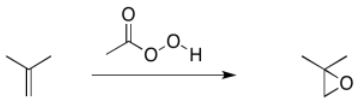
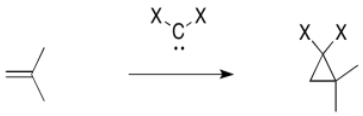
6.9: Cyclopropanation

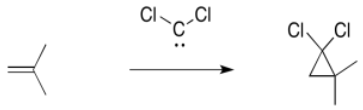
Earlier, we saw that alkenes can donate their pi electrons to oxygen electrophiles in peroxides. The result is transfer of an oxygen atom from the peroxide to the alkene. An epoxide or oxirane ring is formed.



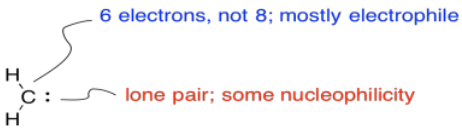
Another, related example is cyclopropanation of an alkene. In alkene cyclopropanation, an alkene is converted into a cyclopropane. A carbon atom is donated to the alkene.



A classic example is the addition of dichlorocarbene to an alkene.



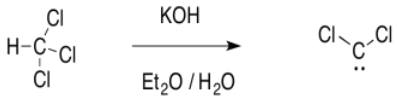
Carbenes are electrophiles because the carbon does not have an octet. The carbon has only two bonds and one lone pair. That's just three electrons, not eight.



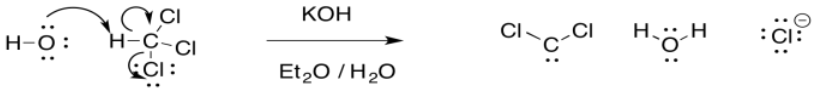
On the other hand, there is a lone pair. The carbene can be nucleophilic, too.

The reaction involves addition of the alkene to an electrophilic carbene. At the same time, that lone pair can donate back, so that a carbocation does not actually form.

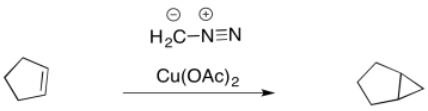
The carbene is sometimes formed through an unusual "alpha"-elimination in the presence of strong base. Strong bases are often alkyllithium reagents, such as CH_3Li, but KOH will work with some compounds.



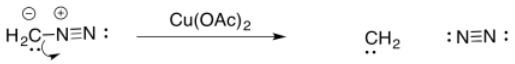
The reaction is unusual because a proton is abstracted from one carbon atom, and a leaving group departs from the same atom. It is much more common to see the leaving group depart from the next atom over, in a beta-elimination.



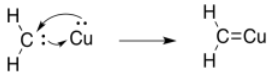
Carbenes are frequently formed from diazo compounds. These include diazomethane, CH_2N_2.



In diazo compounds, an N_2 group is hanging on by a thread. It can easily leave, resulting in a carbene. This reaction is often promoted by metal catalysts, such as copper (II) salts.



The carbene, CH_2, is even less stable than CCl_2. However, in the presence of metal salts, it can be stabilised as a metal carbene complex.

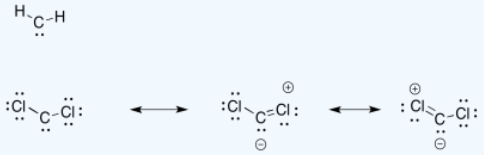


Exercise 6.9.1

Why is a carbene more stable with chlorine atoms attached?

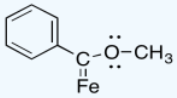
Answer

The chlorines can (weakly) share their electrons to fill the octet on carbon.



Exercise 6.9.2

Some metal carbene complexes, such as the one shown below, are particularly stable. Explain why.

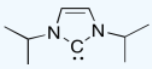


Answer

The oxygen can π-donate to help fill the octet on the carbon.

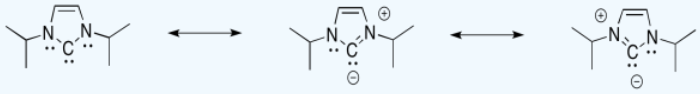
Exercise 6.9.3

Free carbenes, those not attached to a metal ion, are typically so unstable that they can only be generated briefly in solution before they react with a nucleophile, such as an alkene. Arduengo carbenes, such as the one below, are stable enough to be put in a bottle and stored in the refrigerator. Explain why.



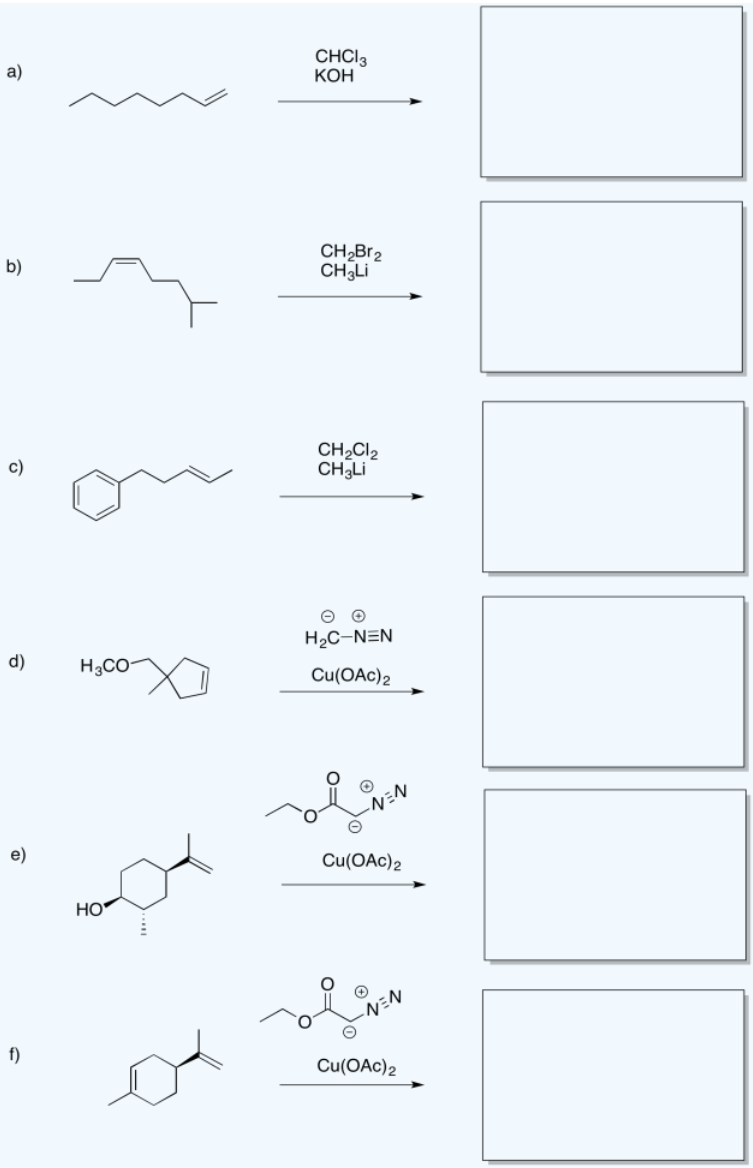
Answer

Not only can the nitrogens π-donate to help fill the octet on carbon, but this is an aromatic system. It is planar, cyclic, fully conjugated, with an odd number of electron pairs in the π-system.



Exercise 6.9.4

Predict the products of the following reactions.



Answer