

NAME: \_\_\_\_\_

1) (3x2=6pts) Define the following terms.

*Electrophile*

*Protic Acid*

*Mechanism*

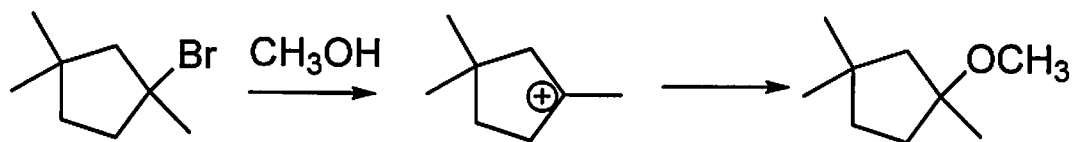
2) (3x2= 6pts) What are the precise chemical meanings of the following three arrows?



3) (2pts) Name two of the things you should check when critically evaluating the curly arrows you have drawn to represent a mechanism.

4) (14 pts) For this reaction:

a) (2+2+2pts) Label the NUCLEOPHILE, ELECTROPHILE and LEAVING GROUP.

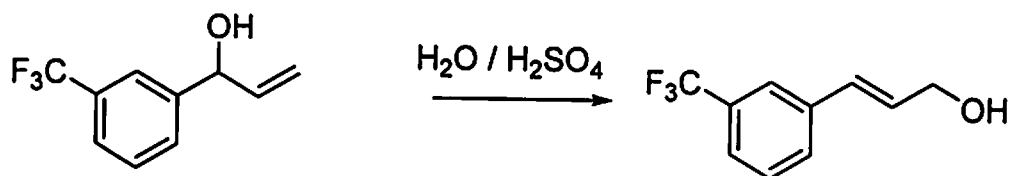


b) (2pts) State the name of this particular type of mechanism (which should include letters and numbers).

c) (2pts) If the starting material was a single enantiomer, what would you expect the stereochemistry of the product to be?

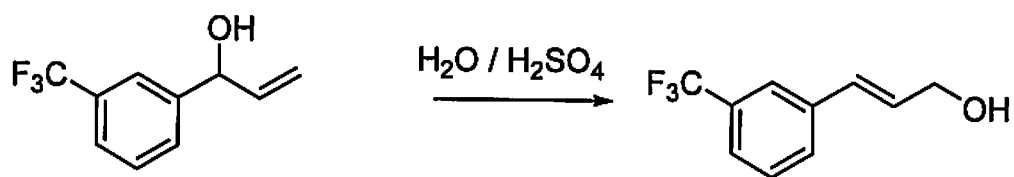
d) (4pts) Draw the mechanism (*i.e. curly arrows*) for this reaction.

5) (13pts) The following reaction is an acid catalyzed isomerization.

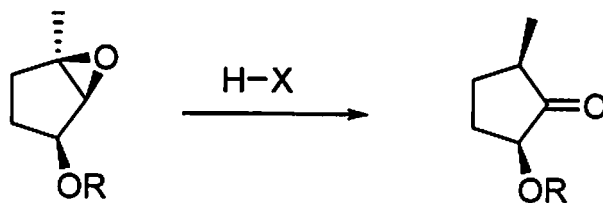


- a) (1pt) What type of isomers are the starting material and product?
- b) (1pt) Identify the most acidic component in this reaction.
- c) (1pt) Acids protonate things, such as lone pairs and  $\pi$  bonds. How many  $\pi$  bonds are in the starting material?
- d) (1pt) How many lone pairs (non-bonding pairs of electrons) are on the Oxygen of the starting material?
- e) (1pt) Provide one reason why lone pairs are usually more easily protonated than  $\pi$  bonds.
- f) (1pt) Provide one reason why for this starting material the  $\pi$  bonds in the ring are less likely to be protonated than the other (acyclic)  $\pi$  bond.
- g) (1pt) What do you think is the energetic driving force that makes this isomerization a favorable process?

h) (6pts) Draw the mechanism (*i.e. curly arrows*) for this reaction.



