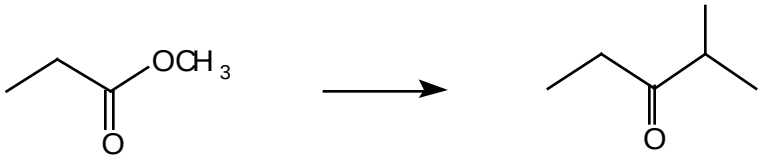
Hour Examination #3, Chemistry 302/302A - 2004

> "If you are obliged to neglect any thing, let it be your chemistry. It is the least useful and the least amusing to a country gentleman of all the ordinary branches of science."
>
> Thomas Jefferson

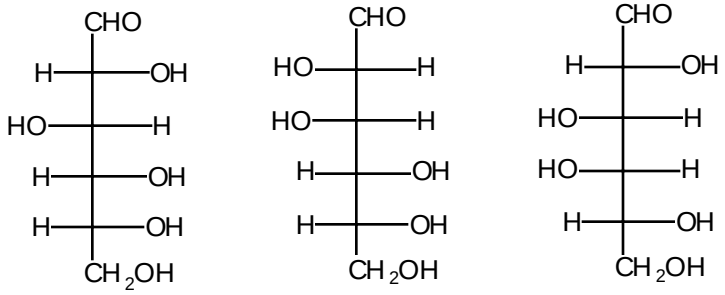
1 (21 points). Devise three different ways to convert methyl propionate into ketone **1**. You may also use isopropyllithium, pyridine, any one-carbon-containing compound, and the DNA from the last rancid yak of Tibet. Need something else? Ask us. Mechanisms are not necessary. What does "different" mean? The judges' decision is final, but here are three hints:

a. acetoacetic ester b. grind it out c. two equivalents of RLi



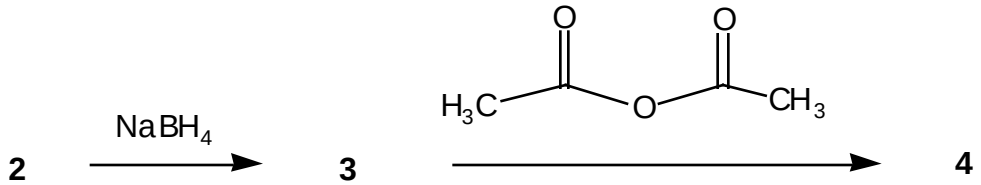
methyl propionate **1**

2 (19 points). Aldohexose **2** was known to be either D-Glucose, D-Mannose, or D-Galactose.



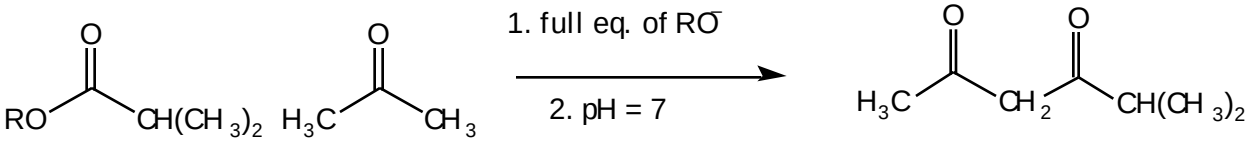
D-Glucose D-Mannose D-Galactose

Reduction with sodium borohydride gives the corresponding D-hexa-alcohol **3**, which was then treated with acetic anhydride to give the corresponding hexa-acetate **4**.



