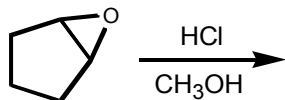


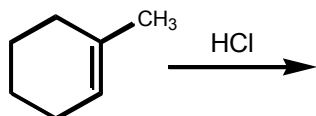
ORGANIC CHEMISTRY I – PRACTICE EXERCISE
Alkene reactions and mechanisms

FOR QUESTIONS 1-24, GIVE THE MAJOR ORGANIC PRODUCT OF THE REACTION, PAYING PARTICULAR ATTENTION TO REGIO- AND STEREOCHEMICAL OUTCOMES.

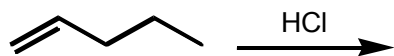
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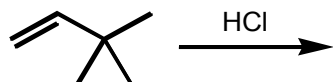
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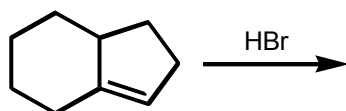
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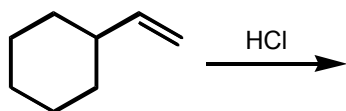
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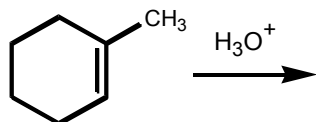
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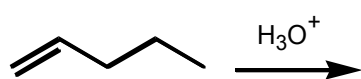
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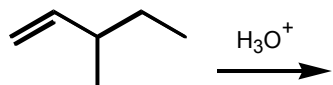
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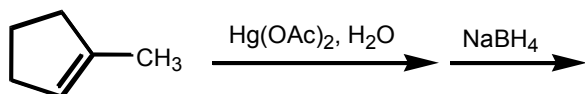
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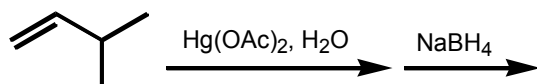
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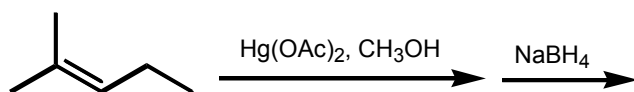
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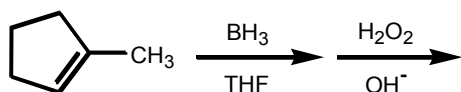
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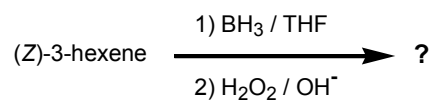
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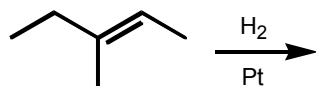
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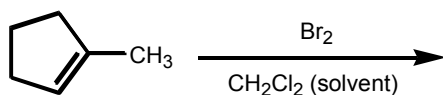
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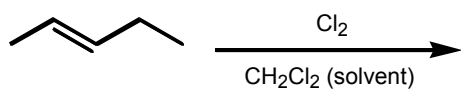
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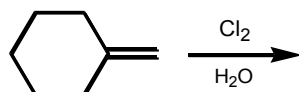
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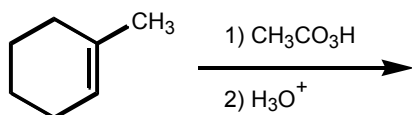
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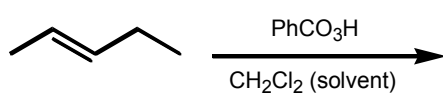
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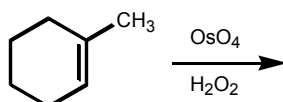
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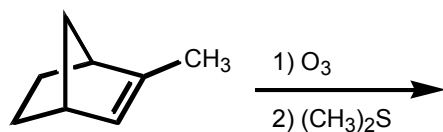
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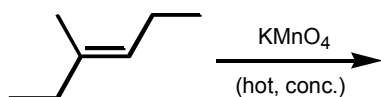
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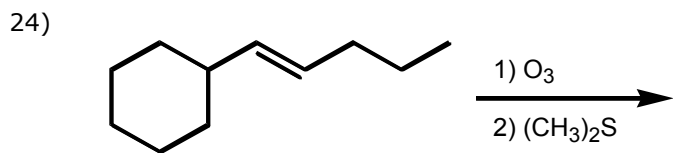


22)



23)

