NAME (Print): ______________________________

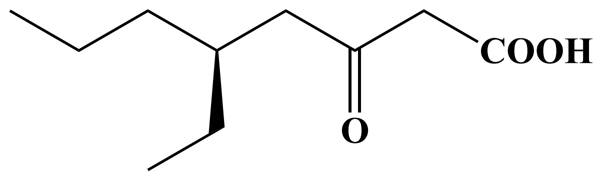
SIGNATURE: ______________________________

Chemistry 320N
Dr. Brent Iverson
7th Homework
March 19, 2024

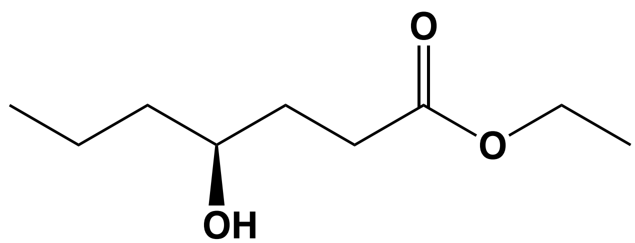
Please print the first three letters of your last name in the three boxes

Score: _________

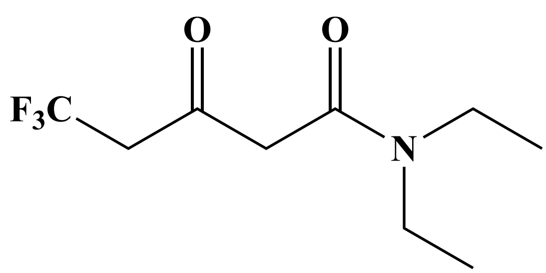
4 pts each) In the space provided, write the IUPAC name (including stereochemistry where appropriate) for the following two molecules:



(*S*)-5-ethyl-3-oxooctanoic acid

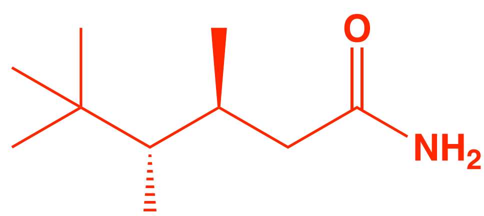


ethyl (*S*)-4-hydroxyheptanoate



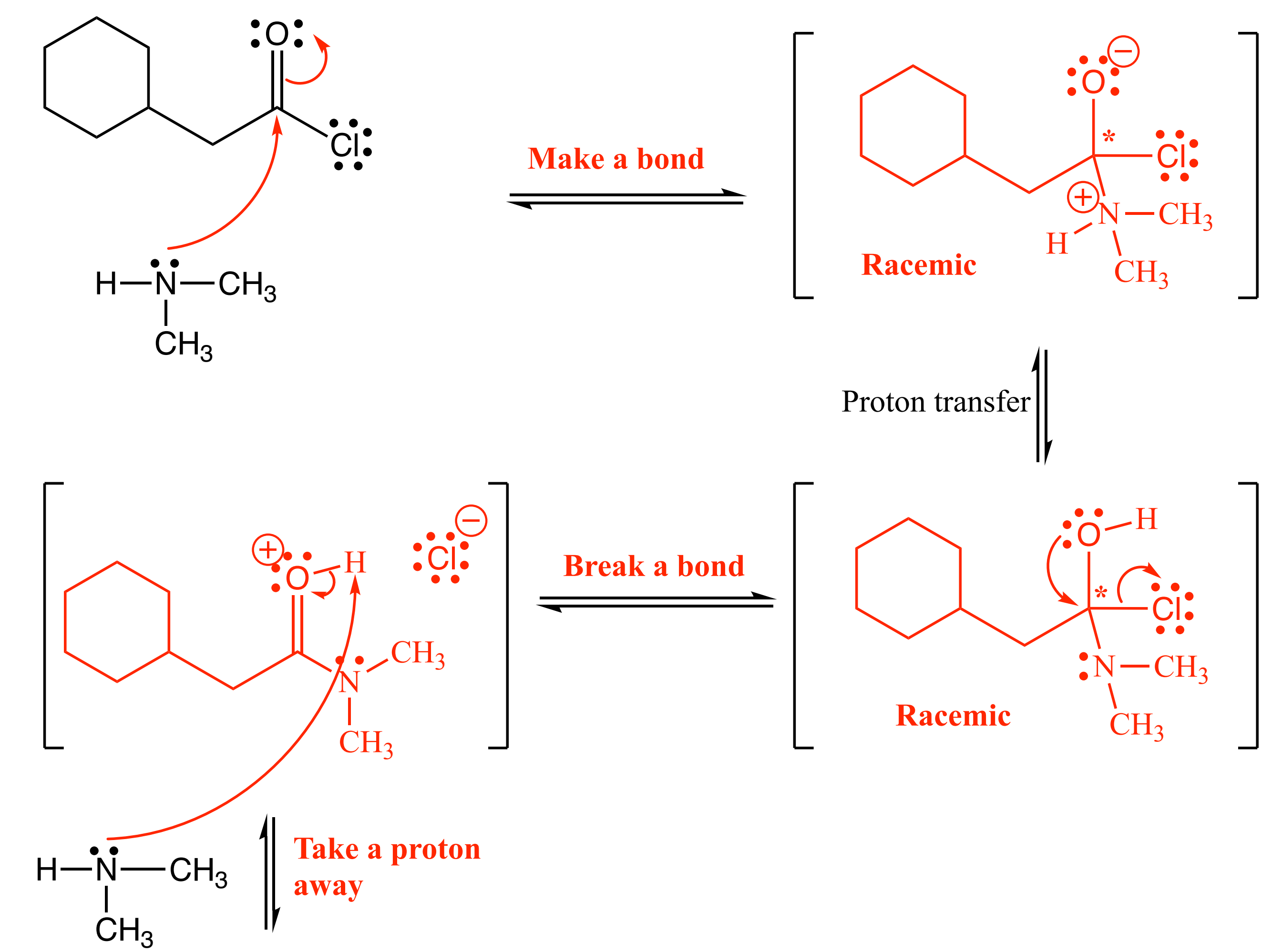
N,*N*-diethyl-5,5,5-trifluoro-3-oxopentanamide

