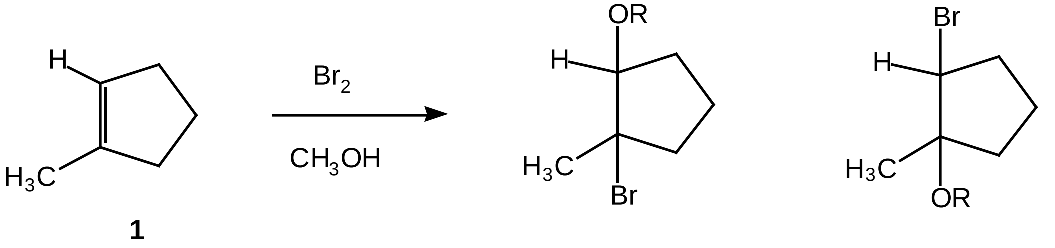
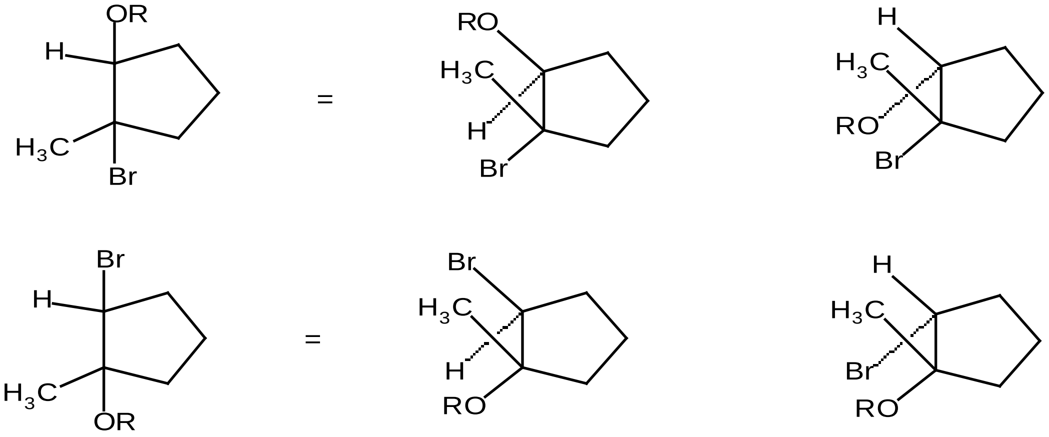
Answers to Hour Examination #3, Chemistry 301-301A - 2004

1. (a) There are two possible regiochemistries, each of which can, in principle, give cis or trans products.



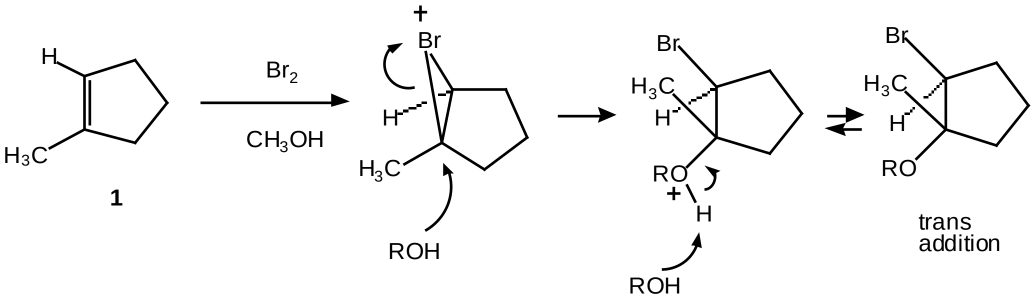
possible regiochemistries - no stereochemistry implied (yet)

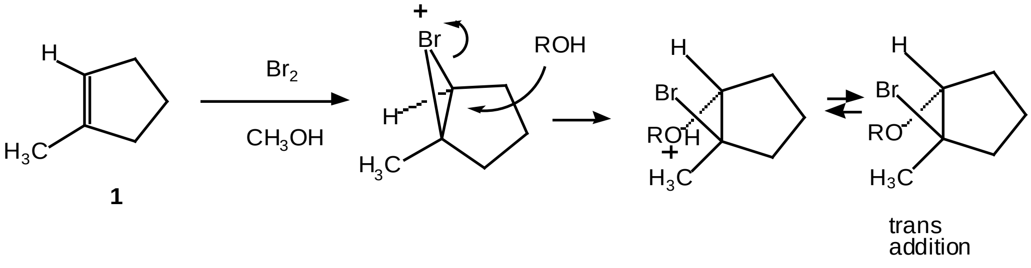
Here are the stereochemical possibities:



