



Pre-Health Post-Baccalaureate Program
CHM2210 Study Guide & Practice Problems

Topics Covered:

Acid-Catalyzed Hydration
Carbocation Rearrangements
Addition of X_2
Addition of XOH
Oxymercuration-Reduction
Hydroboration-Oxidation

Created by Isaac Loy

Acid-Catalyzed Hydration

Subject to carbocation rearrangement (next page). Allows for the selective addition of an alcohol to an alkene at the most substituted position.

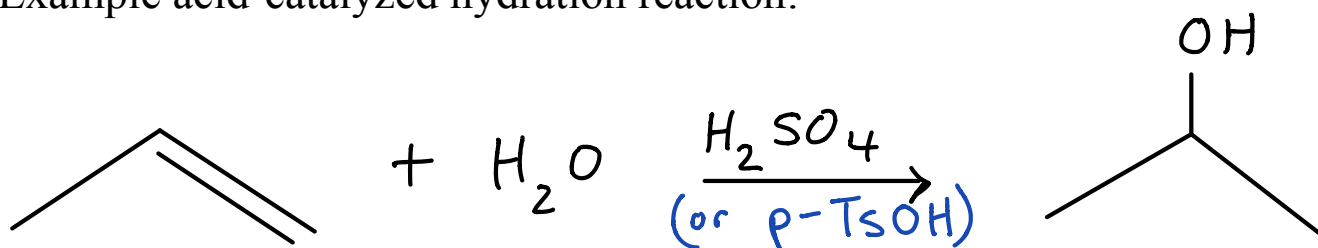
The acid is a catalyst and exists only to protonate water molecules.

The process of adding water to form an alcohol is called hydration.

This reaction follows Markovnikov's rule - H will add to the double-bonded carbon which initially has more hydrogens.

Portmess loves p-Toluenesulfonic acid...

Example acid-catalyzed hydration reaction:



1) What is the mechanism for the above reaction?