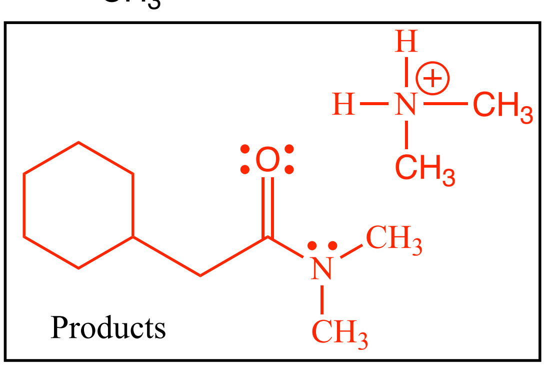
(4 pts) In the space provided, draw the following molecule: **(3*S*,4*S*)-3,4,5,5-tetramethylhexanamide**



Complete the mechanism for the following reaction. **Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK. IF A CHIRAL CENTER IS CREATED IN THE PRODUCTS YOU NEED TO DRAW BOTH ENANTIONMERS, AND LABEL THE PRODUCT MIXTURE AS RACEMIC IF RELEVANT.**

Acid Chlorides Reacting with Amines

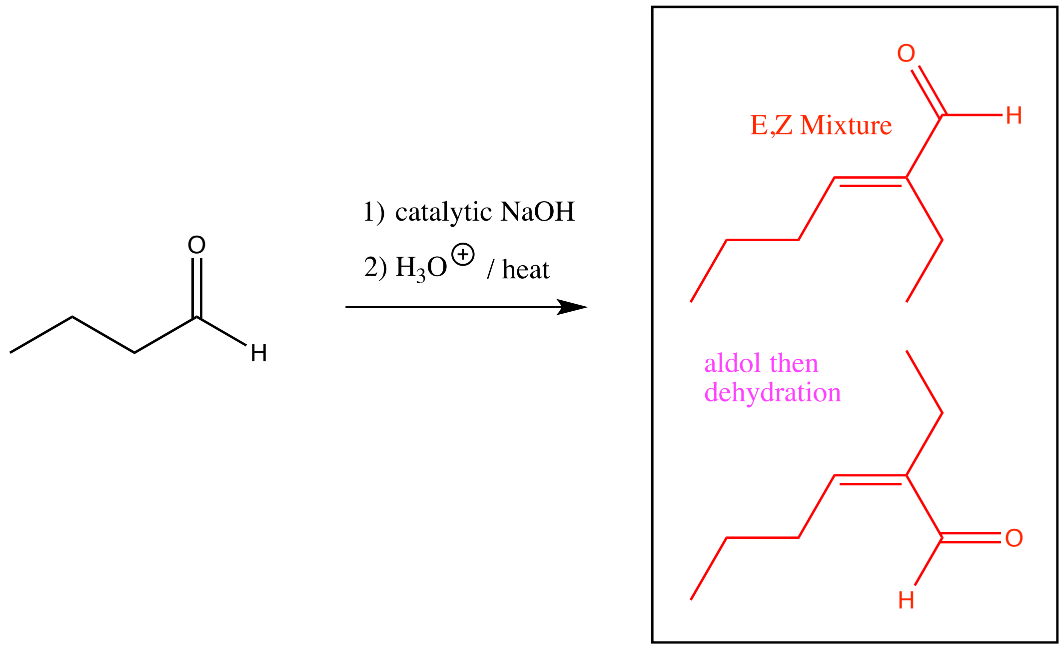


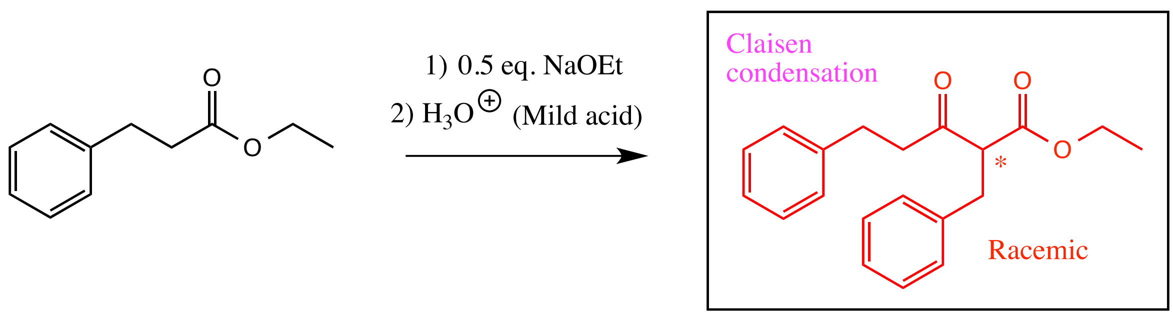


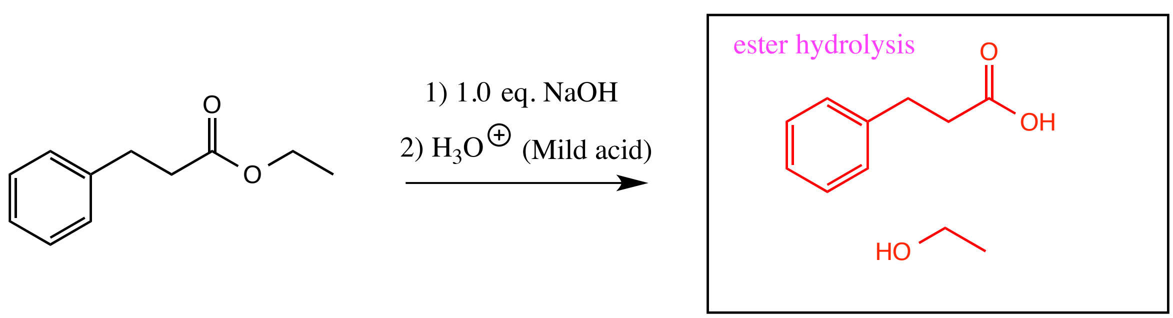
This is an example of Mechanism B

