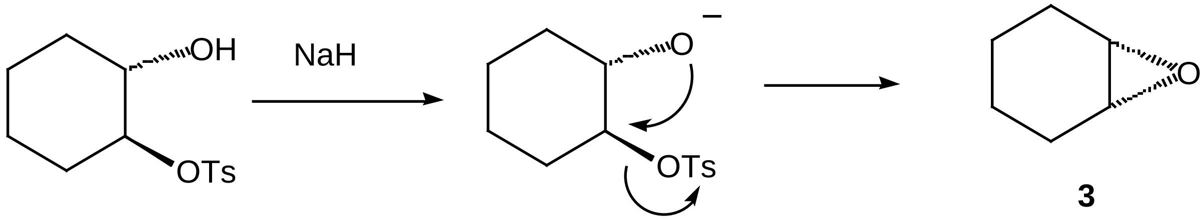
Answers to Hour Examination #2, Chemistry 301-301A - 2004.

1a. In general, sodium hydride forms the alkoxide which then does an intramolecular S_N2 to form the epoxide.



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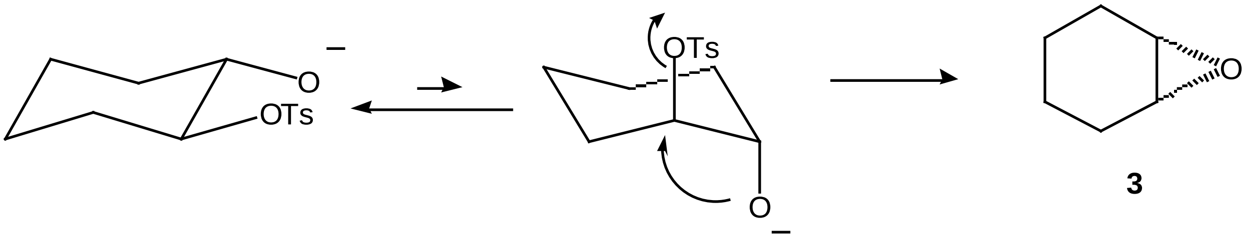
The stereochemical details are critical, however, as the energy minimum chair form cannot undergo the critical S_N2 reaction, and must flip into the less stable diaxial form first so that the critical rear-side displacement can occur:



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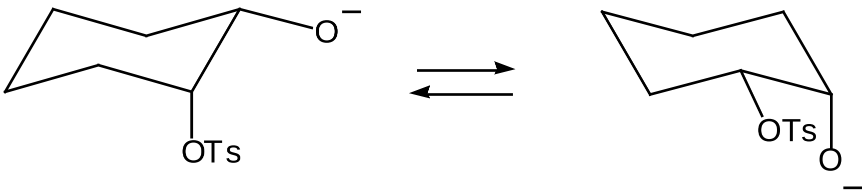
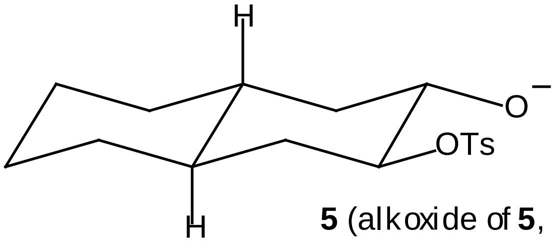
(b) In the cis compound there is no arrangement in which there can be a proper S_N2 displacement (displacement from the rear).



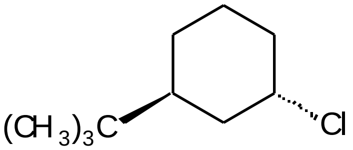
(c) The trans-fused second ring makes the necessary ring flip impossible, and thus the proper arrangement for displacement from the rear cannot be achieved.



no ring flip possible

5 (alkoxide of **5**, really)

2. The problem shows cyclohexanes, so immediately we know we have to draw good chairs, and that the *tert*-butyl group is equatorial:



