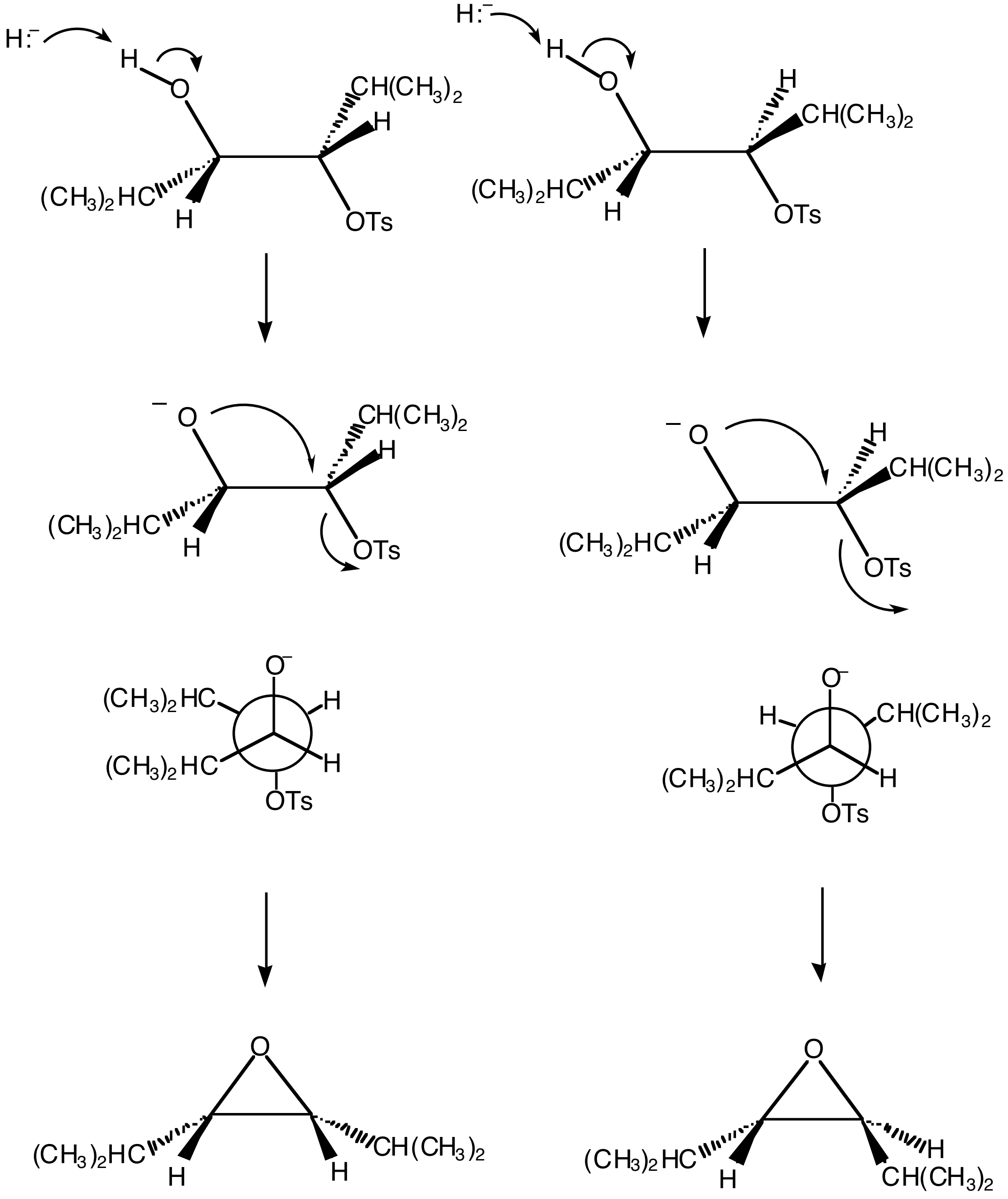
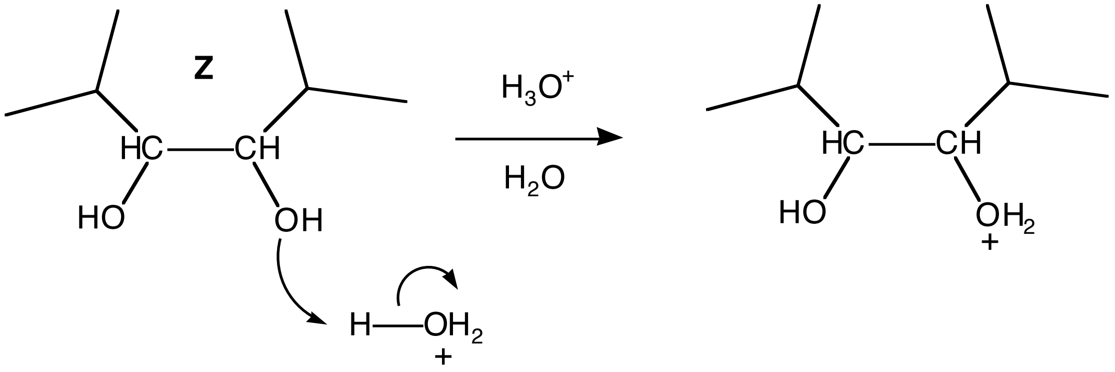
Some Answers to Hour Examination #2, Chemistry 301X - 2006

