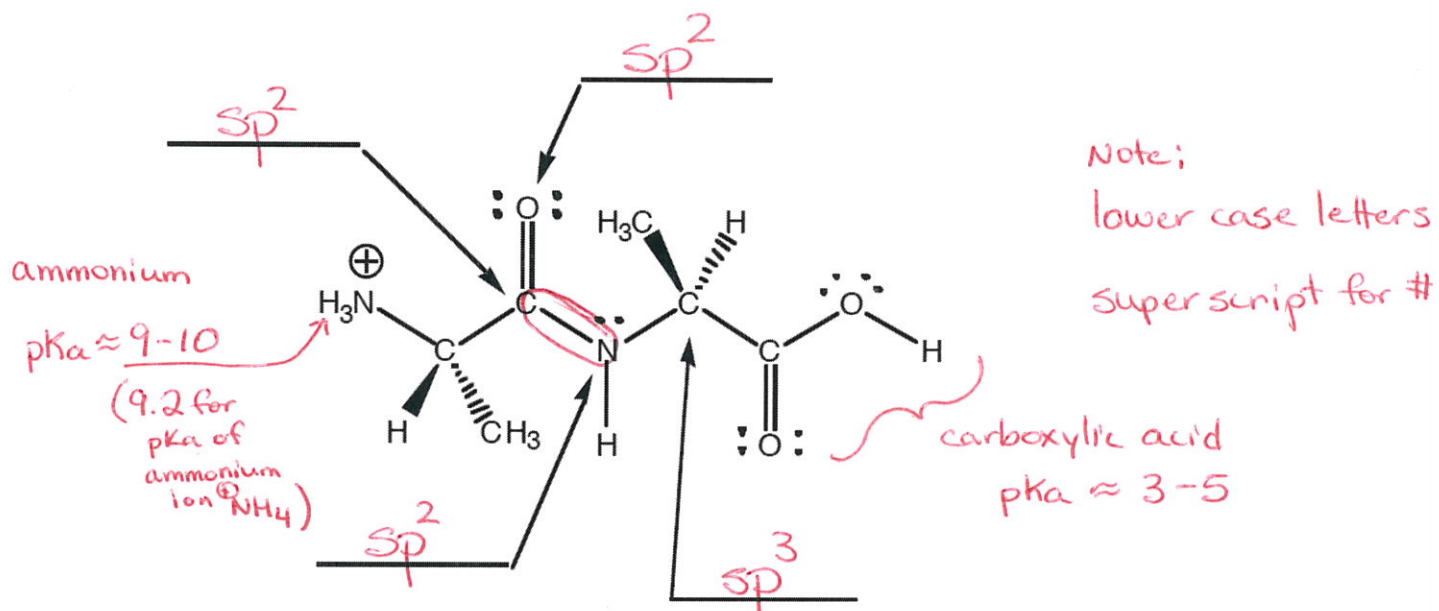


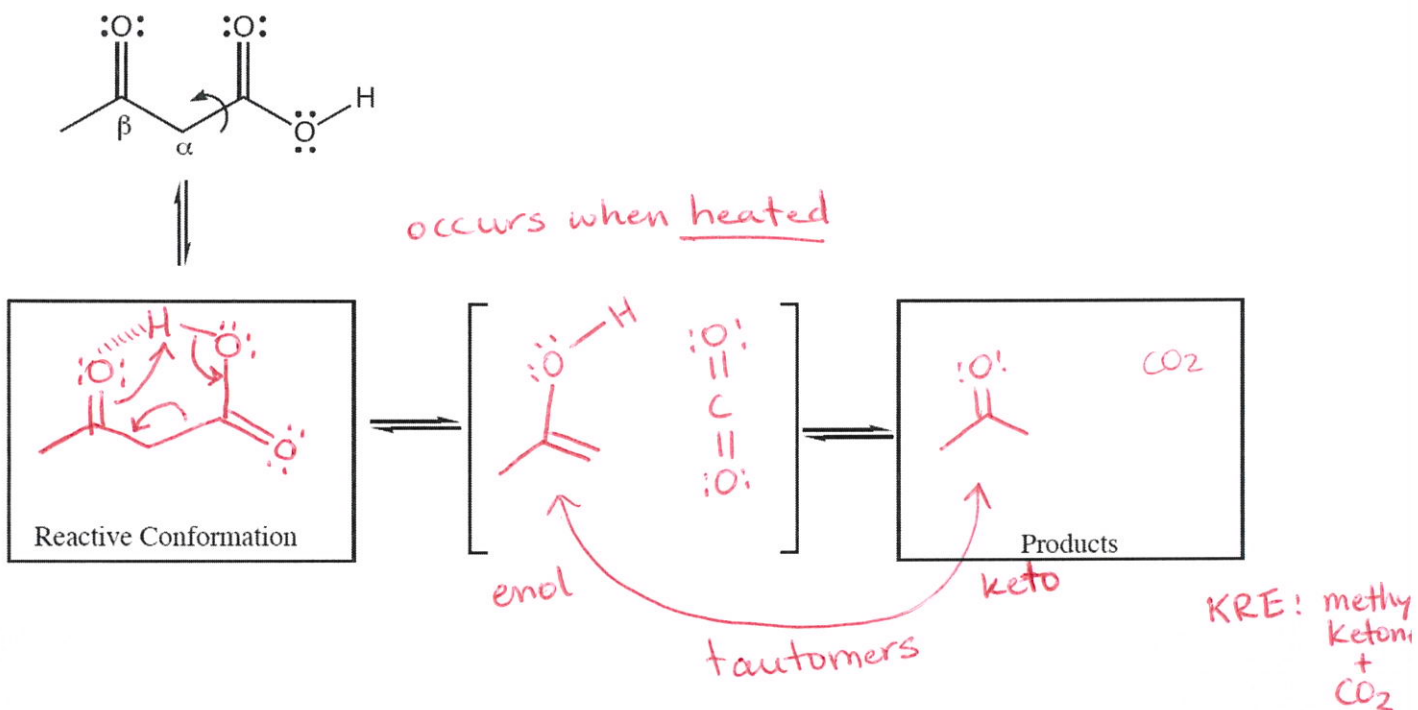
For the structure below, circle all C-N bonds that DO NOT rotate.

As drawn, is the structure at the appropriate protonation state for pH 2.0, pH 7.0, or pH 10.0 ?

On the lines, indicate the hybridization state of each atom indicated by the arrows.

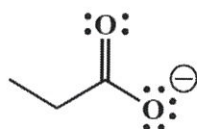


### Decarboxylation of a $\beta$ -Keto Acid



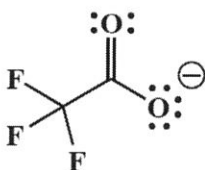
Rank the following in terms of anion stability, with a **1** under the anion that is the most stable and a **4** under the anion that is least stable.

