Chemistry 3B –Exam #2

Student Name: PETE'S KEY

Student ID Number: _____

TA or Section: _____

Student Averages

Point Breakdown

Problem 1	13.5	/ 17
Problem 2	7.4	/ 13
	14.75	/ 23
	7.2	/ 12
Problem 3	10.5	/ 15
Problem 4	13.4	/ 18
Problem 5	13.0	/ 18
Problem 6	11.4	/ 14
	9.5	/ 20
Total	100.6	/ 150

stdev = $\pm \frac{29}{150}$

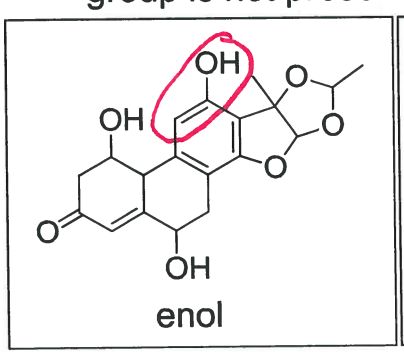
Median = 103.5

Check that you have 10 pages.

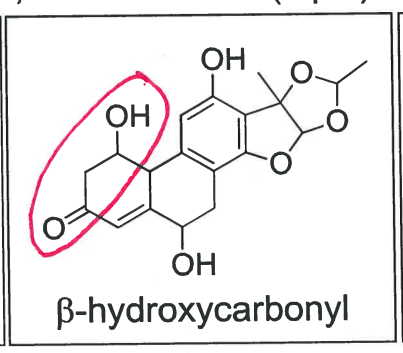
You will have 120 minutes for this exam.

Please Remember: Budget your time well. There are many mechanisms. Acidic conditions are different from basic conditions. READ THE QUESTIONS CAREFULLY; THEY ARE MEANT TO BE HELPFUL!

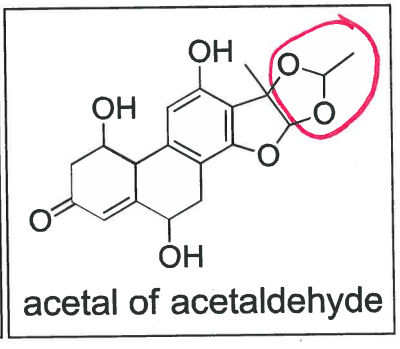
1. A. Circle the named functional group on the molecule in each box. If the group is not present, write "NONE". (9 pts)



enol



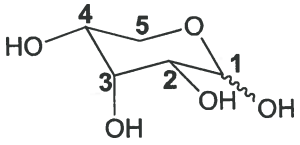
β-hydroxycarbonyl

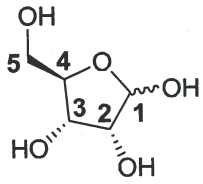


acetal of acetaldehyde

6.6/9

1. B. Match the di-saccharides on the right with their names on the left. There are more possible names than saccharides. (8 points)





Ribose in its cyclic hemiacetal forms

6.8/9

α-1,1-ribopyranose -β-ribopyranose **A**

β-1,1-ribopyranose -β-ribopyranose **B**

α-1,2-ribopyranose -β-ribopyranose **C**

α-1,2-ribopyranose -α-ribopyranose **D**

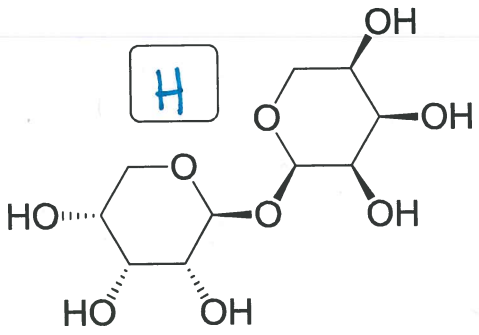
β-1,2-ribopyranose -β-ribopyranose **E**

β-2,4-ribofuranose -β-ribopyranose **F**

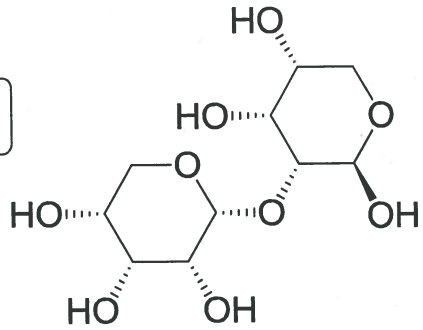
α-2,4-ribofuranose -α-ribopyranose **G**

