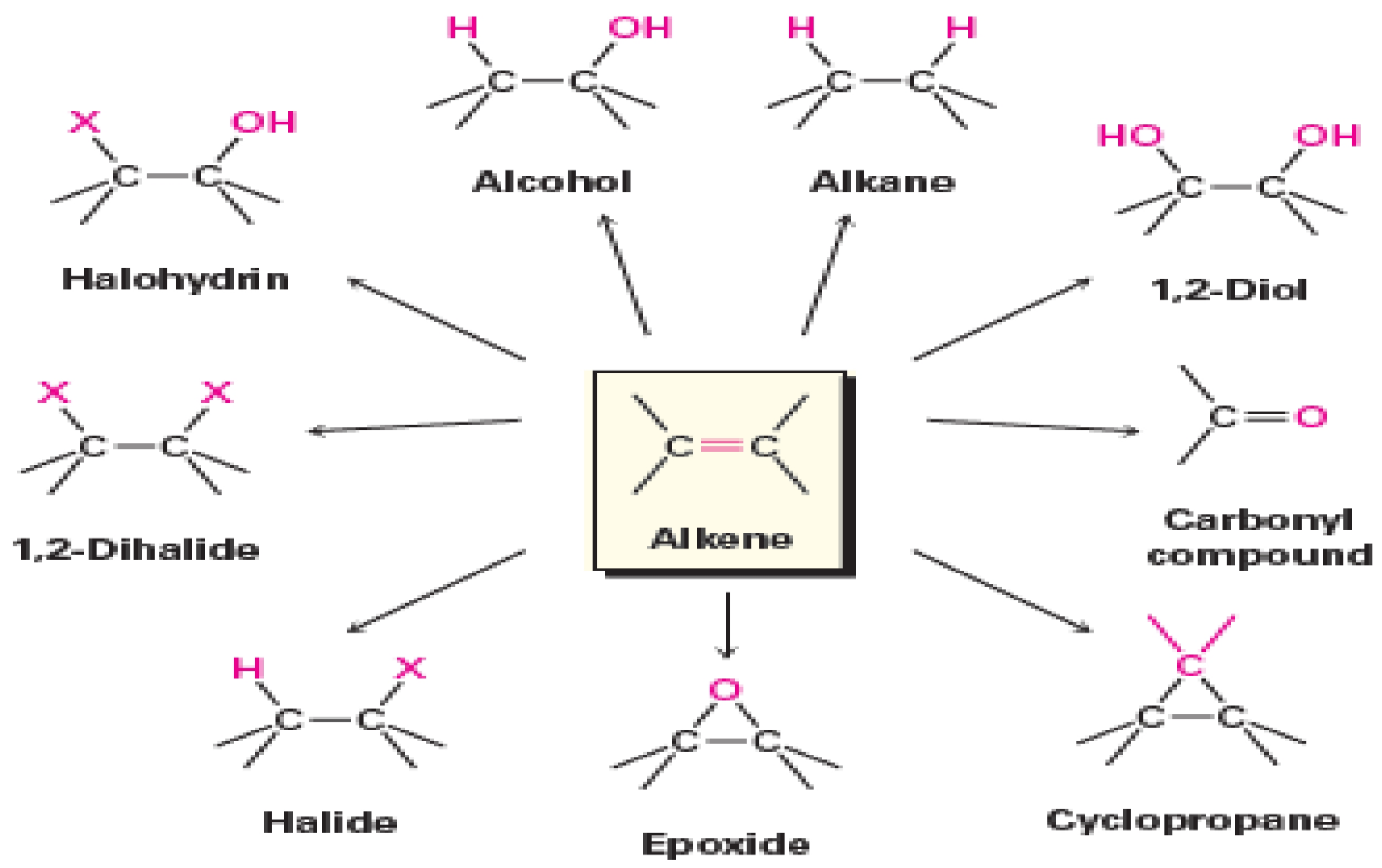


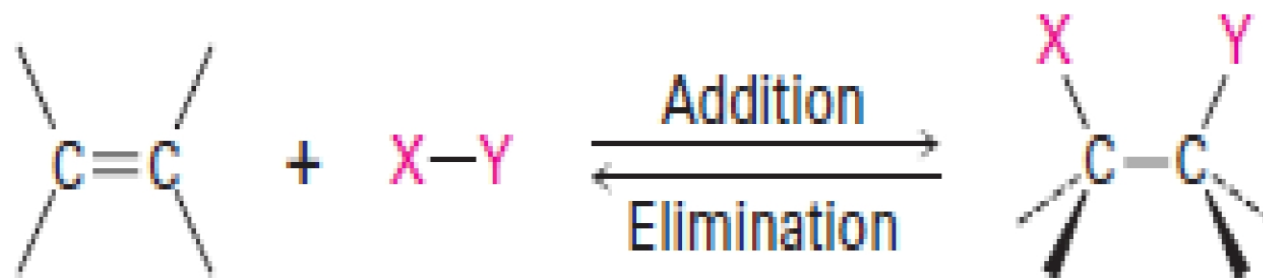
Alkenes: Reactions and Synthesis

Alkene addition reactions occur widely, both in the laboratory and in living organisms. Although we've studied only the addition of HX thus far, many closely related reactions also take place. In this chapter, we'll see briefly how alkenes are prepared and we'll discuss further examples of alkene addition reactions. Particularly important are the addition of a halogen to give a 1,2-dihalide, addition of a hypohalous acid to give a halohydrin, addition of water to give an alcohol, addition of hydrogen to give an alkane, addition of a single oxygen to give a three-membered cyclic ether called an *epoxide*, and addition of two hydroxyl groups to give a 1,2-diol.

