

Experiment 14

Fig. 14-1



ADDITION OF HBr TO ALKENES

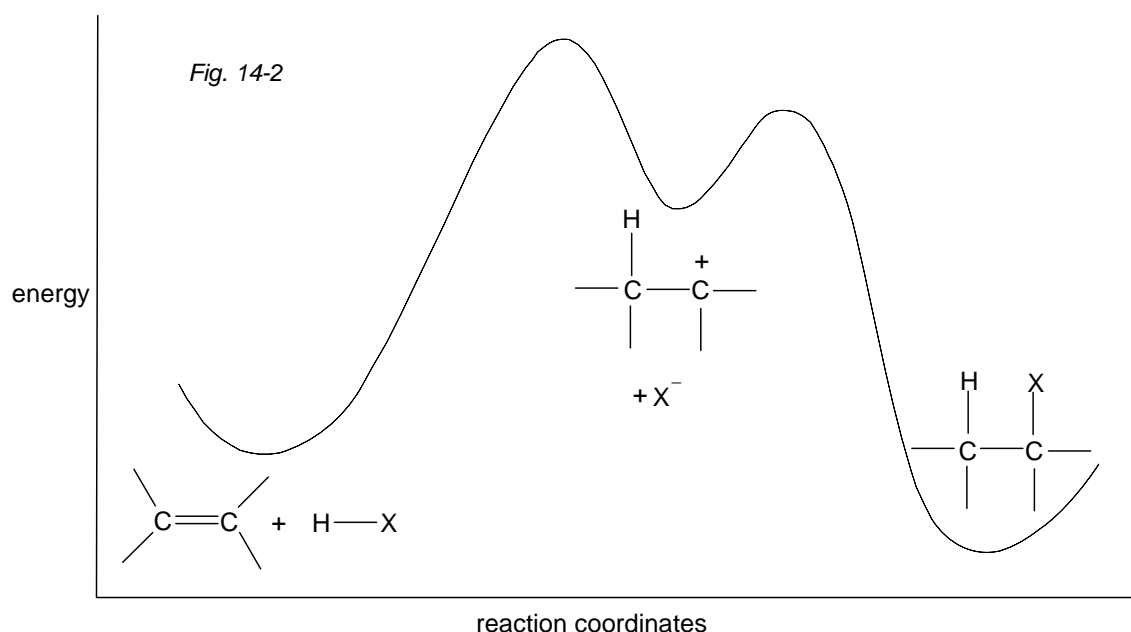
Vladimir V. Markovnikov (1812 -1880)
http://en.wikipedia.org/wiki/Vladimir_Markovnikov

Text Topics

Electrophilic addition to alkenes, Markovnikov addition

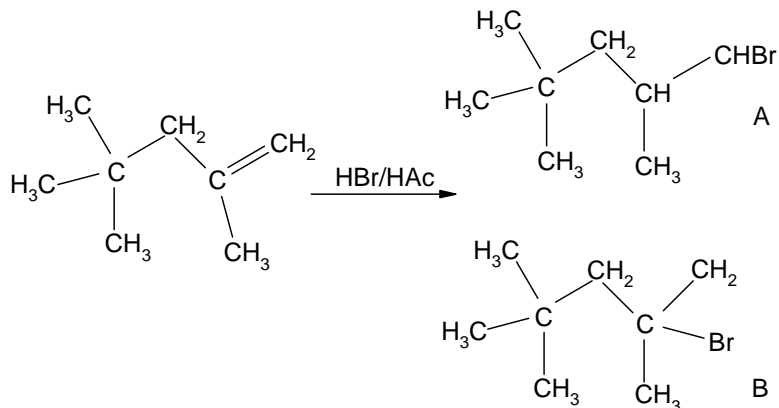
Discussion

Until organic chemistry entered the spectroscopy era around the middle of the 20th century, qualitative chemical tests were the methods of choice for the determination of the presence of functional groups in organic compounds. If a bromine or permanganate solution is added to an alkene, the color of either quickly disappears providing evidence for unsaturation. In an earlier experiment, you studied the mechanism of the addition of bromine to the π bond of cinnamic acid by determining the product structure of the dibromide product. This experiment involves an investigation of the mechanism of the electrophilic addition of HBr to an alkene. Because the alkene that will be used has an asymmetric double bond, there are at least two different bromo compounds that could result from the addition. The scheme below illustrates the commonly accepted reaction profile for the addition of a hydrogen halide to an alkene.



