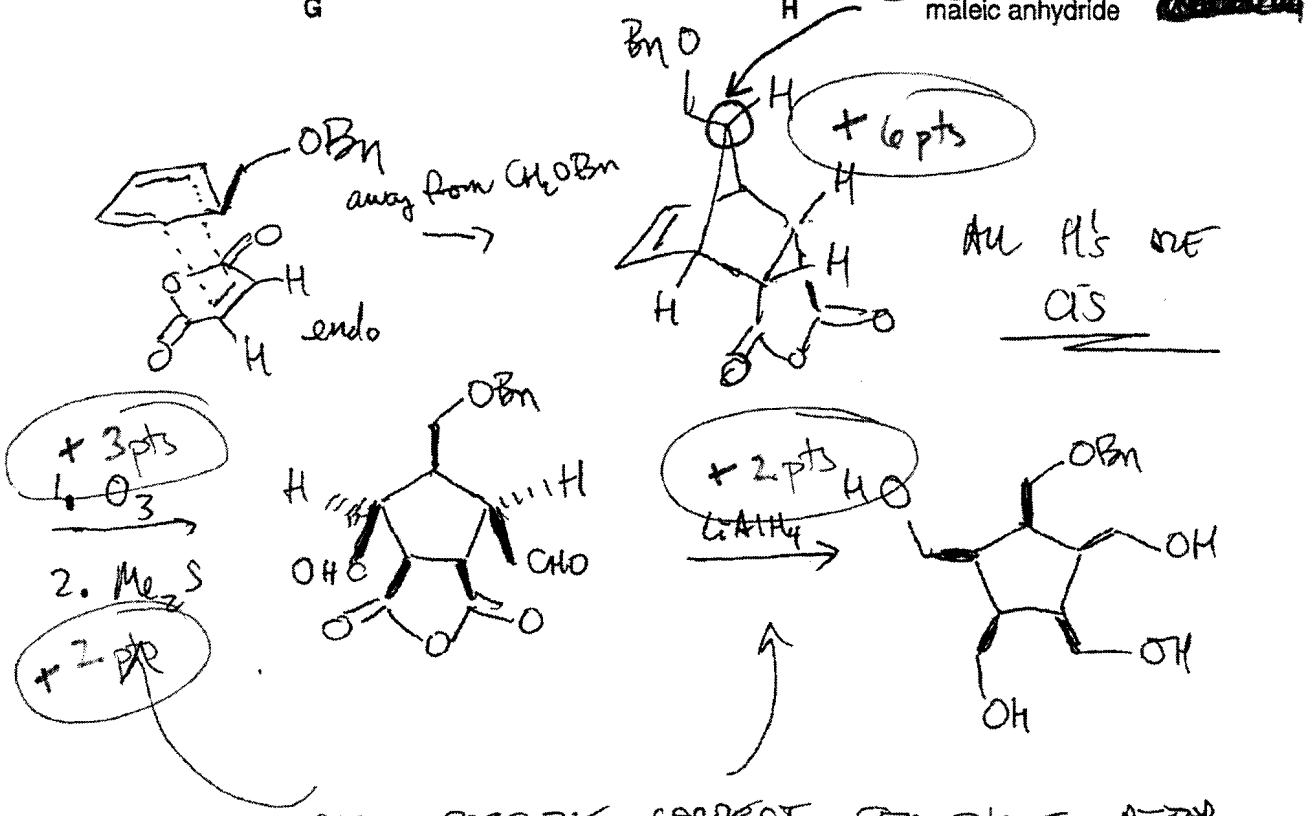
^ ARROW PUSHING & CORRECT STRUCTURE = 10 pts