*(same as most reactive)*



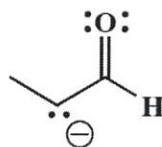
2

resonance delocalized charge



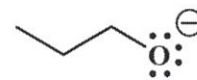
1

resonance + inductive (F's) effects



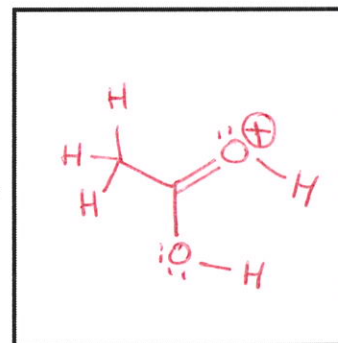
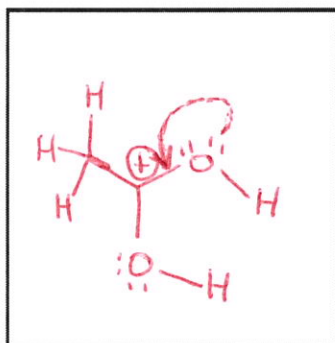
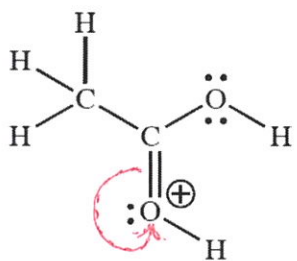
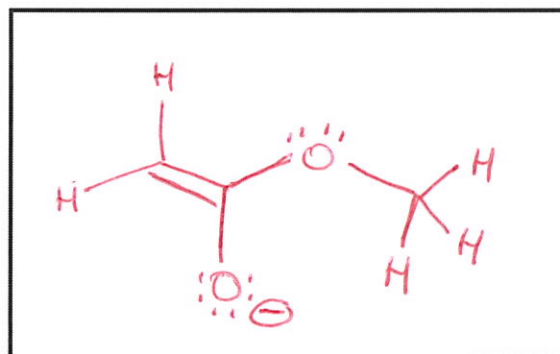
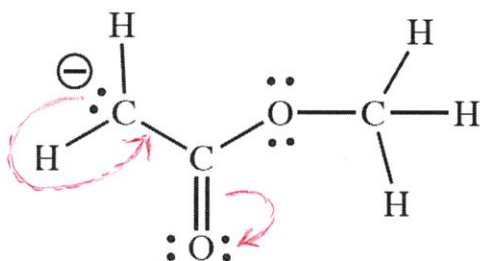
4

⊖ on C much less stable than ⊖ on O (more EN)