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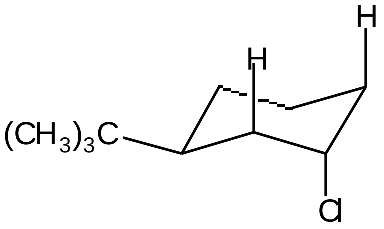
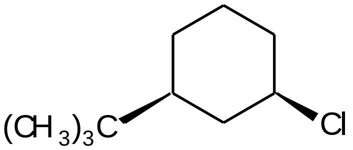


two H's properly aligned for E2



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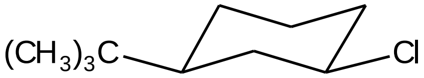
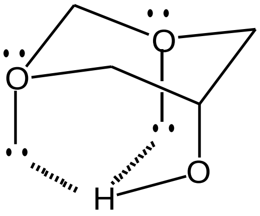
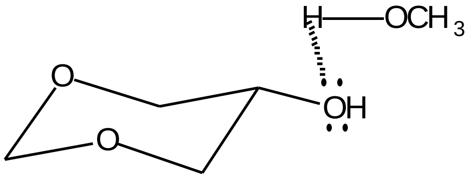


no H properly aligned for E2

Now the answer falls right out- in **8** there is no proper 180° alignment between C-H and C-Cl.

(b) In hexane, only intramolecular hydrogen bonding is possible, and the OH must be axial in order to achieve this stabilizing bonding. In methyl alcohol, intermolecular hydrogen bonding is possible. This effectively increases the size of the OH group and demands an equatorial orientation.

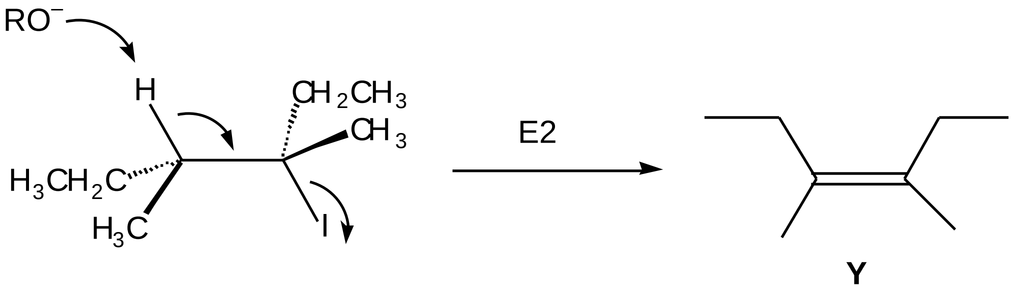




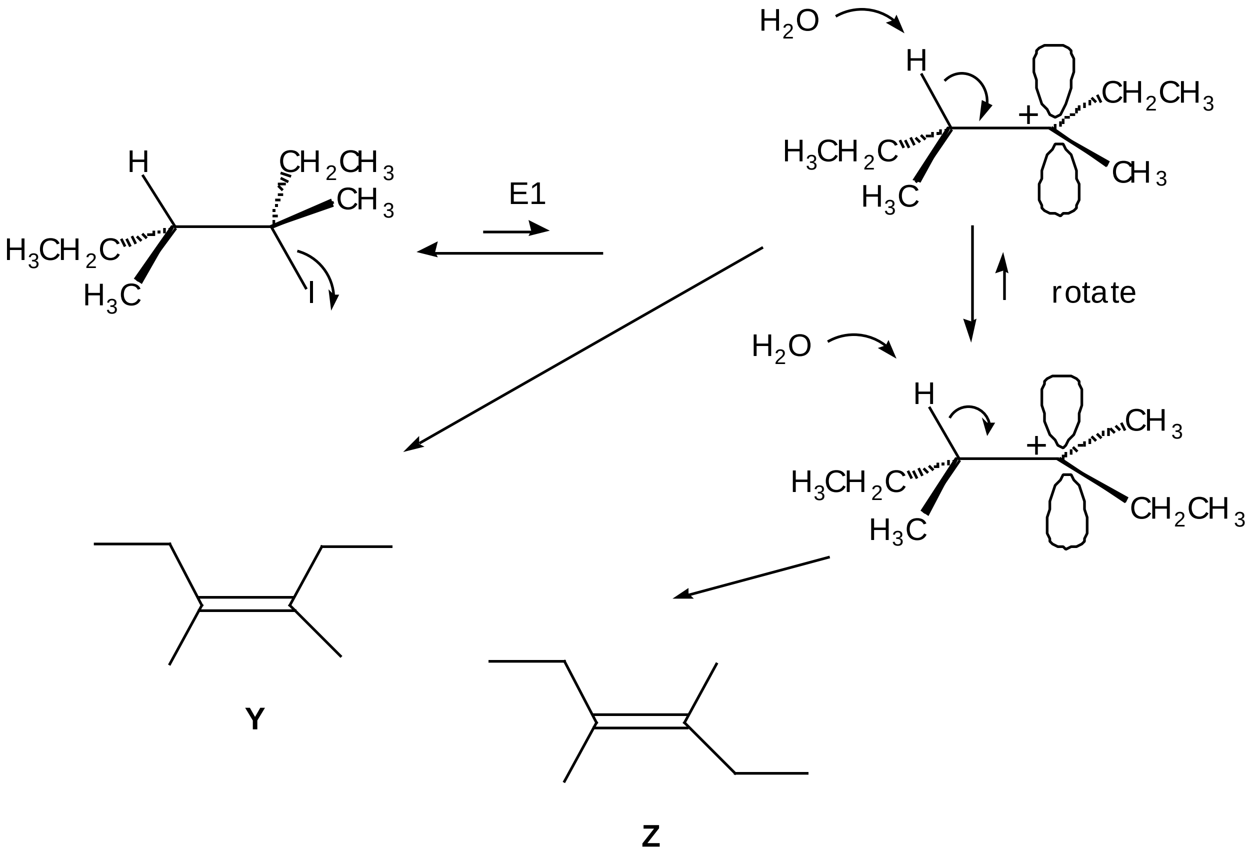
3.
Conditions A are S_N1/E1 (weak base, polar solvent, tertiary substrate).

