

## INTRODUCTION

- Under certain circumstances reaction intermediates can be stable enough to be characterized by x-ray crystallography. The Cambridge Structural Database contains evidence of such species.
- By examining the structure of intermediates we can gain insights into reaction mechanisms. In this module the mechanism for the electrophilic addition of halogens to an alkene will be explored using crystallographic data.

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## OBJECTIVES

- To evaluate possible mechanisms for the electrophilic addition of Br<sub>2</sub> to an alkene based on the stereochemistry of the products that are formed.
- To search the Cambridge Structural Database for evidence of the existence of a cyclic bromonium ion intermediate.
- To account for the observed stability of the adamantylidene-adamantane-bromonium ion.

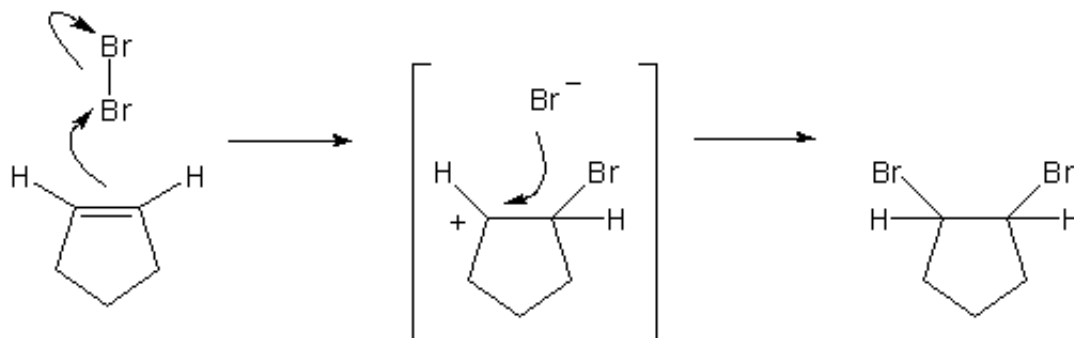
## GETTING STARTED

- This module requires full access to the Cambridge Structural Database System. Specifically, the following software components will be used:
  - *ConQuest*, for search and retrieval of crystal structure data.
  - *Mercury*, for visualisation and examination of crystal structures.

## 1 STEPS REQUIRED

### 1.1 Electrophilic Addition of Br<sub>2</sub> to an Alkene

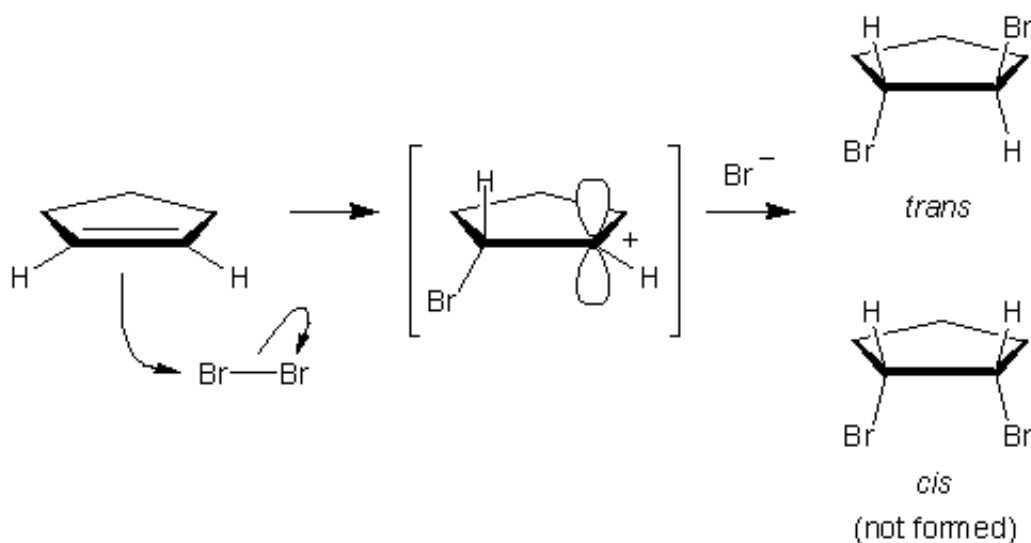
- A possible mechanism for the electrophilic addition of Br<sub>2</sub> to an alkene is outlined below.



