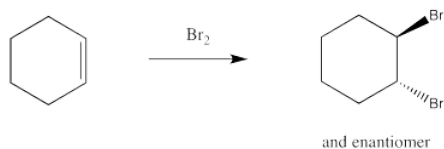


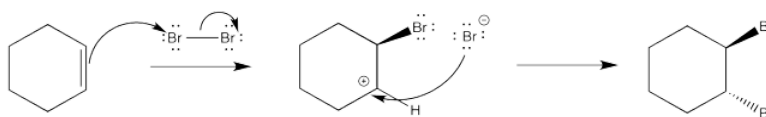
6.4: Stabilized Cations in Electrophilic Addition

Electrophilic addition to alkenes generally takes place via donation of the π -bonding electron pair from the alkene to an electrophile. So far, we have only looked at protic electrophiles, but the reaction proceeds with others, as well. For instance, alkenes react quite easily with bromine.



Dripping a solution of bromine into a solution of alkene provides a clear sign of reaction. The red-brown colour of bromine disappears almost instantly.

Although bromine isn't an obvious electrophile, most of the common diatomic elements can behave that way; the exception is dinitrogen. A fleeting asymmetry of electrons can polarize the molecules to one end. That event leaves one atom partially positive and the other end partially negative. Because these elements tend to form somewhat stable anions, the partially negative atom can be displaced fairly easily.



As before, a nucleophile connects with the cation in a second step. In this case, a dibromide compound is formed. However, it isn't formed in quite the way that is shown below.

We know that the mechanism shown above does not convey the whole picture because it isn't consistent with the stereochemistry of the reaction. The stereochemical outcome is shown below. The enantiomer is formed as well.

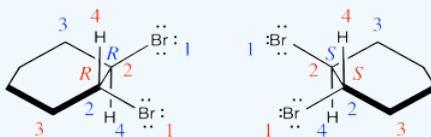


? Exercise 6.4.1

Assign configurations R or S to the product shown in the above mechanism.

Answer

Two products are formed and they are enantiomers.



However, although two enantiomers are formed in the reaction, the corresponding diastereomer is not. The following step does not occur.

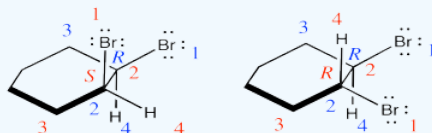


? Exercise 6.4.2

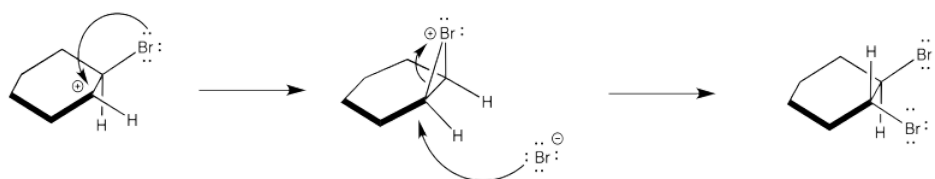
Assign configurations R or S to the product shown in the above mechanism and explain why it is not an enantiomer to the compound in problem EA4.1.

Answer

They are diastereomers. One chiral center has the same configuration in both compounds but the others are opposite.



Instead, the cation that forms in the reaction appears to be stabilized by lone pair donation from bromine. The intermediate species below is called a cyclic bromonium ion. The bromine prevents approach of the nucleophilic bromide from one side, ensuring formation of product through *anti* addition only. The *trans* product forms as a result.