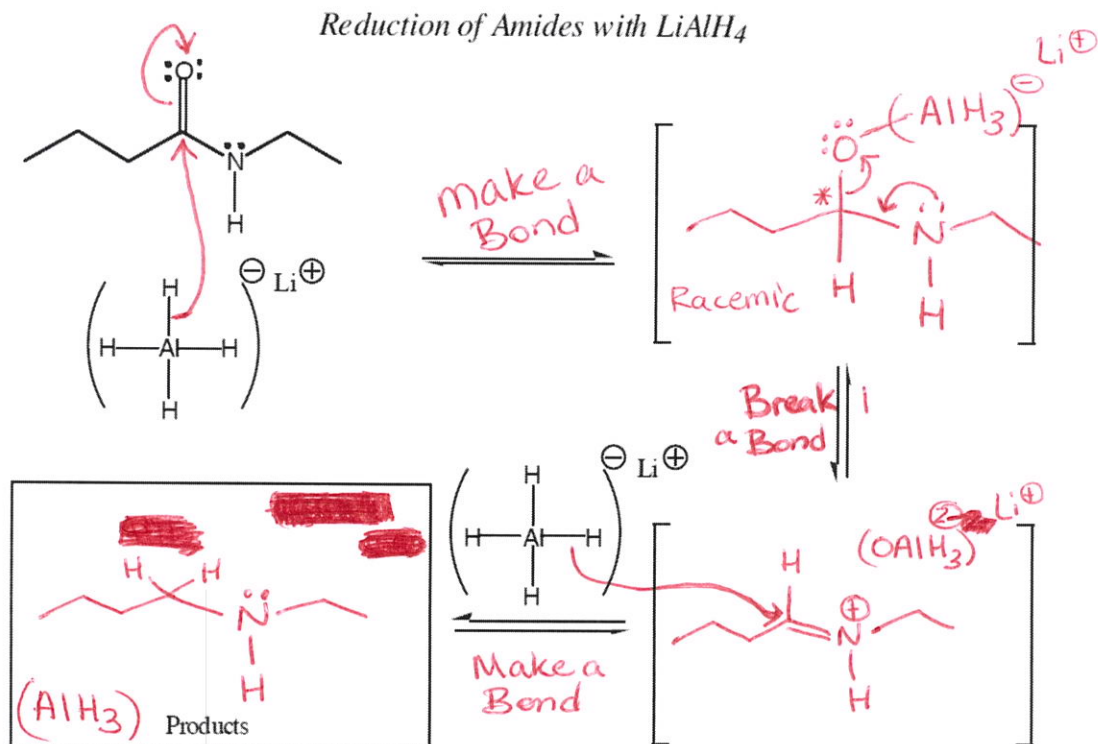


3

For the two molecules below, draw the indicated number of MOST important resonance contributing structures. Be sure to show all lone pairs and formal charges. You do not have to draw any arrows.

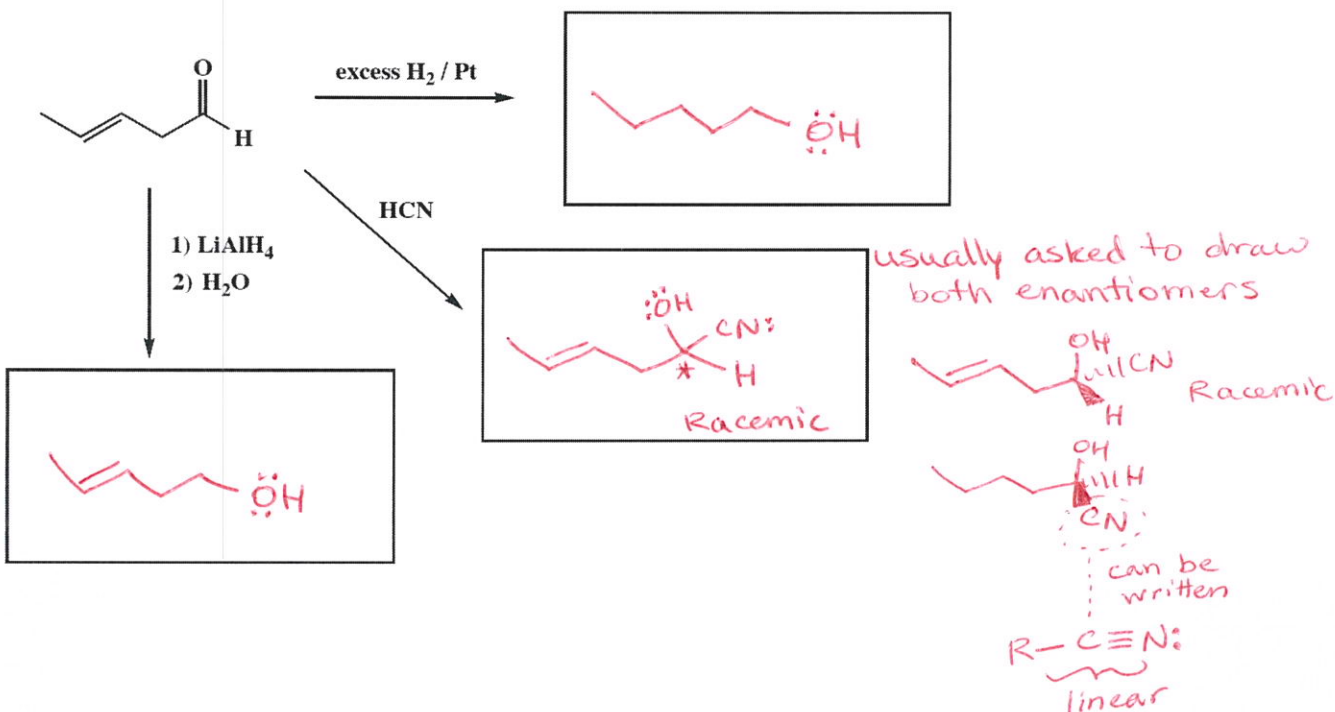


15. (13 points) Complete the following mechanism. Be sure to use arrows to indicate movement of all electrons and show all lone pairs and formal charges. Also, you must show all the products of each step. For resonance stabilized intermediates, you only need to draw one important contributing structure.