Conditions B are E2 (no S_N2 possible, strong base)

In the E2 there is a requirement for anti-periplanar arrangement of the departing groups (H and I), so there is only one possible product, which must be **Y**.



By contrast, in the E1 reaction there is an intermediate carbocation that can be deprotonated in two ways to give **Y** and **Z**. Alkene **Z** is the major product because it, and the TS leading to it, are more stable than **Y** and the TS leading to it, respectively.



4.

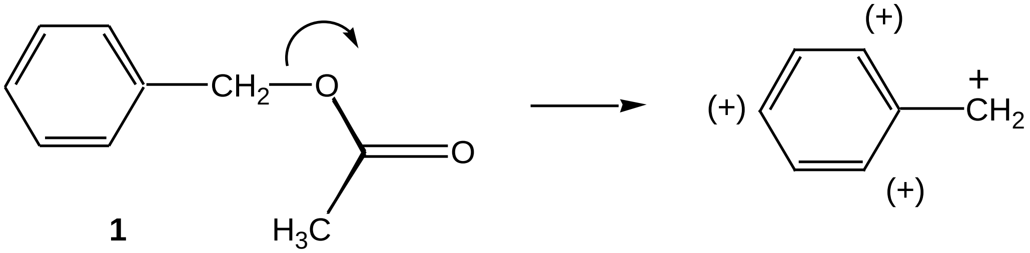
(a) HBr

(b) 1. TsCl 2. $(CH_3)_3CO^-$ 3. HBr

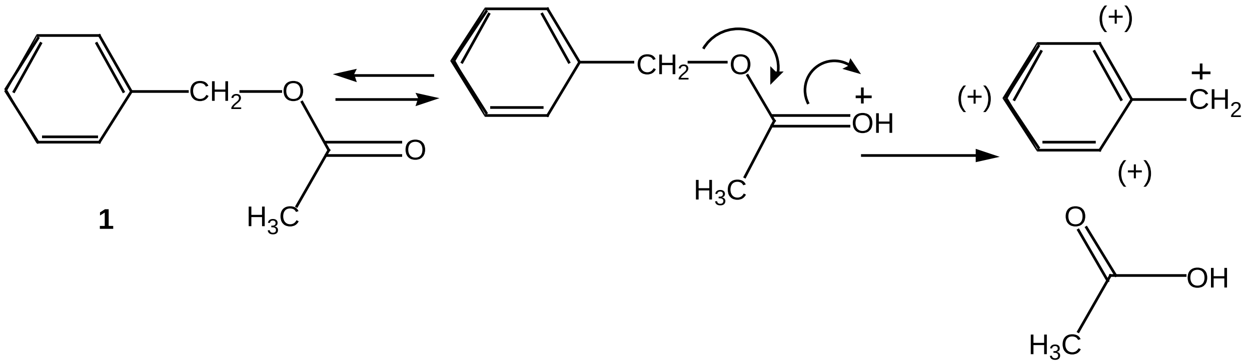
(c) 1. Li (or Mg) + product from (a) or (b) 2. H_2O