6) (23pts) The following is another acid catalyzed isomerization.



a) (2pts) State a difference between a catalyst and a reagent.

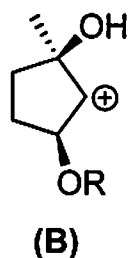
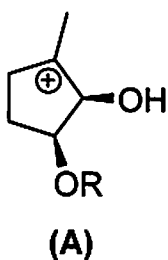
b) (1pt) What is the correct functional group name for a 3 membered ring cyclic ether?

c) (1pt) What do you think is the energetic driving force that makes this isomerization a favorable process?

d) (3pts) In this representation there are bonds shown in three ways: lines, solid (black) wedges, and as dashed wedges. What geometrical (stereochemical) aspect does each type attempt to illustrate?

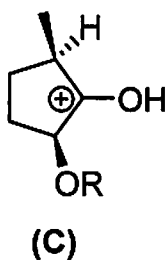
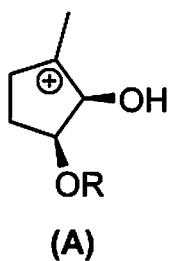
e) (1pt) In the product, the methyl group and the ether linkage both have solid wedge bonds. Provide a term that describes this geometric (stereochemical) relationship.

f) (5pts) This mechanism starts with the protonation of the 3 membered ring cyclic ether Oxygen, which then generates a carbocation. In theory this could result in formation of carbocation **A** or **B**. Draw mechanisms to show formation of carbocations **A** and **B** from the starting material.



e) (1pt) State one reason why carbocation **A** is more stable than **B**.

f) (2pts) Carbocation **A** undergoes a carbocation rearrangement to produce a more stable carbocation **C**. Draw the mechanism for this rearrangement.



g) (1pt) Give one reason why carbocation **C** is more stable than **A**.

h) (4pts) Draw the mechanism that converts carbocation **C** into the final product.

i) (2pts) Briefly explain why in this reaction the methyl group starts off pointing in one direction, but ends up pointing a different way in the product.

**THE NEXT SECTION  
HAS 3  
MECHANISM PROBLEMS**

**X, Y and Z**

**EACH IS WORTH 18 PTS**

**ANSWER ANY 2**

**(For 2x18=36 pts)**

*Partial credit will be awarded for:*

- i) Correct atom labelling between SM and Products*
- ii) "Correct" Organic Chemistry*
- iii) Resonance structures and "justifications"*

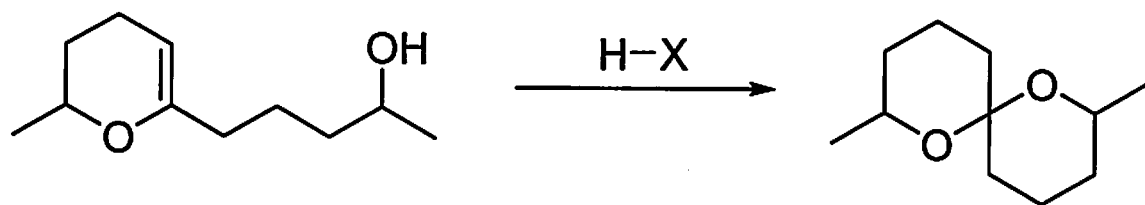
Indicate here which 2 you want counted: \_\_\_\_\_