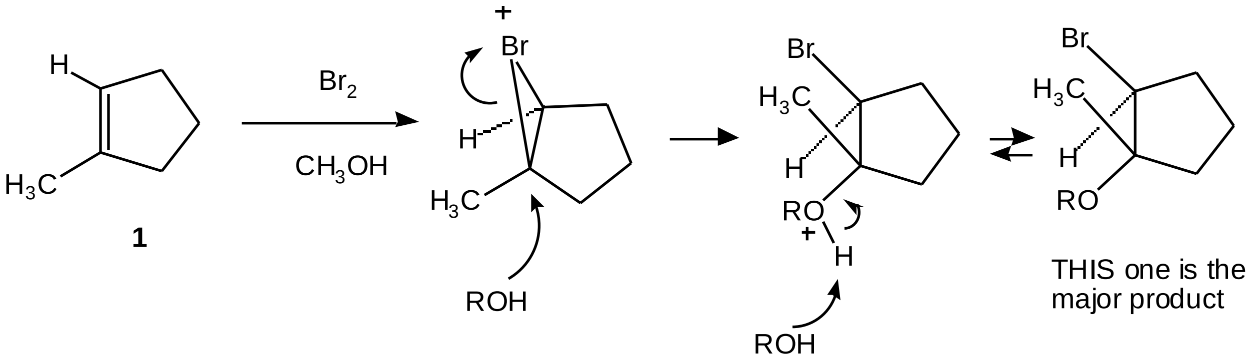
(b) As the starting materials are achiral, there can be no optical activity in the product.

(c) The first step is formation of a bromonium ion. Opening of that ion by methanol is an S_N2 reaction, thus assuring overall trans addition.





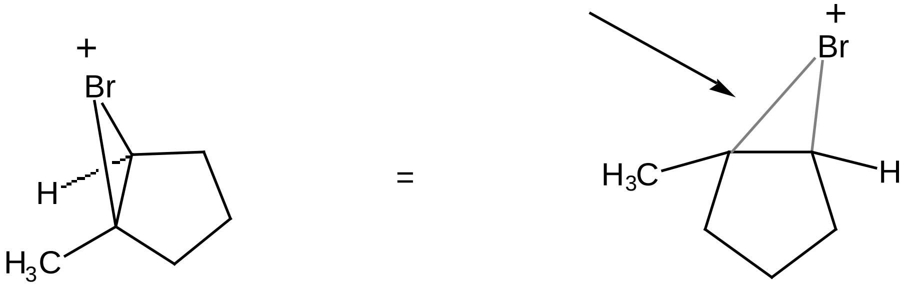
What about the regiochemistry? In fact, the major product is the one in which the RO group winds up on the more substituted carbon of the former alkene. The ‘onium ion is unsymmetric in this case and most of the charge on carbon is on the tertiary carbon, not the secondary carbon. Thus, one bond from carbon to bromine is longer and weaker than the other, and will be much easier to break.



1

THIS one is the major product

easier to break this bond



2.