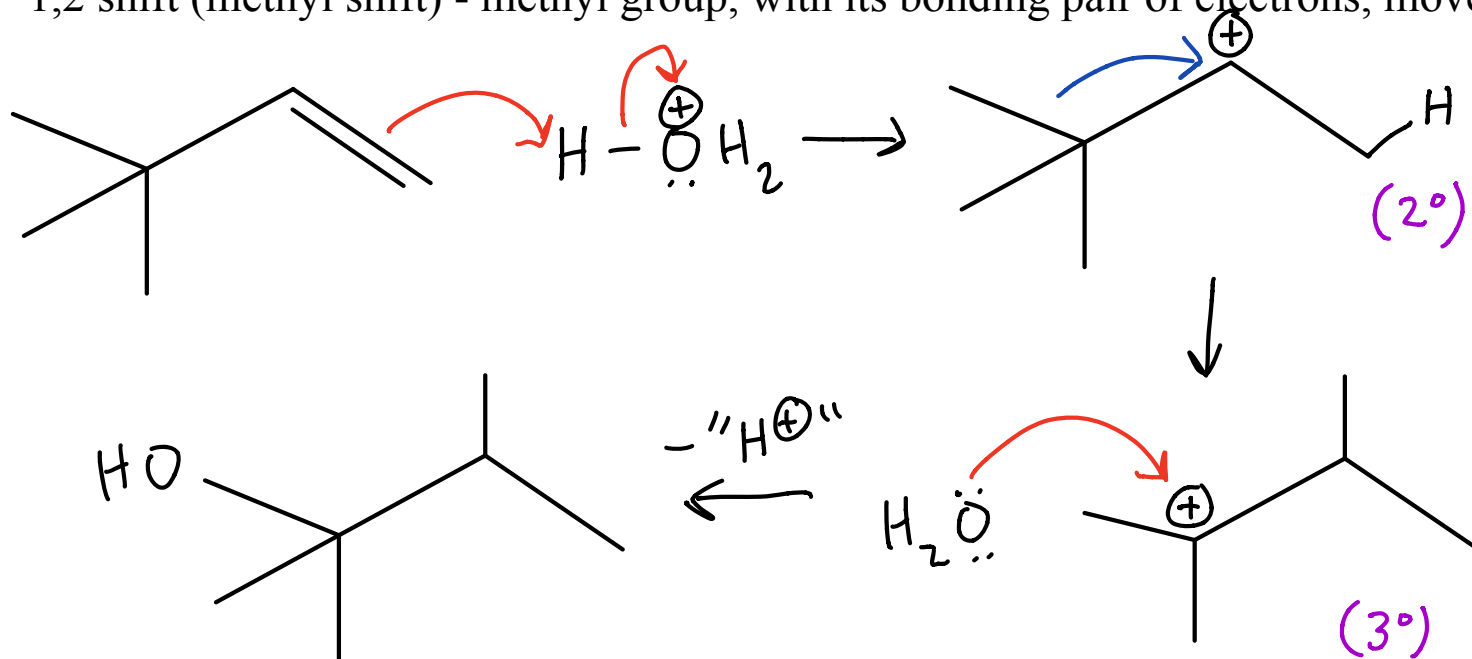
Carbocation Rearrangement

We said previously that 3° carbocations are more stable than 2° carbocations, which are more stable than 1° carbocations.

Because of this, carbocations will rearrange so as to achieve a higher order (and more stable) intermediate.

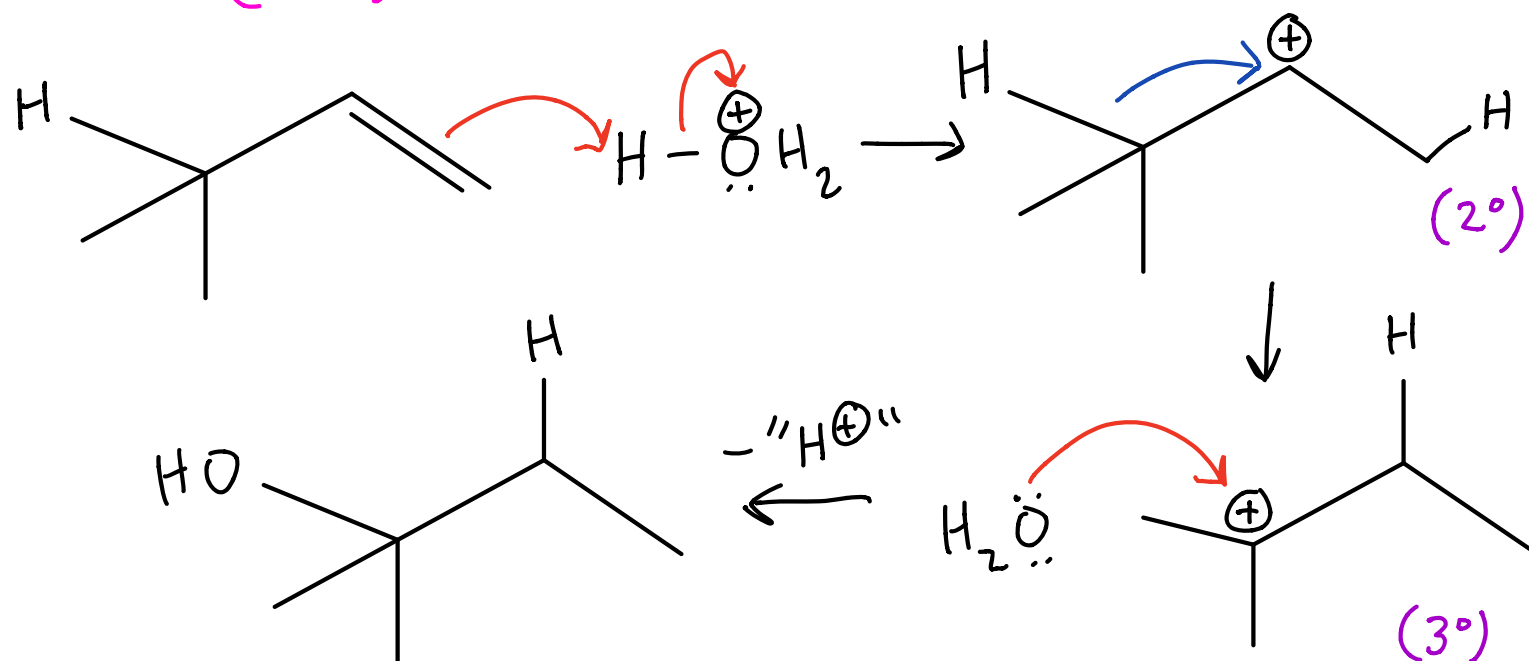
There are two types of rearrangements to be familiar with:

1,2 shift (methyl shift) - methyl group, with its bonding pair of electrons, move



Hydride shift - hydrogen atom, with its bonding pair of electrons, move

($:\text{H}^-$)



Anti-Addition of Halogens

Cl-Cl and Br-Br add to double bonds in an “anti” fashion - that is, they have opposite stereoselectivity.