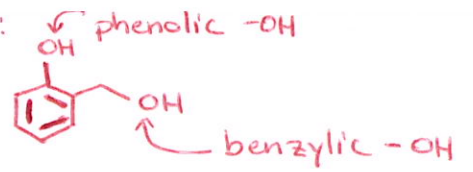


Note: In this reaction the chemist opens the flask and adds water in a second step that quenches any excess LiAlH<sub>4</sub>. Therefore, you need a second step to add water when using this reaction in synthesis even though it is not shown in the mechanism above.

Complete the reactions below:

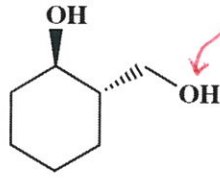


For future: Note



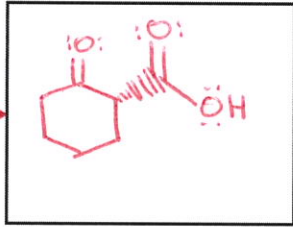
2° alcohol

1° alcohol



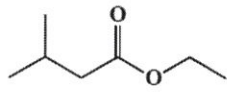
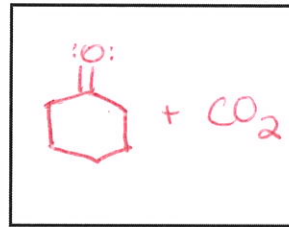
H<sub>2</sub>CrO<sub>4</sub>

not racemic



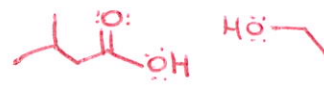
heat

decarboxylation



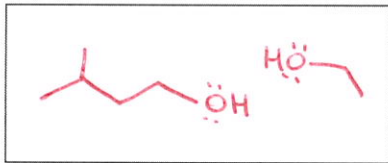
HCl

H<sub>2</sub>O

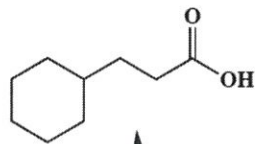
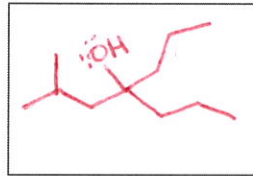