β-1,1-ribopyranose -α-ribopyranose **H**

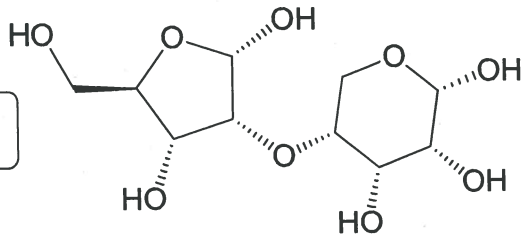
H



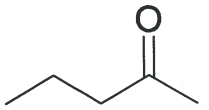
C



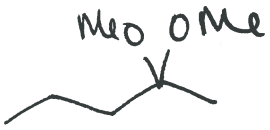
G



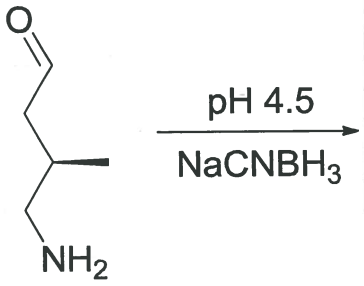
2. Predict the products, reactants, or reagents of the following reactions. Pay special attention to any directions in the answer box. (48 points)



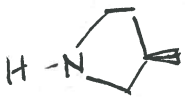
2.6/3



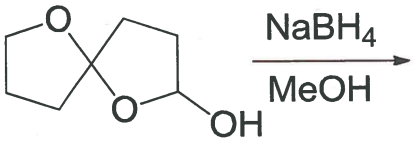
+ H_2O

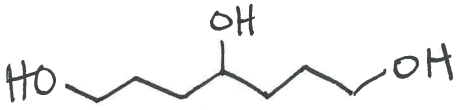


1.4/3

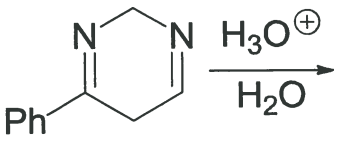


+ H_2O

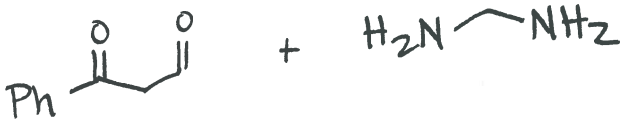




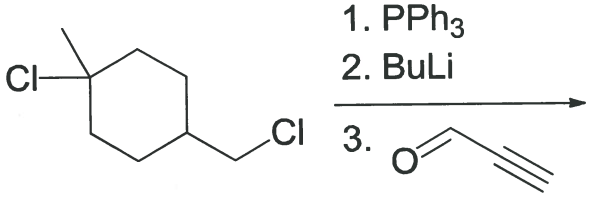
0.8/3

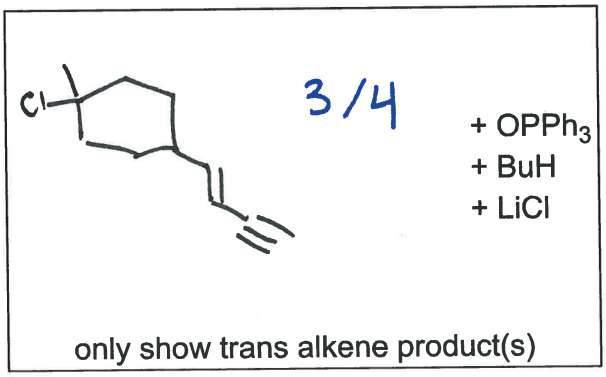


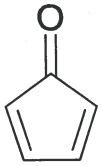
2.5/4



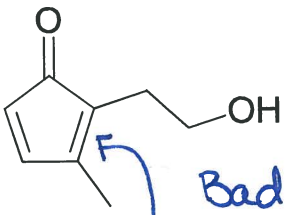
Show the product(s) as neutral