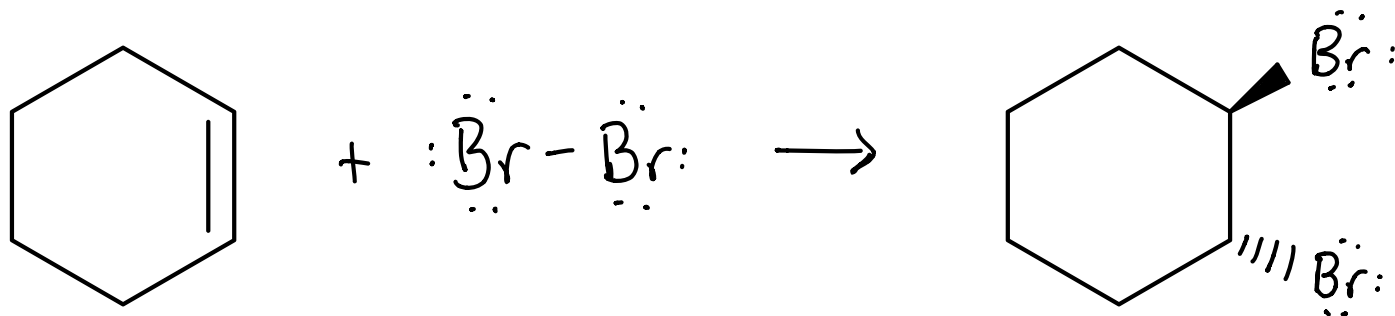
This reaction can happen either with pure halogens as the reagent, or with halogens mixed with an inert solvent such as CH_2Cl_2 .

This reaction occurs at room temperature.

Alkenes that are brominated form dibromoalkanes, which are colorless. The addition of bromine (reddish-brown), then, becomes a useful and easy test to determine if any $\text{C}=\text{C}$ bonds are present in a test sample.

The resulting product is a racemic mixture. (\pm)

Example anti-addition halogenation reaction:



2) What is the mechanism for the above reaction?

Anti-Addition of Halogens with Water

Adding a halogen to an alkene in the presence of water results in the formation of a halohydrin - bonded halogens and hydroxyl groups on adjacent carbon atoms.

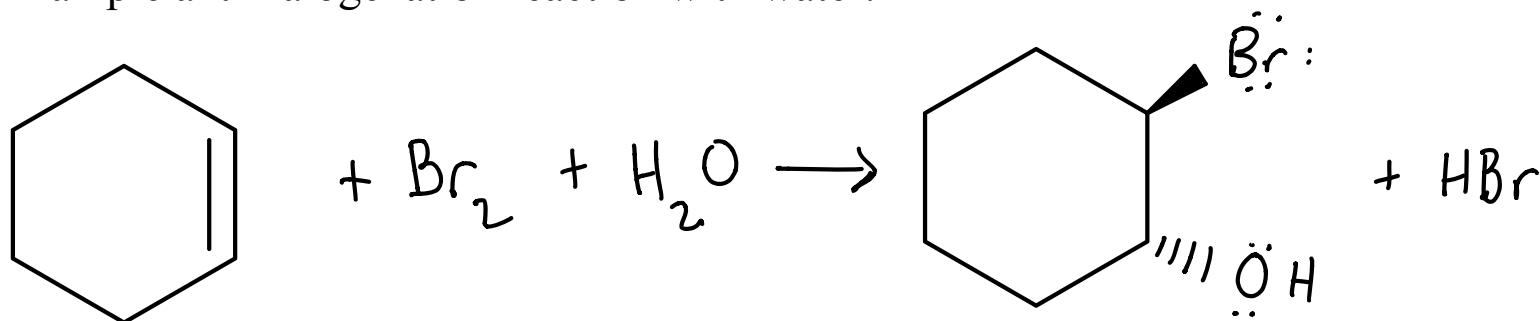
Like the previous reaction, the two groups being added add anti to one another (the mechanism is very similar).

The halogen adds to the less substituted carbon, while the alcohol adds to the more substituted carbon.

Dimethyl sulfoxide (DMSO) is used as a cosolvent to increase the solubility of the alkene.