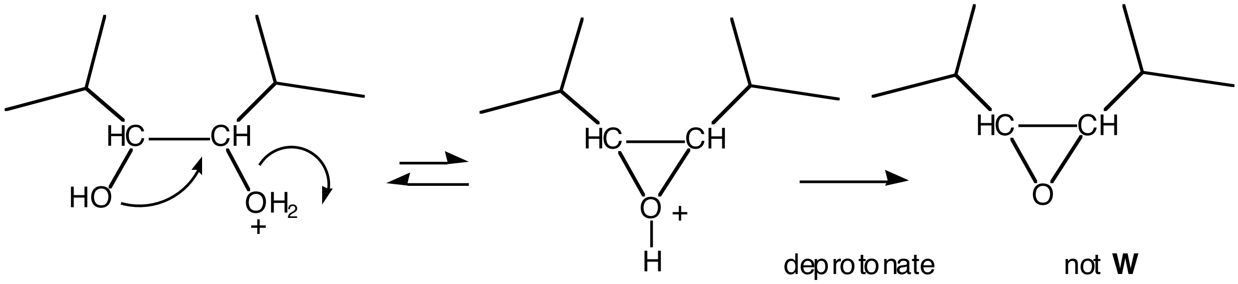
1a and b. Here are the drawings: The two diastereomers are shown at the top and the products at the bottom. In these S_N2 reactions, the leaving group tosylate must be in the position as shown so that the obligatory displacement from the rear is possible. The Newman projections clearly show the gauche interaction in the left hand diastereomer that makes it difficult to achieve the proper orientation.



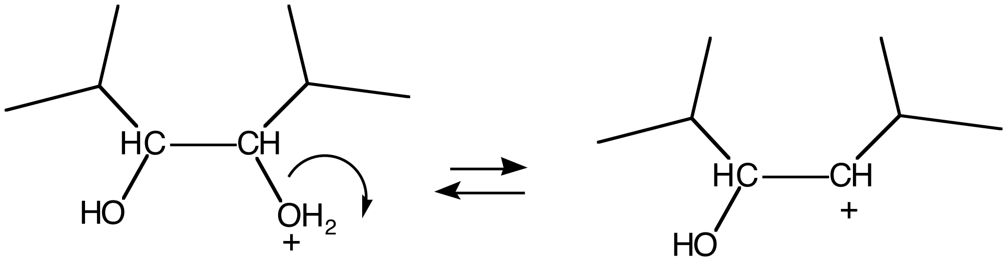
1c. Protonation must be the first step - there simply isn't anything else to do.



Now there are many possibilities: An internal S_N2 would ultimately produce an epoxide, but it has far fewer than six different carbons, so that reaasonable possibility must be discarded.