\_\_\_\_\_

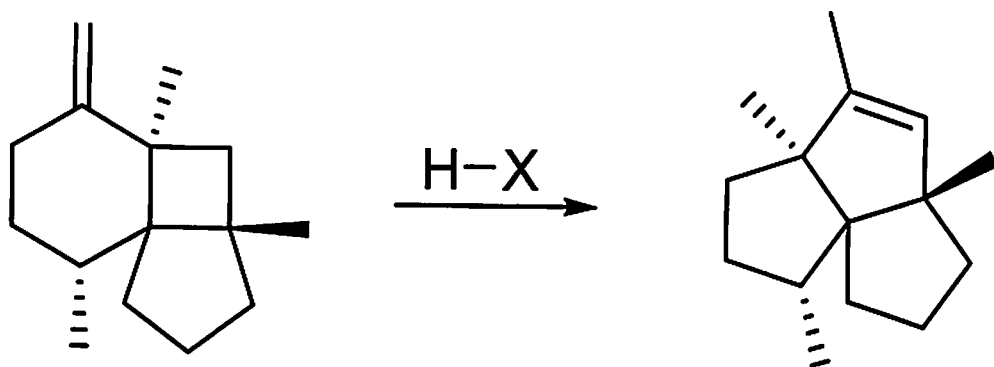
*(You can attempt the remaining question, and I will award up to 5/5 bonus points for that effort).*



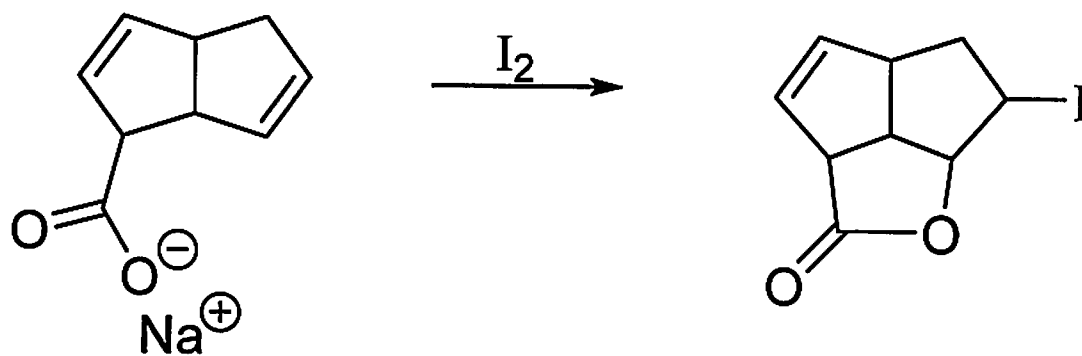
X) Draw the mechanism (*i.e. curly arrows*) for this reaction.



Y) Draw the mechanism (*i.e. curly arrows*) for this reaction.



Z) Draw the mechanism (*i.e. curly arrows*) for this reaction.



NAME: Perfect Answers

1) (3x2=6pts) Define the following terms.

*Electrophile*

A species that receives 2 electrons from a nucleophile.


*Protic Acid*


A species that can act as a  $H^+$  donor.

*Mechanism*

The step by step movement of electrons that describe a chemical reaction.

2) (3x2= 6pts) What are the precise chemical meanings of the following three arrows?

 This "resonance" arrow relates species that differ only in their location of electron density.

 This relates species that are "in equilibrium" with each other.

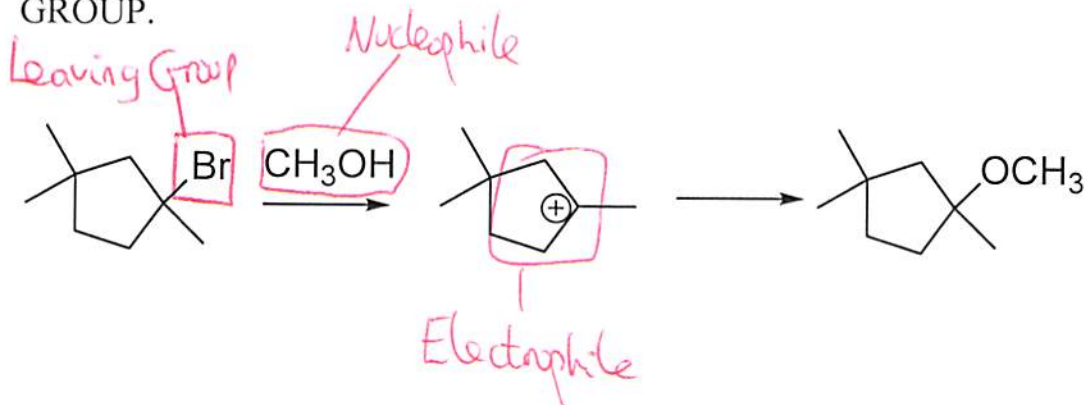
 This means movement of 2 electrons.

