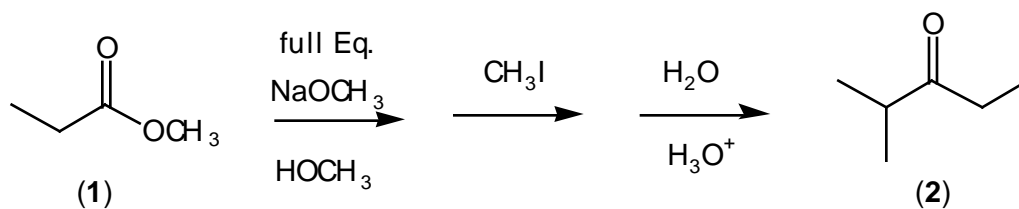
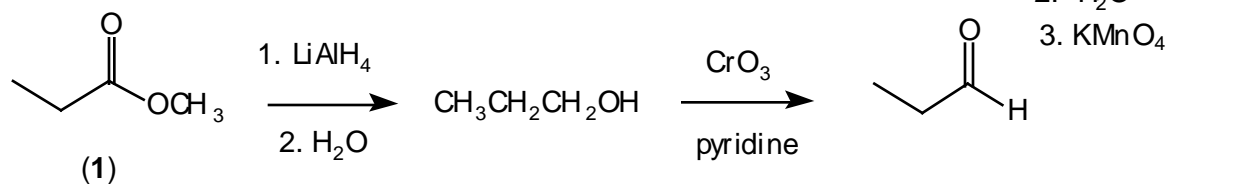
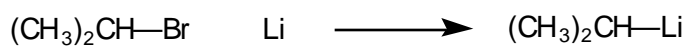
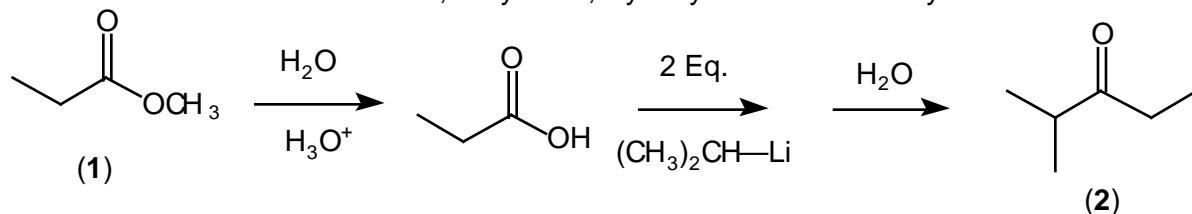


Answers to Hour Examination #3, Chemistry 302X - 2003

1.

