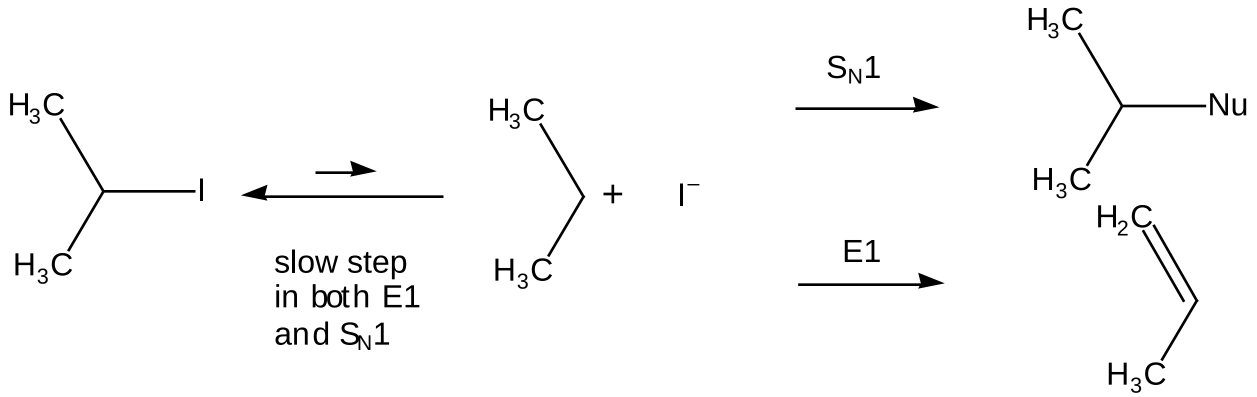
Answers to HT#2, Chemistry 301X, 2005

1. The rate-determining step for the E1 and S_N1 reactions - the ionization shown below - is the same, so the rates must be the same. The E2 and S_N2 reactions have totally different rate-determining steps, so of course their rates are different. Curves can be found all over Chapter 7.



slow step in both E1 and S_N1

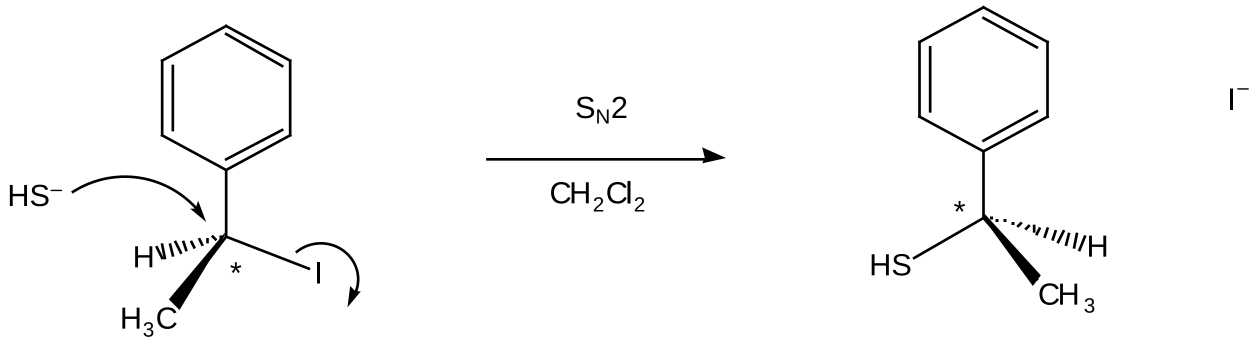
1b. E1, S_N1: pyramidal bridgehead carbocation too unstable to form.

E2: The 2*p* orbitals of the bridgehead double bond do not overlap - there is no real double bond.

S_N2: The nucleophile cannot reach the rear of the putative leaving group.

2.