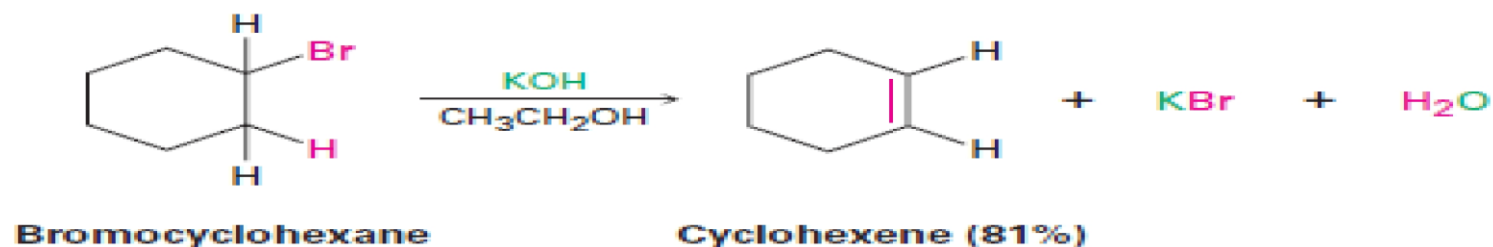


Preparing Alkenes: A Preview of Elimination Reactions

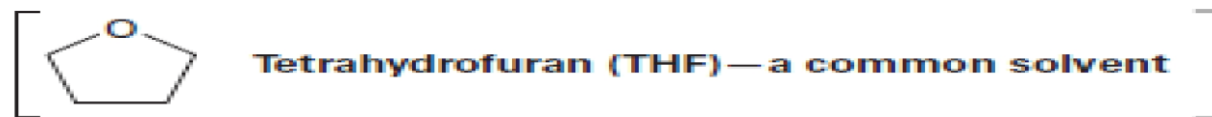
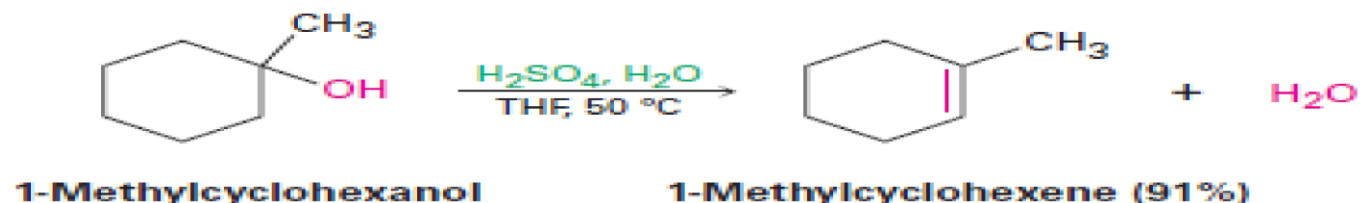
Just as the chemistry of alkenes is dominated by addition reactions, the preparation of alkenes is dominated by elimination reactions. Additions and eliminations are, in many respects, two sides of the same coin. That is, an addition reaction might involve the addition of HBr or H₂O to an alkene to form an alkyl halide or alcohol, whereas an elimination reaction might involve the loss of HBr or H₂O from an alkyl halide or alcohol to form an alkene.