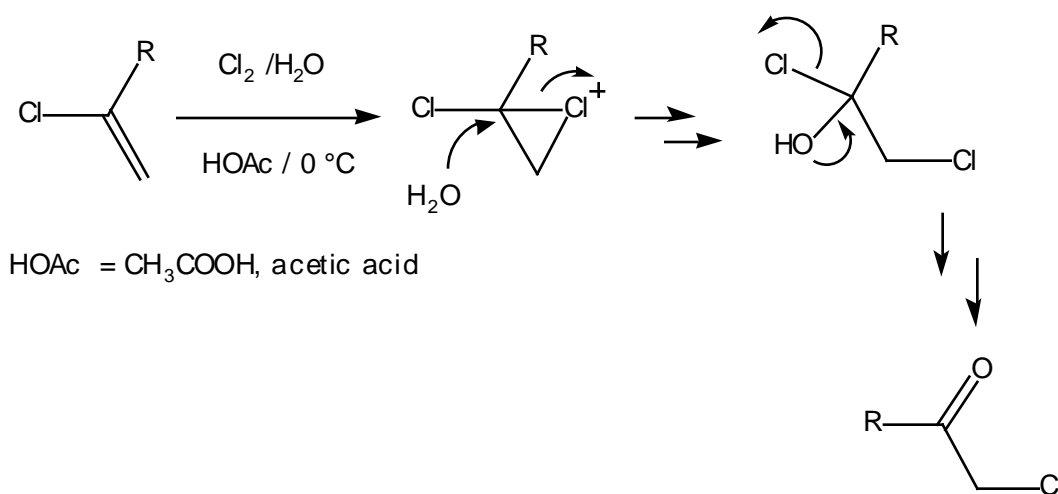


Claisen to the anion, alkylation, hydrolysis and decarboxylation

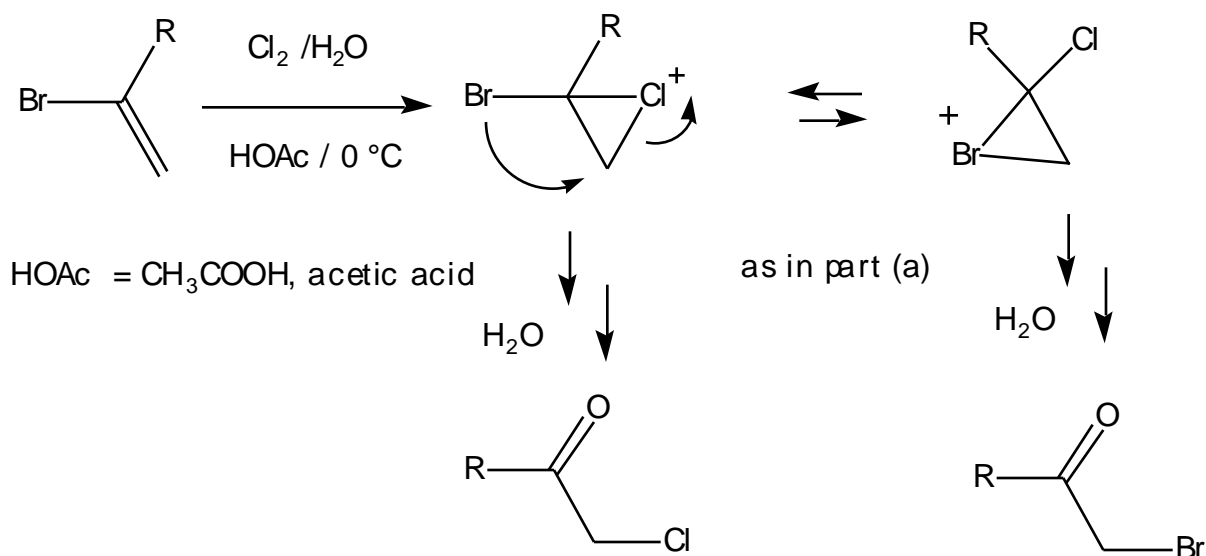


2.

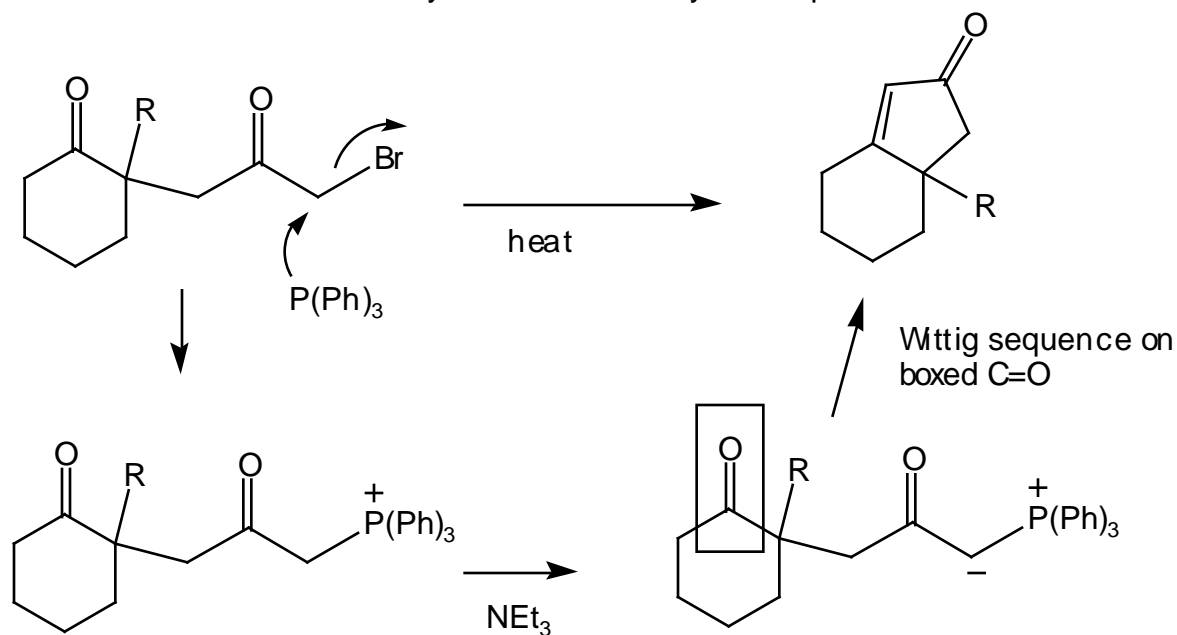
a. Chloronium ion formation is followed by opening by water at the more substituted position (as usual). Loss of chloride and deprotonation finishes it up.



b. But where does that bromide + chloride come from? Take a look at the 'onium ion at the heart of the mechanism. There is an opportunity for NGP to form an equilibrating mixture of chloronium and bromonium ions.