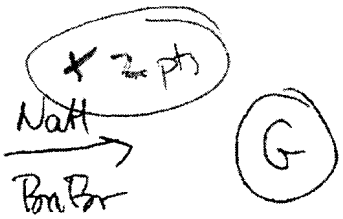
1 OF ABOVE CORRECT: 5 pts

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

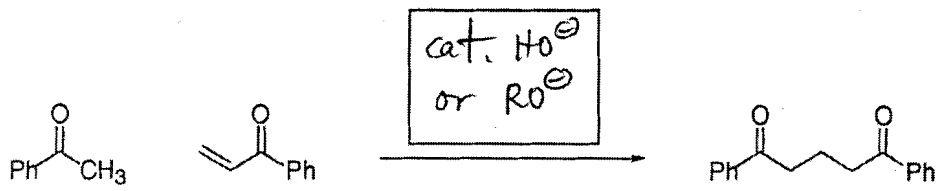
6. **(15 points)** Propose a synthesis of **G** from **H**, maleic anhydride, and benzyl bromide (BnBr = $PhCH_2Br$). (All of the substituents on the five-membered ring in **G** are cis to one another, and your synthesis must establish this relative configuration.) Your synthesis must use **H**, maleic 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.

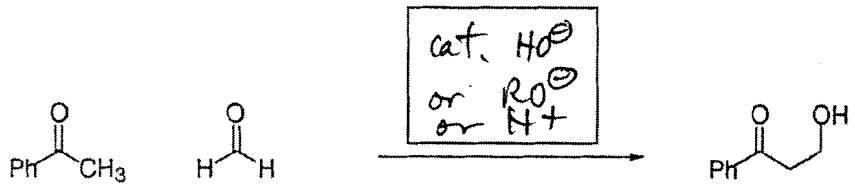


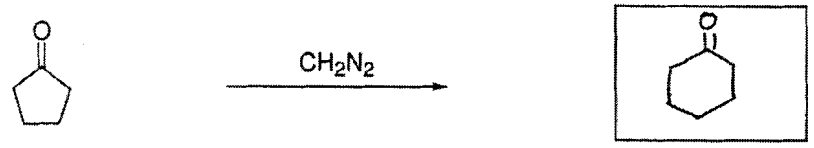


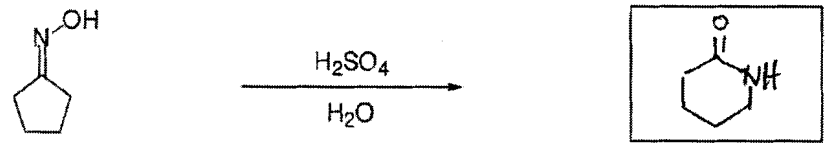


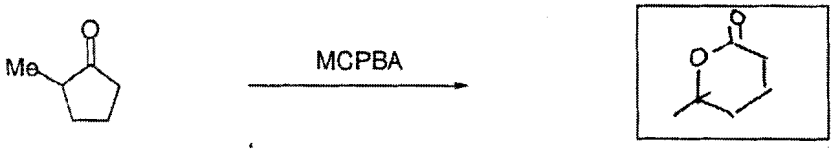
(7) (2 points for each box; 10 points total) Please provide the indicated information. If you use a base or an acid, please specify whether a "catalytic amount", "1 equivalent", etc. is required.

(a) 

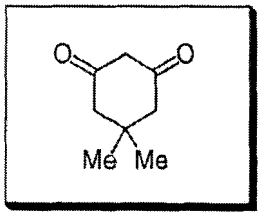
(b) 

(c) 

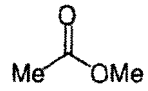
(d) 

(e) 

(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.

