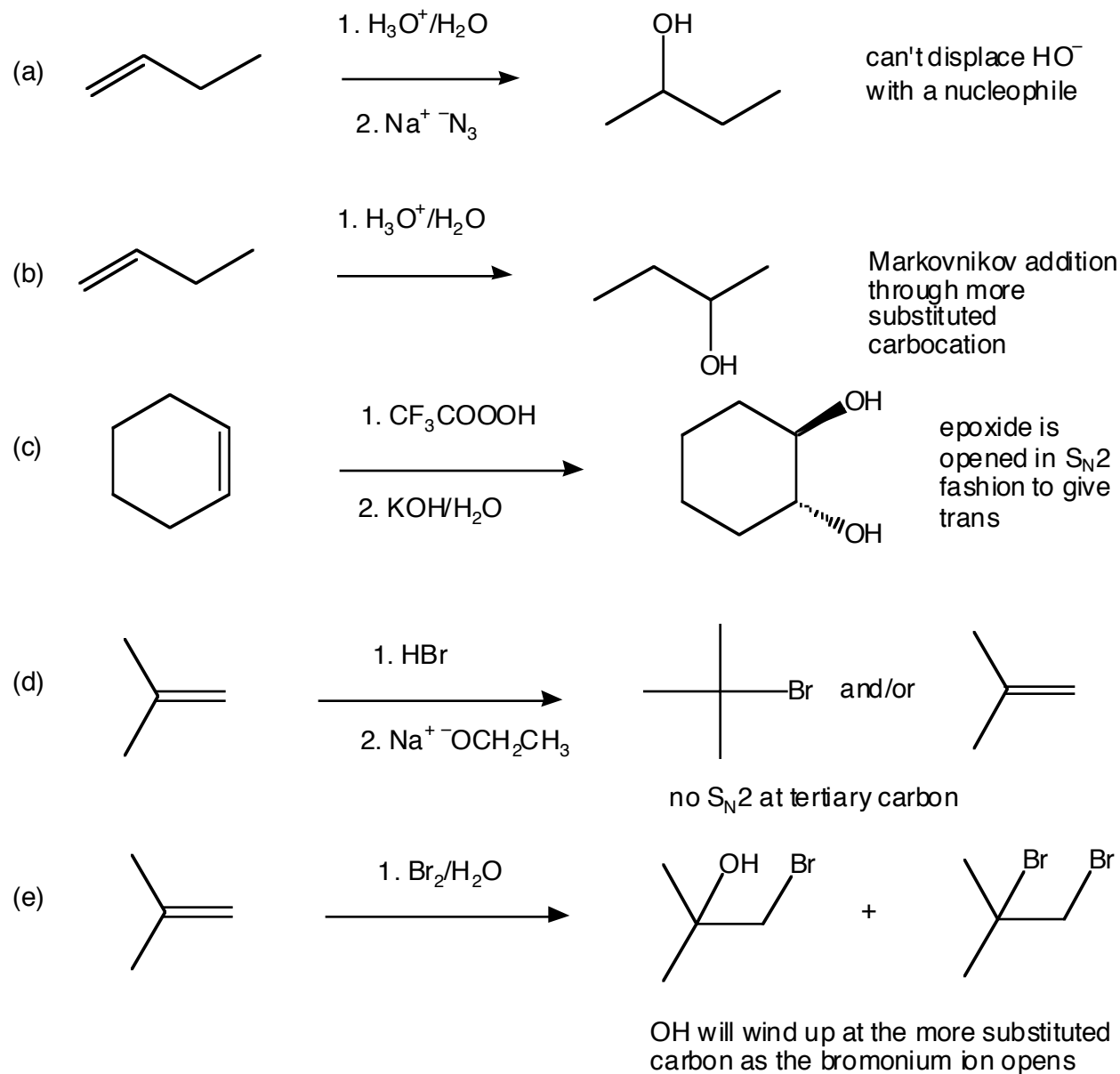


Answers to Hour Examination #3, Chemistry 301X - 2005

1.

real products



Fixes:

(a) 1. $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ 2. TsCl 3. $\text{Na}^+ \text{N}_3^-$