(a)

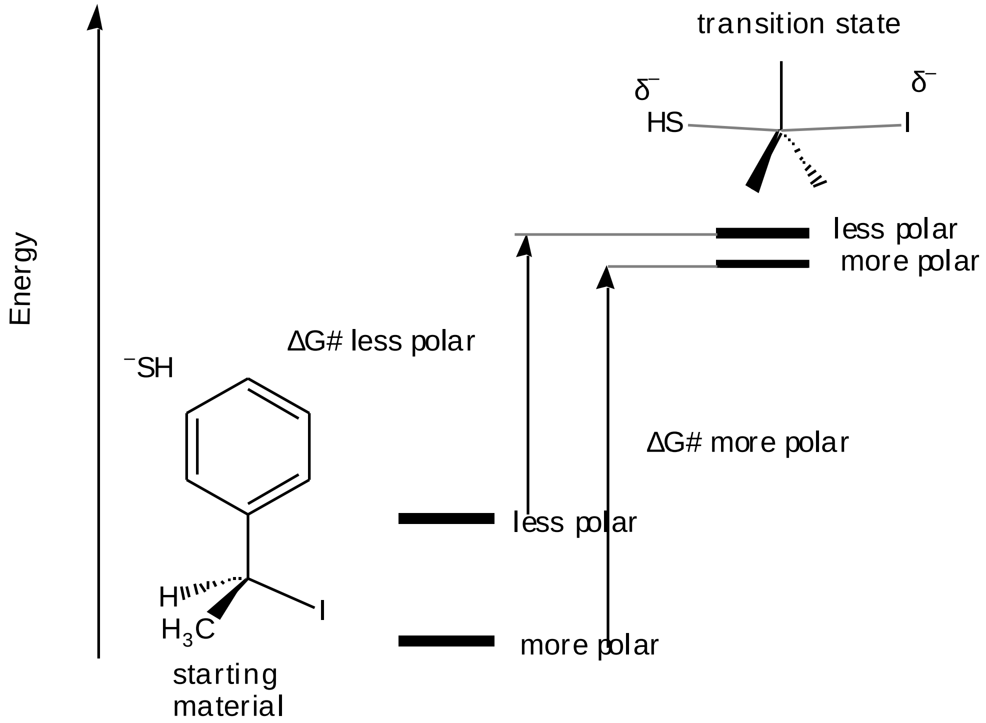


b. *S*

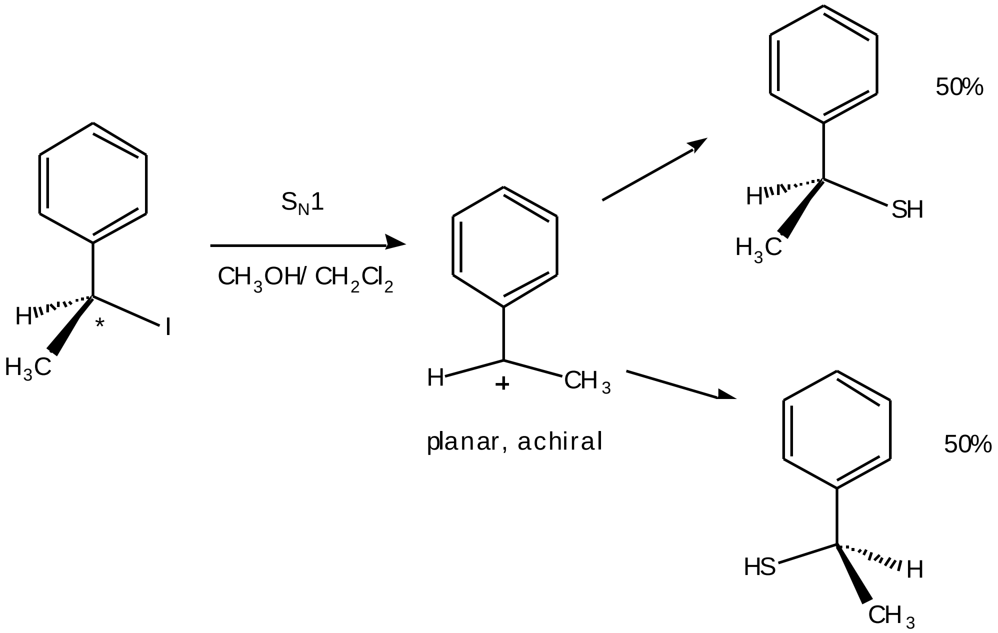
c. *R*

d. you can’t tell.

e. In this case, changing to a less polar solvent would increase the rate of reaction. The ionic starting material, with a thiolate with a full negative charge, is more stabilized by a polar solvent than is the transition state in which the charge is dispersed.

