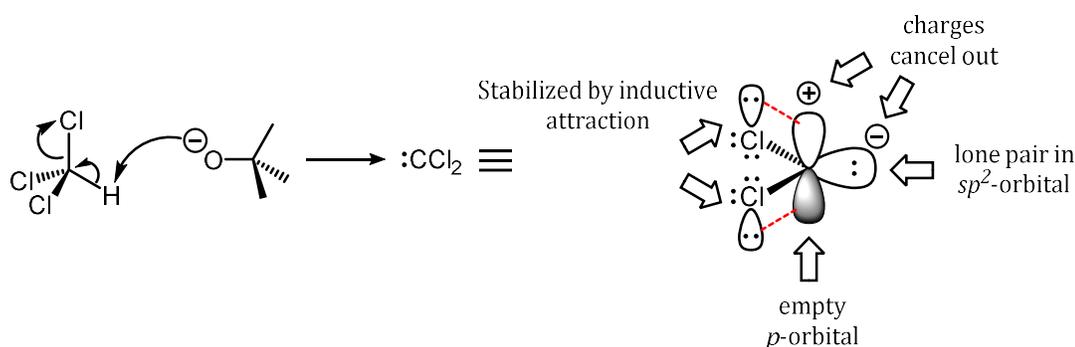


Lesson III.8: Reactions of Alkenes IV: Cyclopropanation and Epoxidation

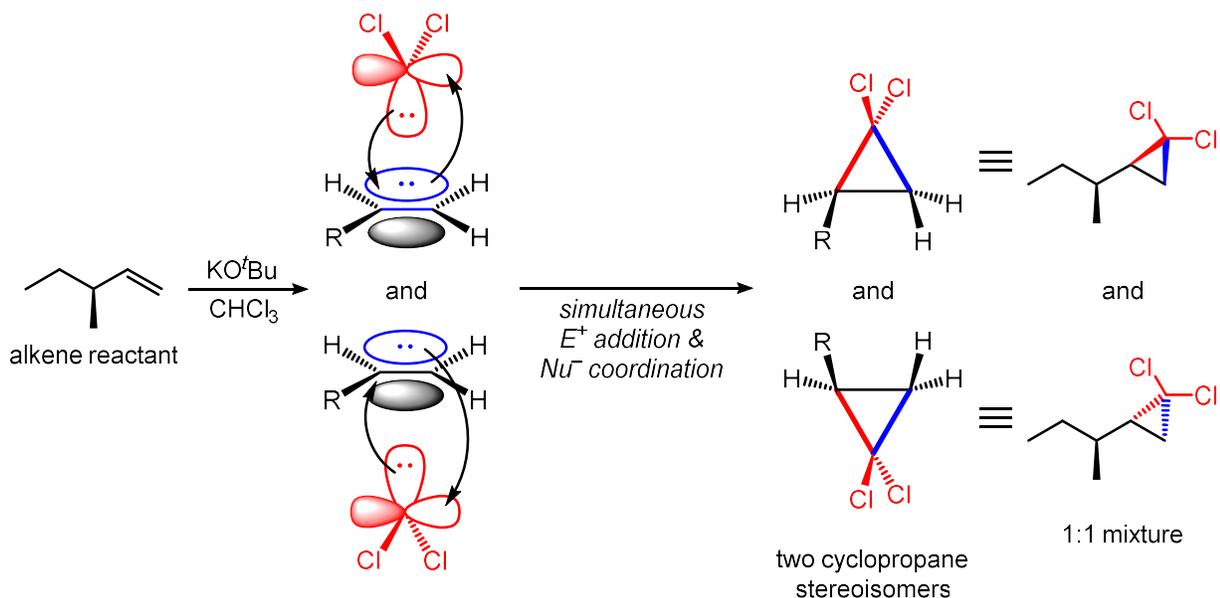
Lesson III.8.1: Cyclopropanation – Simultaneous Nucleophilic and Electrophilic Addition of "CH₂"

In Lessons III.6 and III.7, we learned that sometimes a single atom in a reagent molecule will react as both an electrophile and nucleophile toward a C=C bond, affording an intermediate that contains a 3-membered ring (i.e., halonium and mercurinium, respectively). By carefully selecting an appropriate reagent, we can convert an alkene to a 3-membered ring-containing molecule that is a stable, neutral product.

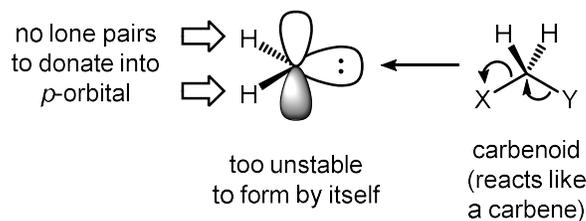
The simplest atom to consider that can react as both electrophile and nucleophile is an atom that has one empty orbital (electrophilic) and one lone pair (nucleophilic). Although this sounds like a very exotic species, one can easily be generated by treating CHCl₃ with KO^tBu. As a strong base but a poor nucleophile, ^tBuO⁻ can only deprotonate CHCl₃. As the H is being removed as H⁺, one of the Cl atoms begins to leave the carbon as Cl⁻, which produces ":CCl₂". This carbon has only 6 valence electrons but is neutral, a species known as a **carbene**. The carbene carbon in :CCl₂ is sp²-hybridized, with an empty p-orbital and a lone pair in an sp²-orbital. Normally, a carbon without an octet would be very unstable, but the lone pairs on the Cl atoms donate into the empty p-orbital and stabilize the carbene via hyperconjugation (Lesson I.11).



Once the dichlorocarbene (:CCl₂) has been generated, the π-electrons in a C=C bond will attack the empty p-orbital to form a bond between the less substituted alkene carbon and the carbene carbon. At the same time as this, the lone pair on the carbene carbon will attack the more substituted alkene carbon to form another C–C bond. The product is a cyclopropane ring, and this reaction is referred to as **cyclopropanation**. Because everything happens in a single, concerted step, the relative spatial orientation of the alkene substituents is retained. If the C=C bond in the reactant has *trans*-stereochemistry, then its substituents will end up *trans*- to each other on the cyclopropane ring. If the C=C bond has *cis*-stereochemistry, the substituents on cyclopropane ring will be *cis*. Remember that :CCl₂ can approach the C=C bond from either above or below, and if the two approaches are identical in energy, then a 1:1 mixture of stereoisomers will be formed.



What do we do if we want a cyclopropane ring without the two Cl atoms? This would require a carbene with the structure $:\text{CH}_2$, but this carbene is too unstable to form, so we must use a species of the form $\text{X}-\text{CH}_2-\text{Y}$ that is not a carbene but does react like one. This type of species is called a "carbenoid".



The reaction of CH_2I_2 with zinc in the presence of copper (written as " $\text{Zn}(\text{Cu})$ ") can generate a carbenoid. When the $\text{I}-\text{CH}_2-\text{ZnI}$ carbenoid is generated, it will react like $:\text{CH}_2$ with the $\text{C}=\text{C}$ bond. The reaction of this carbenoid to form a cyclopropane derivative is called the **Simmons-Smith** reaction. Again, everything happens in a single concerted step, so if we begin the reaction with a *trans*-alkene, those substituents in the cyclopropane ring will also be *trans* to each other. Keep in mind that the carbenoid can react either above or below the plane of the alkene, and if there is no difference in energy between the two approaches, a 1:1 mixture of stereoisomers will be produced.