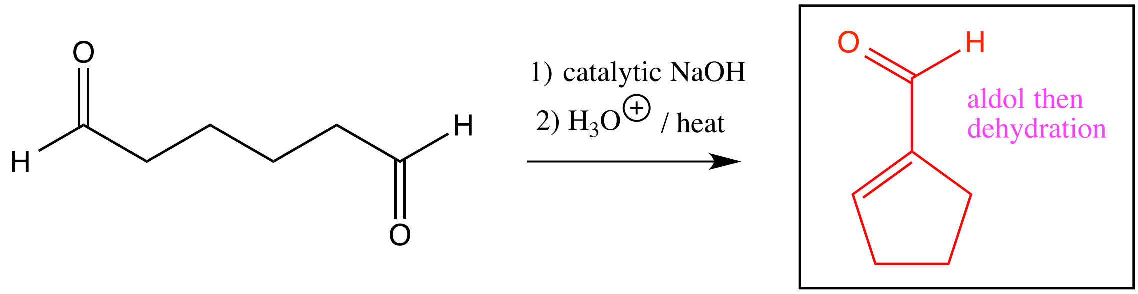
with a protron transfer in the middle

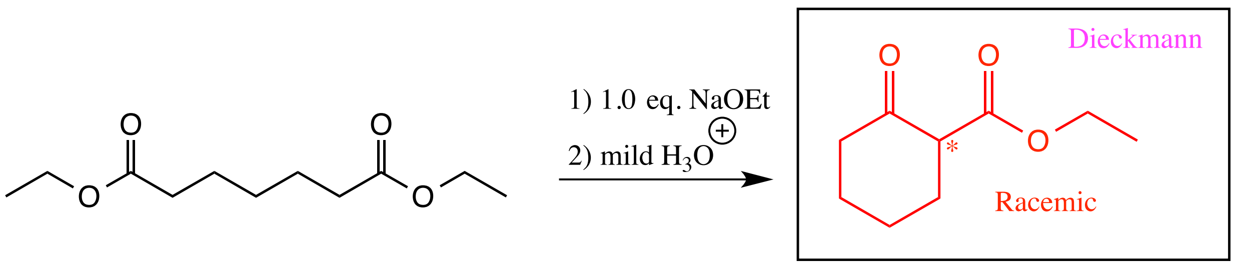
(3 or 5 pts each) Fill in the boxes with the appropriate structure or structures. Because these structures are getting complex, you **do not need to draw both enantiomers. Instead, when a new chiral center is created, just mark it with an asterisk (*) and label the product as "racemic". No need to use wedges and dashes. However, when an E,Z mixture is formed, you must draw both the E and Z products. Notice that H_3O+ is the same as HCl/H_2O**