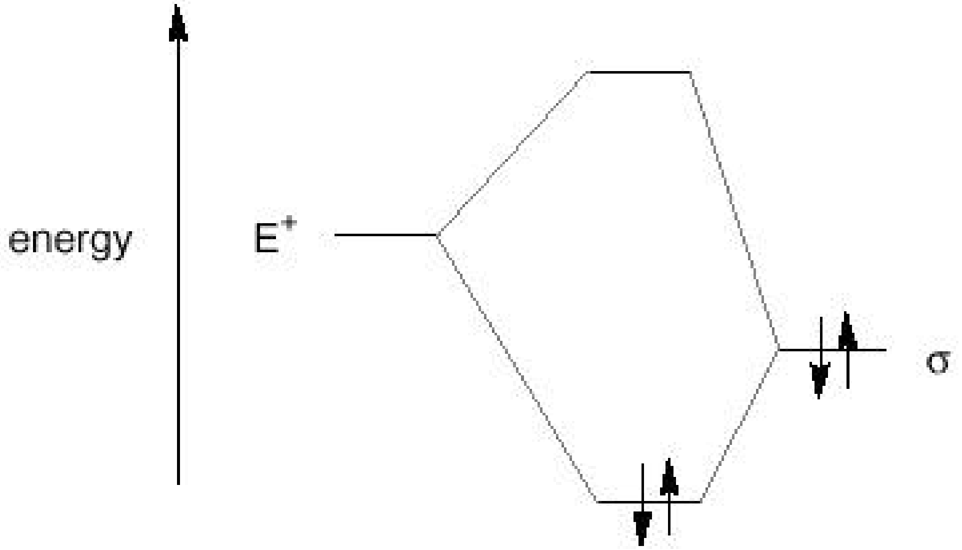


f. In the more polar solvent system, the S_N1 reaction begins to compete with the S_N2 reaction. Ionization leads to a planar cation that is achiral. The achiral intermediate must produce a racemic product. Thus, the rotation of the product, **2**, will be reduced.

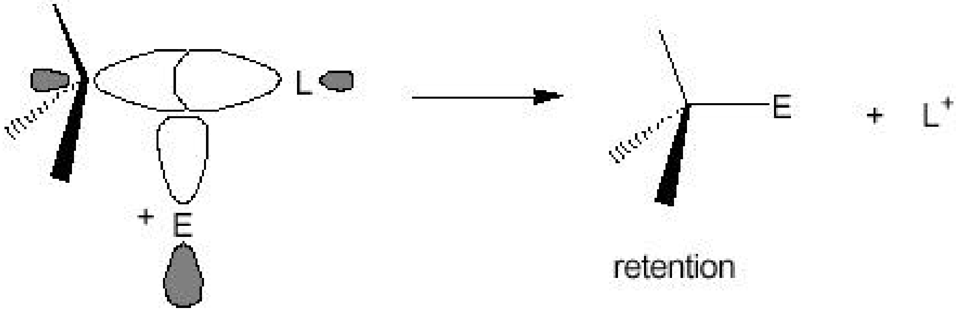


g. It will eventually become pure S_N1 and the product will be racemic - zero rotation.

3. The electrophile E^+ (Lewis Acid) is reacting through its empty orbital, and thus seeks out a source of electrons. It is the same old story: the interaction of filled and empty orbitals is stabilizing.



What can that source of electrons be? The filled σ orbital of the C–L bond is the obvious choice. Where is σ “fat”; where is the electron (and orbital) density? In front, where there is also no symmetry problem - the interaction is bonding everywhere. This simple analysis predicts retention in this reaction.



4. (a) 1. HBr (or DBr)   2. Li   3. D_2O (or H_2O)