The resulting product is a racemic mixture.

Example anti-halogenation reaction with water:



3) What is the mechanism for the above reaction?

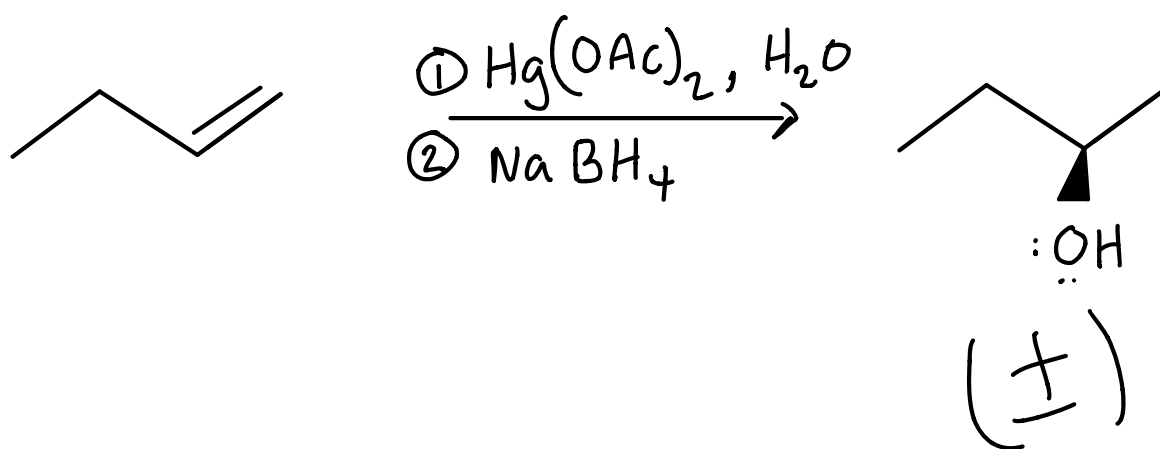
Oxymercuration-Reduction

Unaffected by carbocation rearrangement. Allows for the selective addition of a 2° alcohol to an alkene.

This is a two-step reaction. The first step involves treating an alkene with mercury(II) acetate (often written $\text{Hg}(\text{OAc})_2$), while the second step involves treating the intermediate with sodium borohydride (NaBH_4).

The resulting product is a racemic mixture.

Example oxymercuration-reduction reaction:



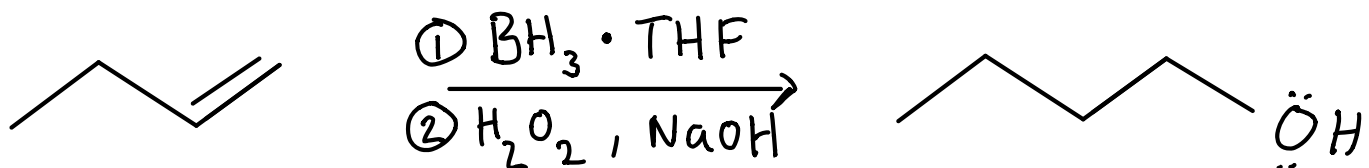
Hydroboration-Oxidation

Unaffected by carbocation rearrangement. Allows for the selective addition of a 3° alcohol to an alkene..