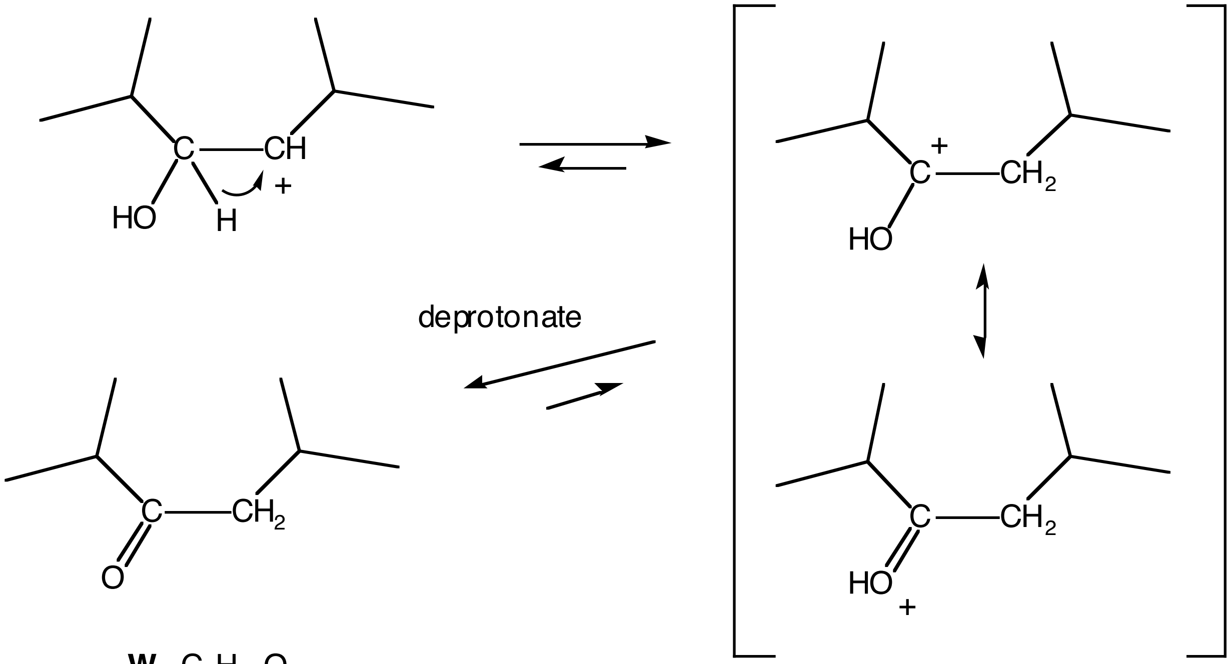


How about an S_N1 reaction of protonated **Z**?



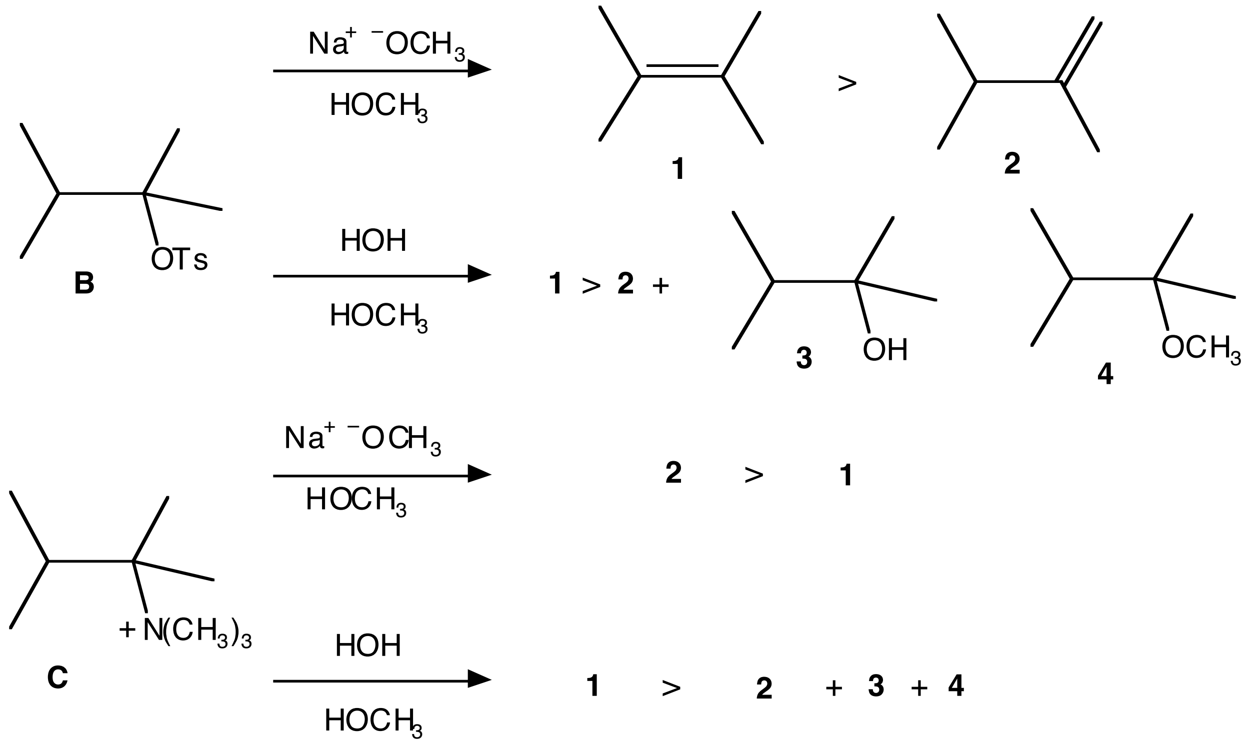
Seems reasonable - very polar medium, no good nucleophile, secondary carbocation.