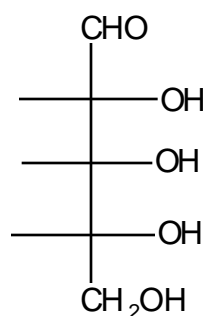


(c) Basically an intramolecular Wittig reaction variation. The adjacent carbonyl group makes the use of the relatively weak base triethylamine possible.

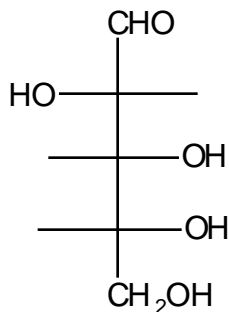


3.

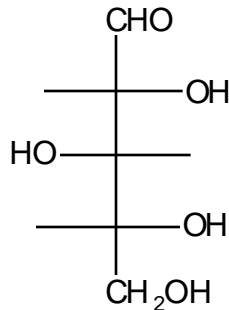
(a) Here are the four D-aldopentoses:



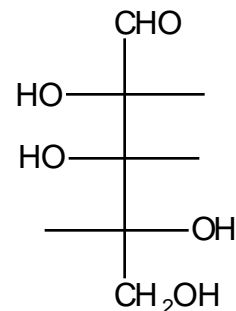
A



B



C



D

(b) conditions 2. A and B or C and D

(c) conditions 3. A and B or C and D

(d) conditions 1. B and D

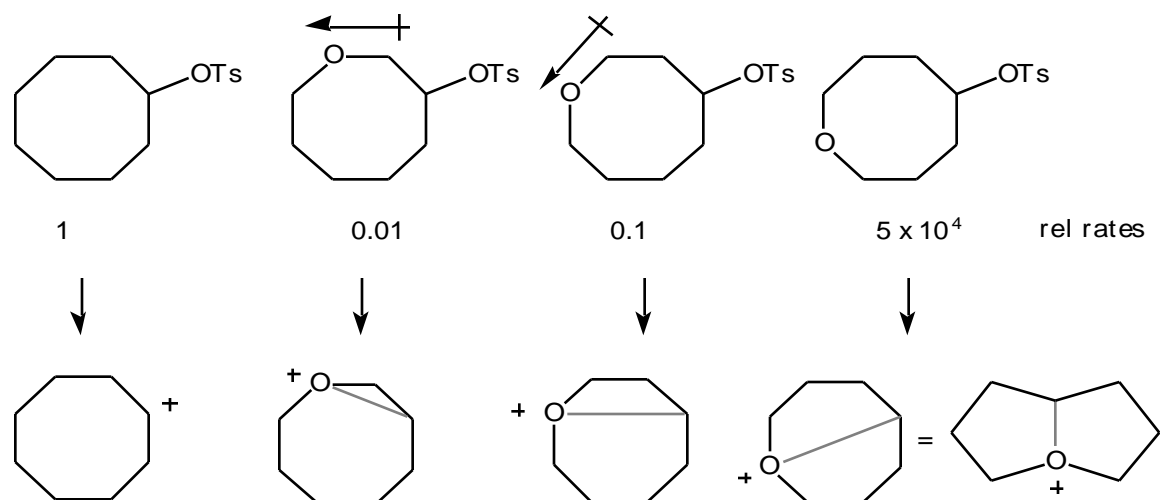
(e) conditions 4. B (also gives D-mannose).

(f) B and D

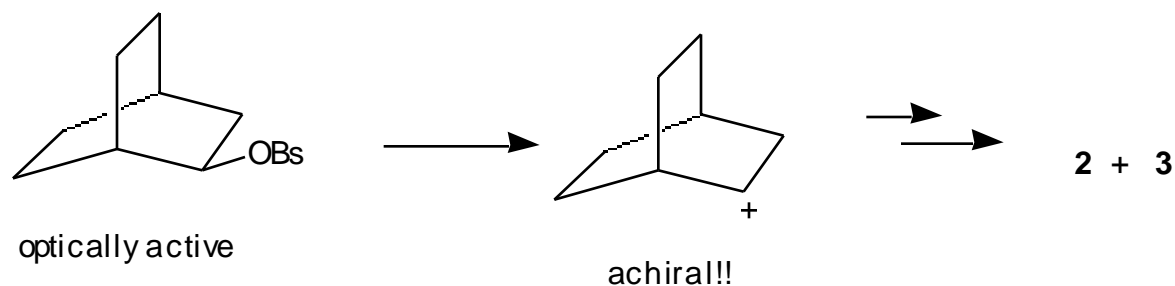
4a.