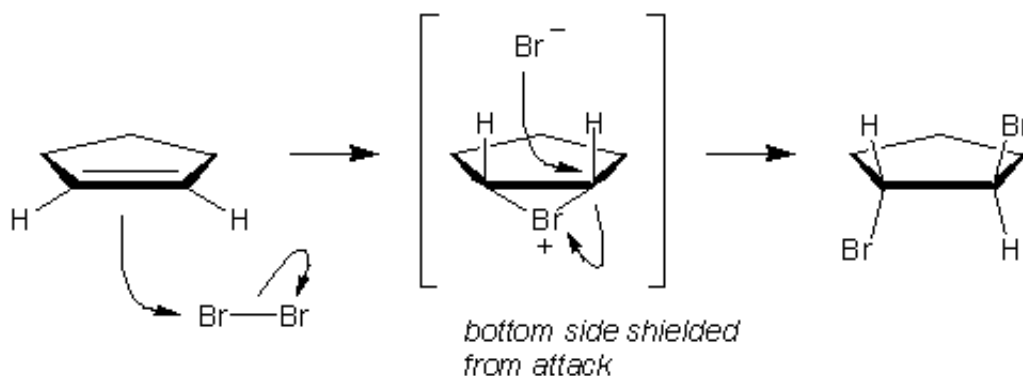
- As a bromine molecule approaches the nucleophilic alkene, the Br-Br bond becomes polarized. The electron pair from the double bond then attacks the polarized bromine forming a C-Br bond and displacing a bromide ion. The intermediate electrophilic carbocation then immediately reacts with the nucleophilic bromide ion to give the dibromo addition product.
- Although this mechanism looks reasonable it is not consistent with the known facts. In particular, it does not explain the stereochemistry of halogen addition.

### 1.2 Investigate the stereochemistry of halogen addition

- Lets look again at the addition reaction of bromine with cyclopentene. We will assume that Br<sup>+</sup> adds to cyclopentene from the bottom face to form the carbocation intermediate shown below:



- Since the positively charged  $sp^2$  carbon is planar, it could be attacked by the bromide ion in the second step of the reaction from either the top or bottom face to give a mixture of products. One product has the two bromine atoms on the same side of the ring (*cis*), the other has the bromines on opposite sides (*trans*).
- However, we actually find that only *trans*-1,2-dibromocyclopentene is produced. None of the *cis* product is formed. Therefore, the mechanism proposed above cannot be correct.
- In order to explain the stereochemistry of halogen addition it has been suggested that the true reaction intermediate is not a carbocation, but is instead a bromonium ion. A bromonium ion is a symmetrical three-membered ring containing a bridged bromine atom carrying a positive charge.
- If a bromonium ion is formed as an intermediate it would *shield* one face of the molecule. Attack by the bromide ion in the second step could then only occur from the opposite, *unshielded* face to give the *trans* product exclusively.

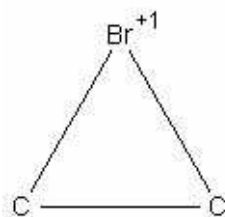


- This mechanism would explain the observed stereochemistry of halogen addition reactions.

However, can we find further evidence for the existence of the bromonium ion intermediate?

### 1.3 Search for evidence, in the Cambridge Structural Database, that the cyclic bromonium ion actually does exist.

- Start *ConQuest* and hit the **Draw** button to open the *Draw* window.
- Sketch the cyclic bromonium ion shown below. Remember to specify a charge of +1 on the bromine. This can be done, e.g. by right-clicking on the Br atom at selecting **Charge**, followed by **Positive** and then +1 from the resulting pull-down menus.



- Hit **Search**, then in the *Search Setup* window hit **Start Search**.
- As soon as you start the search, the *ConQuest* interface moves to the *View Results* pane. After a few moments, the refcodes of any hit structures will appear in the list on the right-hand side.
- You should retrieve two hits (refcodes *DAKVUG* and *WEVPIW*). Both are examples of adamantylidene-adamantane-bromonium ions. Examine these two structures.
- We can now confirm that bromonium ions are indeed real.