The two most common elimination reactions are *dehydrohalogenation*—the loss of HX from an alkyl halide—and *dehydration*—the loss of water from an alcohol. Dehydrohalogenation usually occurs by reaction of an alkyl halide with strong base such as potassium hydroxide. For example, bromocyclohexane yields cyclohexene when treated with KOH in ethanol solution.

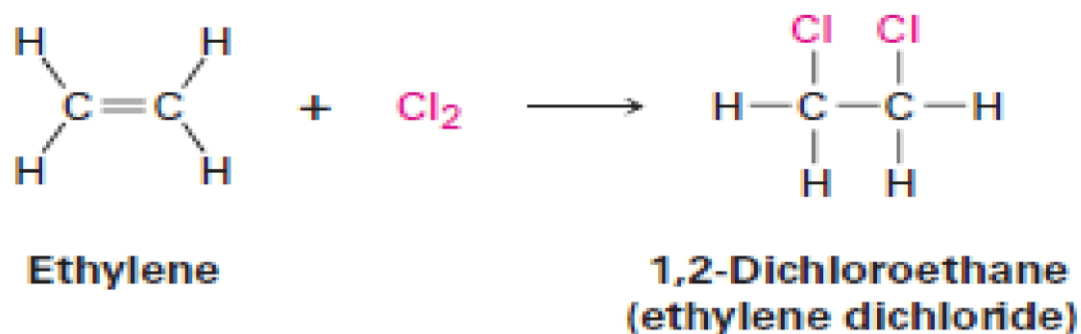


Dehydration is often carried out in the laboratory by treatment of an alcohol with a strong acid. For example, when 1-methylcyclohexanol is warmed with aqueous sulfuric acid in tetrahydrofuran (THF) solvent, loss of water occurs and 1-methylcyclohexene is formed.

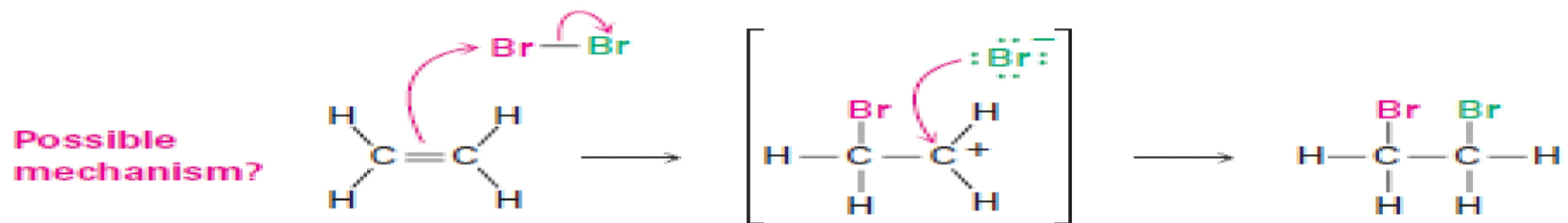


Halogenation of Alkenes: Addition of X₂

Bromine and chlorine add rapidly to alkenes to yield 1,2-dihalides, a process called *halogenation*. For example, more than 25 million tons of 1,2-dichloroethane (ethylene dichloride) are synthesized worldwide each year, much of it by addition of Cl₂ to ethylene. The product is used both as a solvent and as starting material for the manufacture of poly (vinyl chloride), PVC. Fluorine is too reactive and difficult to control for most laboratory applications, and iodine does not react with most alkenes.