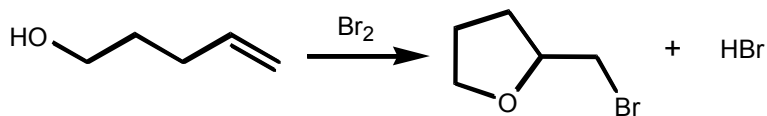




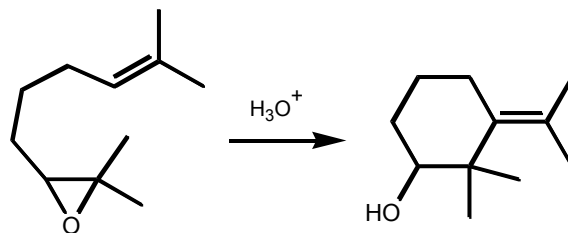
25) Treatment of cyclopentene with peroxybenzoic acid

- A) results in oxidative cleavage of the ring to produce an acyclic compound
- B) yields a meso epoxide
- C) yields an equimolar mixture of enantiomeric epoxides
- D) gives the same product as treatment of cyclopentene with OsO_4
- E) none of the above

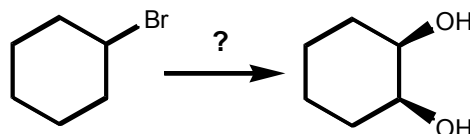
26) Provide a detailed, step-by-step mechanism for the reaction shown below.



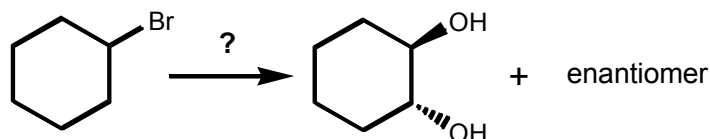
27) Provide a detailed, step-by-step mechanism for the reaction shown below.



28) Provide the reagents necessary to complete the following transformation. The synthesis may involve more than one step.



29) Provide the reagents necessary to complete the following transformation. The synthesis may involve more than one step.

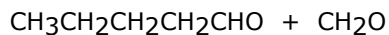


30) Provide the reagents necessary to convert 3-methyl-2-butanol to 2-methyl-2-butanol. The synthesis may involve more than one step.

31) Both (*E*)- and (*Z*)-hex-3-ene are subjected to a hydroboration-oxidation sequence. How are the products from these two reactions related to each other?

- A) The (*E*)- and (*Z*)-isomers generate the same products but in differing amounts.
- B) The (*E*)- and (*Z*)-isomers generate the same products in exactly the same amounts.
- C) The products of the two isomers are related as constitutional isomers.
- D) The products of the two isomers are related as diastereomers.
- E) The products of the two isomers are not structurally related.

32) What alkene would yield the following products upon ozonolysis?



33) Addition of Br₂ to (*E*)-hex-3-ene produces

- A) a meso dibromide
- B) a mixture of enantiomeric dibromides which is optically active
- C) a mixture of enantiomeric dibromides which is optically inactive
- D) (*Z*)-3,4-dibromo-3-hexene
- E) (*E*)-3,4-dibromo-3-hexene

34) The mechanism for the acid-catalyzed hydration of alkenes is the reverse of the acid-catalyzed dehydration of alcohols. This illustrates the principle of _____.

35) Which of the following is the best reaction sequence to accomplish a Markovnikov addition of water to an alkene with minimal skeletal rearrangement?

- A) water + dilute acid
- B) water + concentrated acid
- C) oxymercuration-demercuration
- D) hydroboration-oxidation
- E) none of the above

36) Which of the following additions to alkenes occur(s) specifically in an anti fashion?

- A) hydroboration-oxidation
- B) addition of Br₂
- C) addition of H₂
- D) addition of H₂O in dilute acid
- E) both A and B

37) Which of the following additions to alkenes occur(s) specifically in an syn fashion?

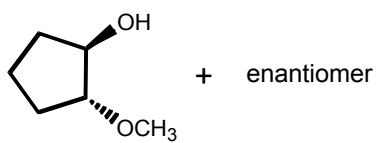
- A) dihydroxylation using OsO₄, H₂O₂
- B) addition of H₂
- C) hydroboration
- D) addition of HCl
- E) A, B, and C

38) HBr can be added to an alkene in the presence of peroxides (ROOR). What function does the peroxide serve in this reaction?