This ion can form a very stable (resonance!) carbocation through a dreaded hydride shift. Deprotonation leads to **W**, with the right number of carbons and a carbonyl group.



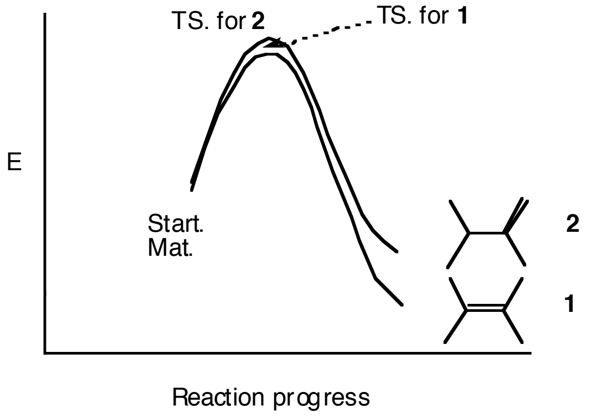
W, $C_8H_{16}O$

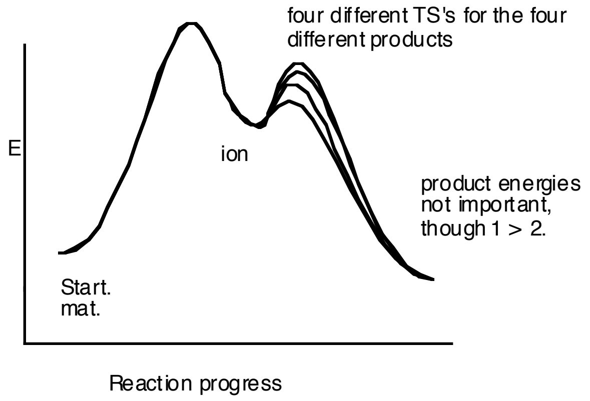
2.



The first reaction is a fairly straightforward pair of E2’s. The only semi-subtle point is to get the energy difference between the two TS’s smaller than that between the two products.

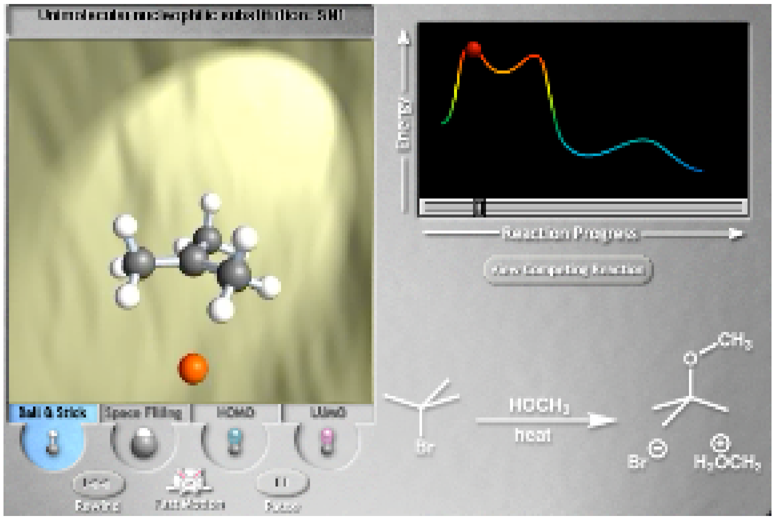
In the second case, there is a common intermediate from which four different paths emerge. For two of the products (**3** and **4**) there is a final deprotonation step (not shown).