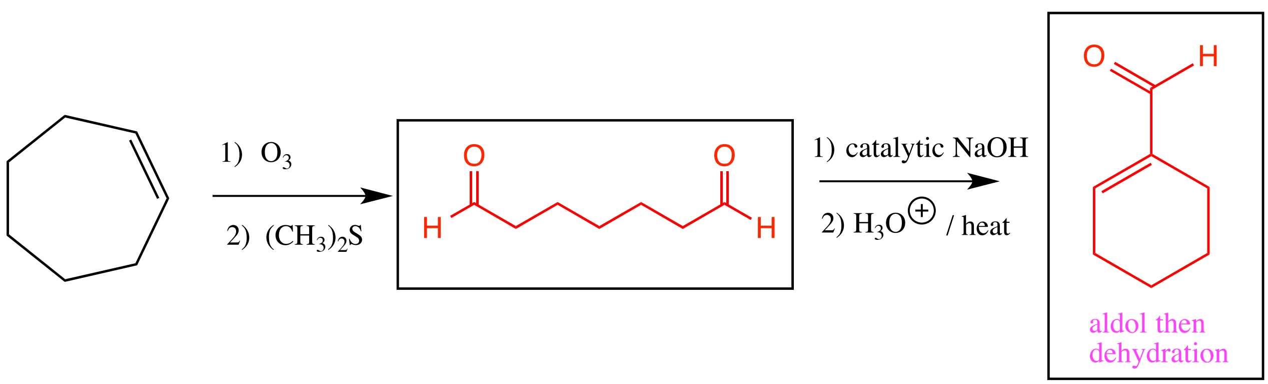


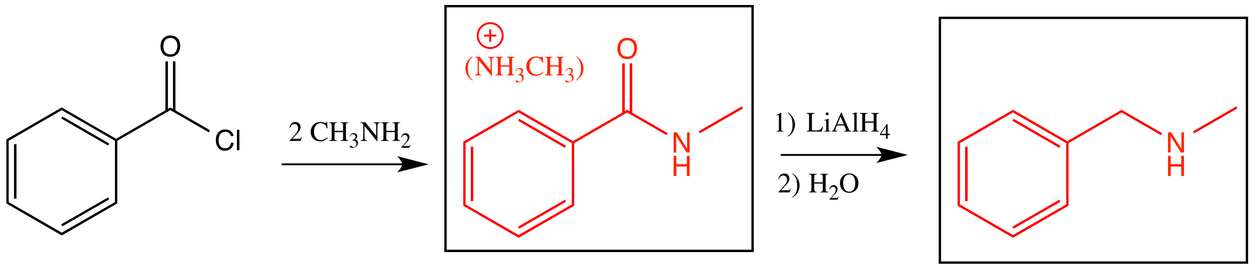


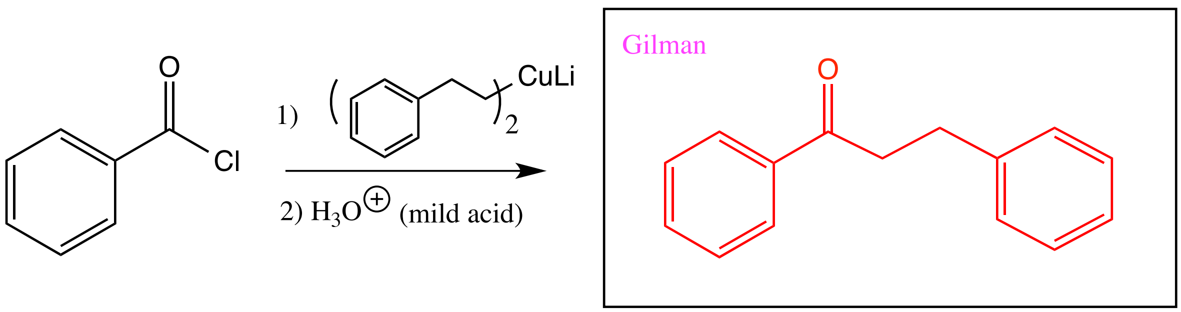


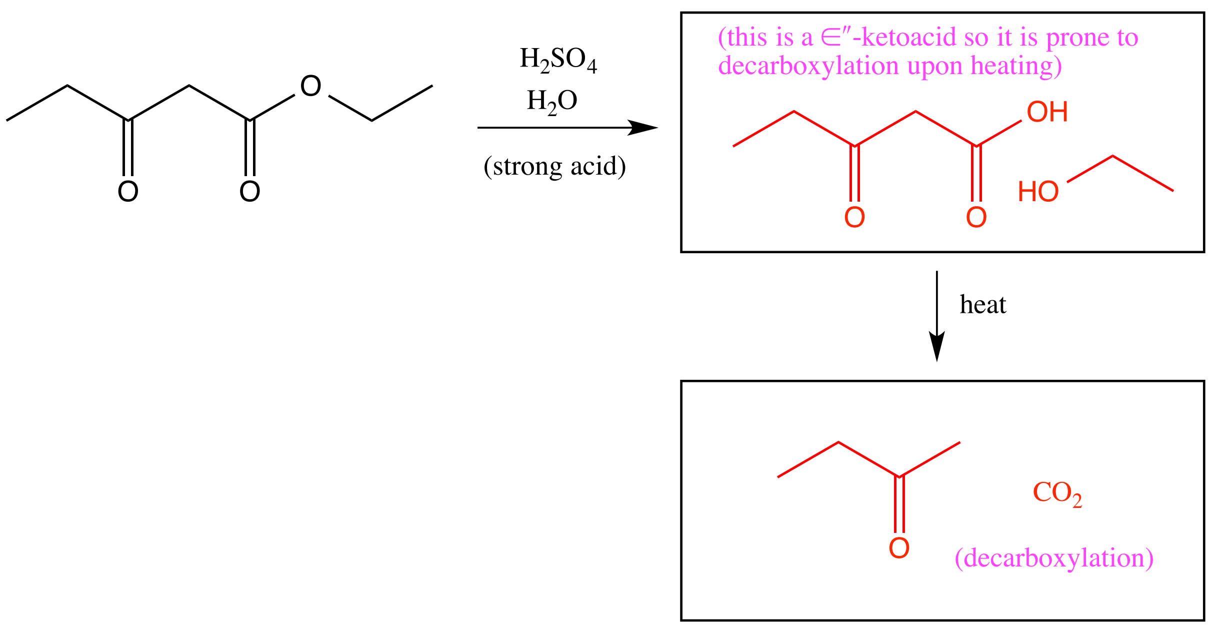

1) catalytic NaOH
2) $H_3O^{\oplus}$ / heat
aldol then dehydration


1) 1.0 eq. NaOEt
2) mild $H_3O^{\oplus}$
Dieckmann
Racemic


1) O_3
2) $(CH_3)_2S$
1) catalytic NaOH
2) $H_3O^{\oplus}$ / heat
aldol then dehydration