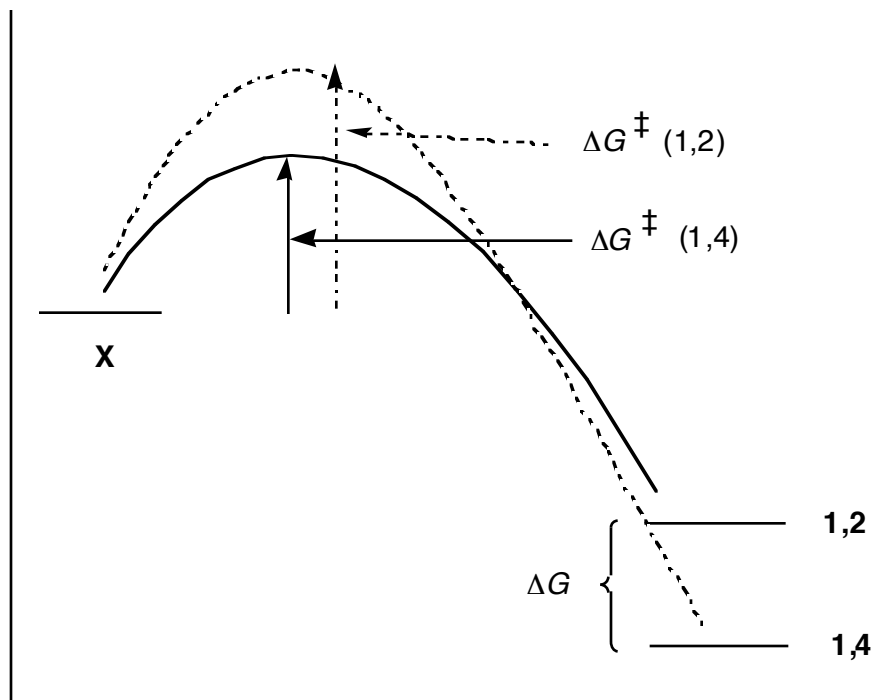
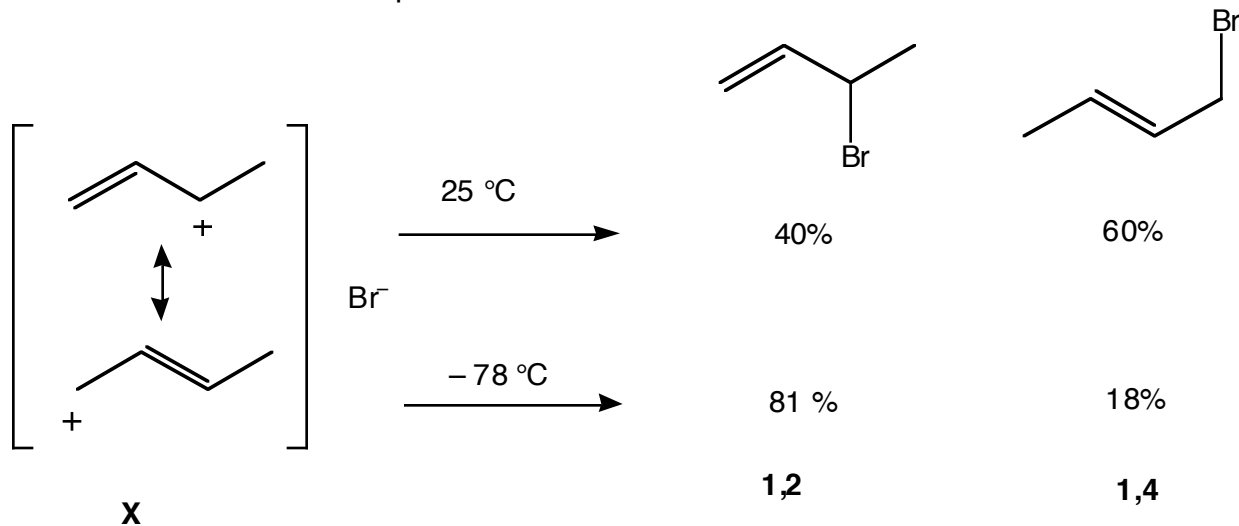
(b) 1. BH_3 2. HOOH/HO^-

(c) KMnO_4

(d) 1. $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ 2. NaH 3. $\text{CH}_3\text{CH}_2\text{I}$

(e) 1. CF_3COOOH 2. HBr

2. The data demand that the activation energy for formation of the lower energy 1,4-addition product must be higher than the activation energy for formation of the higher energy product of 1,2-addition. At high temperature (25 °C) the reaction is controlled by thermodynamics - there is enough available energy so that all the barriers can be crossed in both directions. At lower energy (− 78 °C) the reaction is kinetically controlled - controlled by the relative activation barriers for the two possible reactions.