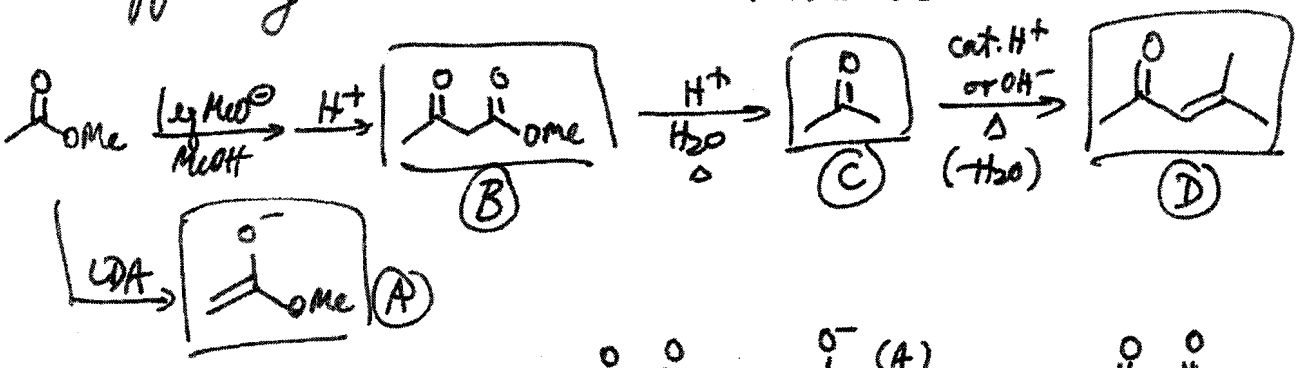


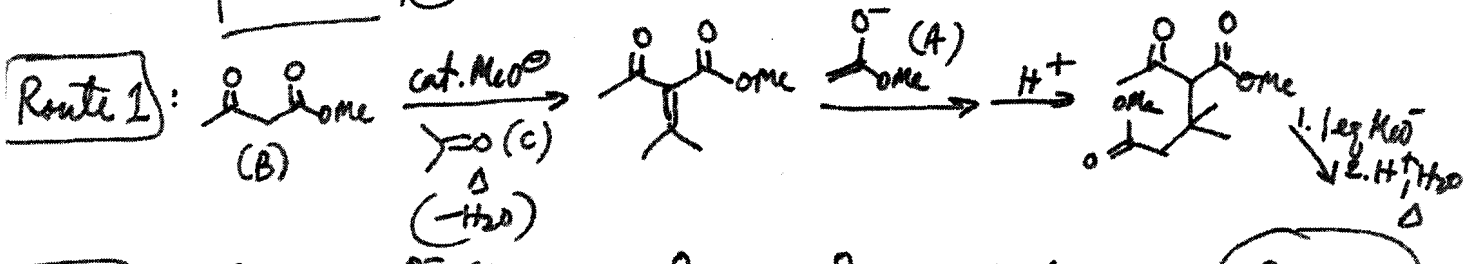
target compound

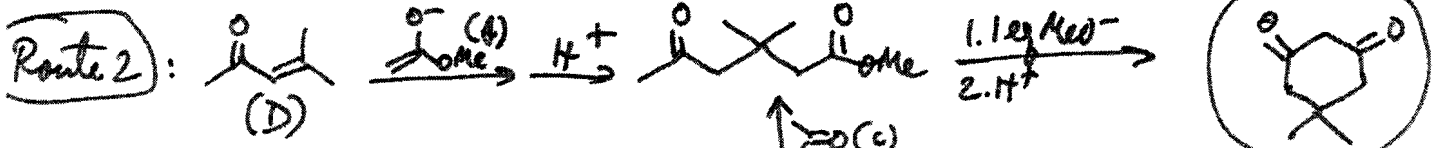


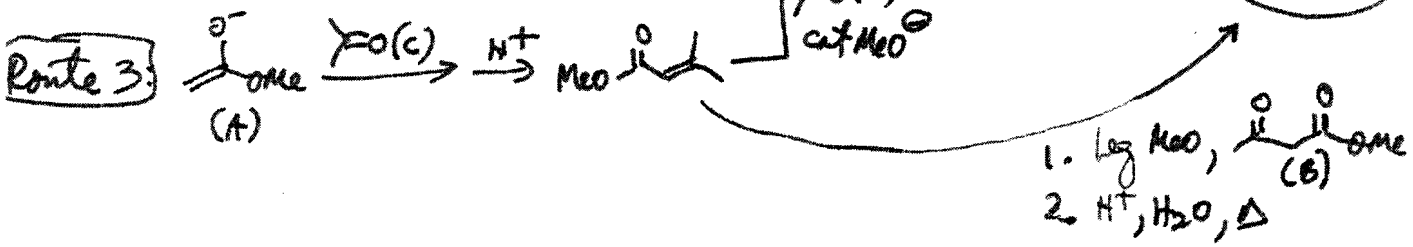
methyl acetate

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

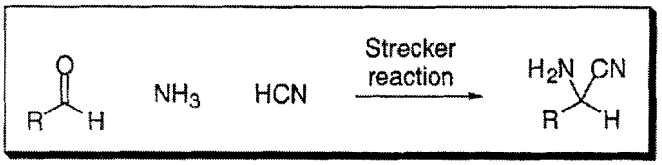


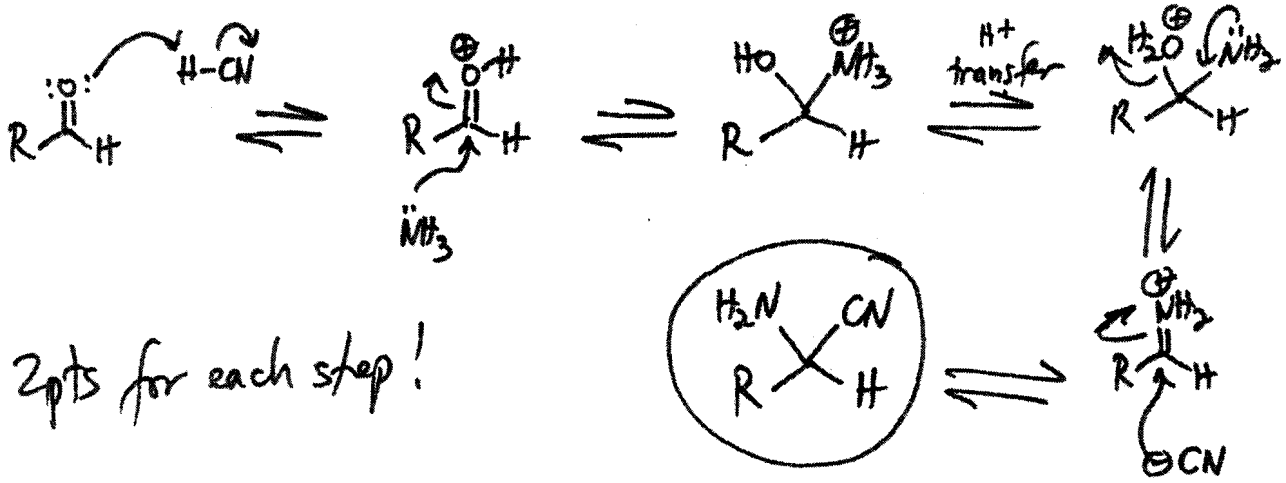






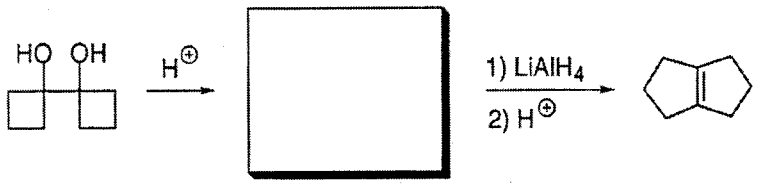
(9) (10 points) The Strecker reaction, followed by a hydrolysis reaction, is an excellent method for synthesizing amino acids, which are the building blocks of proteins. Provide the best mechanism for this process. Please show all arrow pushing. Note: You do NOT have to draw the mechanism for the hydrolysis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