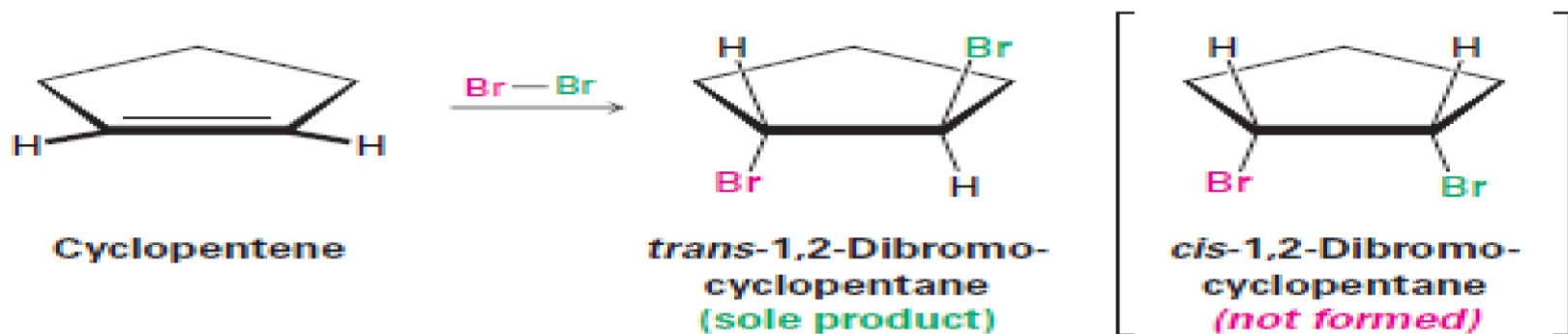


A possible mechanism for the reaction of bromine with alkenes might involve electrophilic addition of Br⁺ to the alkene, giving a carbocation intermediate that could undergo further reaction with Br⁻ to yield the dibromo addition product.

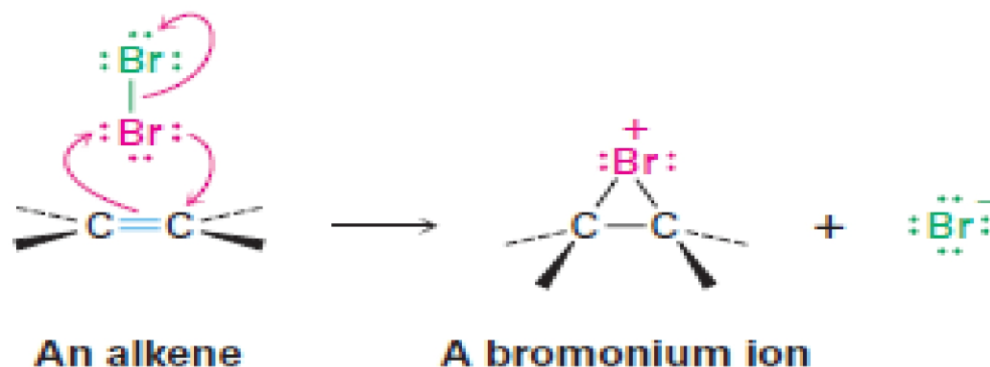


Although this mechanism seems plausible, it's not fully consistent with known facts. In particular, it doesn't explain the *stereochemistry* of the addition reaction. That is, the mechanism doesn't tell which product stereoisomer is formed.