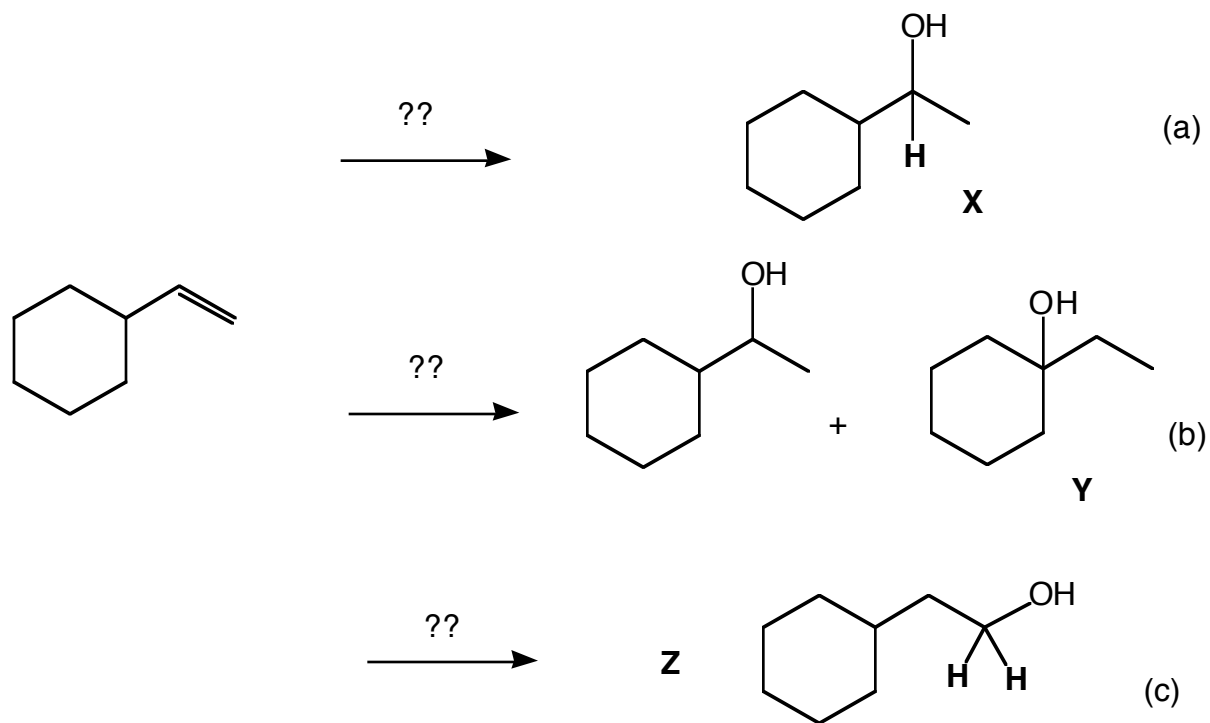


3.

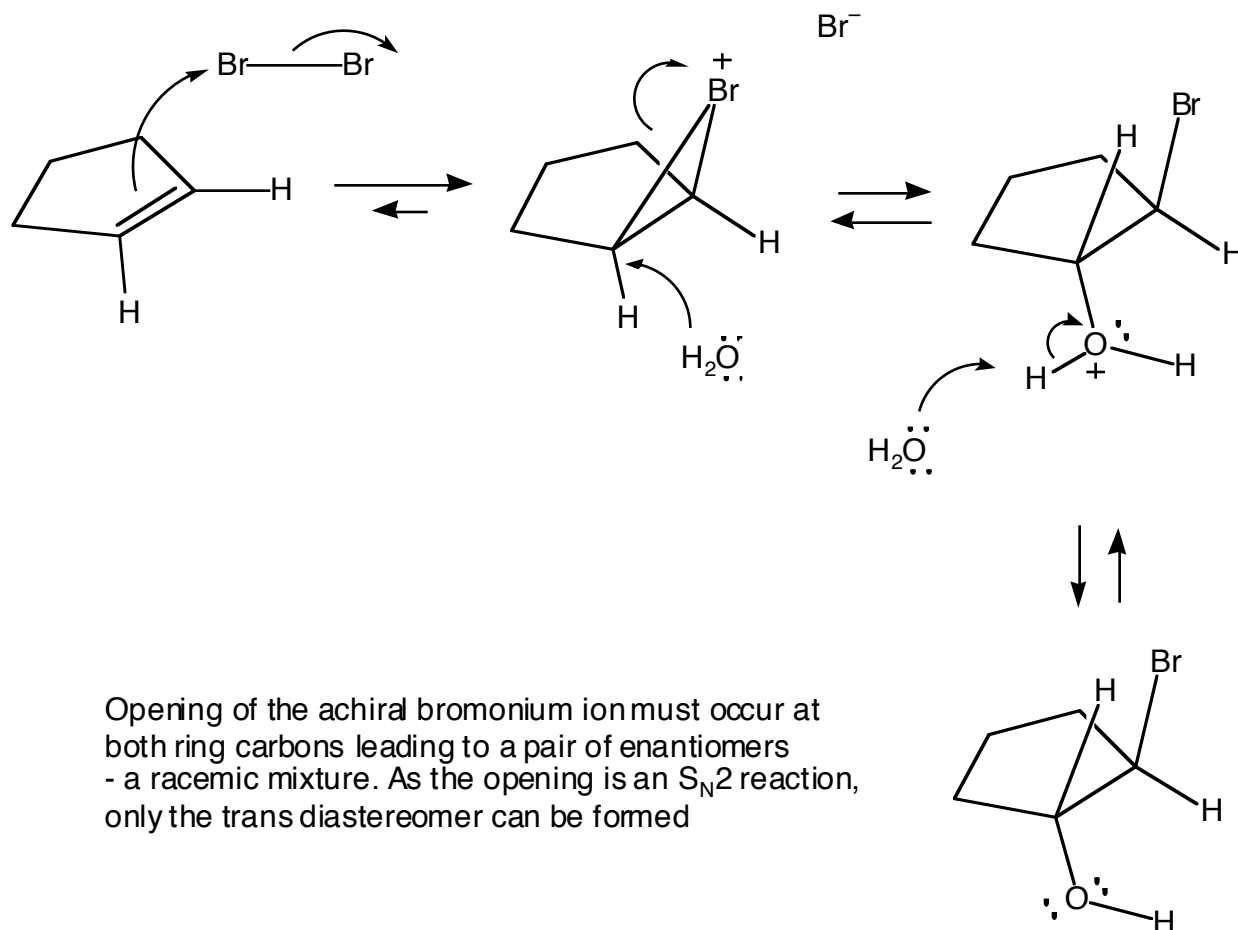
(a) 1. $\text{Hg}(\text{OAc})_2 / \text{H}_2\text{O}$ 2. $\text{NaBH}_4 / \text{HO}^-$