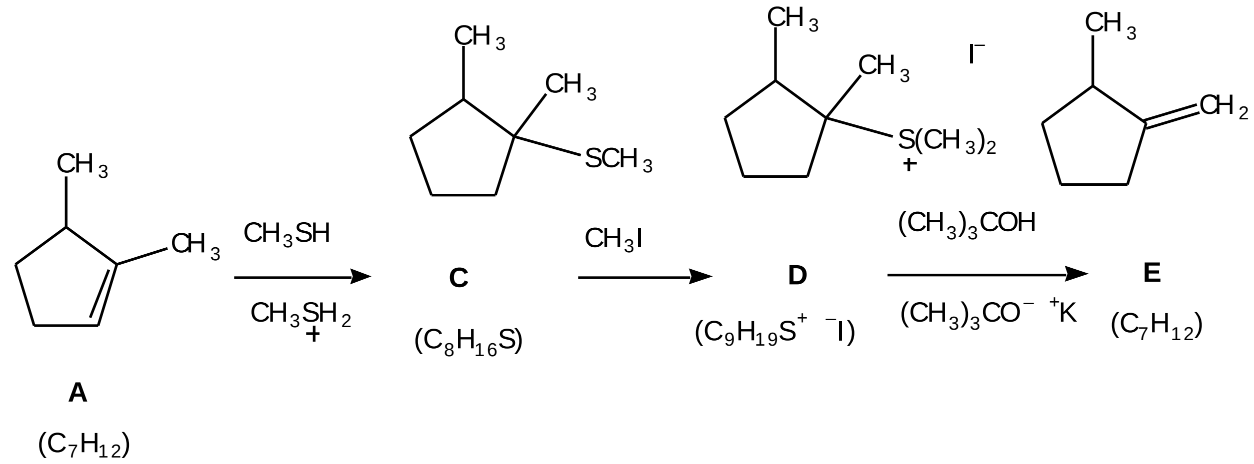
(b) HCl

(c) 1. HBr   2. Mg/ether

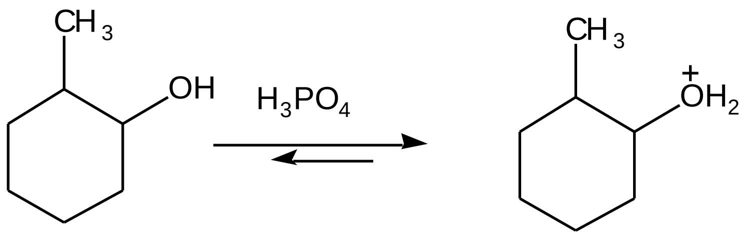
(d) 1. H_3O^+/H_2O 2. TsCl

(e) 1. H_3O^+/H_2O 2. NaH   3. CH_3I - there are several other ways.

5.

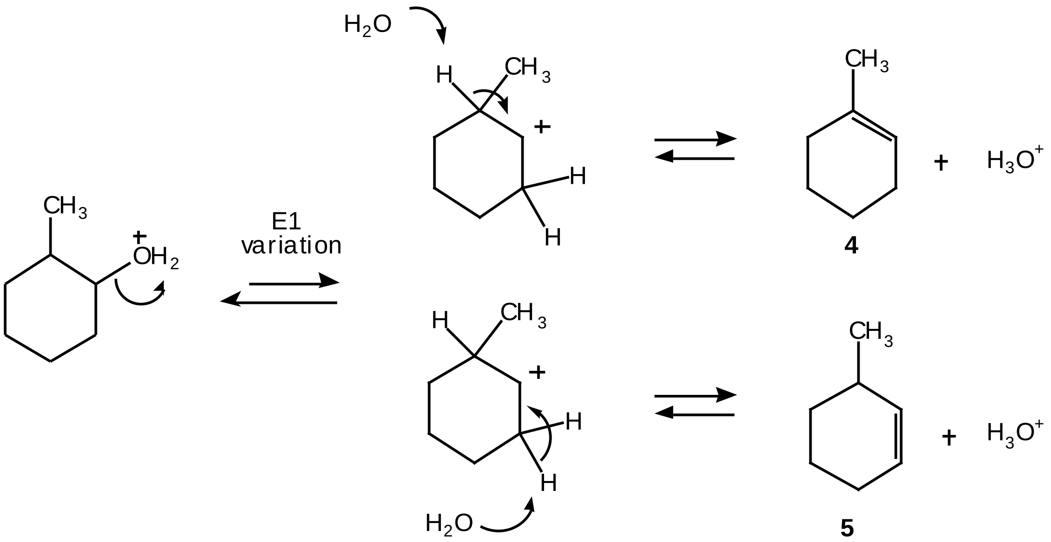

CH3
CH3
A
(C7H12)
CH3SH
CH3SH2 +
CH3
CH3
SCH3
C
(C8H16S)
CH3I
CH3
CH3
S(CH3)2 +
I−
D
(C9H19S+ −I)
(CH3)3COH
(CH3)3CO− +K
CH3
CH2
E
(C7H12)

6. The clue “first order” surely points you towards the E1 reaction - at least we hope so. The first step is protonation of the alcohol.