In the first compound, solvolysis leads to a secondary carbocation. Base rate is set at 1. In the second and third molecules, participation would involve a strained bicyclic system in the intermediate and in substantial strain in the TS leading to that intermediate. Thus there is no rate advantage here. In the last case, strain is minimal in the bicyclo[3.3.0] system and there is substantial participation by the well-placed oxygen atom. The rate of ion formation is much faster than that of the base compound.

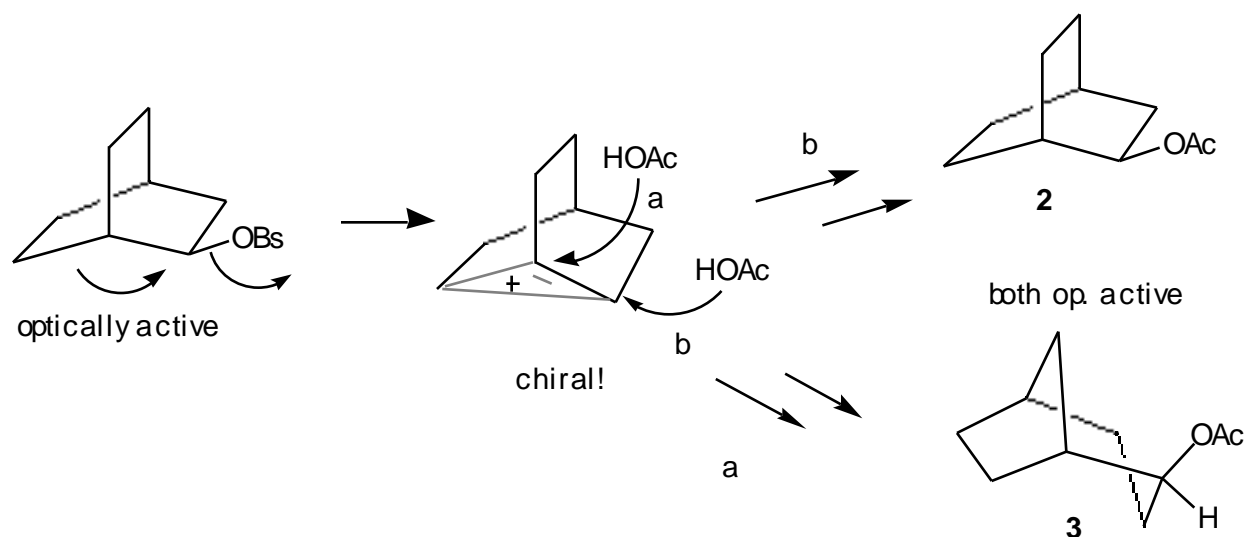
But why are the middle compounds slow? The dipole in the C-O bond will inhibit formation of any cation. That effect is also present somewhat in the last compound but is overwhelmed by participation.



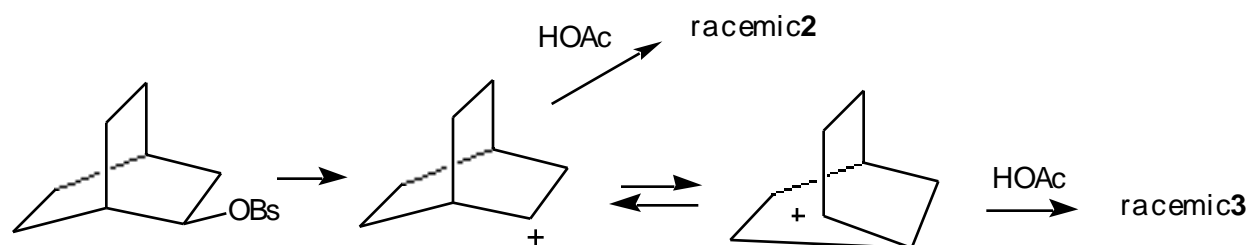
b. For one thing, isolation of optically active products tells you that no achiral intermediate can precede them. Thus, ionization to an open secondary carbocation cannot be happening.



The results are nicely rationalized by a bridged ion:



The observation of two products can be accommodated by *both* a bridged ion (see above) and a pair of equilibrating open ions, so finding both **2** and **3** tells you nothing about the nature of the ion, bridged or not, that is involved in the mechanism.



5.