(b) $\text{H}_3\text{O}^+ / \text{H}_2\text{O}$

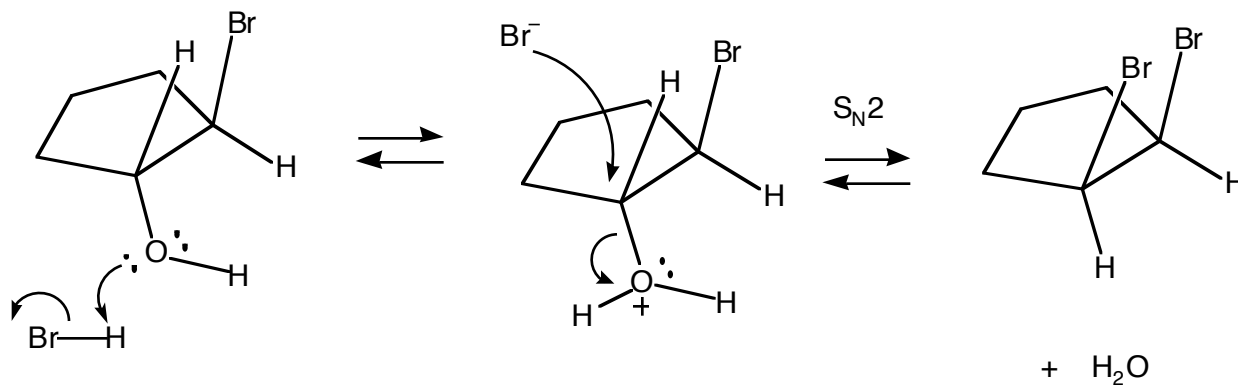
(c) 1. B_2H_6 2. $\text{HOOH} / \text{HO}^-$