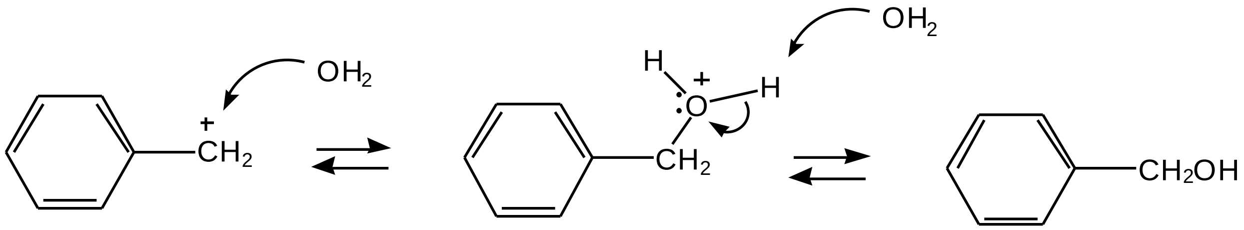
(d) 1. NaH 2. CH_3I

5. Benzyl acetate forms a primary carbocation in an S_N1 reaction, and that event is surely unusual. However this is no normal primary cation, as it is well stabilized by resonance. Accordingly, the benzyl cation is unusually stable, and can be formed under appropriate S_N1 conditions.

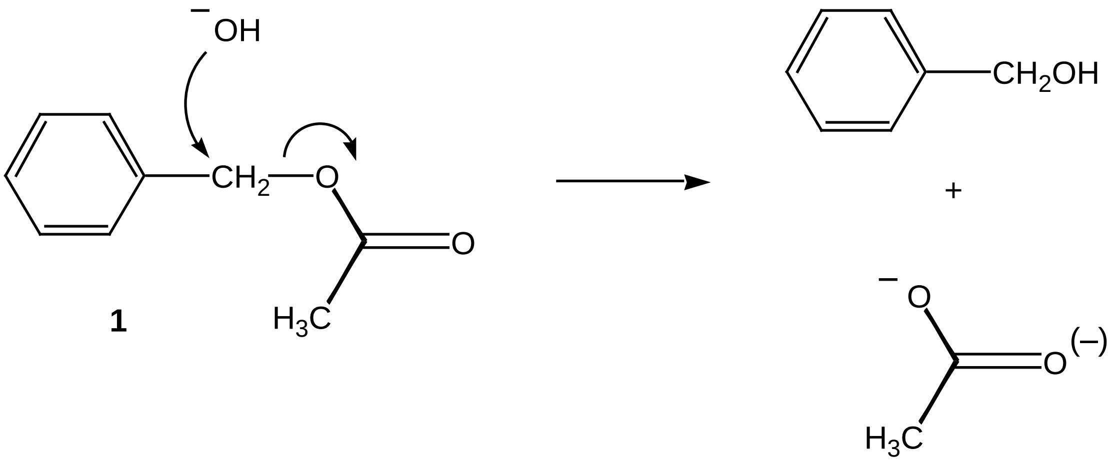


At pH = 1, the leaving group will be protonated, and the S_N1 reaction is off and running, as the mediocre leaving group is transformed into a good leaving group. The reaction is, of course, first order in acetate **1**. Note protonation of the carbonyl (C=O) oxygen.





At pH = 10, we are in basic conditions (E2/S$_N$2, not E1/S$_N$1 conditions), and hydroxide will displace acetate in a standard S$_N$2 reaction, first order in substrate (**1**) and first order in nucleophile.



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