1. LiAlH<sub>4</sub>

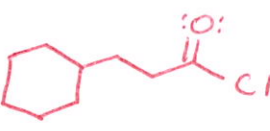
2. H<sub>2</sub>O



1. 2. H<sub>3</sub>O<sup>+</sup>



SOCl<sub>2</sub>

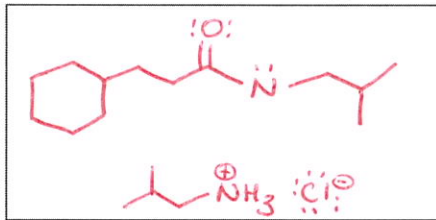


+ SO<sub>2</sub> + HCl

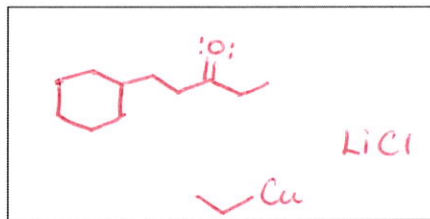
H<sub>3</sub>O<sup>+</sup>

heat

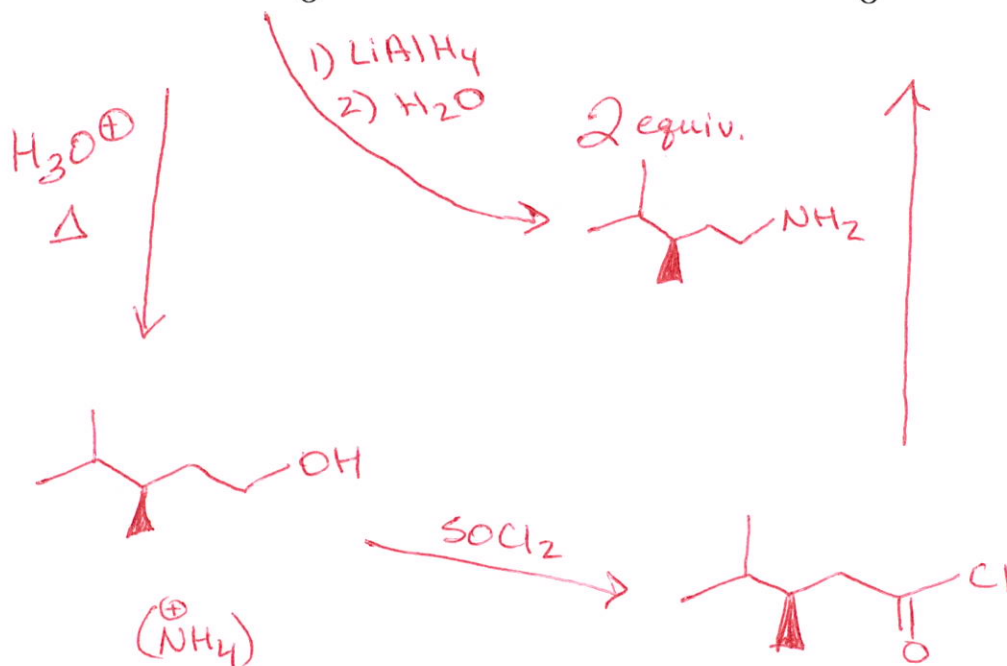
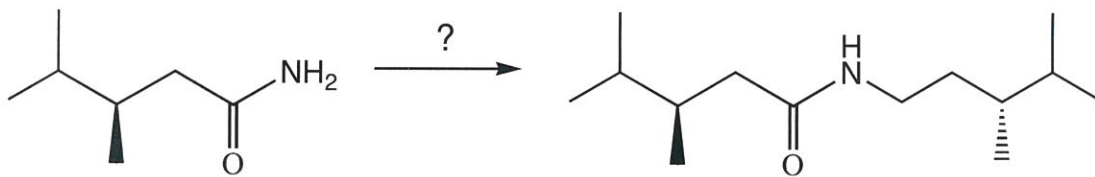
2. (CH<sub>3</sub>)<sub>2</sub>CH-NH<sub>2</sub>



(CH<sub>3</sub>)<sub>2</sub>CuLi

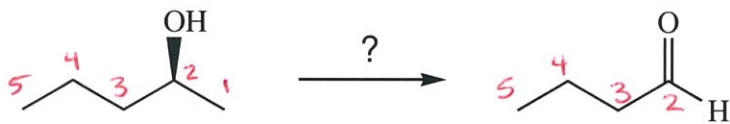


All of the carbons of the product must come from the given starting material.