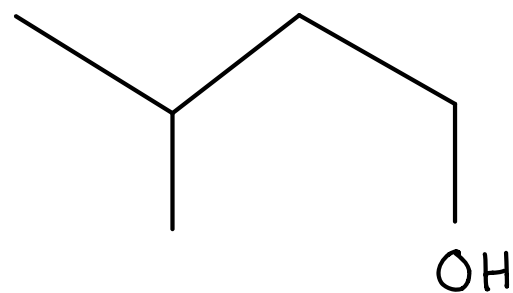
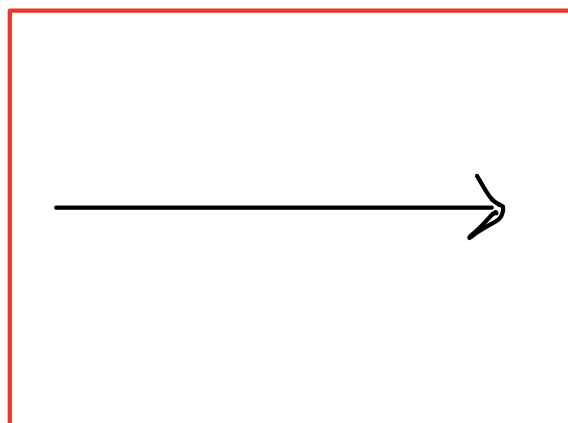
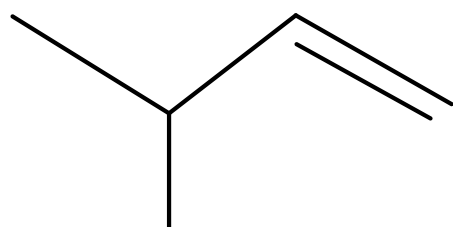
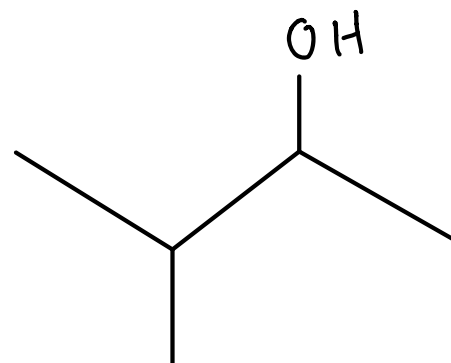
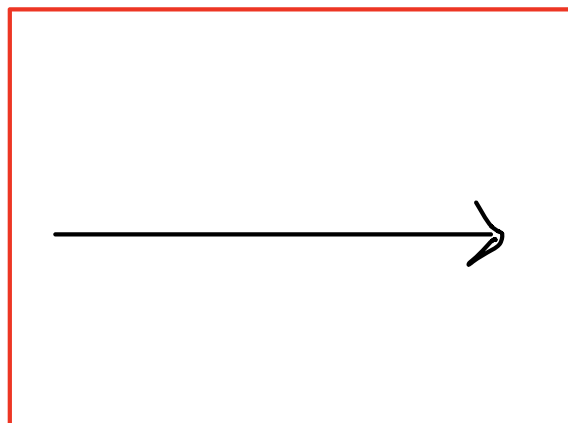
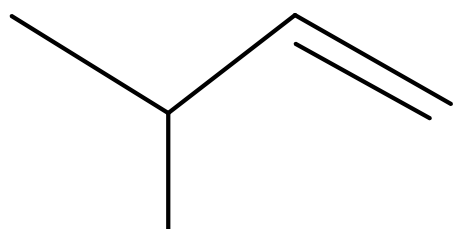
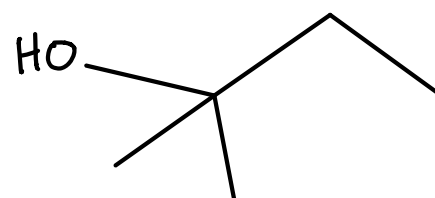
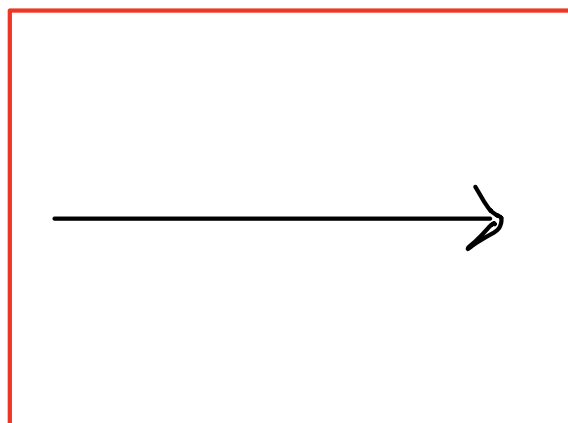
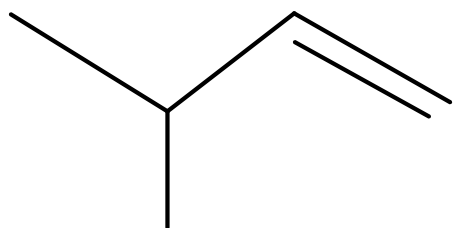
This is also a two-step reaction. The first step involves adding borane (BH_3) to an alkene which bonds to the less substituted carbon in a syn fashion, while the second step involves oxidizing the intermediate with hydrogen peroxide (H_2O_2) with sodium hydroxide (NaOH).

Borane must be prepared in an ether solution, typically with tetrahydrofuran (THF).