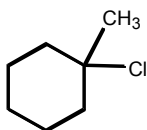
- A) nucleophile
- B) electrophile
- C) radical chain initiator
- D) acid catalyst
- E) solvent

ANSWERS

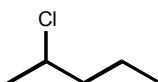
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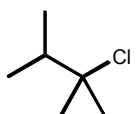
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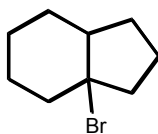
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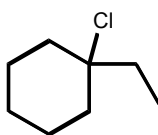
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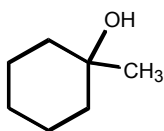
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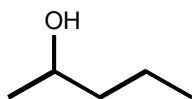
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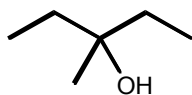
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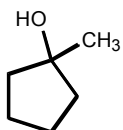
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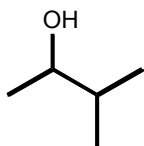
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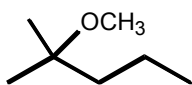
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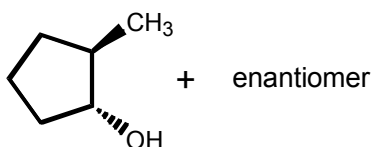
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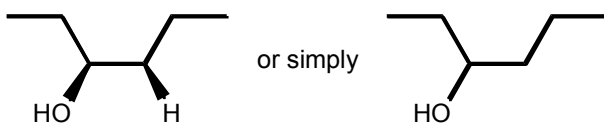
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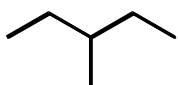
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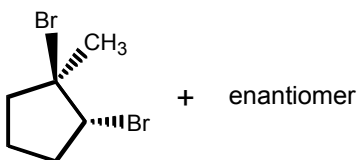
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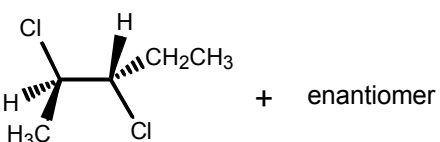
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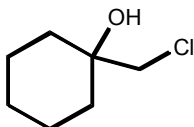
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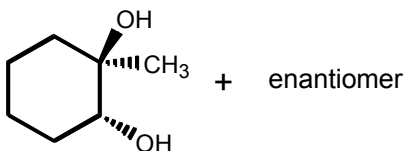
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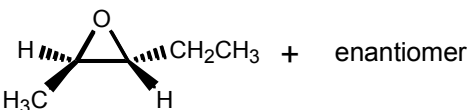
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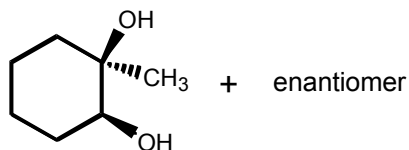
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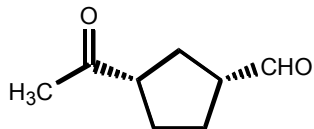
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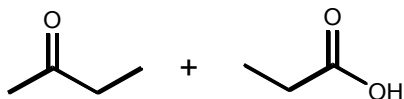
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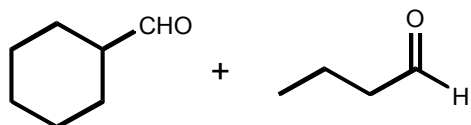
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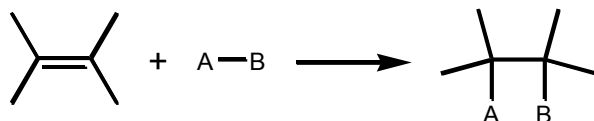


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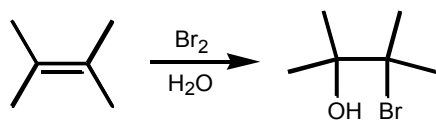


25) B

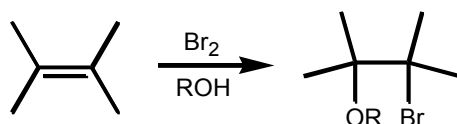
26) This mechanism is best approached by working backwards. The product shown is an ether-bromide, with the oxygen and the bromine atoms on adjacent carbons. Every time two functional groups are on adjacent carbons it suggests the possibility that they might be formed by an addition to the C=C double bond. This can be represented generically thus:



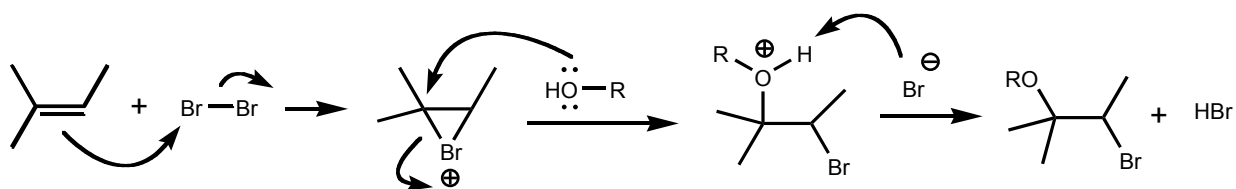
An addition of bromine in the presence of water produces such result, adding Br to one carbon and OH to the other (section 8-11 in the textbook).