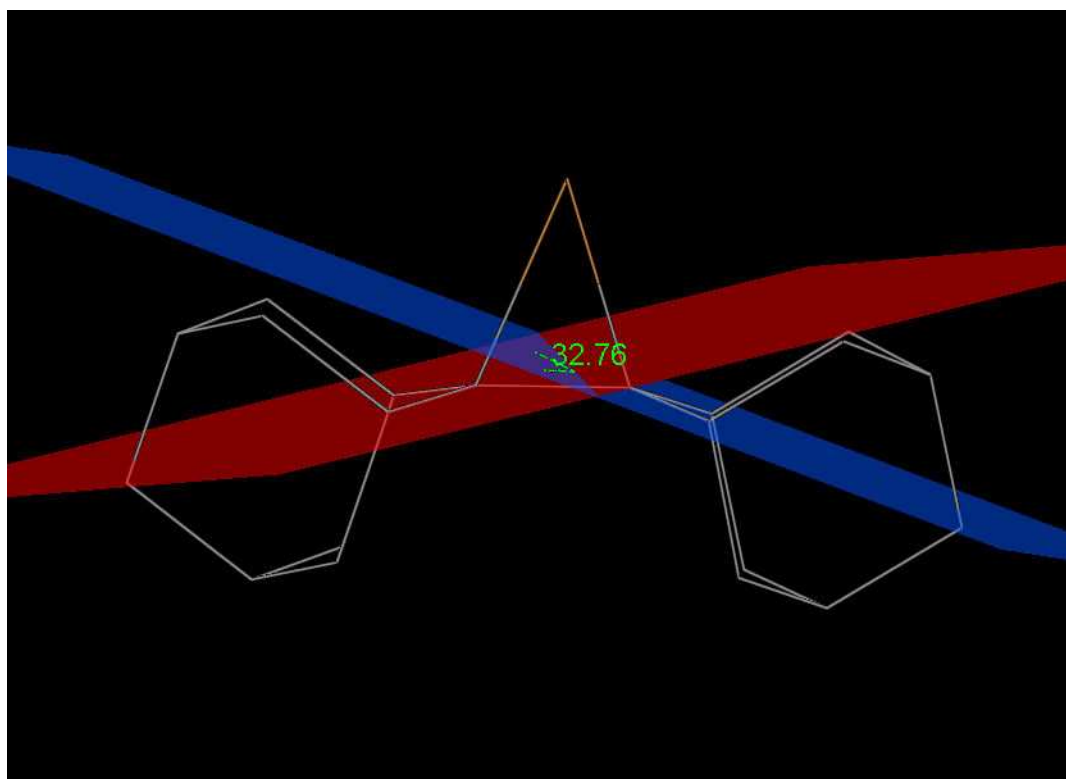
### 1.4 Find other examples of halonium ions

- Search for other examples of halonium ions (F, Cl, I) in the Cambridge Structural database (CSD).
- Write out the journal references for any halonium ions you find.
- To write out a file containing the journal references click on **File** in the top-level menu and select **Export Entries as...** from the pull-down menu. Then click on the file type bar and select **TXT: Text representation** from the pull-down menu. Turn the output off for everything except Bibliographic information (using the check-boxes in the Select options section of the window). Hit **Save** to save the file of journal references.
- When viewing CSD entries that which have a Digital Object Identifier (DOI) a clickable hyperlink to the original literature source will be available from the Author/Journal tab in the *View Results* pane. Articles are normally accessed via CrossRef (<http://www.crossref.org>) though links are also available where appropriate through the IUCr and LitLink. A subscription to the

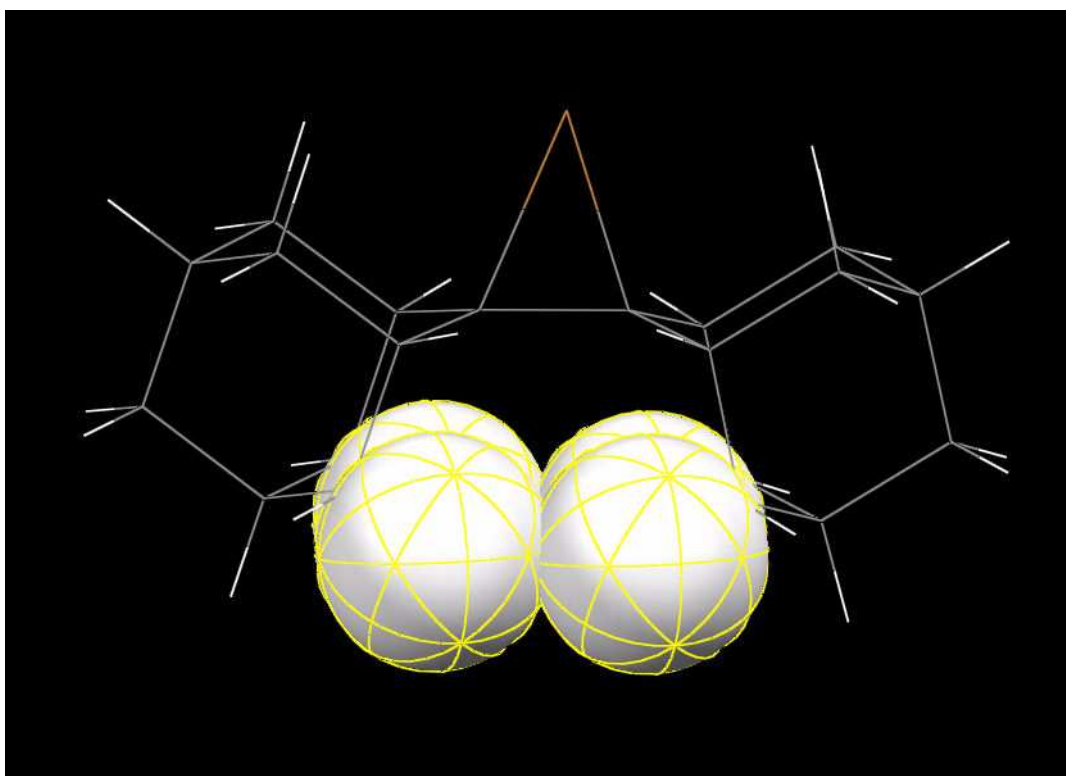
publication in question will normally be required to view the on-line article.