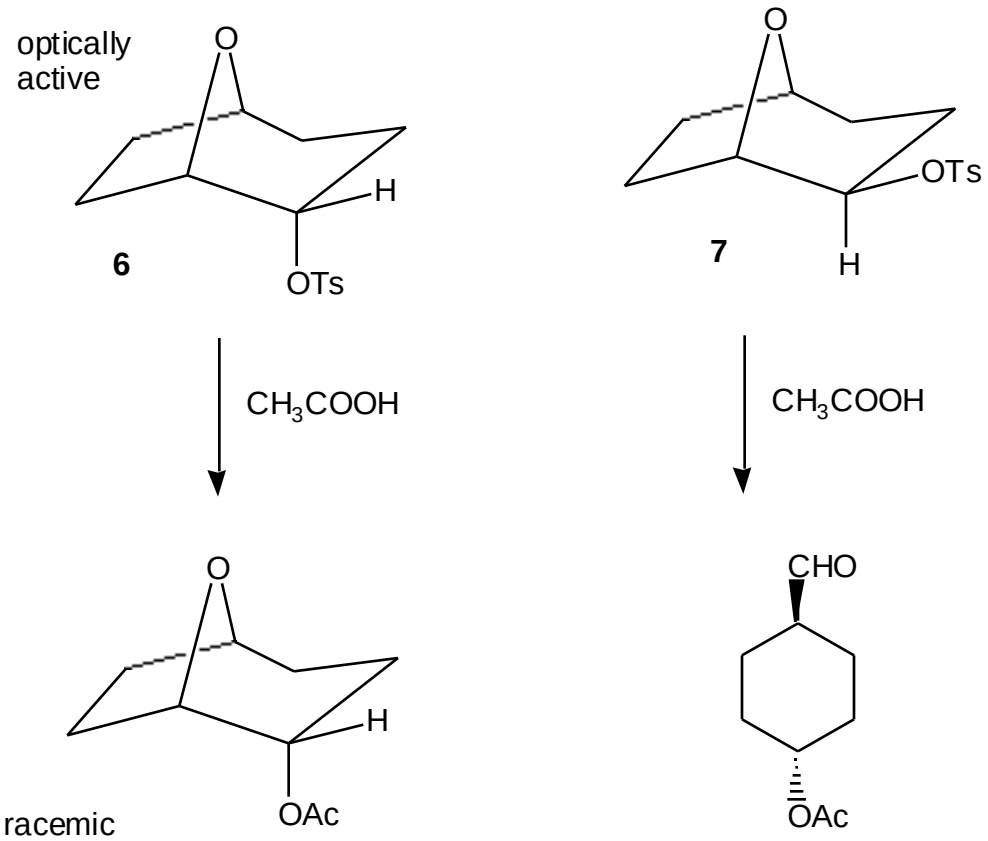
The hexa-acetate **4** was optically active and showed three singlets of equal intensity in the ^{1}H NMR spectrum between δ 2-2.15 ppm. Deduce the structures of **2**, **3**, and **4** and explain your reasoning.

3 (20 points). Explain why the following “crossed Claisen” condensation succeeds. In particular, why is there a good yield of product **5**? Shouldn’t the aldol condensation of acetone severely reduce the yield? Shouldn’t the self-condensation of the ester lead to a Claisen product that reduces the yield of **5**? Yes, you will have to analyze the mechanism of this reaction.

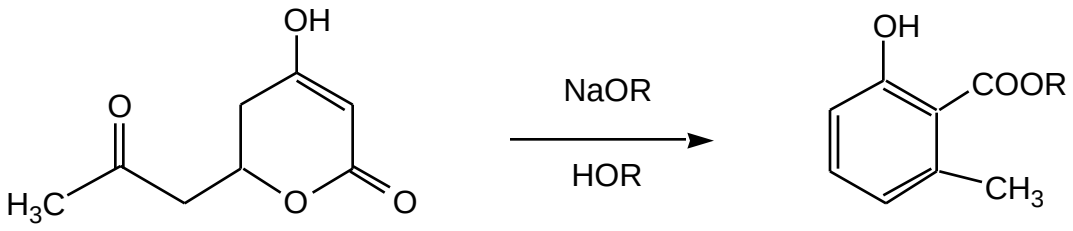


5

4 (20 points). Provide mechanisms for the following changes, and explain why **6** and **7** react differently.



5 (20 points). Provide a mechanism for the following change, Please note that an ester, COOR, is formed, not an acid, COOH, or carboxylate, COO^-.



“I pledge that I have not violated the Honour Code on this examination.”