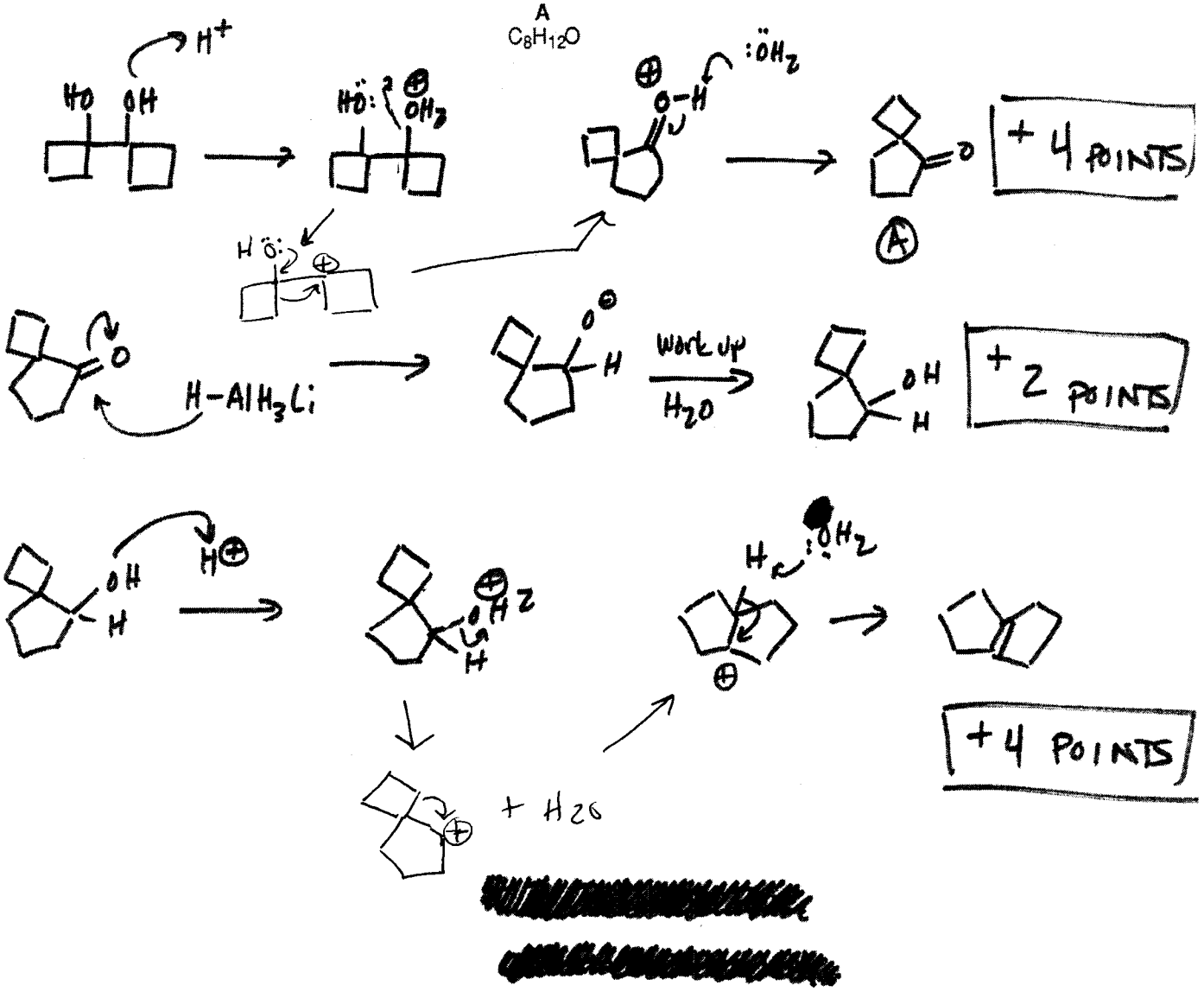


2pts for each step!

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



A
$C_8H_{12}O$



*FULL CREDIT FOR ALL STEPS AND CLEAN, THOROUGH MECHANISM.