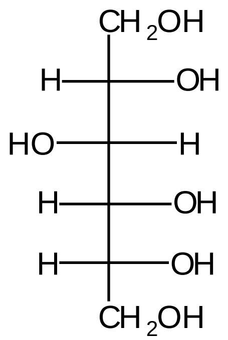
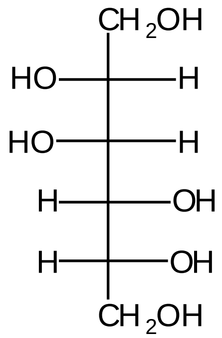
Answers to Hour Examination #3, Chemistry 302/302A - 2004

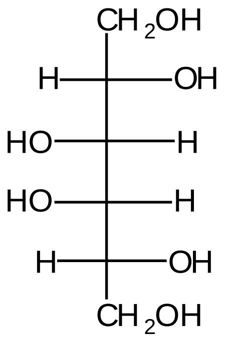
1.

(a)	(b)	(c)
1. CH_3OH/CH_3O^- 2. CH_3I 3. H_3O^+, heat	1. H_3O^+/H_2O 2. 2 Eq. $(CH_3)_2CHLi$ 3. H_2O	1. $LiAlH_4$ 2. H_2O 3. CrO_3/pyridine 4. 1. $(CH_3)_2CHLi$, 2. H_2O 5. $KMnO_4$

2. The borohydride reduction leads to the following three possibilities for **3**.

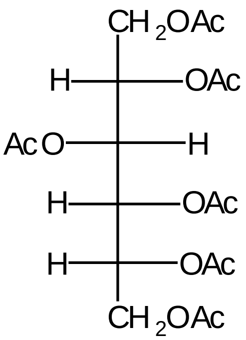




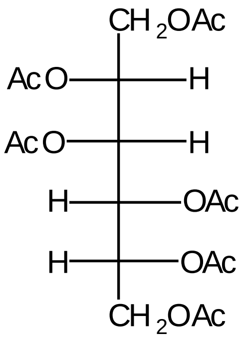


The corresponding hexa-acetates are A, B, and C:

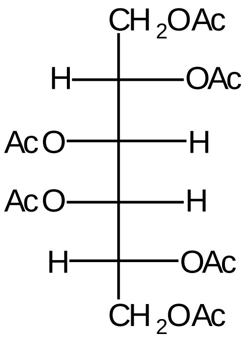
A



B

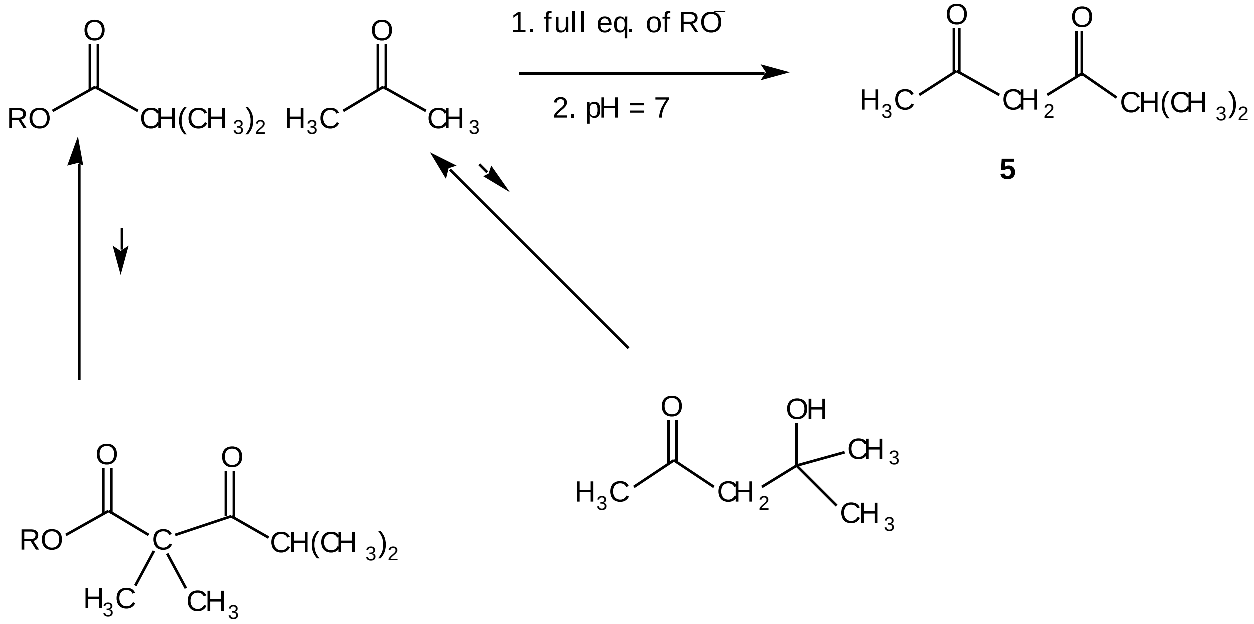


C



Acetate C is optically inactive and is eliminated. Acetate B has three different methyl groups but acetate A has six!. The hexa-acetate is B, and the starting sugar must be D-D-mannose.