3) (2pts) Name two of the things you should check when critically evaluating the curly arrows you have drawn to represent a mechanism.

- Arrow should start at the two electrons that are moving.
- Arrow should show exactly where those 2 electrons go.
- The direction of the arrow should make "scientific" sense.

4) (14 pts) For this reaction:

a) (2+2+2pts) Label the NUCLEOPHILE, ELECTROPHILE and LEAVING GROUP.



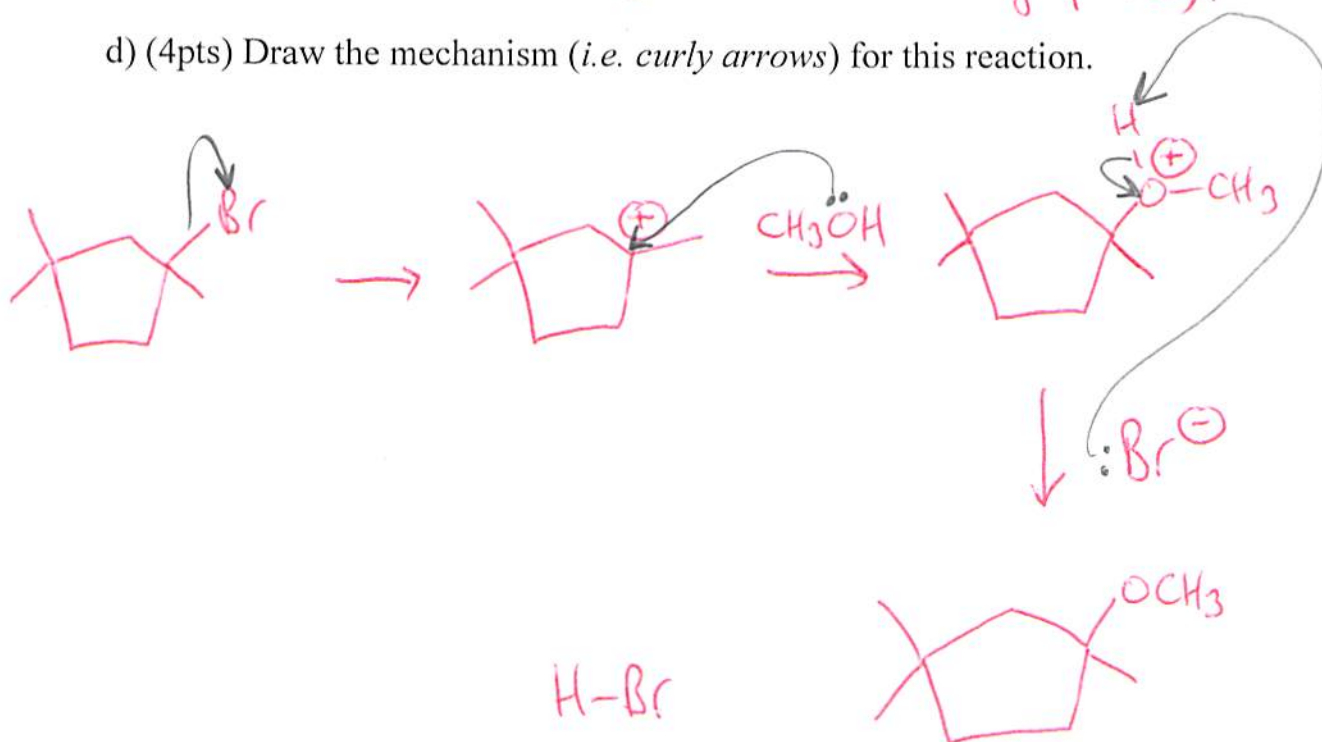
b) (2pts) State the name of this particular type of mechanism (which should include letters and numbers).