O
Cl
2 CH3NH2
(NH3CH3)
O
N
H
1) LiAlH4
2) H2O
N
H

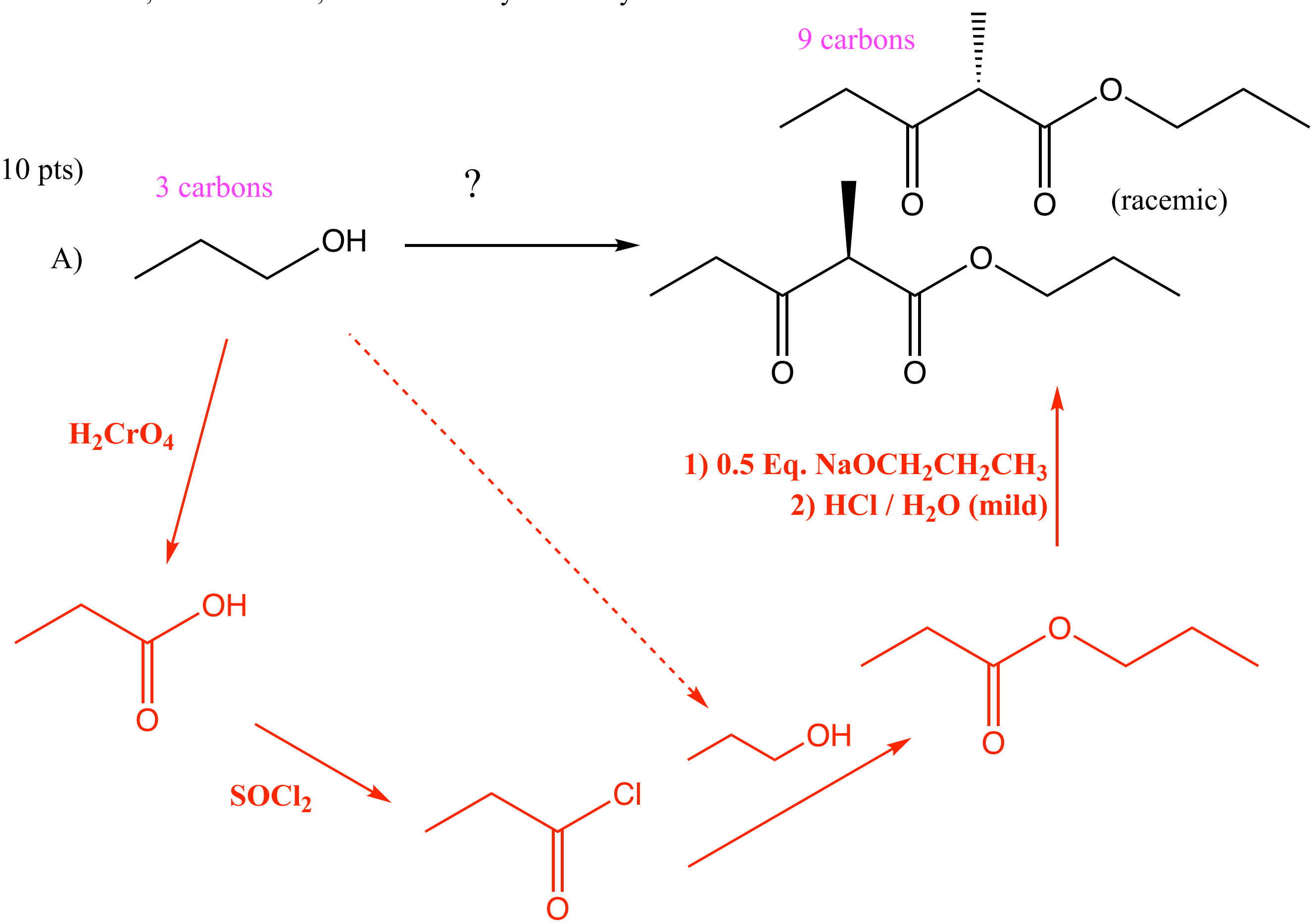

O
Cl
1)
CuLi
2
2) H3O (mild acid)
Gilman
O


O
O
O
H2SO4
H2O
(strong acid)
(this is a ∈″-ketoacid so it is prone to
decarboxylation upon heating)
OH
HO
O
O
heat
CO2
O
(decarboxylation)

These are enolate synthesis problems. In each case, all of the carbons of the products must come from the listed starting materials. You may use any reagents we have discussed this semester or last semester. Show all molecules synthesized along the way. For each step, you will only get full credit if the product you list is the major product of that transformation. Use wedges and dashes for all chiral centers. Remember to work backwards, count carbons, and make sure you know your KRE's.

(10 pts)