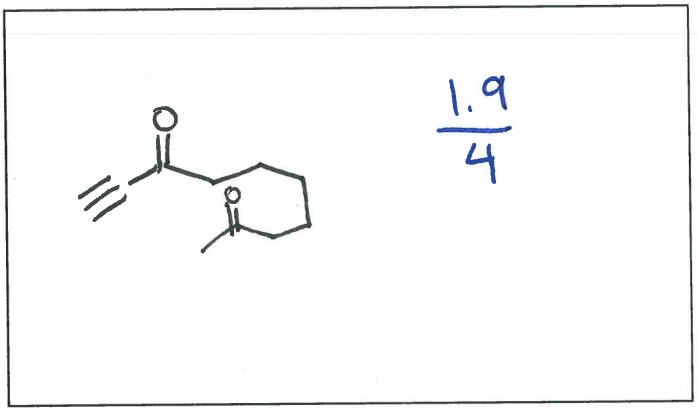


1. Me_2CuLi
2.
3. $H_3O^{\oplus}$

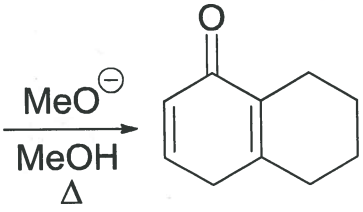


6/6

Bad Question. Typo. product should not have that π bond.

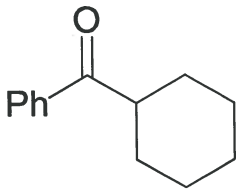


1.9/4

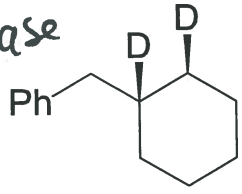


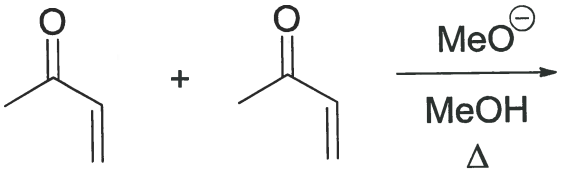
Product of a Robinson Annulation

3.8/8

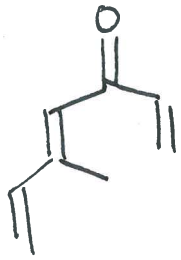


1. HBr, Br_2
2. LDA or other base
3. D_2, Pd/C
4. Zn(Hg), HCl



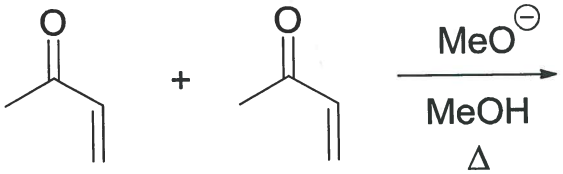


2.5/4

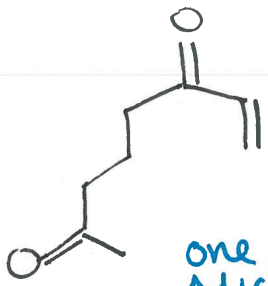


+ H_2O

E Aldol Condensation product



2.6/4

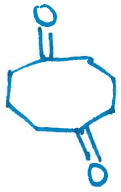


one Michael Addition

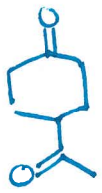
Michael Addition product (1,4)

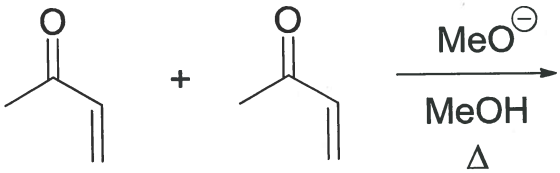
Also Accepted:

2 Michael Additions

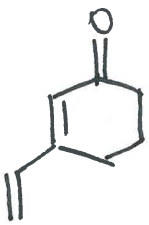


and





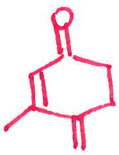
2/4



+ H_2O

Robinson Annulation product

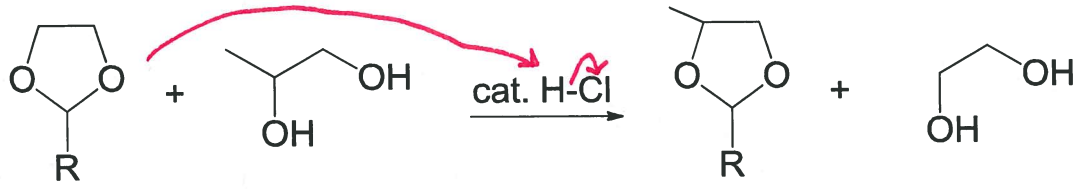
common answer **incorrect**



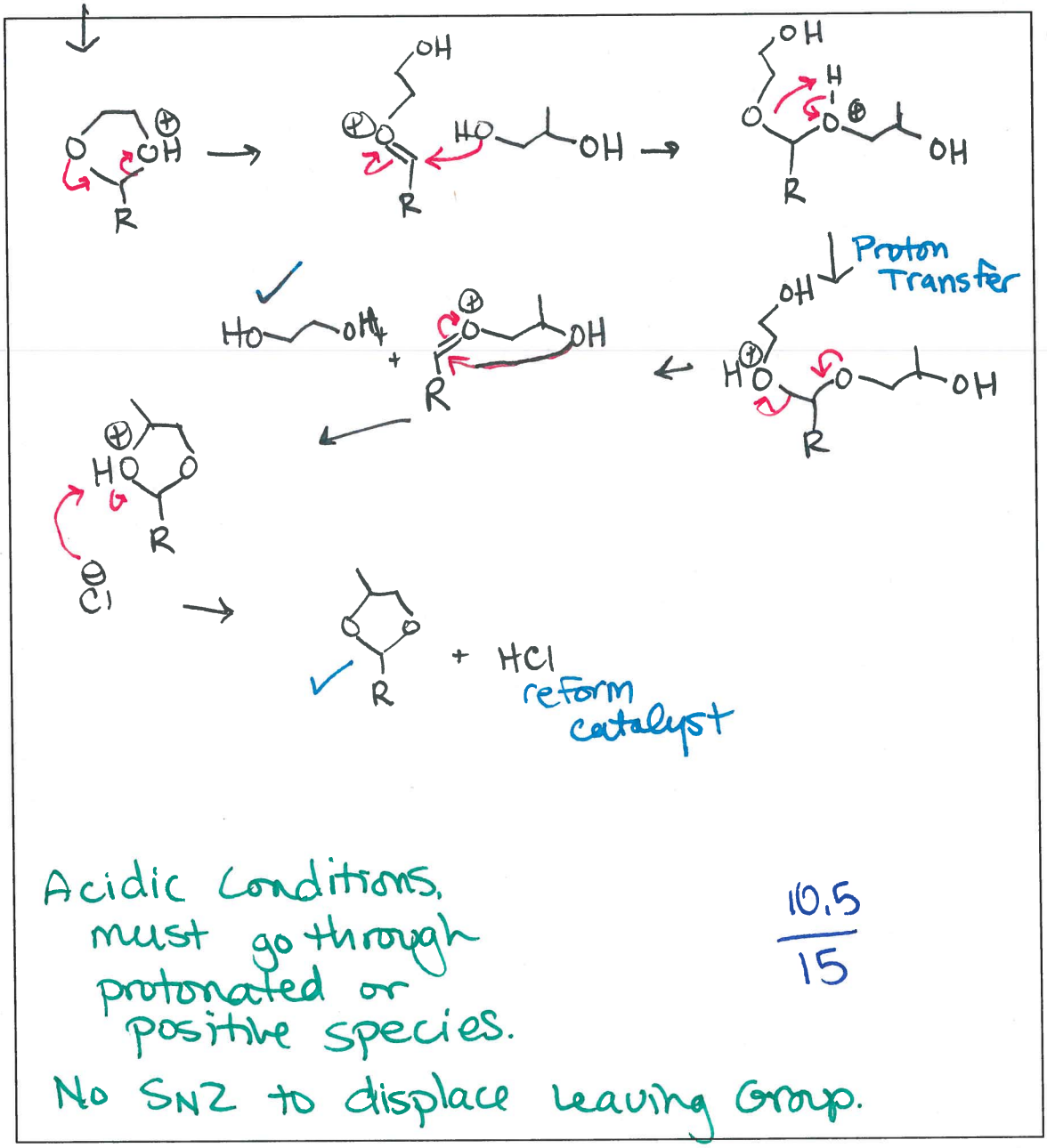
via

as first enolate. Not reasonable.

3. Show a mechanism converting NanoKid into NanoGreenBeret. You **may use** intramolecular "proton transfers" if they are appropriately **labeled with correct arrows**. (15 pts)