This suggests the possibility that an alcohol could be used instead of water, with similar results, except that this would add Br to one carbon and RO to the other one.



The mechanism of this reaction would be similar to that with water. Bromine adds first to form a three membered ring intermediate, followed by nucleophilic attack by the alcohol from the back. Let's use an unsymmetrical alkene to illustrate the point that the most highly substituted carbon gets the RO group preferentially.



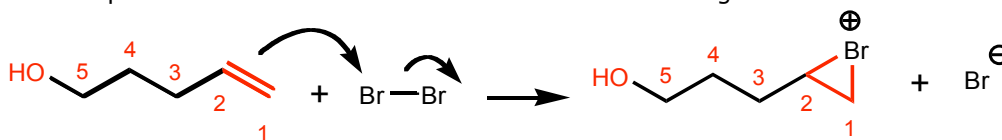
The molecule in question has an oxygen (ether group) and a bromine on adjacent carbons. We can make a similar reasoning as above that such arrangement forms from the reaction between a C=C bond and Br₂ in the presence of an alcohol, a group that also happens to be present in the starting material.



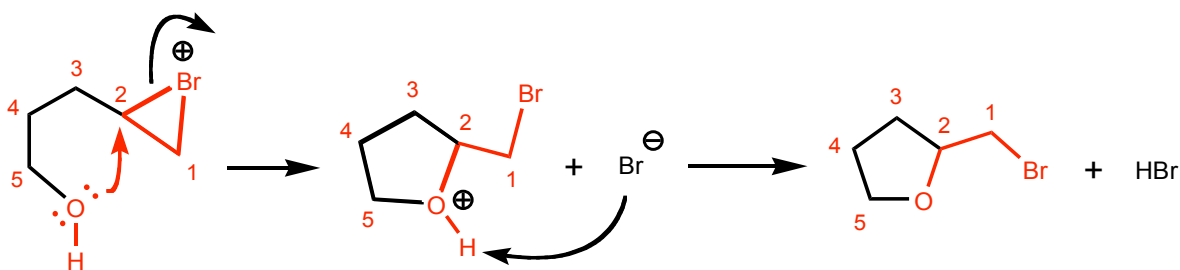
The ether and bromine groups are on adjacent carbons, suggesting that the original double bond was between C₁ and C₂. Notice the oxygen on C₅

The starting material also happens to have 5 carbons, with the double bond on C₁ and C₂, and the oxygen on C₅.

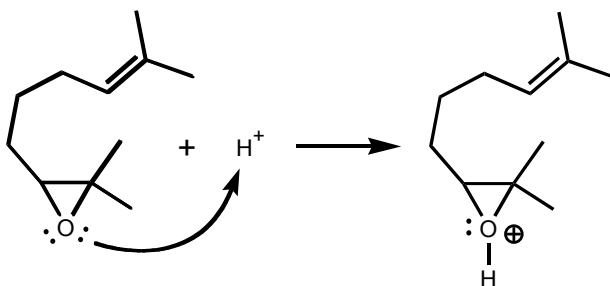
With this scenario in place, we can now start the mechanism from the first step, which would be the attack of the pi-bond on bromine to form a three membered ring intermediate.



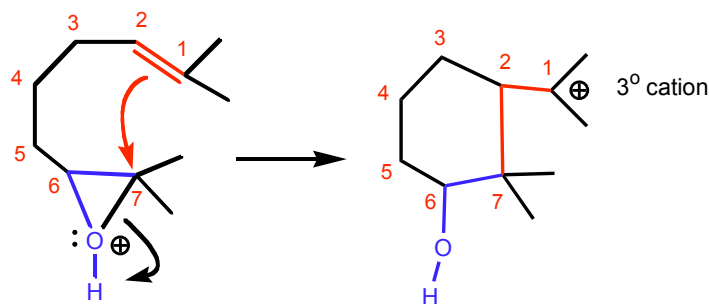
The alcohol group is now poised to attack the three membered ring at the most highly substituted carbon. The carbon chain is long enough to allow for flexibility of movement without introducing strain.



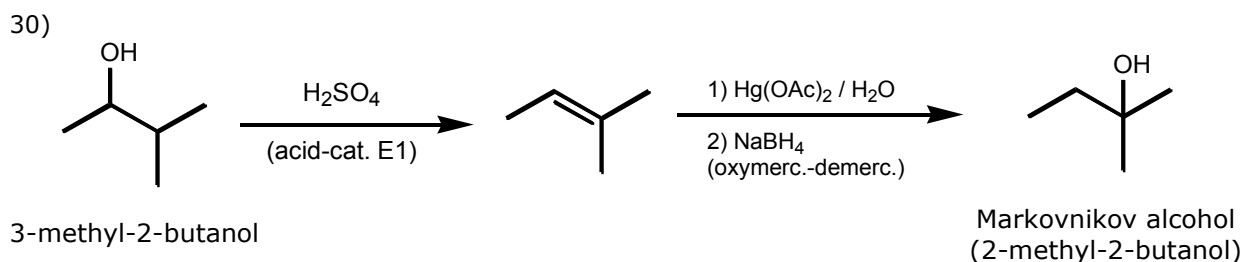
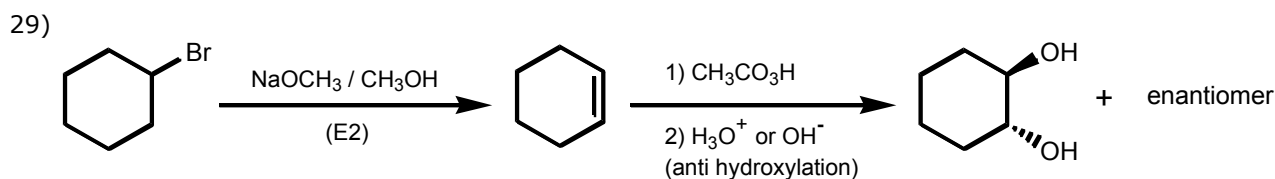
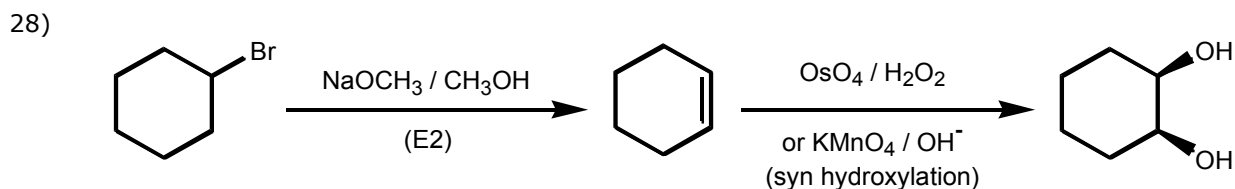
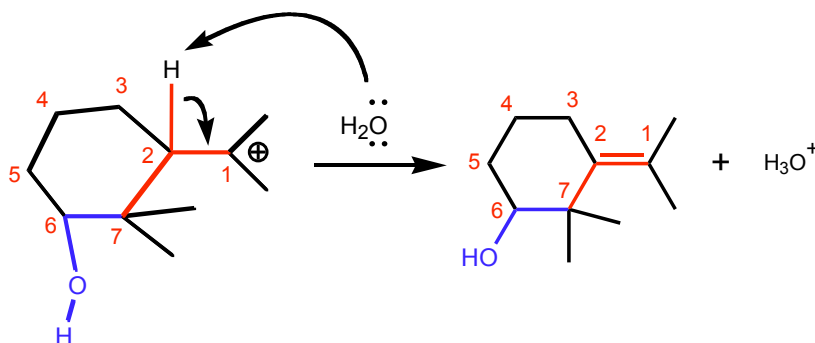
27) When the starting material gets placed in acid, two (basic) sites can get protonated: the oxygen atom and the pi-bond. The pi-bond is a weak base,. Energy must be expended to break it in order to protonate it and form a carbocation. The oxygen is also basic, but its unshared electrons are not tied up in bonding and are ready to react. Protonation occurs at the oxygen first.



The pi-bond is now poised to attack the three membered ring from the back at the most highly substituted carbon, to open it. At the same time, a tertiary carbocation forms at one of the carbons originally sharing the pi-bond. A new bond forms between carbons 2 and 7, which results in formation of a new 6-membered ring.



The tertiary cation undergoes an elimination reaction, losing the adjacent proton to make the new pi-bond present in the product.



31) B 32) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ 33) A 34) microscopic reversibility

35) C 36) B 37) E 38) C