### 1.5 Explain the stability of the halonium ions found in the CSD.

- Halonium ions are electrophiles and react immediately to form the addition product. However, the structures we have examined are clearly stable enough to be characterized by x-ray crystallography. What structural characteristics, possessed by all examples of halonium ions in the CSD, give rise to this special stability?
- Open Mercury and read in the file *halonium\_ions.gcd*. Browse the structures by clicking on each of the refcodes in the *Structure Navigator* on the right hand side of the main Mercury window.
- You will notice that all examples of halonium ions in the CSD are produced by halogen addition to 2-(adamant-2-ylidene)adamantane (refcode *ADYLAD01*). This very hindered alkene forms halonium ions that are resistant to nucleophilic attack.
- Examine closely the structure of adamantylidene-adamantane-bromonium tribromide (refcode *DAKVUG*). The dihedral angle between the substituent planes of the carbons connecting the adamantyl rings is 32.76 degrees. This distortion from planarity results in close interatomic contacts between the H atoms on some of the carbons of the two adamantane groups. Consequently, there is severe steric crowding on the bottom face. The relevant distances are: 2.00 Å for H10 and H15 on C8 and C12, respectively; 2.01 Å, for H1, H24 on C2, C18; 2.14 Å for H9, H17 on C7, C13; and 2.15 Å for H13, H25 on C10, C19.
- It is this severe crowding at the side opposite to the Br atom which prevents access of a nucleophile to the ion. This unusual feature is the likely source of the stability of the bromonium ion.



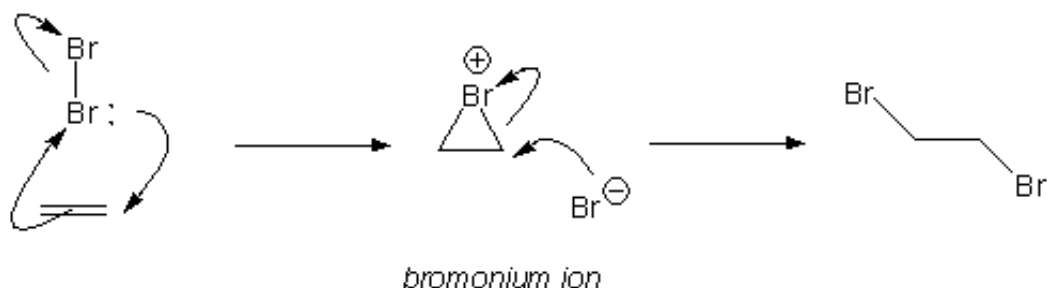
*Image showing the dihedral angle between the substituent planes of the carbons connecting the adamantyl rings in CSD refcode DAKVUG.*



*Image showing severe crowding at the side opposite to the Br atom prevents access of a nucleophile to the ion*

## SUMMARY OF KEY CONCEPTS

- The electrophilic addition of halogens to an alkene proceeds via a three-membered halonium ion intermediates to give the trans addition product.



- Halonium ions were first postulated in 1937 by Roberts and Kimball to account for the observed diastereoselectivity in halogenation of alkenes, see: *The Halogenation of Ethylenes* Irving Roberts, George E. Kimball *J. Am. Chem. Soc.*; **1937**; 59(5); 947-948. The halonium ion postulate is an excellent example of deductive logic: from experimental results the mechanistic details of alkene electrophilic reactions were deduced.
- Very hindered alkenes form halonium ions that are resistant to nucleophilic attack. Such ions are sufficiently stable to be characterized by x-ray crystallography. Thus, almost 50 years after halonium ions were first proposed we have structural evidence that confirms their existence.