(a) H_3O^+/H_2O

(b) 1. BH_3 (B_2H_6) 2. $HOOH/HO^-$

(c) product from (b) and HBr

(d) HBr

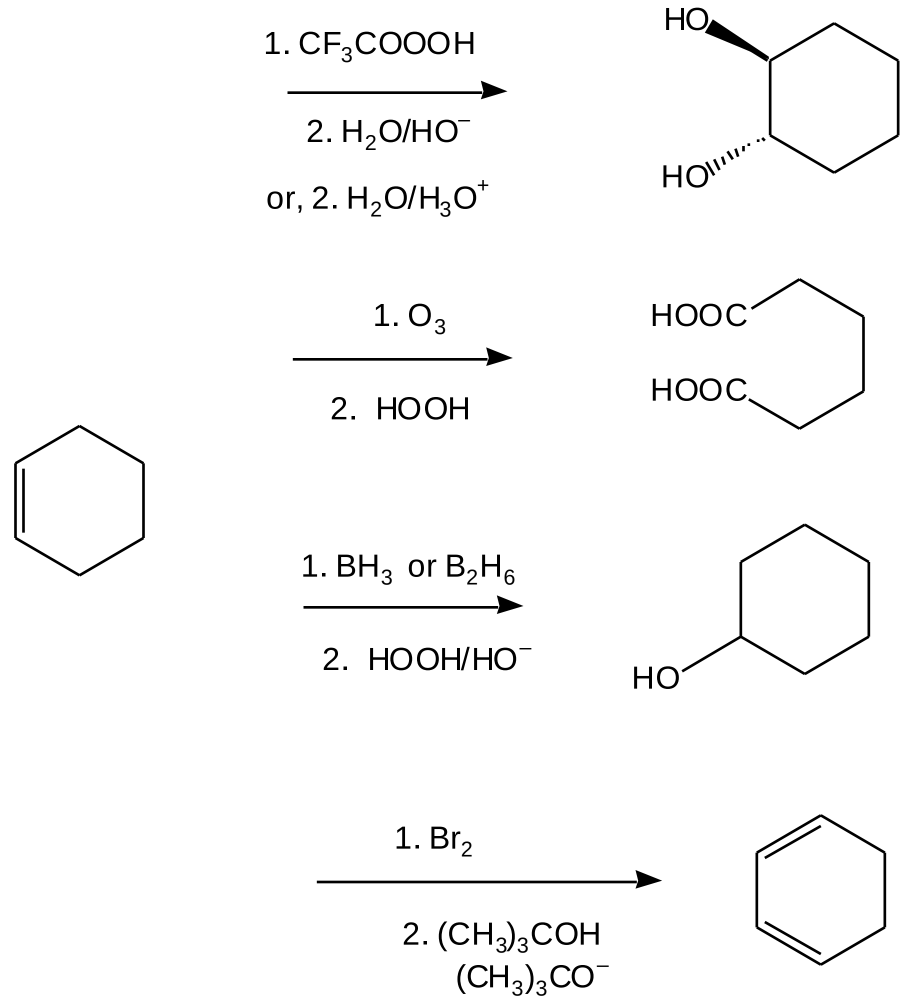
(e) 1. CF_3COOOH 2. H_3O^+/H_2O

(f) product from (b) ---> 1. NaH 2. CH_3I

(g) CH_2N_2 and light (or heat)

(h) 1. O_3 2. HOOH

3a.



3b. There are, of course many ways to do each. From the top:

a) real compound will have strong OH stretch at ~3300 - 3500 cm^{-1}

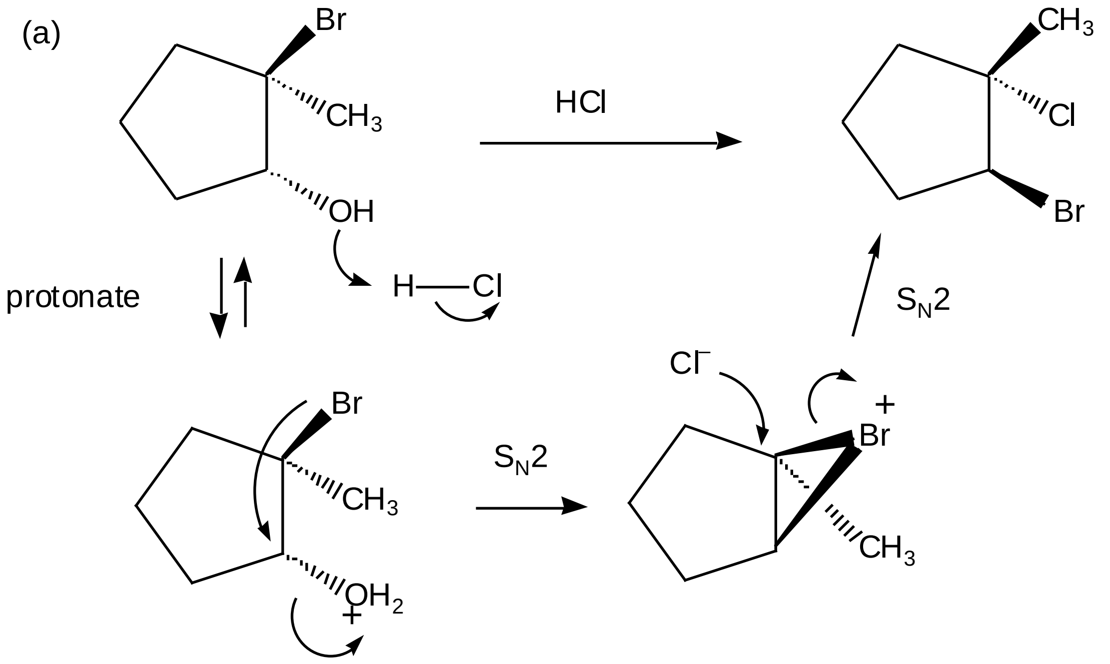
b) real compound will lack the “aldehyde couplet” at 2850 and 2750 cm^{-1}