$\text{S}_\text{N}1$

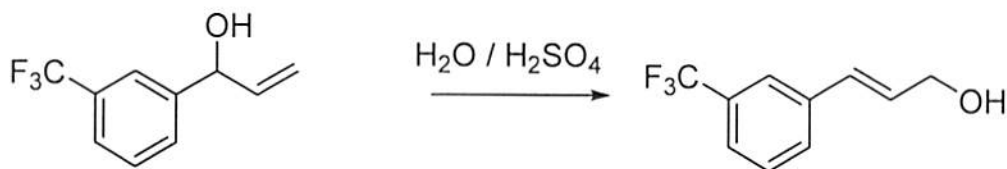
c) (2pts) If the starting material was a single enantiomer, what would you expect the stereochemistry of the product to be?

A racemic mixture (both enantiomers of product).

d) (4pts) Draw the mechanism (i.e. curly arrows) for this reaction.



5) (13pts) The following reaction is an acid catalyzed isomerization.



a) (1pt) What type of isomers are the starting material and product?

Structural isomers

b) (1pt) Identify the most acidic component in this reaction.

$\text{H}_2\text{SO}_4$  (Sulphuric Acid)

c) (1pt) Acids protonate things, such as lone pairs and  $\pi$  bonds. How many  $\pi$  bonds are in the starting material?

4  $\pi$  bonds

d) (1pt) How many lone pairs (non-bonding pairs of electrons) are on the Oxygen of the starting material?

2 lp.

e) (1pt) Provide one reason why lone pairs are usually more easily protonated than  $\pi$  bonds.

lone pairs are non-bonding electrons, and so are more available than  $\pi$  bonds which are already involved in covalent bonding.

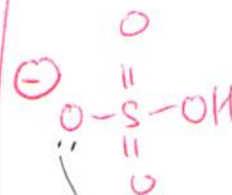
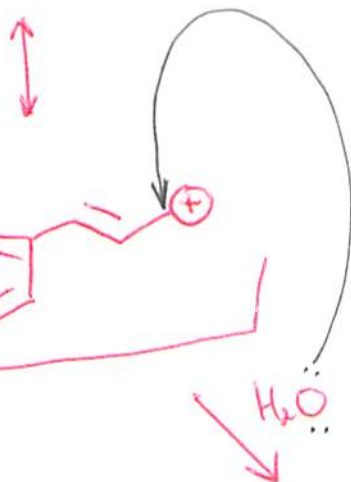
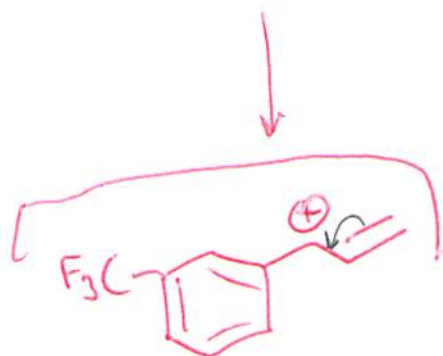
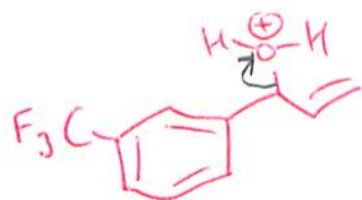
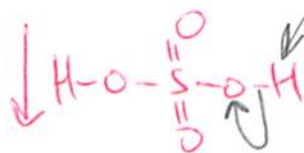
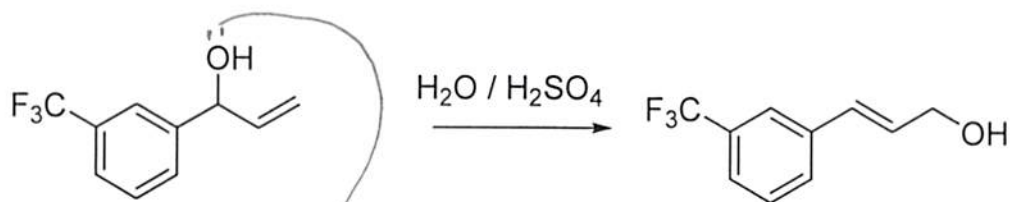
f) (1pt) Provide one reason why for this starting material the  $\pi$  bonds in the ring are less likely to be protonated than the other (acyclic)  $\pi$  bond.

