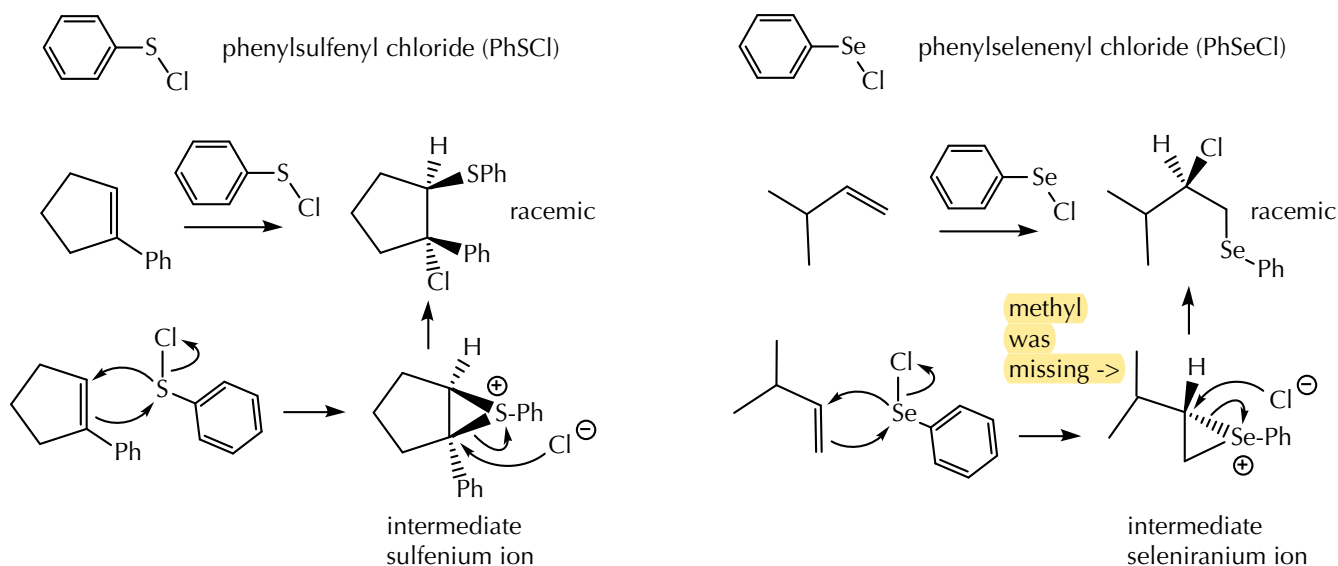


When an interhalogen compound reacts with a pi bond, the halonium ion forms using the most electrophilic of the two halogen atoms (i.e., the less electronegative atom). Thus, chlorine monofluoride (ClF) reacts with pi bonds to give a chloronium ion that is then captured by the released fluoride ion; bromine monochloride (BrCl) gives a bromonium ion, and iodine monochloride (ICl) gives an iodonium ion.

The regioselectivity in the addition reactions of diatomic interhalogens follows the same Markovnikov-like generalization discussed throughout this section: the halonium ion intermediate is structurally unsymmetrical and the positive charge is shared between the halogen atom and the carbon atom that can better stabilize positive charge. Finally, the reactivity of halogen atoms, to give halonium ion intermediates, is not unique and it is mirrored by other atoms (Figure 0918).

Figure 0918

#### Addition reactions with benzenesulfonyl chloride and benzeneselenenyl chloride.



In organic chemistry, two atoms that are commonly observed to give intermediates analogous to halonium ions are sulfur and selenium atoms. Reagents of the general form RSCl and RSeCl give addition reaction products that are consistent with cationic three-membered rings involving sulfur and selenium, respectively, followed by the nucleophilic opening of the positively charged ring according to the Markovnikov-like regioselectivity.

As with the diatomic interhalogen compounds, chlorine is more electronegative than either sulfur or selenium, making sulfur and selenium the electrophilic atoms. There is no fundamental mechanistic difference in how these reagents react with pi bonds to give anti addition products compared with any of the other examples in this chapter.

The reactions and mechanisms for two frequently used reagents, PhS-Cl (benzenesulfonyl chloride) and PhSe-Cl (benzeneselenenyl chloride), both begin with the 3-arrow mechanism to give a cationic, three-membered ring intermediate. As with the halonium ions, the nucleophile that opens the positively charged ring can be the released chloride ion, other anions, or neutral nucleophiles. These ring opening reactions can also be carried out intermolecularly or intramolecularly.

An important feature about the role of analogies in organic chemistry is compellingly exemplified in this first section of Chapter 9: Understanding the details of the anti addition reaction of molecular bromine serves as a powerful mechanistic concept that allows for the understanding of, and prediction for, the reactions of many other chemical reagents.