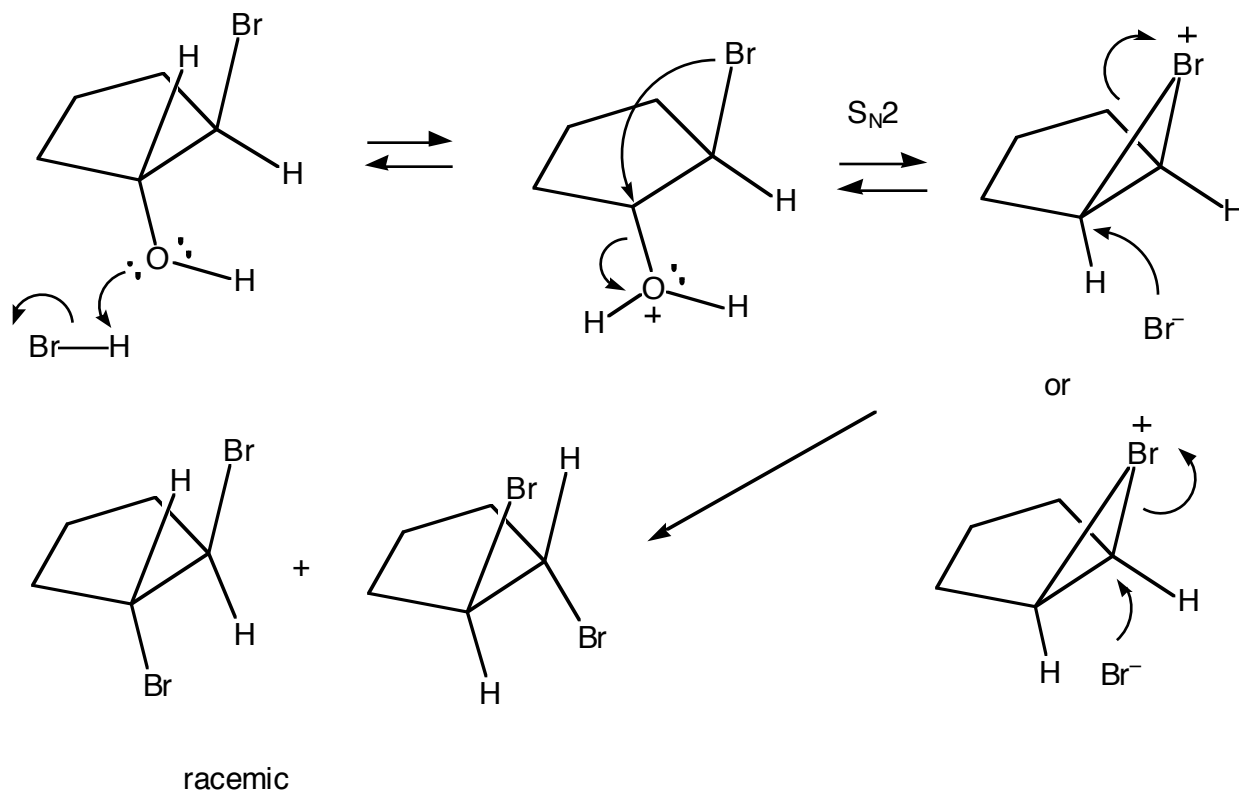
4. (a) Cyclopentene should form the two enantiomers of *trans*-1-bromo-2-hydroxycyclopentane, which is just what happens.



(b) Reaction of one of the enantiomers of the *trans* bromo - hydroxy product with HBr will begin with protonation of the OH to produce a good leaving group. I. B. expected the usual displacement by bromide to give the *cis* 1,2-dibromo compound, a meso compound.



But in the protonated alcohol, the bromine is poised in great position to reform the achiral bromonium ion, which can open in S_N2 fashion in two ways to give the racemic *trans*-1,2-dibromocyclopentane.

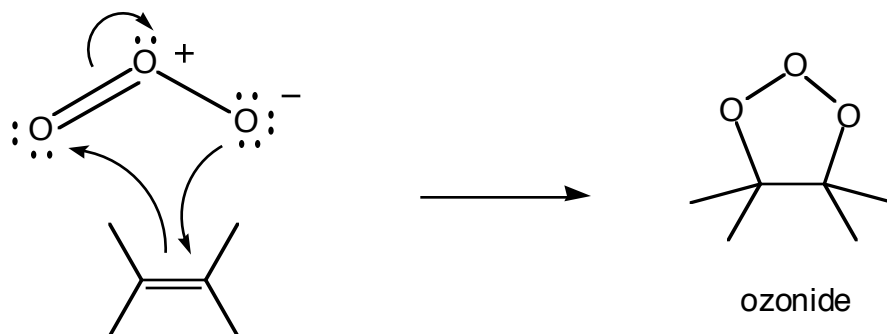


Please note that an answer that lost water from the protonated alcohol in S_N1 fashion, followed by capture by bromide must give the meso *cis* compound and *optically active* *trans* compound. A mechanism in which water is lost in S_N1 fashion and then the bromonium ion is formed is OK.