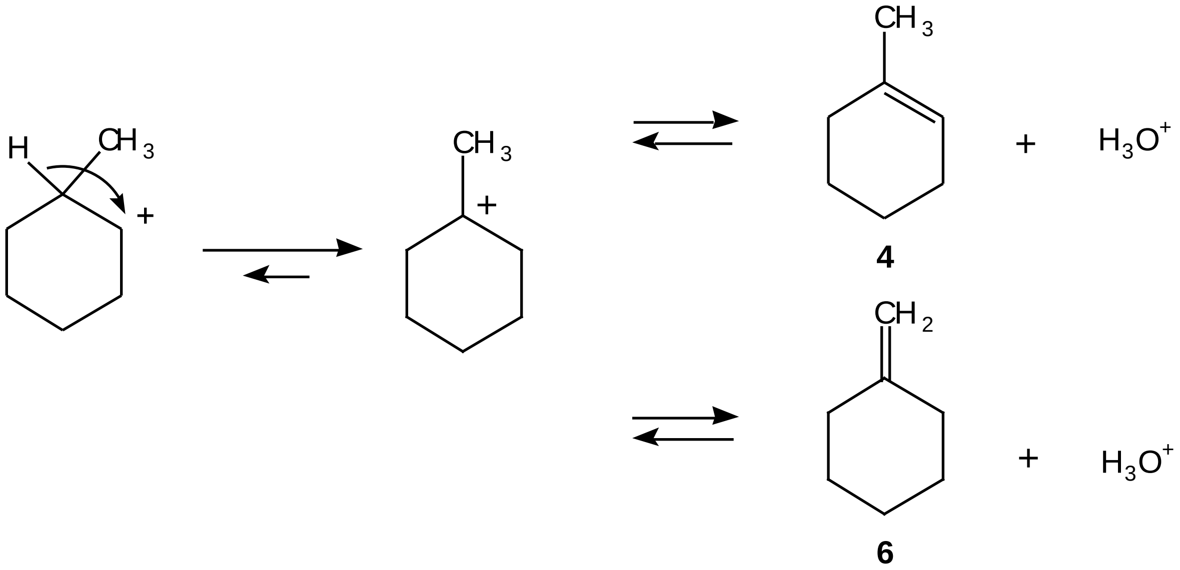
3

Water is now lost. There are two different protons that can be removed - notice they are plucked by a Lewis base, not just ejected into solution:

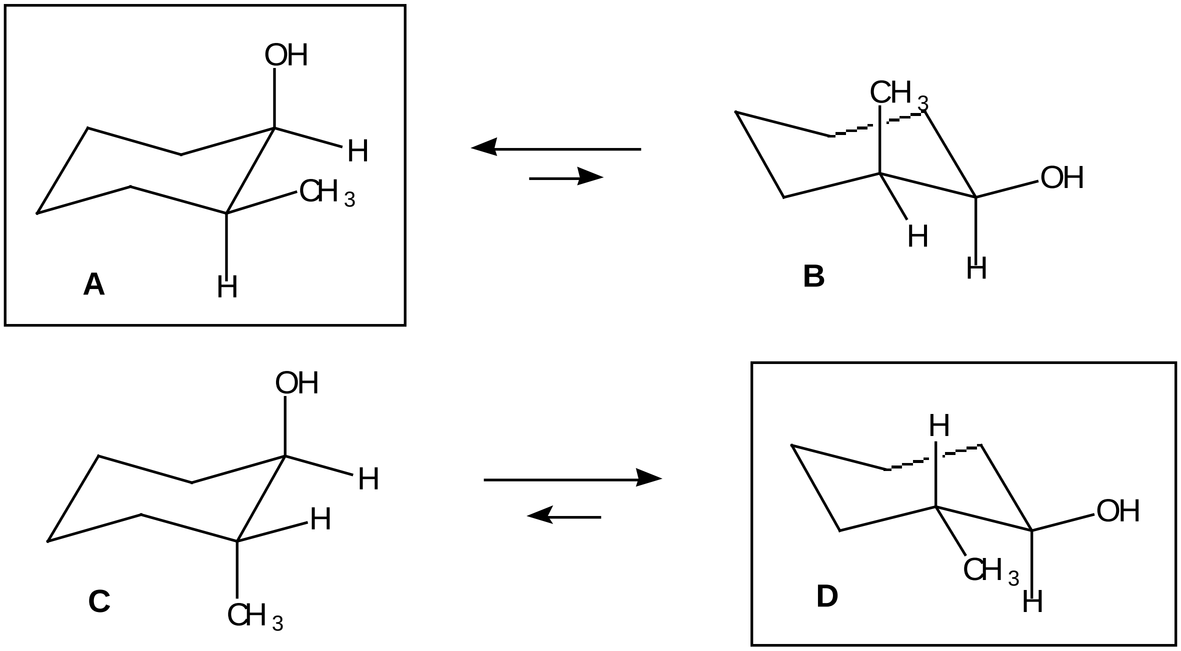


Compound **4** is the major product because the TS leading to it contains a partially formed trisubstituted double bond, which is more stable than the partially formed disibstituted double bond in the TS leading to **5**.