The ring is a 6 $\pi$  aromatic system and therefore those  $\pi$  electrons are especially unreactive.

g) (1pt) What do you think is the energetic driving force that makes this isomerization a favorable process?

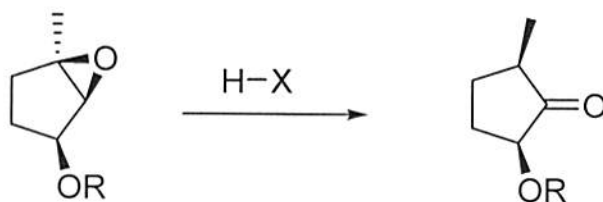
The production of conjugation (albeit with aromatic system).

h) (6pts) Draw the mechanism (i.e. curly arrows) for this reaction.





6) (23pts) The following is another acid catalyzed isomerization.



a) (2pts) State a difference between a catalyst and a reagent.

A reagent is used and overall consumed in a reaction (requiring a stoichiometric equivalent), whereas a catalyst is used but regenerated.

b) (1pt) What is the correct functional group name for a 3 membered ring cyclic ether?

Epoxide.

c) (1pt) What do you think is the energetic driving force that makes this isomerization a favorable process?

Release of ring strain (of the epoxide).

d) (3pts) In this representation there are bonds shown in three ways: lines, solid (black) wedges, and as dashed wedges. What geometrical (stereochemical) aspect does each type attempt to illustrate?

— means covalent bond in the plane of the paper.

▲ means the bond is coming out of the plane toward the viewer.

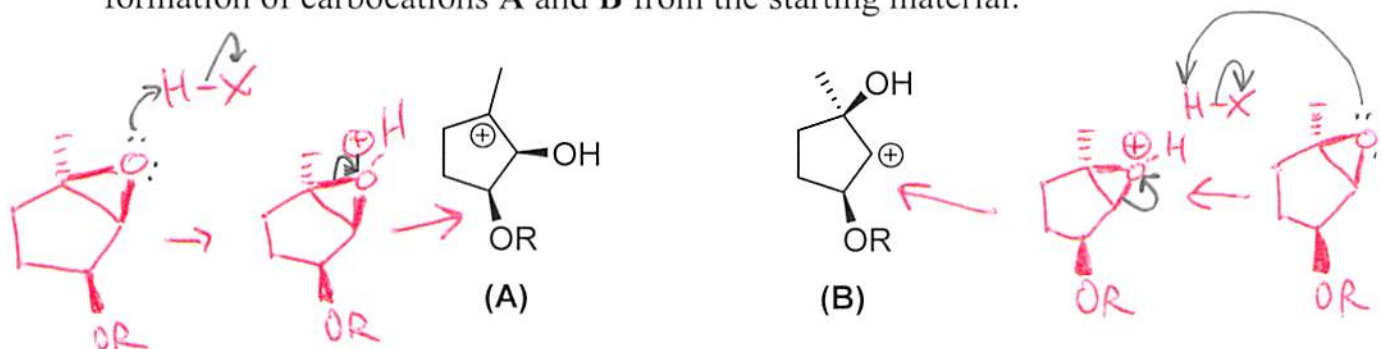
||||| means the bond is going away from the viewer.