NanoKid *NanoGreenBeret*

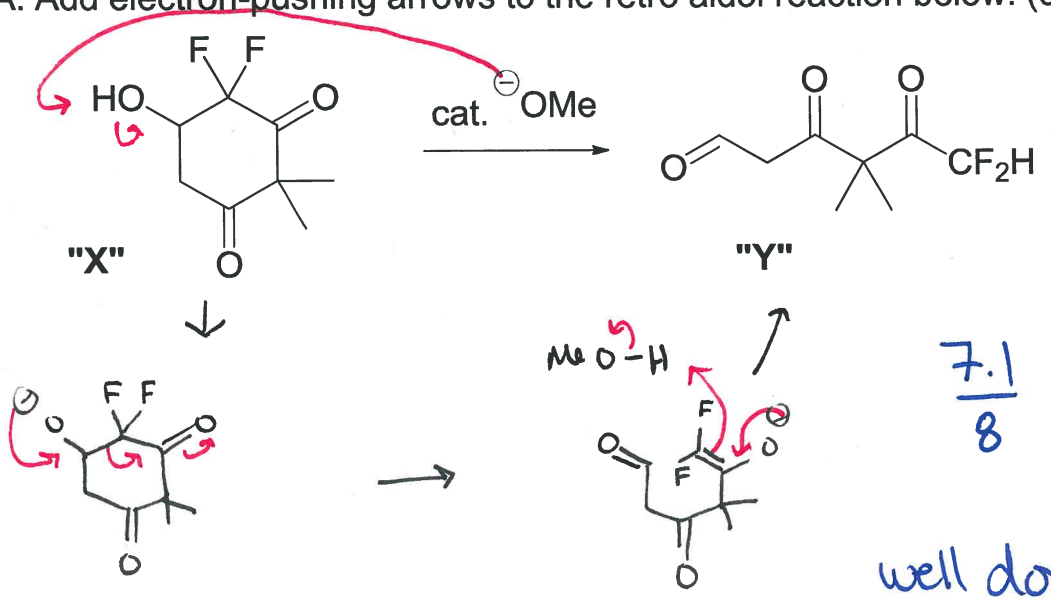


Acidic Conditions, must go through protonated or positive species.

No S_N2 to displace leaving Group.

10.5/15

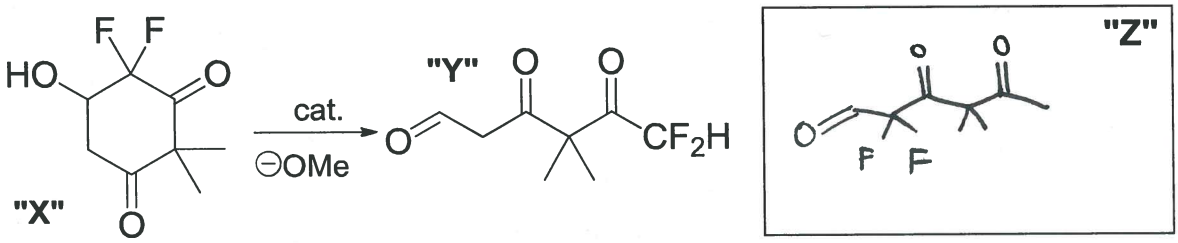
4. A. Add electron-pushing arrows to the retro aldol reaction below. (8 pts)



7.1/8

well done, team!

4. B. Predict the other possible retro-aldol product (not a tautomer of **"Y"**) and place it in the box labeled **"Z"** below. (4 points)

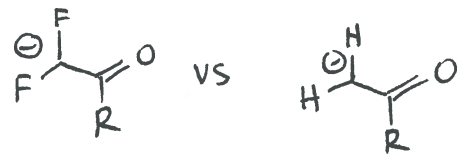


3.1/4

4. C. The only observed product of the above reaction is product **"Y"**. Explain the experiment result in 25 words or fewer. You may also draw one or two relevant chemical structures. (6 points)

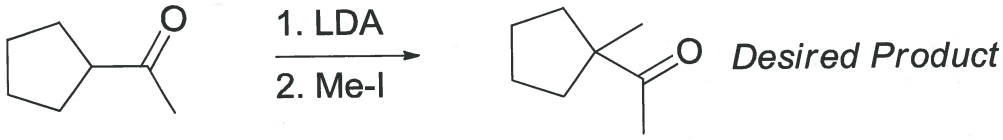
"Y" is the only observed retro aldol product because:
the enolate leading to "Y" is much more stable than the alternative b/c the Fluorines stabilize the ⊖ charge.

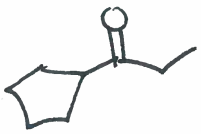
3.2/6



Must specify ⊖ stability.