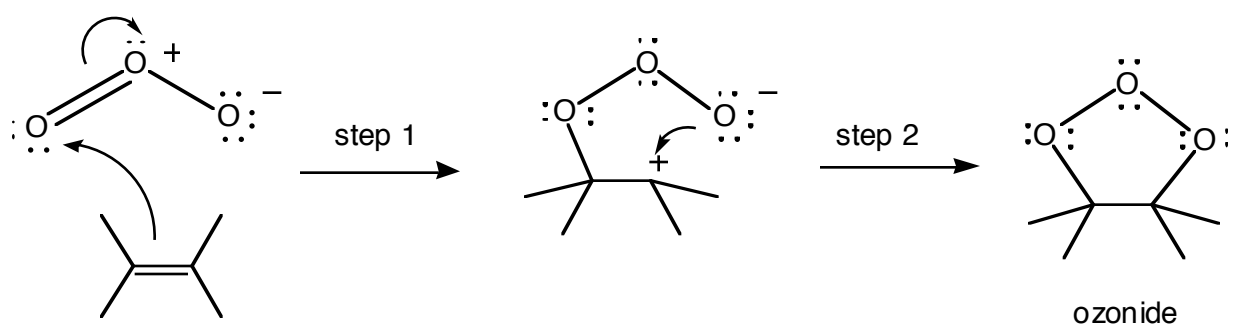
5.

(a)

concerted - both bonds formed in a single step

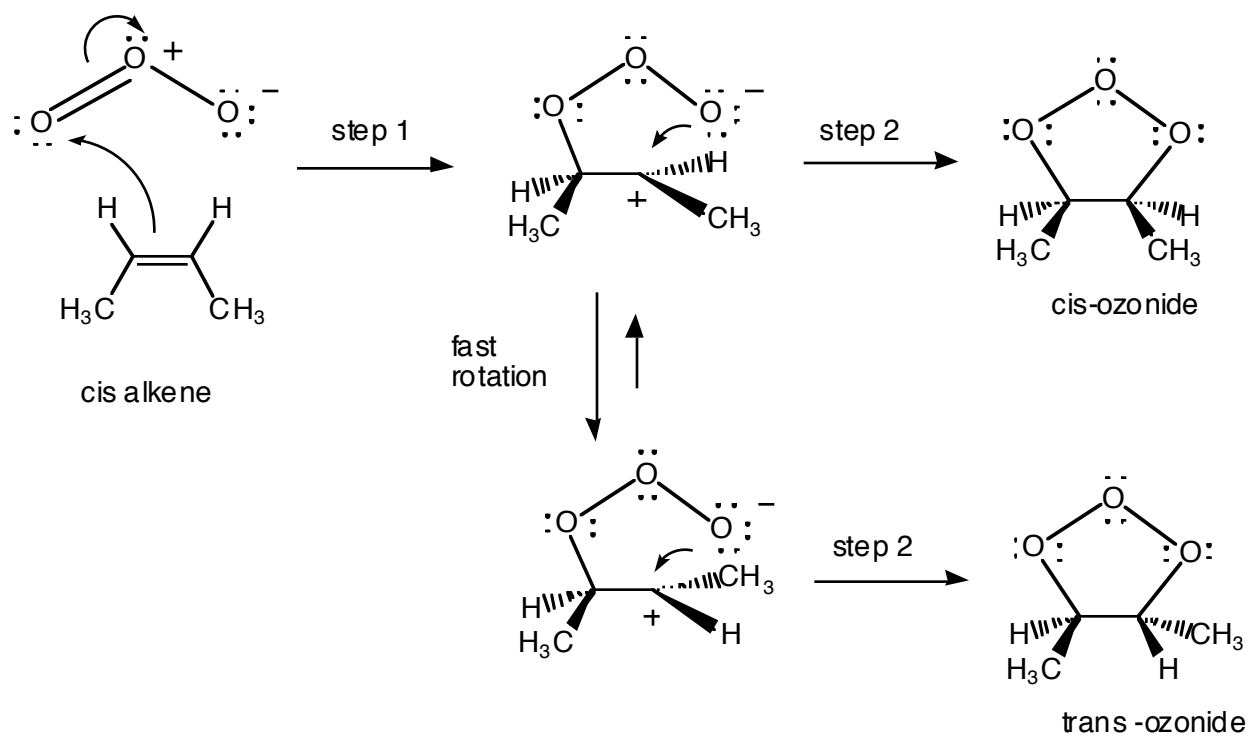


two-step - the bonds are formed in separate steps

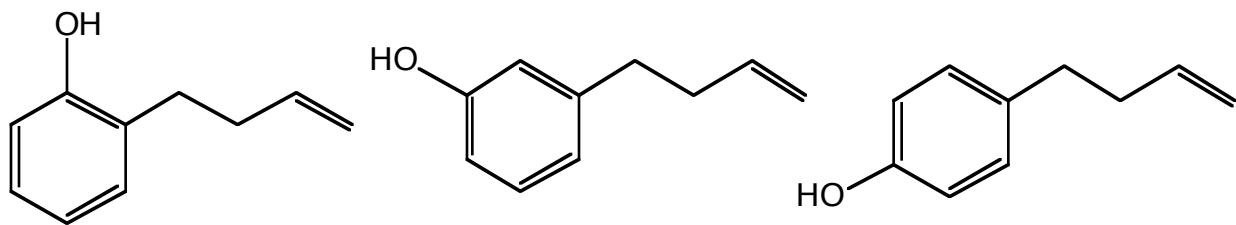


(b) The best way is to probe for rotation in the putative intermediate. Any alkene with "sides" will do - *cis*-2-butene is traditional. If stereochemistry is scrambled, the mechanism is two-step. If not, one step.