e) (1pt) In the product, the methyl group and the ether linkage both have solid wedge bonds. Provide a term that describes this geometric (stereochemical) relationship.

cis (or syn)



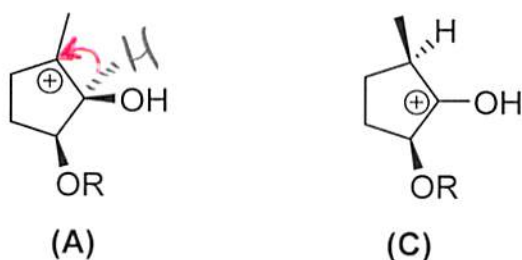
f) (5pts) This mechanism starts with the protonation of the 3 membered ring cyclic ether Oxygen, which then generates a carbocation. In theory this could result in formation of carbocation **A** or **B**. Draw mechanisms to show formation of carbocations **A** and **B** from the starting material.



e) (1pt) State one reason why carbocation **A** is more stable than **B**.

*Tertiary versus Secondary cation (More alkyl substitution).*

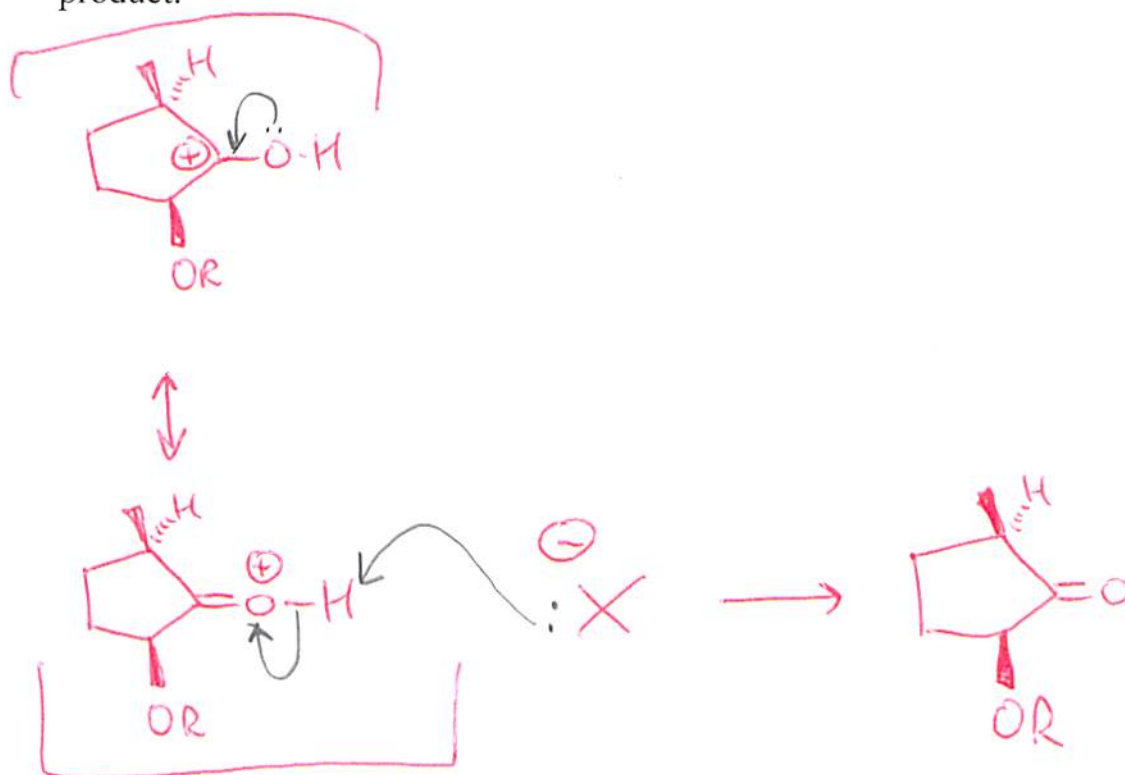
f) (2pts) Carbocation **A** undergoes a carbocation rearrangement to produce a more stable carbocation **C**. Draw the mechanism for this rearrangement.



g) (1pt) Give one reason why carbocation **C** is more stable than **A**.