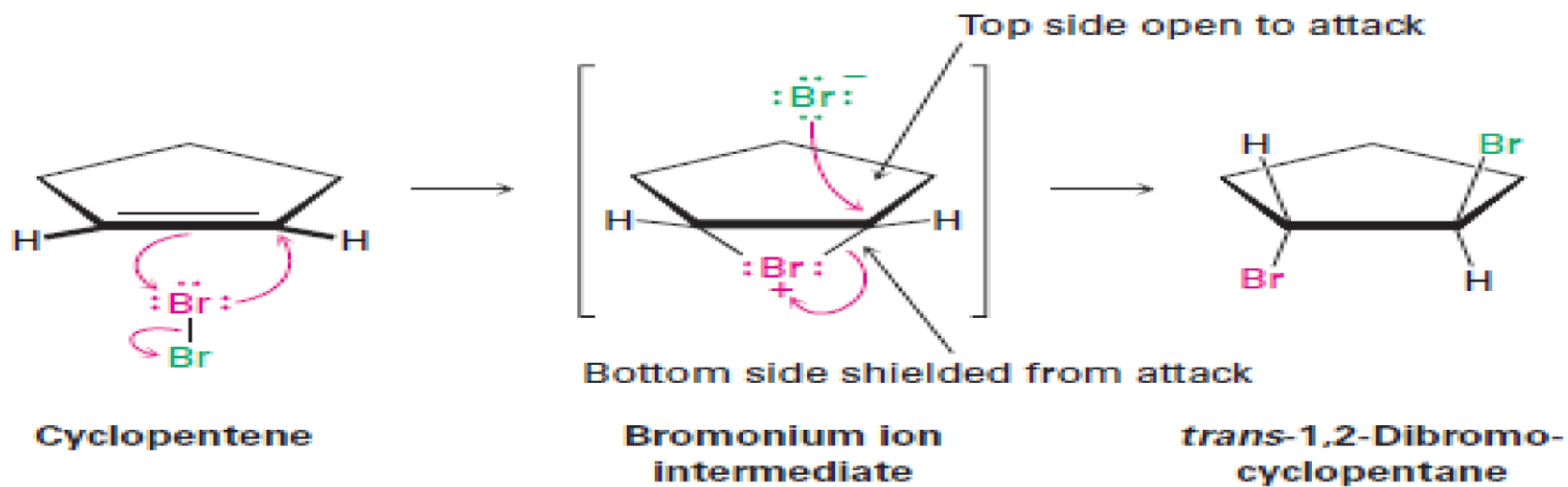
When the halogenation reaction is carried out on a cycloalkene, such as cyclopentene, only the *trans* stereoisomer of the dihalide addition product is formed, rather than the mixture of *cis* and *trans* isomers that might have been expected if a planar carbocation intermediate were involved. We say that the reaction occurs with **anti-stereochemistry**, meaning that the two bromine atoms come from opposite faces of the double bond—one from the top face and one from the bottom face.



An explanation for the observed stereochemistry of addition was suggested by George Kimball and Irving Roberts, who proposed that the reaction intermediate is not a carbocation but is instead a **bromonium ion**, R_2Br^+ , formed by electrophilic addition of Br^+ to the alkene. (Similarly, a ***chloronium ion*** contains positively charged, divalent chlorine, R_2Cl^+ .) The bromonium ion is formed in a single step by interaction of the alkene with Br_2 and the simultaneous loss of Br^- .

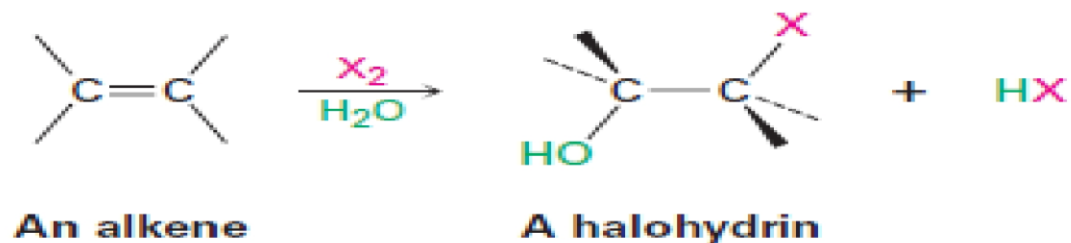


How does the formation of a bromonium ion account for the observed anti-stereochemistry of addition to cyclopentene? If a bromonium ion is formed as an intermediate, we can imagine that the large bromine atom might “shield” one side of the molecule. Reaction with Br^- ion in the second step could then occur only from the opposite, unshielded side to give **Trans** product.