5. A. A student proposes the following synthesis. It will not yield the desired product. Indicate the problem, provide the actual products, and suggest a change to the synthesis which will make it work. (9 pts)

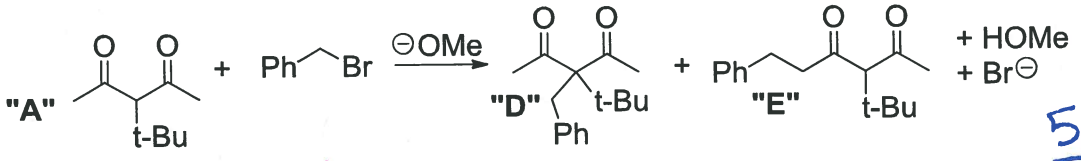


Problem:	Actual Products:	Proposed Change:
LDA creates least subbed enolate		use enamine approach. 1. R_2NH, pH 4.5 2. MeI 3. H_2O

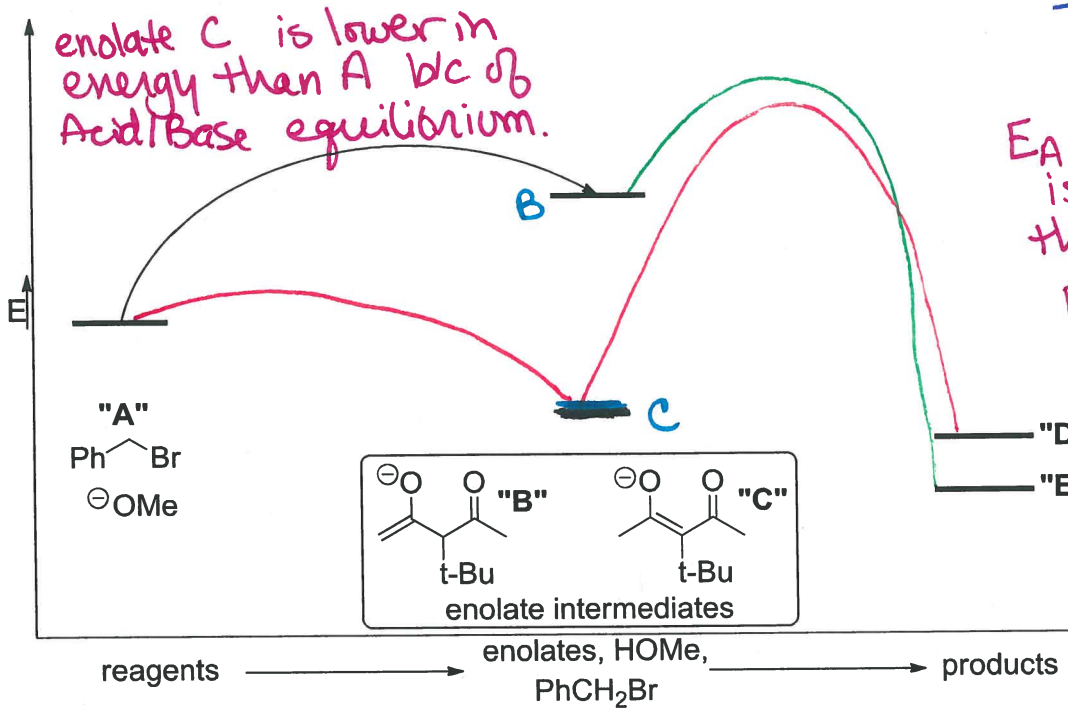
7.6/9

Awesome

5. B. Finish the energy diagram for the following enolate alkylation reaction. Place the remaining enolate energy level, label the levels according to the labeling scheme below, and add the remaining energy curves. The last step is rate determining. (9 pts)



5.4/9

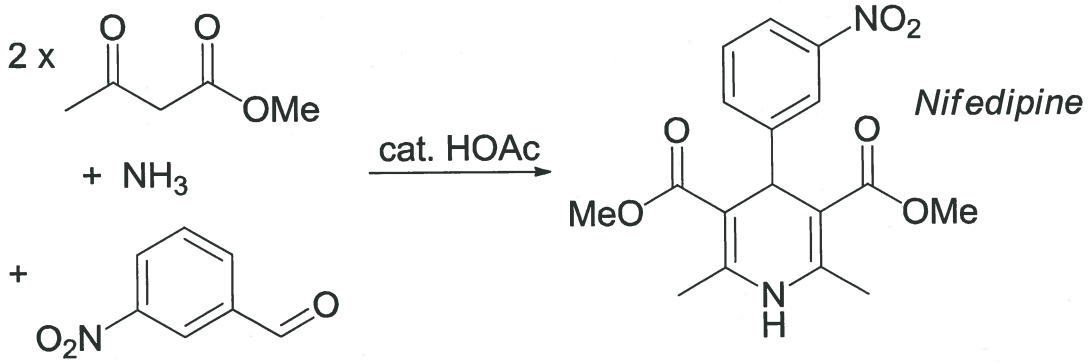


E_A for C→D is larger than E_A of B→E b/c of sterics in the T.S.