Example hydroboration-oxidation reaction:

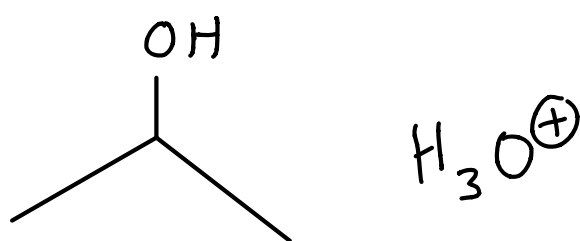
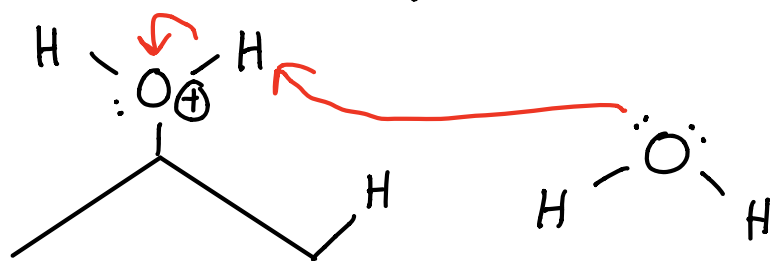
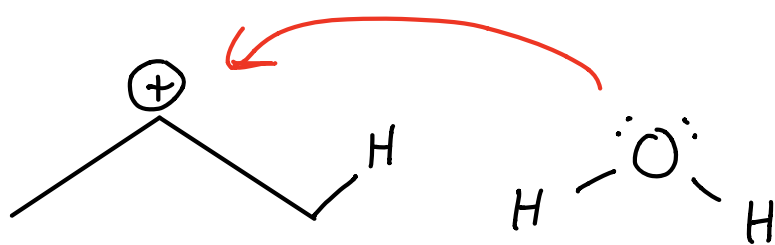
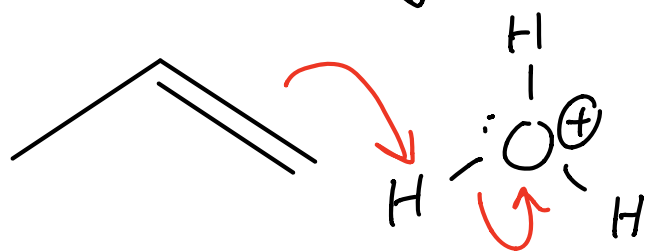
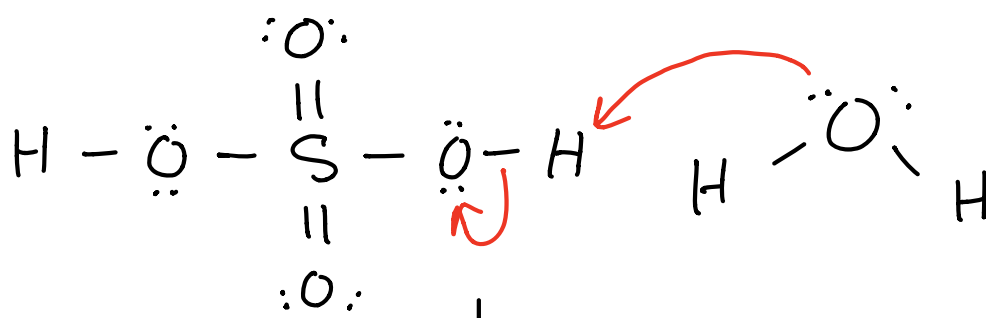


4) In the red boxes below, fill in the necessary reagents and reaction conditions to satisfy the overall chemical equations.