*Resonance (using the oxygen lone pairs).*

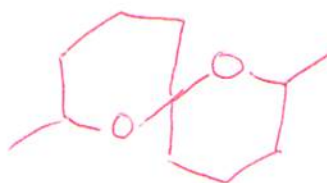
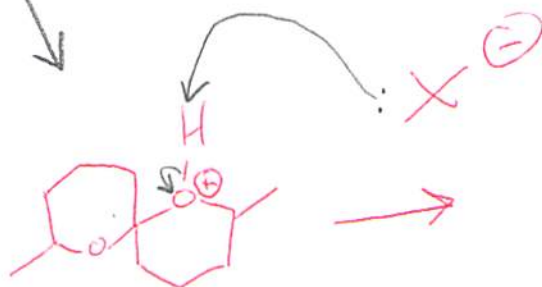
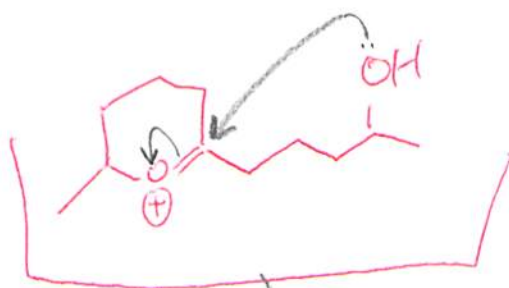
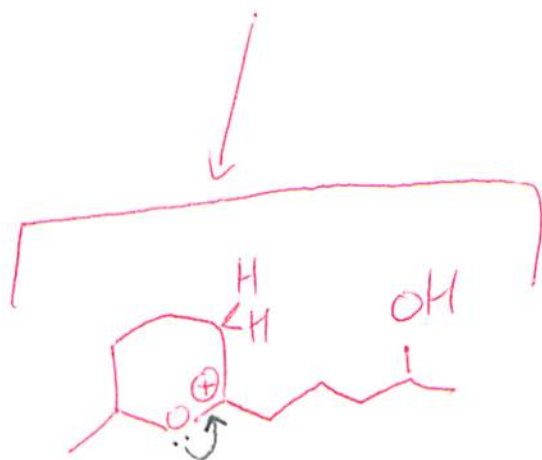
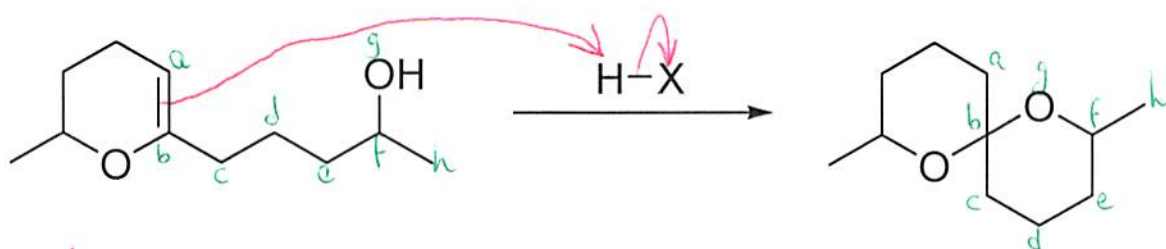
h) (4pts) Draw the mechanism that converts carbocation C into the final product.



i) (2pts) Briefly explain why in this reaction the methyl group starts off pointing in one direction, but ends up pointing a different way in the product.

The stereochemistry is lost when the planar carbocation is generated in cation A. Then when the hydride shift (carbocation rearrangement) occurs, it must proceed with the H pointing away, and this is delivered behind the methyl group, thus pushing the methyl group forward (section f).

X) Draw the mechanism (i.e. curly arrows) for this reaction.





Z) Draw the mechanism (i.e. curly arrows) for this reaction.