(c) real compound has no low field signal for the C=O carbon in the ^{13}C NMR spectrum (~ 200 ppm)

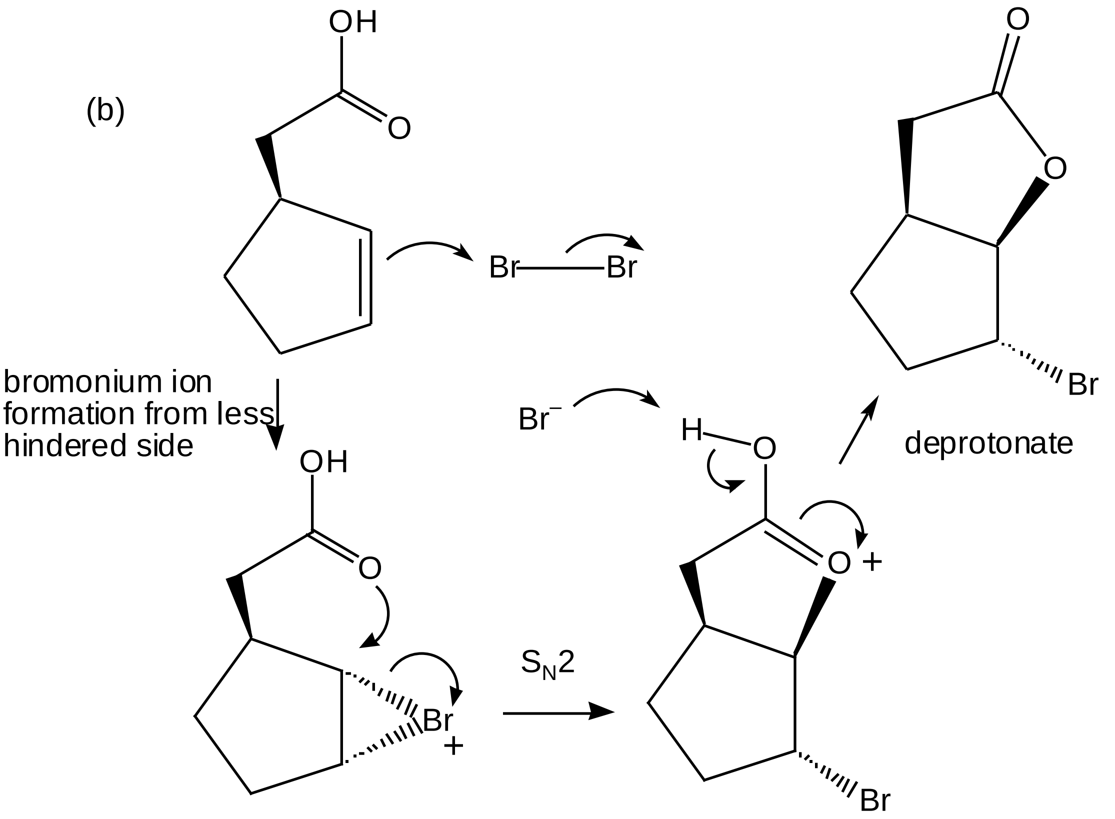
(d) real product has three different carbons (and three different hydrogens) whereas the wrong compound has two different carbons and two different hydrogens.

4.