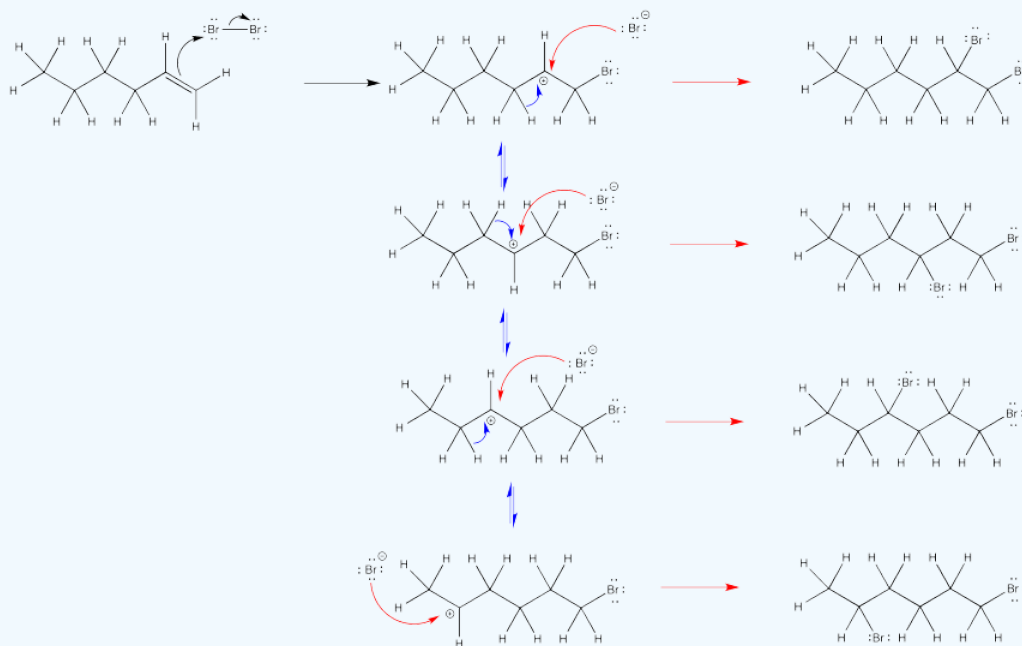


? Exercise 6.4.3

Additional evidence of the stabilized bromonium comes from the observation of just one product in the bromination of 1-hexene. How many products would be expected in the absence of a stabilized cation? Explain with a mechanism.

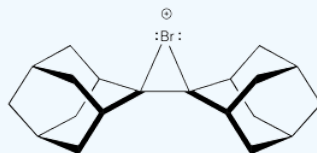
Answer

The second bromine could occupy any of the secondary positions if there were a true carbocation. That doesn't happen; the second bromine occupies only the position next to the other bromine.



? Exercise 6.4.4

Bromonium ions like the one shown below have been isolated and characterized by X-ray crystallography in at least one case. Explain why the intermediate was isolated in this case, rather than a dibromo product.



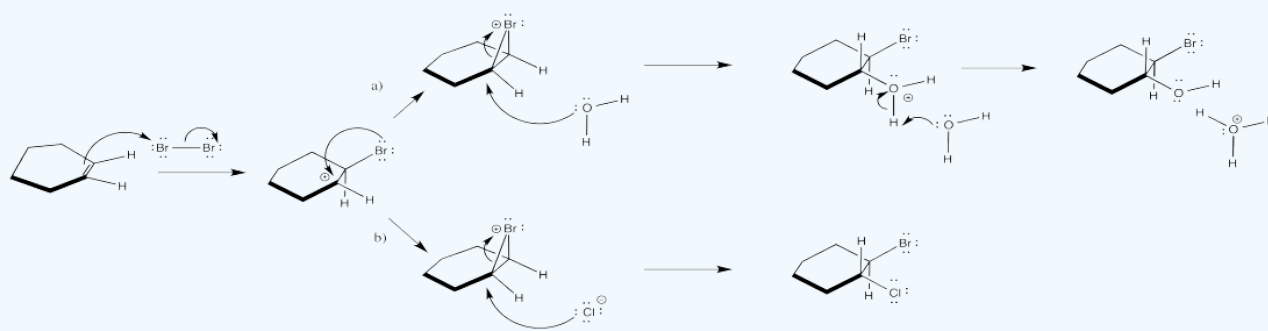
? Exercise 6.4.5

In some cases, the reaction of an alkene with bromine does not provide dibromo products. Show products of the reaction of cyclohexene under the following conditions and justify your choices with mechanisms.

a) Br_2 in water b) Br_2 and $\text{NH}_4^+ \text{Cl}^-$ in THF

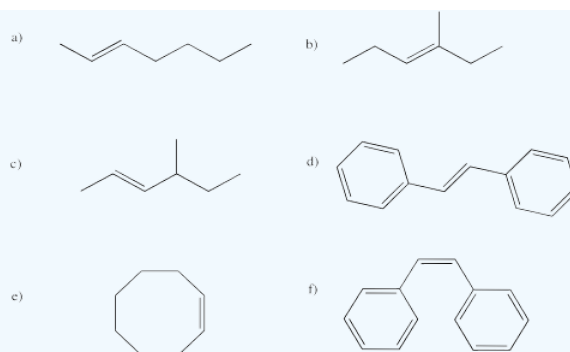
Answer

The nucleophile in the second step changes under different conditions.

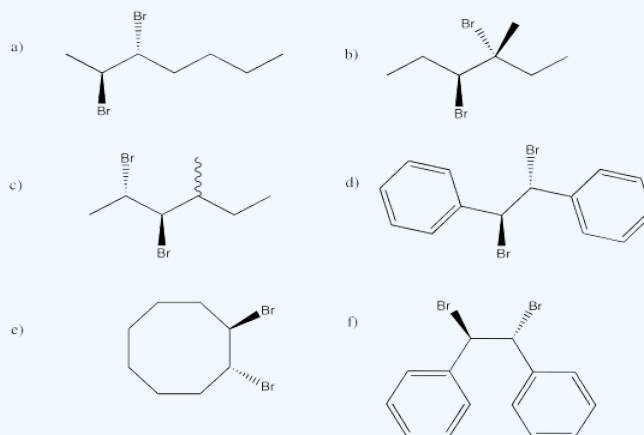


? Exercise 6.4.6

Provide products for the reaction of bromine with each of the following compounds.



Answer



& enantiomer in each case

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