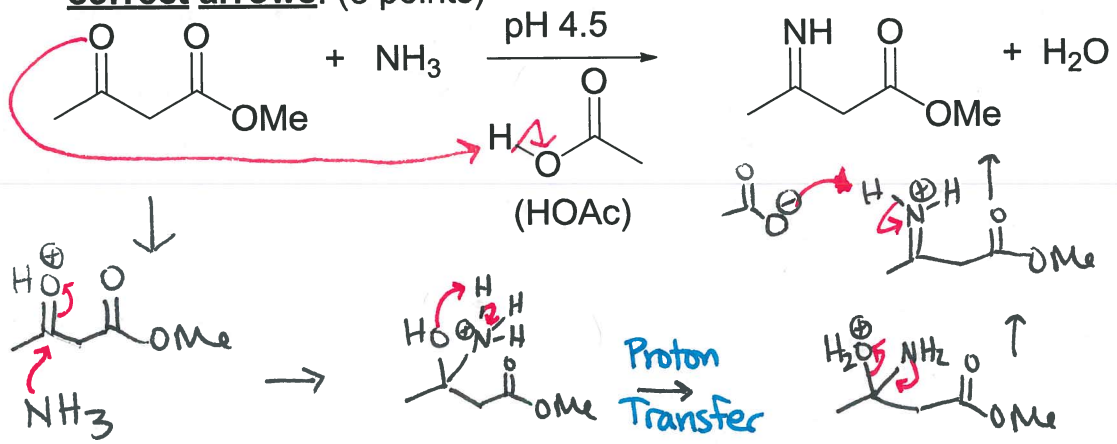
⇓

E_A is not the same as height of the energy curve. It's the dif between that peak and the start

6. The Hantzsch dihydropyridine synthesis is a 4 component reaction that yields dihydropyridines, common calcium ion channel blockers. This reaction is used to create Nifedipine, a hypertension and chest pain drug.



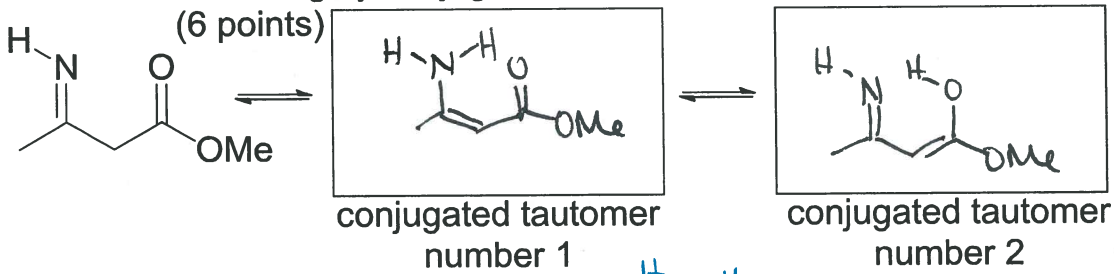
6. A. Provide a mechanism for the following transformation. You **may use** the shortcut "proton transfers" if they are properly **labeled and show correct arrows**. (8 points)



7/8

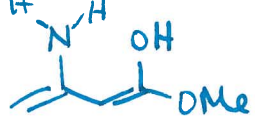
Booya!

6. B. Draw the two highly conjugated tautomers of the immine below. (6 points)



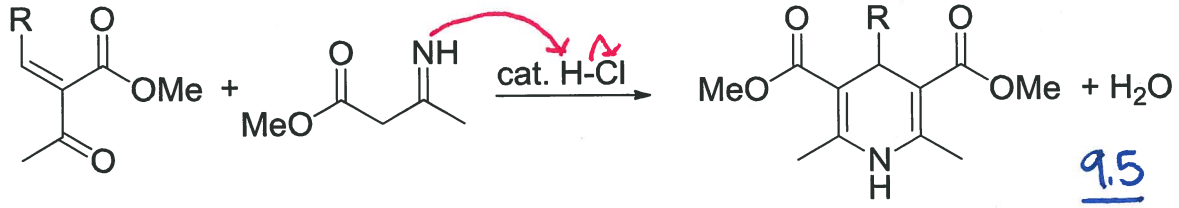
4.4/6

Also correct:



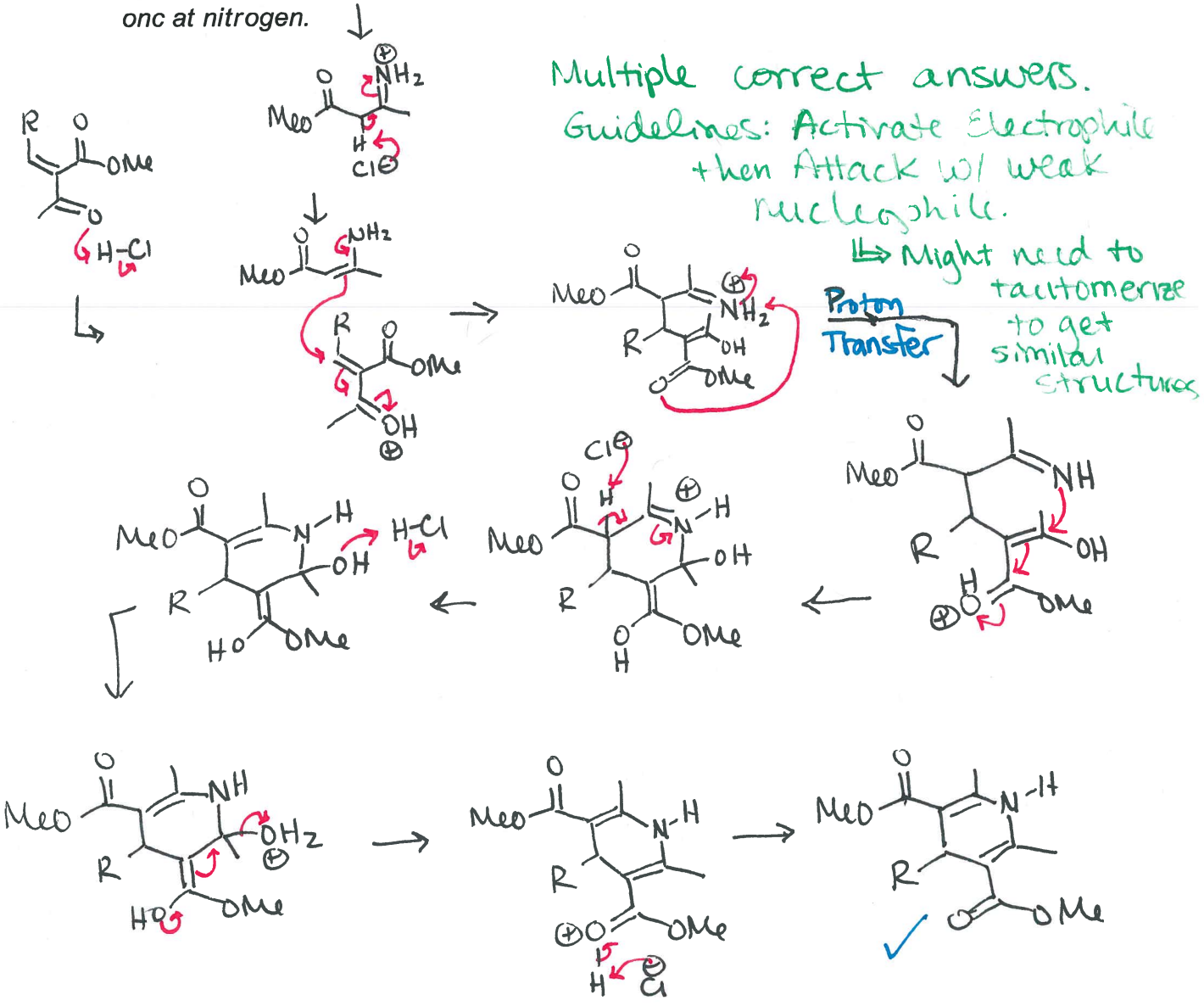
double tautomer.

6. C. Provide a mechanism for the following reaction. You **may use** intramolecular proton transfers if they are appropriately **labeled with appropriate arrows**. (20 points)



9.5/20

Hint: First step, show the mech for generating an enamine.
Hint: You will need to use the enamine as a nuclophile twice. Once at carbon and onc at nitrogen.



common correct creative answers:
① electrocyclization.
② immine Nitrogen as nucleophile