

8.9: ADDITION OF CARBENES TO ALKENES - CYCLOPROPANE SYNTHESIS

OBJECTIVES

After completing this section, you should be able to

- describe, and write the detailed mechanism for, the formation of a carbene, such as dichlorocarbene.
- describe the structure of a carbene in terms of the hybridization of the central carbon atom.
- write an equation for the formation of a substituted cyclopropane from an alkene and a carbene.
- identify the reagents, the alkene, or both, needed to prepare a given substituted cyclopropane by addition of a carbene to a double bond.
- identify the substituted cyclopropane formed from the reaction of a given alkene with the reagents necessary to form a carbene.

KEY TERMS

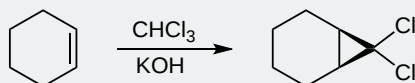
Make certain that you can define, and use in context, the key terms below.

- carbene ($R_2C:$)
- carbenoid
- Simmons-Smith reaction
- stereospecific

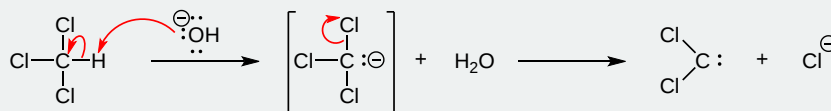
STUDY NOTES

A *carbenoid* is best considered to be a reagent which, while not actually a carbene, behaves as if it were an intermediate of this type.

Dichlorocarbenes can also form cyclopropane structures and are created in situ from reagents such as chloroform and KOH.



The detailed mechanism of the formation of dichlorocarbene is given below. Note that the deprotonation of chloroform generates the trichloromethanide anion, which spontaneously expels the chloride anion.



The highly strained nature of cyclopropane compounds makes them very reactive and interesting synthetic targets. Additionally cyclopropanes are present in numerous biological compounds. One common method of cyclopropane synthesis is the reaction of carbenes with the double bond in alkenes or cycloalkenes. Methylene, H_2C , is simplest carbene, and in general carbenes have the formula R_2C . Other species that will also react with alkenes to form cyclopropanes but do not follow the formula of carbenes are referred to as carbenoids.

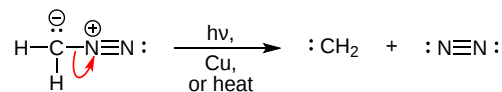
INTRODUCTION

Carbenes were once only thought of as short lived intermediates. The reactions of this section only deal with these short lived carbenes which are mostly prepared in situ, in conjunction with the main reaction. However, there do exist so called persistent carbenes. These persistent carbenes are stabilized by a variety of methods often including aromatic rings or transition metals. In general a carbene is neutral and has 6 valence electrons, 2 of which are non bonding. These electrons can either occupy the same sp^2 hybridized orbital to form a singlet carbene (with paired electrons), or two different sp^2 orbitals to form a triplet carbene (with unpaired electrons). The chemistry of triplet and singlet carbenes is quite different but can be oversimplified to the statement: singlet carbenes usually retain stereochemistry while triplet carbenes do not. The carbenes discussed in this section are singlet and thus retain stereochemistry.

The reactivity of a singlet carbene is concerted and similar to that of electrophilic or nucleophilic addition whereas, triplet carbenes react like biradicals, explaining why stereochemistry is not retained. The highly reactive nature of carbenes leads to very fast reactions in which the rate determining step is generally carbene formation.

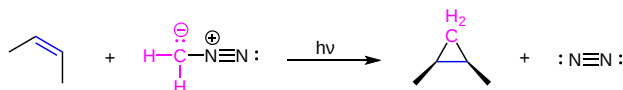
PREPARATION OF METHYLENE

The preparation of methylene starts with the yellow gas diazomethane, CH_2N_2 . Diazomethane can be exposed to light, heat or copper to facilitate the loss of nitrogen gas and the formation of the simplest carbene methylene. The process is driven by the formation of the nitrogen gas which is a very stable molecule.

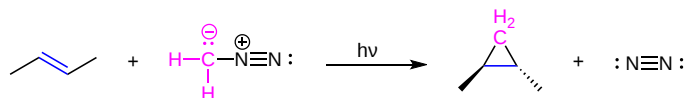


CARBENE REACTION WITH ALKENES

A carbene such as methylene will react with an alkene which will break the double bond and result with a cyclopropane. The reaction will usually leave stereochemistry of the double bond unchanged. As stated before, carbenes are generally formed along with the main reaction; hence the starting material is diazomethane not methylene.



In the above case *cis*-2-butene is converted to *cis*-1,2-dimethylcyclopropane. Likewise, below the *trans* configuration is maintained. This shows that the reactions are stereospecific, only a single stereoisomer is obtained as the product.



ADDITIONAL TYPES OF CARBENES AND CARBENOIDS

In addition to the general carbene with formula R_2C there exist a number of other compounds that behave in much the same way as carbenes in the synthesis of cyclopropane. **Halogenated carbenes** are formed from halomethanes. An example is dichlorocarbene, Cl_2C . The mechanism for the formation of dichlorocarbene is above in the study notes. These halogenated carbenes will form cyclopropanes in the same manner as methylene but with the interesting presence of two halogen atoms in place of the hydrogen atoms.

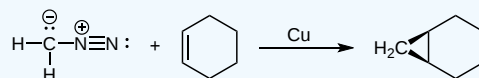
Carbenoids are substances that form cyclopropanes like carbenes but are not technically carbenes. One common example is the stereospecific Simmons-Smith reaction which utilizes the carbenoid - ICH_2ZnI . The (iodomethyl) zinc iodide is formed in situ via the mixing of Zn-Cu with CH_2I_2 . If this ICH_2ZnI is in the presence of an alkene, a CH_2 group is transferred to the double bond to create cyclopropane. Since this reacts as a carbene, the same methods can be applied to determine the product.

? EXERCISE 8.9.1

Knowing that cycloalkenes react much the same as regular alkenes what would be the expected structure of the product of cyclohexene and diazomethane facilitated by copper metal?

Answer

The product will be a bicyclic ring, Bicyclo[4.1.0]heptane.



? EXERCISE 8.9.2

What would be the result of a Simmons-Smith reaction that used *trans*-2-pentene as a reagent?

Answer

The stereochemistry will be retained making a cyclopropane with *trans* methyl and ethyl groups. *Trans*-1-ethyl-2-methylcyclopropane

? EXERCISE 8.9.3

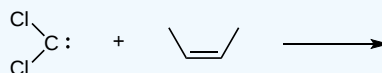
What starting material could be used to form *cis*-1,2-diethylcyclopropane?

Answer

The *cis* configuration will be maintained from reagent to product so we would want to start with *cis*-3-hexene. A Simmons Smith reagent, or methylene could be used as the carbene or carbenoid.

? EXERCISE 8.9.4

What would the following reaction yield?



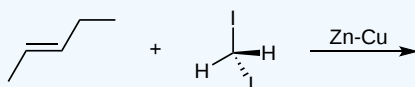
Answer

The halogenated carbene will react the same as methylene yielding, *cis*-1,1-dichloro-2,3-dimethylcyclopropane.



? EXERCISE 8.9.5

Draw the product of this reaction. What type of reaction is this?



Answer

This is a Simmons-Smith reaction which uses the carbenoid formed by the CH_2I_2 and Zn-Cu . The reaction results in the same product as if methylene was used and retains stereospecificity. Iodine metal and the Zn-Cu are not part of the product. The product is *trans*-1,2-ethyl-methylcyclopropane.

REFERENCES

1. Vollhardt, K. Peter C. and Schore, Neil E. Organic Chemistry: Structure and Function. New York: Bleyer, Brennan, 2007.
2. Abdel-Wahab, Aboel-Magd A. Ahmed, Saleh A. and Dürr, Heinz. "Carbene Formation by Extrusion of Nitrogen" in CRC Handbook of Organic Photochemistry and Photobiology. CRC Press, 2004.

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