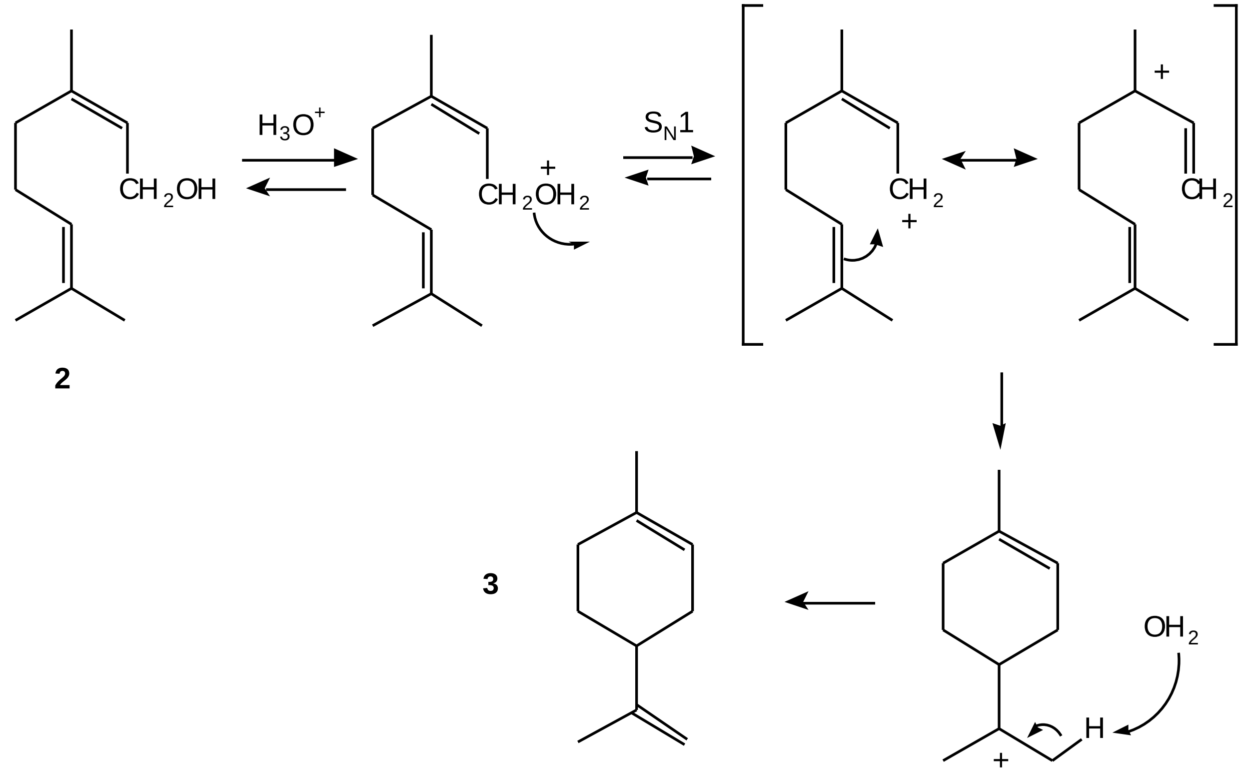
(a)


Br
CH3
OH
HCl
CH3
Cl
Br
H—Cl
protonate
SN2
Cl⁻
+
Br
CH3
Br
CH3
OH2
+
SN2

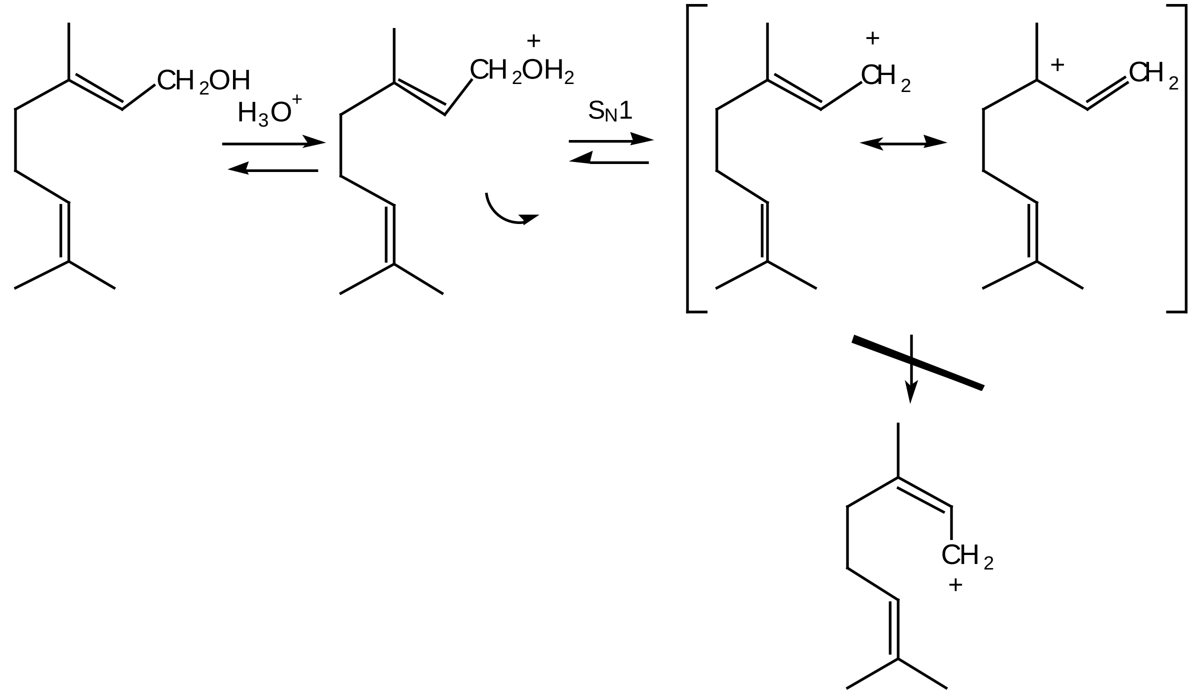
(b)