But where does **6** come from? It can’t be formed from the intially produced carbocation. There must be a hydride shift to make the more stable tertiary cation from the originally formed secondary cation. Now a proton can be plucked to give **4** (again) or **6**.

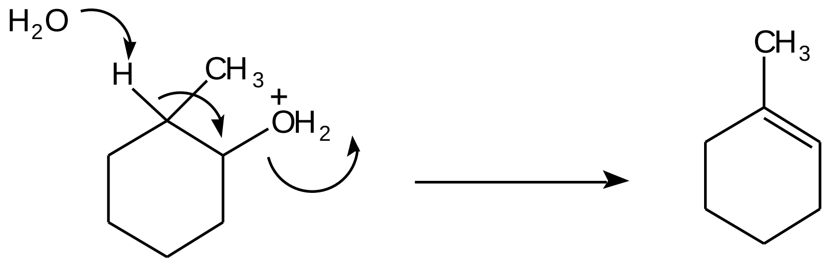


(b) Here are all four chairs. The energy minimum forms are boxed. Note that OH is smaller than CH_3.

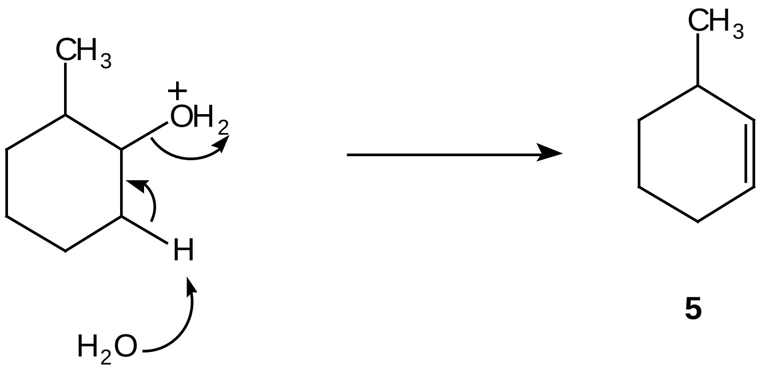


c. **A** is faster than **D**. Chair **D** is lower energy than chair **A** (or chair **B**), and thus is further from the transition state, and slower to react.

d. No, a changing product distribution is not consistent with a pure S$_N$1 reaction. Were the process to be pure S$_N$1, the intermediate carbocation formed from **3** is the same in each case, and must lead to exactly the same distribution of products. It appears that there is a competing E2 elimination to give **4** and **5**.



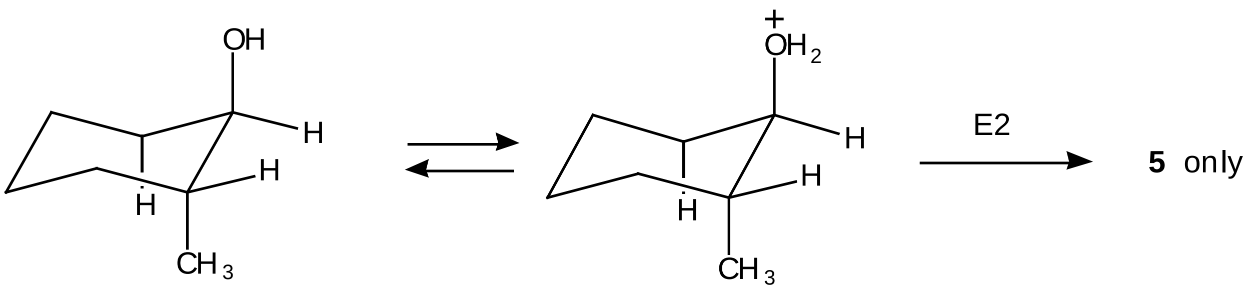
4



5

Compound **4** is still the major product because the transition state for **4** contains a partially formed trisubstituted double bond and the transition state for **5** contains a less stable partially formed disubstituted double bond.

Note that the less reactive trans isomer (chair **C**) can only give **5** in this E2 process.



So, as the slower E2 process becomes significant, more **5** is formed.