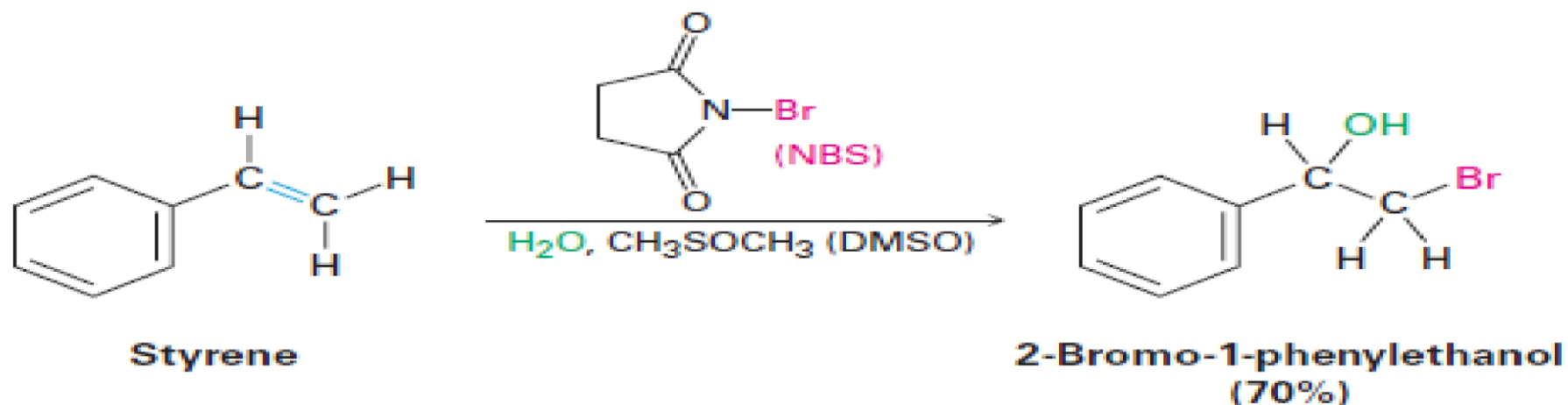


Halohydrins from Alkenes: Addition of HOX

Another example of an electrophilic addition is the reaction of alkenes with the hypohalous acids HO-Cl or HO-Br to yield 1,2-halo alcohols, called **halohydrins**. Halohydrin formation doesn't take place by direct reaction of an alkene with HOBr or HOCl, however. Rather, the addition happens indirectly by reaction of the alkene with either Br₂ or Cl₂ in the presence of water.



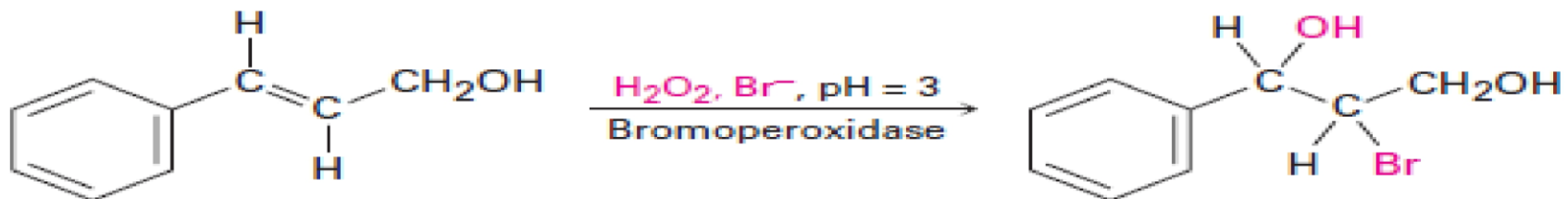
In practice, few alkenes are soluble in water, and bromohydrin formation is often carried out in a solvent such as aqueous dimethyl sulfoxide, CH_3SOCH_3 (DMSO), using a reagent called *N*-bromosuccinimide (NBS) as a source of Br_2 . NBS is a stable, easily handled compound that slowly decomposes in water to yield Br_2 at a controlled rate. Bromine itself can also be used in the addition reaction, but it is more dangerous and more difficult to handle than NBS.



Note that the aromatic ring in the above example does not react with Br_2 under such conditions, even though it appears to contain three carbon–carbon double bonds.

There are a number of biological examples of halohydrin formation, particularly in marine organisms. As with halogenation, halohydrin formation is carried out by halo peroxidases, which function by oxidizing Br_2 or Cl_2 ions to the corresponding HOBr or HOCl bonded to a metal atom in the enzyme. Electrophilic addition to the double

bond of a substrate molecule then yields a bromonium or chloronium ion intermediate, and reaction with water gives the halohydrin. For example:



Hydration of Alkenes: Addition of H₂O by Oxymercuration

Water adds to alkenes to yield alcohols, a process called *hydration*. This reaction takes place on treatment of the alkene with water and a strong acid catalyst. Acid-catalyzed alkene hydration is particularly suited to large-scale industrial procedures, and approximately 300,000 tons of ethanol are manufactured each year in the United States by hydration of ethylene. The reaction is of little value in the typical laboratory, however, because it requires high temperatures 250 °C in the case of ethylene and strongly acidic conditions.