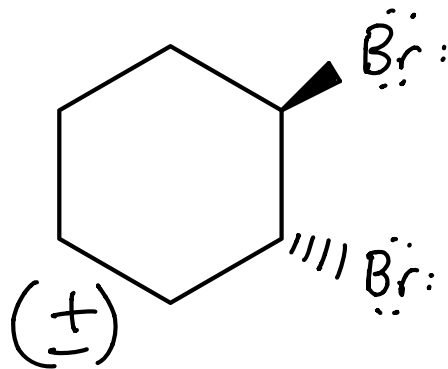
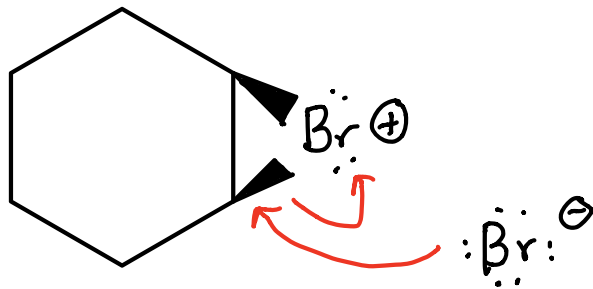
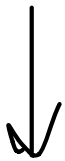
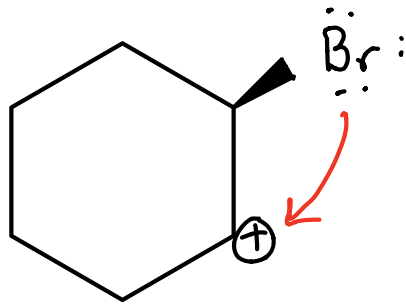
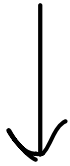
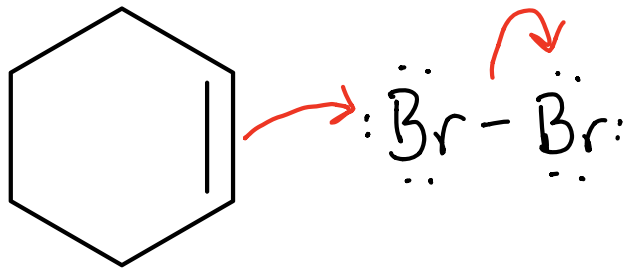


Solutions

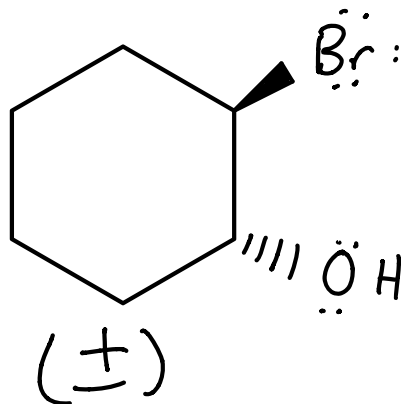
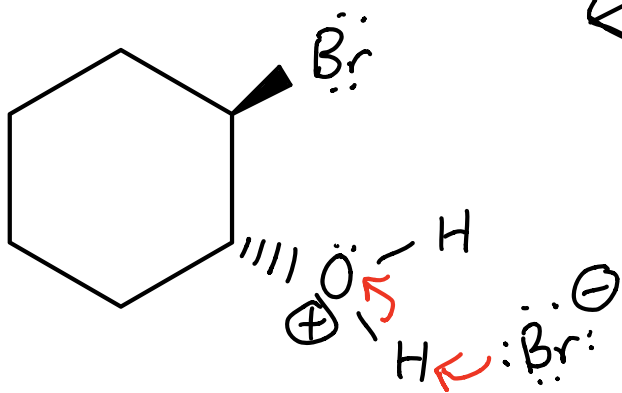
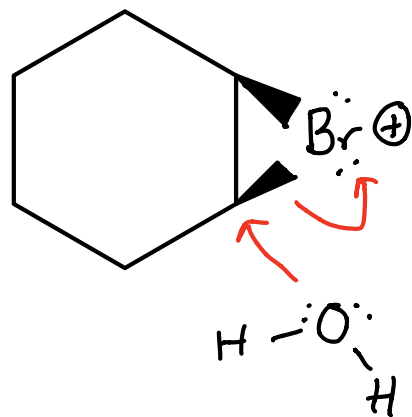
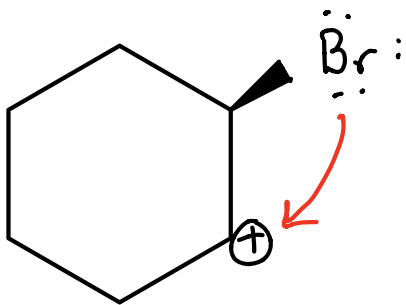
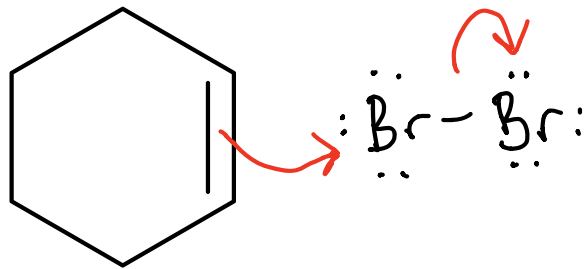
①



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③



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