OH
O
Br—Br
O
O
Br
bromonium ion
formation from less
hindered side
Br⁻
H
O
deprotonate
OH
O
Br
+
SN2
O +
Br

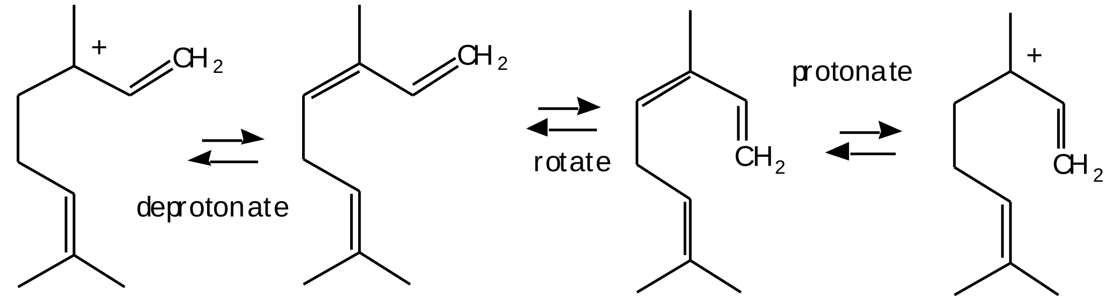
5. Here is a straightforward **2** -> **3** mechanism:

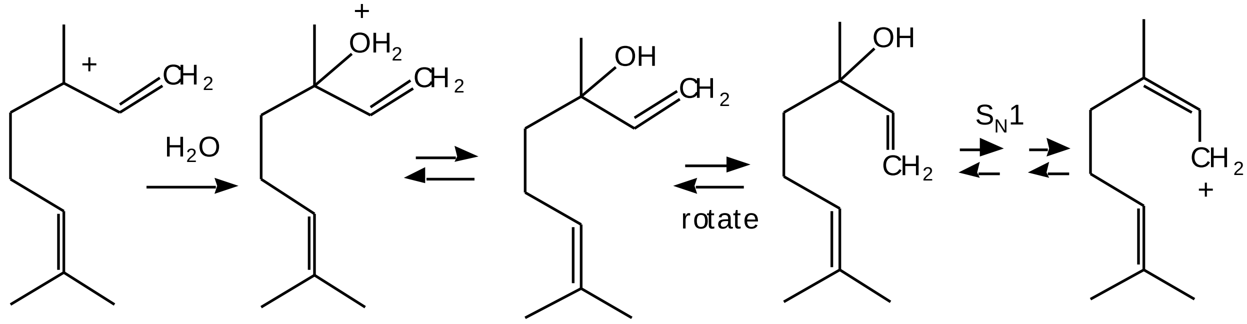


The isomeric **4** is more difficult because of stereochemical problems. The allyl cation is made up of overlapping 2*p* orbitals, and there is not free rotation. You can't just trivially turn it over so the ring closure can take place.



There are several possible solutions. First, you might just note that the stereochemical isomerization necessary will not be as costly as the 66 kcal/mol required to isomerize around a simple alkene. Alternatively, you might write a deprotonation, rotate, reprotonation scheme. Finally, you might capture that allyl cation with water to give **A**, rotate, and then do another S_N1. There are many possible variations.





A