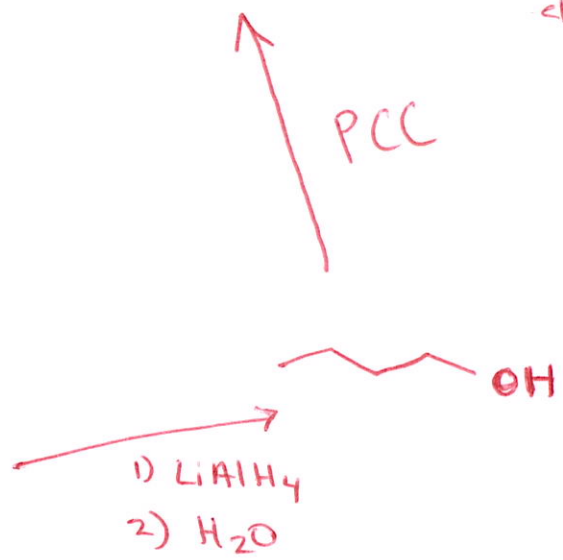
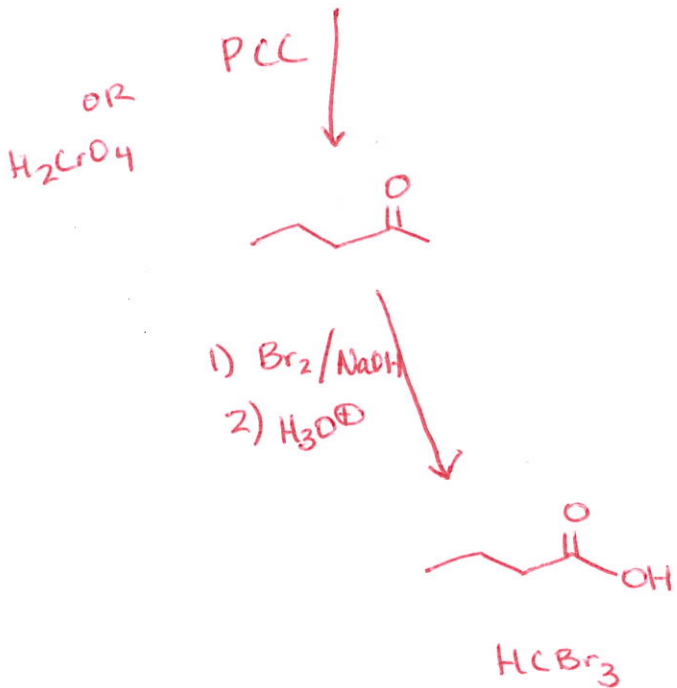


- see C-N bond so amide could have "re-formed" from acid chlor and an amine
- acid chloride comes from carboxylic acid
- can easily make the amine for last step by reducing the amide starting material

All of the carbons of the product must come from the given starting material.



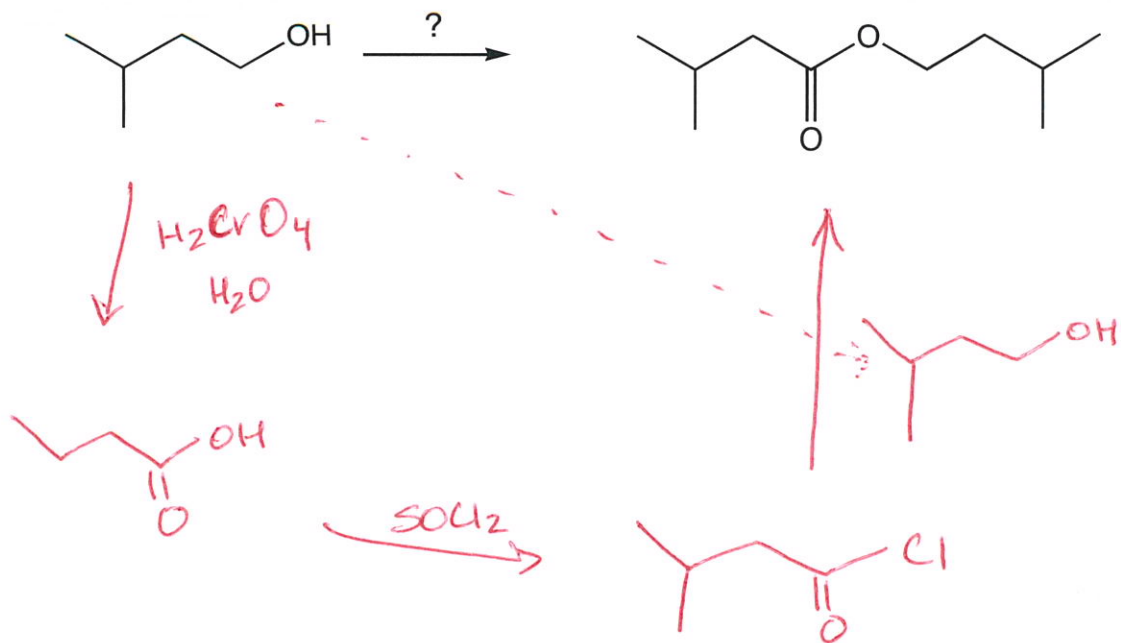
- lost a carbon  
 (could use ozonolysis, decarboxylation, or haloform rxn choose; Haloform can easily make methyl ketone starting material why not others)