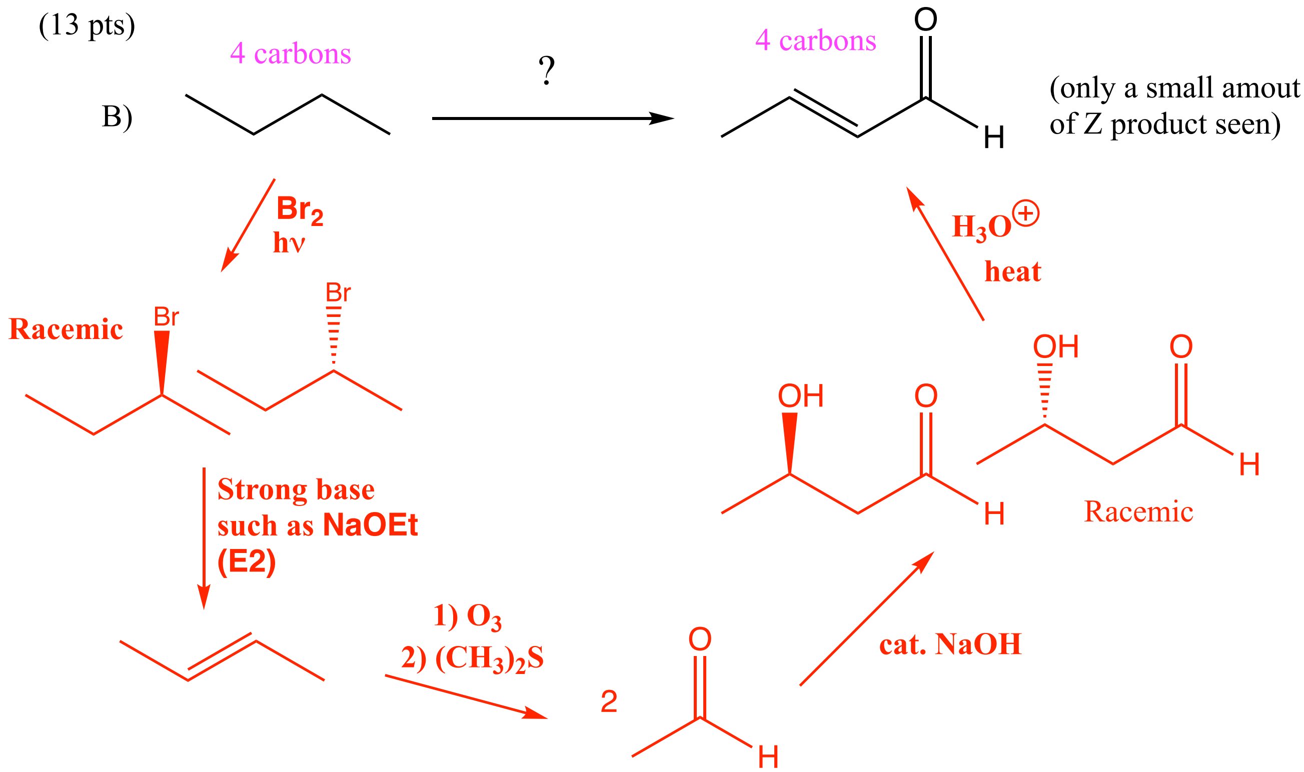
A)



Notice that the product has 9 carbon atoms, and the staring material has 3. Therefore, assume 3 starting molecules have ended up in the product. **Recognize** the product is a β-ketoester, the KRE for a Claisen condensation. Therefore predict the last step to be a Claisen condensation using $NaOCH_2CH_2CH_3$ to match the ester group. The required ester can be derived from the starting alchohol by first oxidizing to the carboxyic acid using chromic acid (Jones reagent) followed by $SOCl_2$ then reaction of the resulting acid chloride with the starting alcohol. You could have carried out a Fischer esterification using catalytic H_2SO_4, the carboxylic acid and starting alcohol.

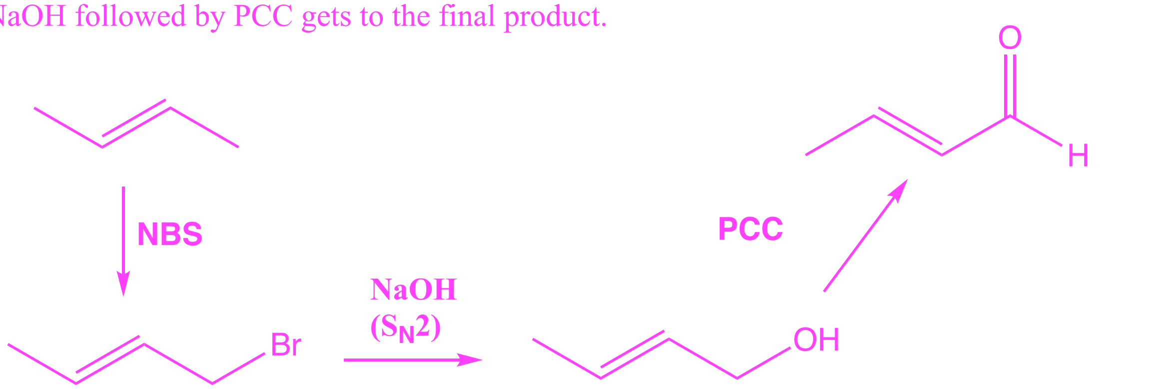
(13 pts)

B)