two-step - the bonds are formed in separate steps

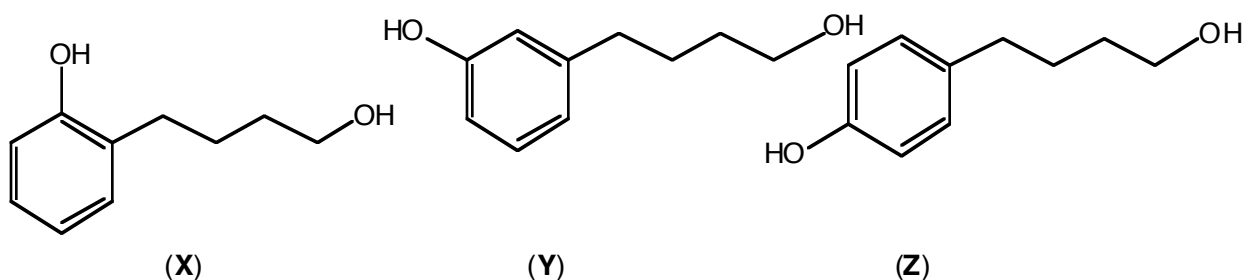


6. The three possibilities for **1** are:



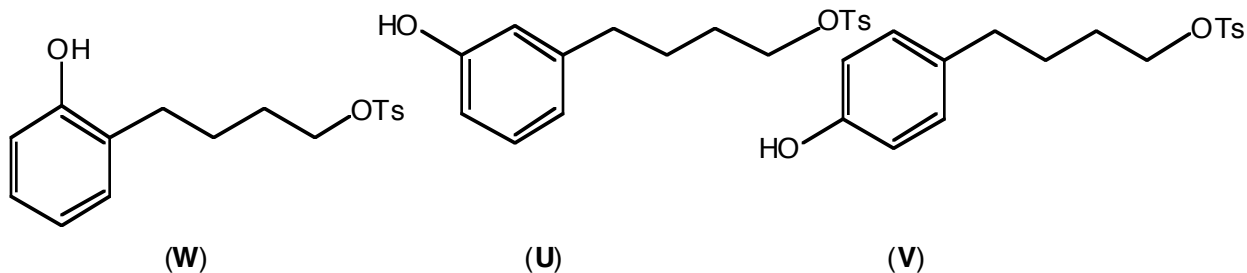
Reaction one is a hydroboration/oxidation. The product is an alcohol, and there are no surprises here at all. There are still three possibilities, **X**, **Y**, and **Z**:

1

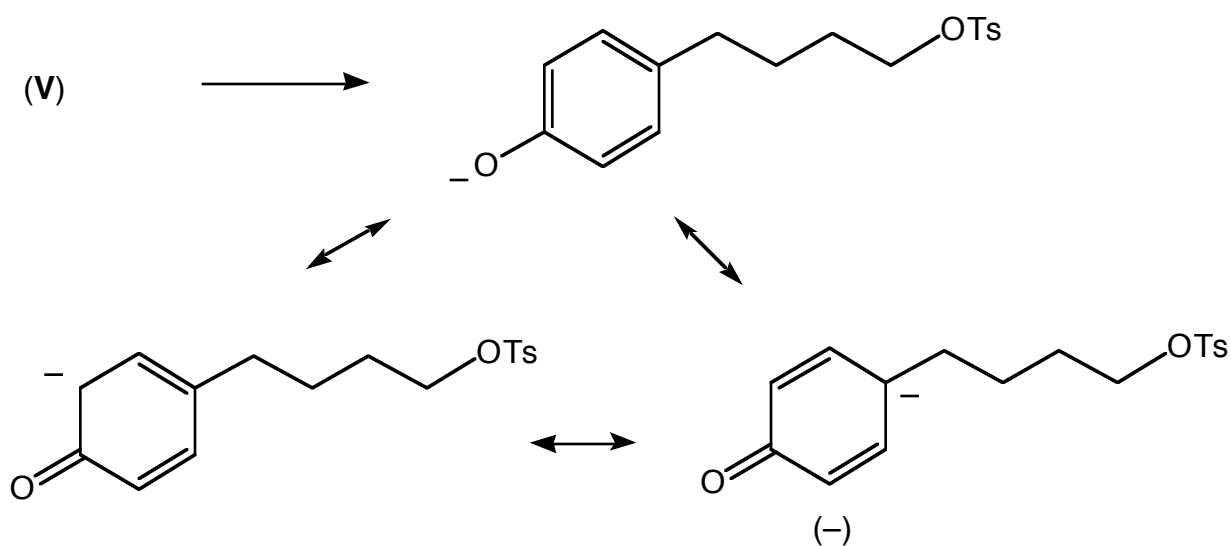
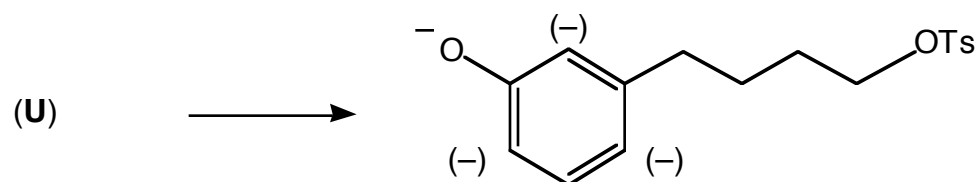
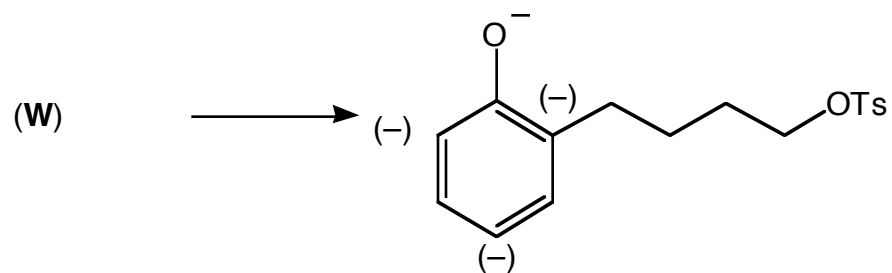


Reaction two makes a tosylate out of an alcohol - still three possibilities, **W**, **U**, and **V**

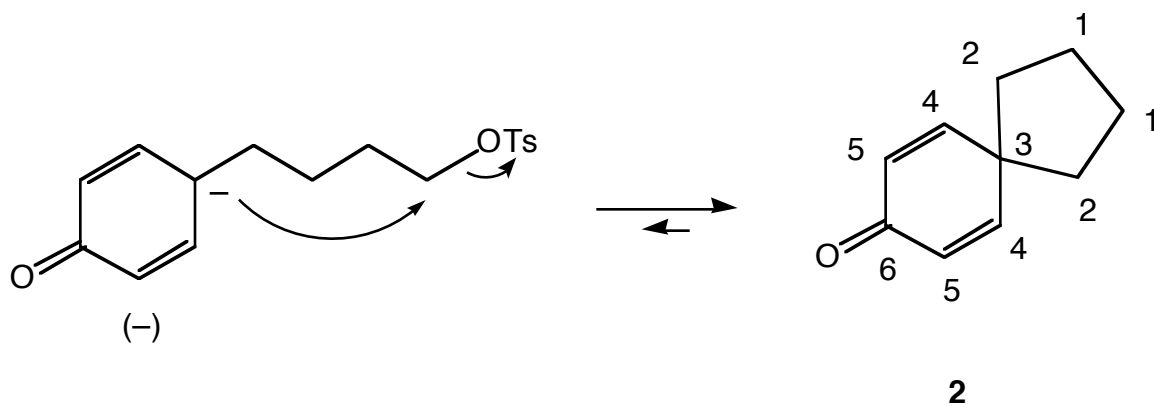
:



The third reaction does the trick. Look at the formula- the tosylate is lost. That is hardly surprising, as that is tosylate's job - to be a leaving group. But this is no ordinary S_N2 displacement or $E2$ elimination. Both of these reactions would leave an OH in the molecule and the IR specifically tells you there is no OH left. Something must happen that destroys the OH (some of the "action" must be at the OH on the ring). The strong band at 1670 cm^{-1} is indicative of a conjugated carbonyl group, and the ^{13}C NMR tells you that there are only six different carbons in **2**. There has been a fair amount of symmetrization. What can happen in base, if there is no displacement or elimination? Well, if the OH has to go away, let's start there - how about a deprotonation by carbonate? The result is a well resonance stabilized intermediate in each case. For **V**, some resonance forms are drawn out, for others the forms are indicated with "(−)".



Now many intramolecular displacements of OTs are possible, but only the one shown yields a product with only six different carbons.



The structure of **1** must be:

