9.9: ADDITION OF HALOGENS

Learning Objective

- predict the products/specify the reagents for halogenation of alkenes

INTRODUCTION

As the halogen molecule, for example Br_2, approaches the double bond of an alkene, electrons in the double bond repel electrons in the bromine molecule causing polarization of the halogen bond. This interaction induces a dipole moment in the halogen molecule bond allowing one of the halogens to gain a partial positive charge and take the role of electrophile. The nucleophilic pi electrons form a bond to the electrophilic halogen while the halogen molecular bond heterolytically breaks to release bromide as a leaving group. The halogen addition is not regioselective but stereoselective. Stereochemistry of this addition is analogous to the oxymercuration mechanism. In this reaction, a bromonium (halogenium) ion froms as the intermediate. The bromonium ion formation stabilizes the positive charge and prevents carbocation rearrangement. In the second step, the bromide released from the first step takes the role of thenucleophile and reacts with the cyclic bromonium ion with back side orientation. Therefore, the stereochemistry of the product is a **vicinial dihalides** through **anti-addition**.

$$R_2C{=}CR_2 + X_2 \rightarrow R_2CX{-}CR_2X \tag{9.9.1}$$

Halogens that are commonly used in this type of the reaction are: Br_2 and Cl_2. In thermodynamical terms I_2 is too slow for this reaction because of the size of its atom, and F_2 is too vigorous and explosive. Solvents that are used for this type of electrophilic halogenation are inert (e.g., CCl_4) can be used in this reaction.

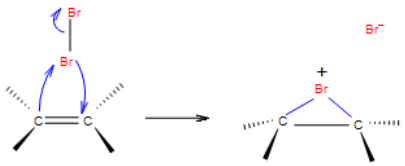
Because halogen with negative charge can attack any carbon from the opposite side of the cycle it creates a mixture of steric products.Optically inactive starting material produce optically inactive achiral products (meso) or a racemic mixture.

ELECTROPHILIC ADDITION MECHANISM CONSISTS OF TWO STEPS.

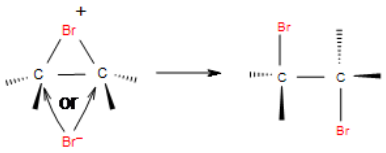
Before constructing the mechanism let us summarize conditions for this reaction. We will use Br_2 in our example for halogenation of ethylene. Halogens can act as electrophiles due to polarizability of their covalent bond. Addition of halogens is stereospecific and produces vicinial dihalides with anti-addition. Cis starting materials will give a mixture of enantiomers and trans starting materials produce a meso compound.

Nucleophile	pi electrons of alkene double bond
Electrophile	halogen (Cl_2 or Br_2)
Regiochemistry	none
Stereochemistry	anti-additon

Step 1: The addition the Br-Br bond polarizes, heterolytic cleavage occurs and Br with the positive charge forms a intermediate cycle with the double bond.

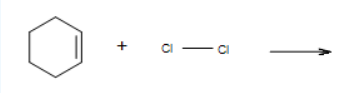


Step 2: The bromide anion reacts with either carbon of the bridged bromonium ion from the back side of the ring. The ring opens up and the two halogens are in the **anti-position** relative to each other.



Exercise

1. What is the mechanism of adding Cl_2 to the cyclohexene?

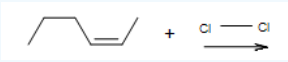


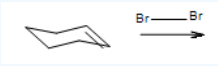
2. A reaction of Br_2 molecule in an inert solvent with alkene follows?

a) syn addition

b) anti addition

c) Morkovnikov rule

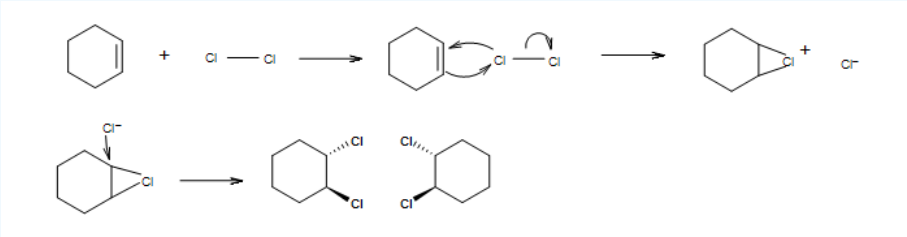
3. 

4. 

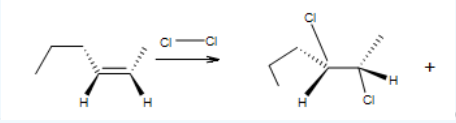
5. Predict the product of the product of 1,2-dimethylcyclopentene reacting with Br_2 with proper stereochemistry.

6. Predict the products for 1,2-dimethylcyclpentene reacting with HCl, give the proper stereochemistry. What is the relationship between the two products?

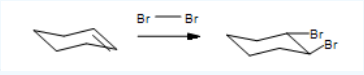
Answer

1. 

2. b

3. 

enantiomer

4. 

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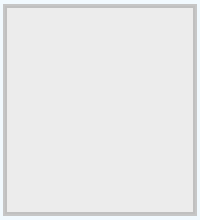
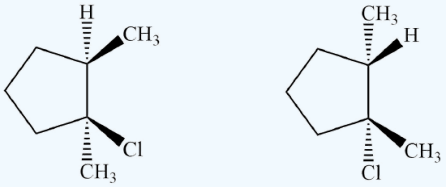


6.



These compounds are enantiomers.

REFERENCES

1. Vollhard,K.Peter C., and Neil E.Schore.Organic Chemistry:Structure and Function.New Yourk: W.H.Freeman and Company 2007
2. Chemestry-A Europian Journal 9 (2003) :1036-1044

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