**ChemActivity 18**

**Epoxide & Bromonium Ring Opening**
(How can we explain the products produced by some electrophilic additions?)

**Model 1: Epoxides**
A three-member ring containing 1 oxygen and 2 carbons is called an epoxide.

**Figure 1: Nucleophile Colliding with an Alcohol vs. an Epoxide**

Rxn I is thermo-neutral (neither up-hill nor down-hill), as indicated by the reaction arrows. Although hydroxide is a poor leaving group, it is also a very good nucleophile. These balance each other and make Rxn I neither up-hill nor down-hill. Rxn II is downhill.

**Critical Thinking Questions**
1. Draw curved arrows to illustrate each reaction mechanism in Figure 1. Both are one-step reactions.

2. Both reactions in Figure 1 are examples of $S_2$ type mechanisms. Identify the nucleophile, electrophilic atom (carbon), and leaving group in each.

3. Explain the following statement. The leaving group in Rxn II doesn't actually depart like a normal leaving group because it is attached with two bonds, and only one of them breaks.
4. Consider the following mechanisms of epoxide ring opening. Construct an explanation for why "opposite-side collision" is favored over "same-side collision."

![Opposite-Side Collision by HO⁻](image1.png)  
Opposite-Side Collision by HO⁻  
![Same-Side Collision by HO⁻](image2.png)  
Same-Side Collision by HO⁻

5. In the diagram labeled "Opposite-Side Collision by HO⁻," the hydroxide collides with the carbon on the side opposite from what? (That is, why is this called opposite-side collision?)

6. Is the "Opposite-Side Collision by HO⁻" mechanism at the top of the page consistent with the fact that epoxide ring openings (like the reaction below) yield ONLY trans product? Explain.

![Reaction Diagram](image3.png)  
trans only  
No cis product!

7. Upon neutralization with dilute HCl, the trans product in CTQ 6 becomes a di-ol (di-alcohol) as shown below.

![Neutralization Reaction](image4.png)  
trans di-ol

a) Use curved arrows to show the mechanism of this acid-base neutralization reaction.

b) A second trans di-ol (not shown) is produced when the epoxide in CTQ 6 is treated with hydroxide followed by dilute HCl. Draw this second trans di-ol. (Hint: it is a stereoisomer of the trans di-ol shown above.)
Model 2: Bromonium Ion Intermediate (vs. Carbocation)

Br₂ is called "polarizable" because electrons in the large orbitals that make up the Br—Br bond can slosh back and forth. Think of waves in a bathtub. At a given moment more water can be at one end of the tub than the other.

\[ \text{Sloshy Bathtub} \]

excess of electrons

more water at this end

lack of electrons

In Figure 2a, the electrons in Br—Br have "sloshed" to the left, leaving a partial + charge on one Br atom. At this moment, the π electrons of an alkene, acting as a nucleophile, react with the electrophilic Br atom.

**Figure 2a: Polarized Br—Br as Electrophile and Nucleophile**

![Image of polarized Br—Br as electrophile and nucleophile]

carbocation

**Critical Thinking Questions**

8. In the box above, draw a carbocation that might result from this reaction. Be sure to put the + charge on the correct carbon.

**Figure 2b: Carbocation vs. Bromonium Ion**

![Image of carbocation vs. bromonium ion]

carbocation

very small activation barrier

bromonium ion

9. The carbocation in Figure 2b is not stable because there is no activation barrier preventing it from changing into a much lower potential energy bromonium ion.

a) Add the missing formal charge to the Br of the bromonium ion in Figure 2b.

b) A carbocation intermediate is not observed in this reaction, it may be that it forms but immediately changes into the bromonium ion shown. Add curved arrows to show a mechanism for changing the carbocation in Figure 2b into a bromonium ion.
10. Bromonium ion ring opening is very similar to epoxide ring opening.
   a) Label one of the arrows going from Br on the diagram below "same-side collision" and label the other one "opposite-side collision," as appropriate.
   b) Predict which type of collision (same-side collision or opposite-side collision) [circle one] is more likely in a bromonium ring opening reaction and explain your reasoning.

![Diagram of bromonium ion ring opening]

ONLY ONE of these products forms [circle one]

c) Circle the more likely of the two products shown above.

11. Consider the following reaction, which yields the product shown below, right.

![Diagram of reaction with product shown]

a) According to the product shown, which is a stronger nucleophile: bromide or cyanide (CN)?

b) Is the reaction of the nucleophile with the bromonium ion Markovnikov or Anti-Markovnikov? Label the product "Markov," or "anti-Markov."