3. The aldol condensation of acetone is endothermic. It will surely take place, but monomeric acetone is always the major compound in equilibrium with the aldol product, and thus is available for the crossed Claisen. The Claisen condensation of the starting ester leads to a β-keto ester with no doubly α hydrogens and so cannot be successful. Also, acetone is a far stronger acid than the ester [p*K*a (acetone) = 19.3 p*K*a (ester) = 24]. Thus it will be the enolate of acetone that reacts with the ester carbonyl.



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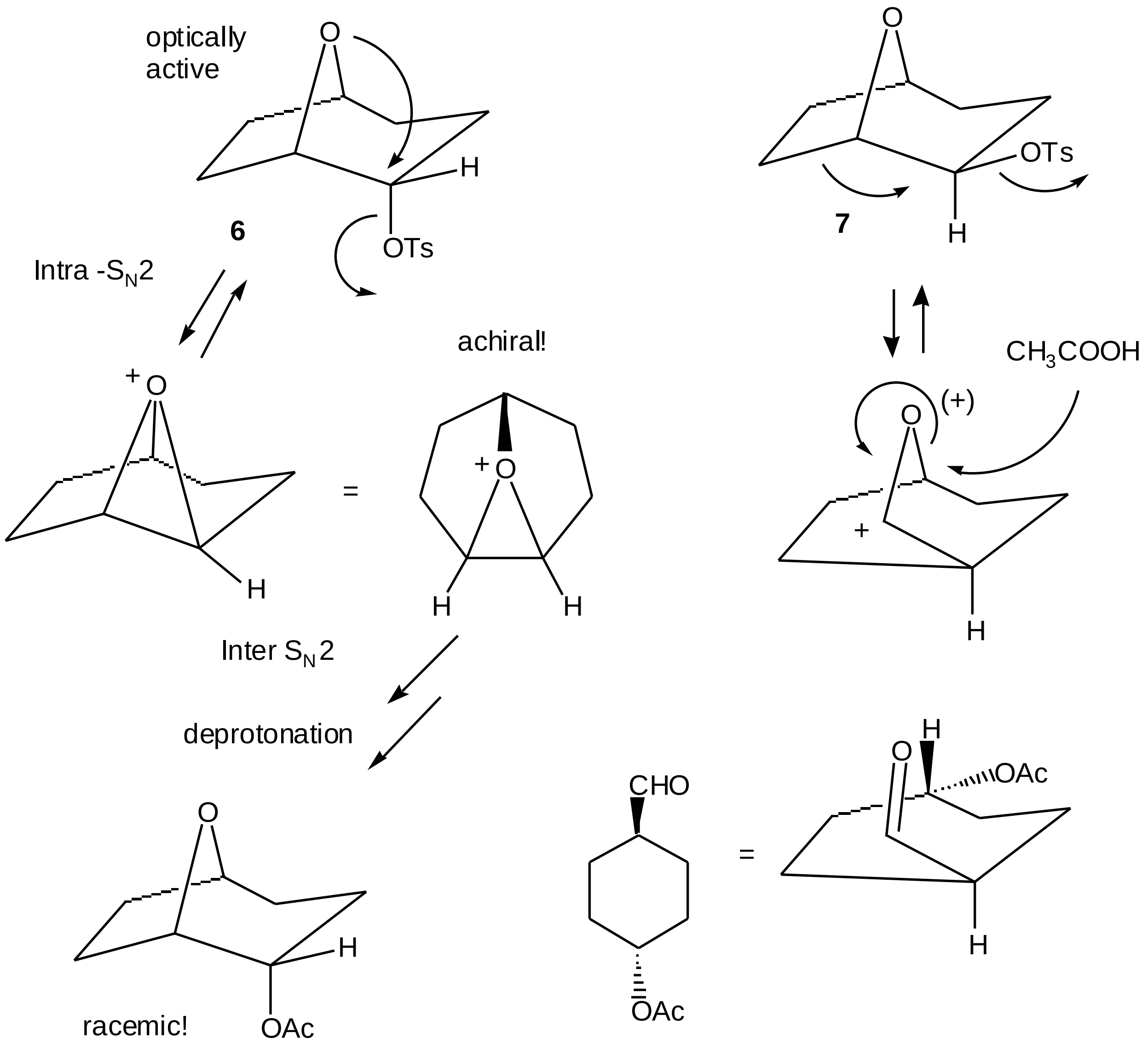
4. In each case it is the pair of electrons that is in position to assist in the ionization of the tosylate that participates. The second example can be written either with bridged or unbridged ions. When the oxygen participates, the backside S_N2 yields an achiral intermediate oxonium ion that, of course, must lead to racemic product.



5. Here is a reasonable pathway for this open-close problem.