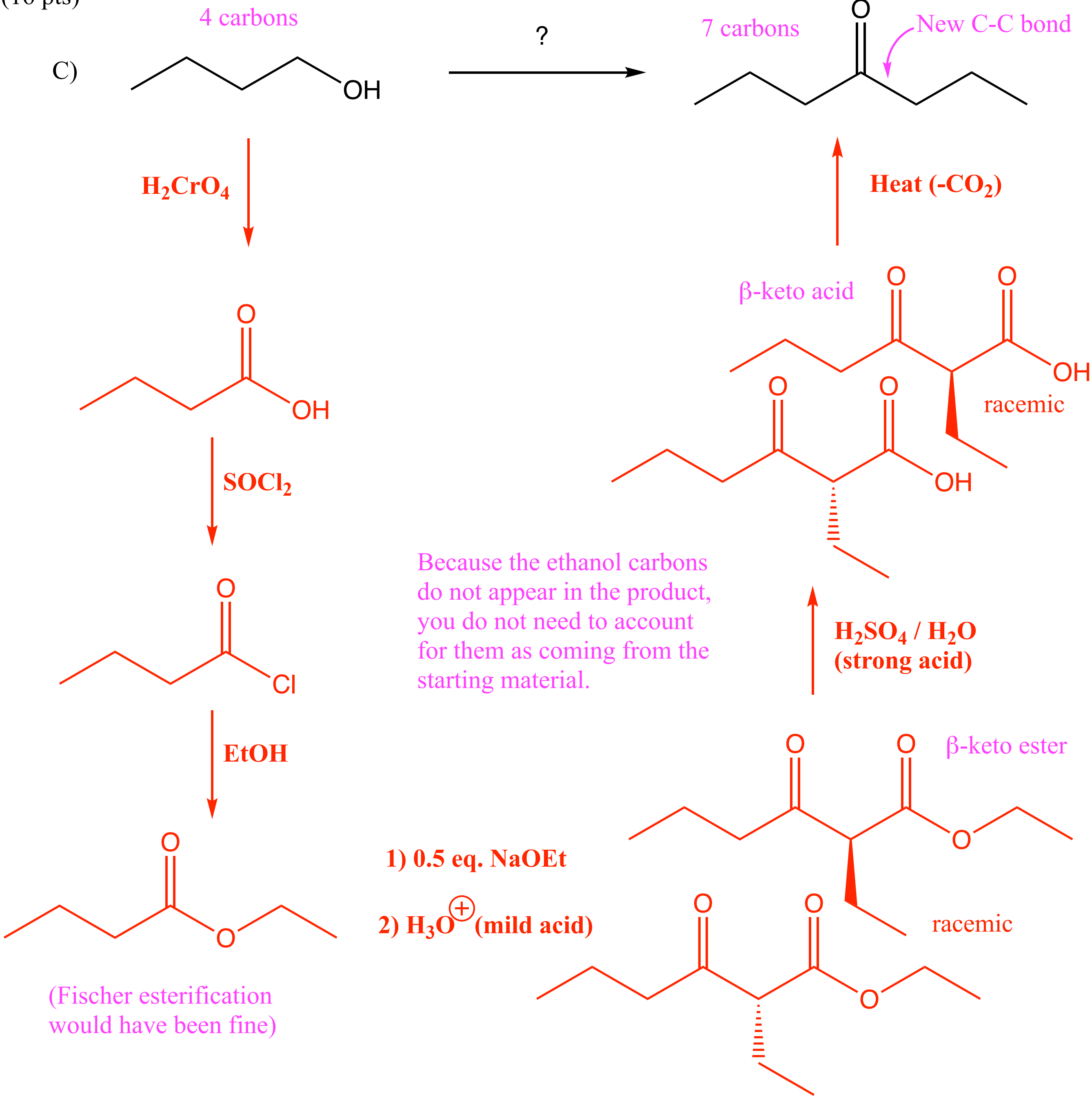
Notice that the product has 4 carbon atoms just like the starting material. **Recognize** the product as an α,β-unsaturated aldehyde, the KRE for reaction of an aldol reaction followed by dehydration. **Recognize** that the aldol product comes from the aldol reaction of acetaldehyde. The acetaldehyde can be produced by the ozonolysis of 2-butene, which is derived from the E2 elimination of 2-bromobutane. 2-Bromobutane comes from the reaction of butane with Br_2 and light, the only reaction that can use an alkane as a starting material.

An alternative route also uses 2-butene, followed by NBS to put a Br atom on the end. An S_N2 reaction using NaOH followed by PCC gets to the final product.



(16 pts)

C)



Recognize the product as being a ketone with 7 carbons. The starting alcohol has 4. Therefore, assume th there is a new C-C bond formed as shown and 1 carbon must be lost. The most logical way to lose a singl carbon is from a decarboxylation step. For this to occur, the carboxylic acid would have to be β to the carbonyl so putting all of this information together predict the β-βíketo acid intermediate shown. **Recogni** the β-keto acid intermediate as being derived from the corresponding β-keto ester, that in turn, is the produ of a Claisen condensation with the ester of butanoic acid. **Recognize** that the ester could be derived by reacting butanoic acid with an alcohol such as ethanol in the presence of catalytic H_2SO_4. Finally, **recogni** that butanoic acid can be derived from the oxidation of the starting 1-butanol with H_2CrO_4.

An alternative aldol approach is also possible for this one as shown