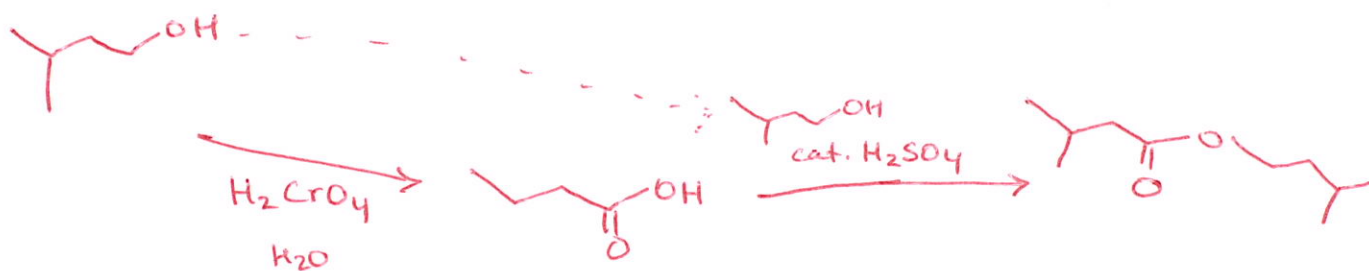
- decarboxylation  
 KRE: methyl ketone = pro  
 doesn't look like a possibility towards end of synt  
 - ozonolysis

to cleave 1C need terminal alkene which is non-Zaitsev product which is less stable and so not formed in high yields  
 major product Zaitsev more stable alkene  
 minor product non-Zaitsev less stable alkene

All of the carbons of the product must come from the given starting material.

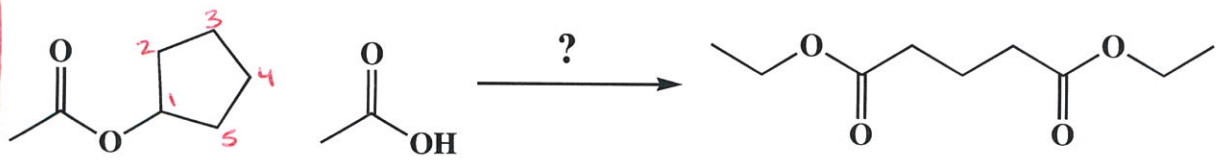


could also do:

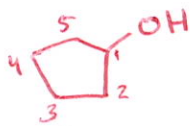


All of the carbons of the product must come from the given starting materials.

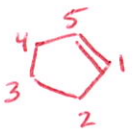
\*  $H_3O^+$   
can be  
 $H_2O/HCl$



OR  
1)  $LiOH$   
2) mild  $H_3O^+$



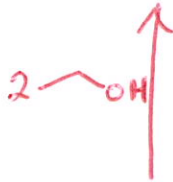
$H_2SO_4$



1)  $O_3$   
2)  $(CH_3)_2S$



1)  $LiAlH_4$   
2)  $H_2O$



2  $SOCl_2$



excess  $H_2CrO_4$

OR

2  $CCO$   
cat.  $H_2SO_4$   
(Fischer esterification)