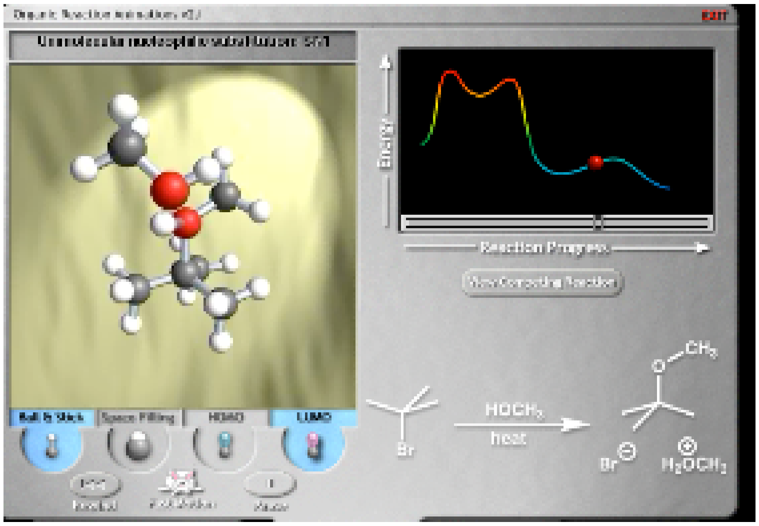


3.

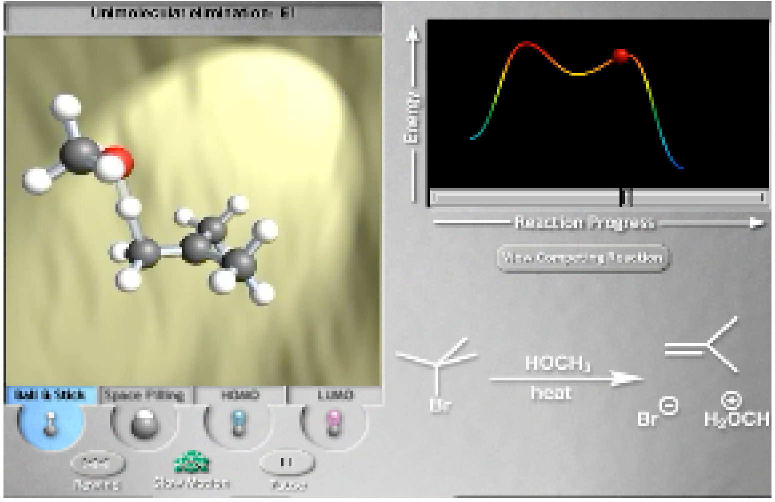
A: Close to the TS for the E1 or S_N1 reaction



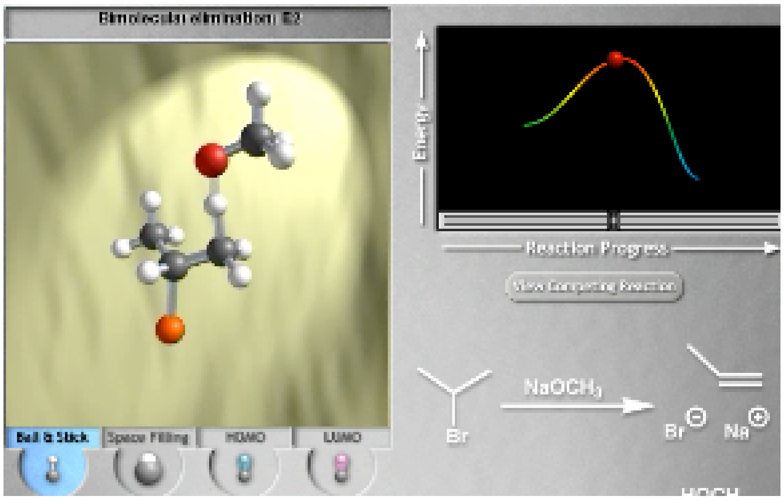
B: deprotonation step in S_N1



C: Deprotonation step in the E1 reaction



D: Just about the TS for the E2 elimination.



4. Most of these targets have many possible routes. Here are samples:

(a) $(CH_3)_3C-O^-$ ^+Na (E2 elim). Could also do the E2 on (i)

(b) let (a) react with HCl

(c) (a) + H_3O^+/H_2O

(d) 1. (c) + NaH 2. CH_3I

(e) 1. Li 2. D_2O

(f) 1. (a) +DCl 2. Li 3. D_2O

(g) HS^-

(h) 1. (g) + NaH 2. CH_3I

(i) (c) + TsCl

(j) 1. (c) + NaH 2. (i)

5. Like so many problems, this one hinges on the formation of two diastereomers, one of which can do an S_N2 reaction with the obligatory inversion. The other is forced to do a “front side SN2” and such reactions are unknown (you know why). So, deprotonation of **G** occurs, but the thiolate simply reprotonates on acidification to pH = 7.