One of the alkene options for reasons involving boiling points, cost and possible product structures (including rearrangement considerations) for this experiment will be 2,4,4-trimethyl-1-pentene. If the carbocation mechanism illustrated above is operative, the H⁺ could add either on carbon 1 or carbon 2.

Addition of H^+ to carbon 1 leads to the formation of **A** and addition of H^+ to carbon 2 leads to **B**. The reaction could produce one or the other or a mixture of the two possible products. It will be up to you to determine the product structure(s) and whether the information provides any insight into the mechanism of the reaction. The product will be analyzed using nmr. The solvent plays an important role in this reaction and acetic acid seems to give the best results.



An interesting nomenclature issue centers on the carbon skeleton used in this experiment. 2,2,4-Trimethylpentane is used as a standard for octane ratings of gasoline and has been assigned a rating of 100. Mixtures with n-heptane (octane rating of 0) are used to determine the octane rating of commercial gasoline. In other words, if testing reveals that a gasoline sample causes the same knocking in an engine as an 87% 2,2,4-trimethylpentane, 13% n-heptane mixture, the gasoline receives an octane rating of 87. Unfortunately, the commercial name of 2,2,4-trimethylpentane is isooctane. Why is this a poor choice for a name?

Procedure

(Please note that other alkenes such as 1-octene, 1-hexene and styrene will probably work for this experiment but have not been tested in our laboratory. This experiment was adapted from the articles by T. M. Brown et.al, and H. M. Weiss but note that small amounts of hazardous carbon tetrachloride are used. Marty Jones uses ether and while it is probable that ether can be substituted for CCl_4 , preparation for the nmr will be more difficult.) This experiment can be performed in test tubes, vials with v shaped bottoms or small round bottom flasks. Use a calibrated plastic pipet to transfer 0.25 mL of 2,2,4-trimethyl-1-pentene to a reaction vessel. In a hood, carefully open a bottle of 30% solution of hydrogen bromide in acetic acid. The bottle will probably fume upon opening. Keep the bottle in the hood at all times. Use a 1 mL glass pipet to transfer 1 mL of the hydrogen bromide solution to the reaction vessel. Stir thoroughly for a about a minute and allow the mixture to sit for few more minutes. Add 2 mL of carbon tetrachloride to the vessel and mix being careful to avoid contact with the hazardous liquid. Add 10 mL of water to the mixture and stir again. Use a Pasteur pipet to withdraw and transfer the organic layer to a clean test tube or vessel trying as best as possible to minimize the amount of water during transfer. To the remaining aqueous phase, add a couple of milliliters of carbon tetrachloride and mix. Use the Pasteur pipet to again withdraw the organic layer and combine the two organic layers. Add about 10 mL of saturated sodium bicarbonate solution slowly with mixing (foaming might occur) to the organic liquid and mix. Use a clean Pasteur pipet to transfer the organic layer to a final clean test tube. The organic layer will probably appear to be cloudy due to the presence of water. Add anhydrous sodium sulfate to the organic liquid until the liquid clarifies. Use another clean Pasteur pipet to transfer the solution to an nmr tube. Determine the H-nmr spectrum and analyze the spectrum to determine the product structure.

References

<http://faculty.adams.edu/~mbjones/Chem321/Addition%20of%20HBr%20to%20octene%202005.pdf>
Brown, T. M.; Dronsfield, A. T.; Ellis, R. *J. Chem. Ed.*, **1990**, *67*, 518.
Weiss, H. M. *J. Chem. Ed.*, **1995**, *72*, 848.

Prelaboratory Preparation - *Experiment 14*

First, be sure to list all the goals of the experiment. Write a detailed mechanism that illustrates electron movement for the carbocation mechanism and predict the structure of the expected product and possible minor product. Indicate how nmr can be used to distinguish between the two most probable products. Suggest other plausible mechanisms, if any, for the reaction. Locate this type of addition reaction on the *Reaction-Map of Organic Chemistry* in **Appendix C** and include the reaction number in your report.

Observations

Report all relevant observations.

Conclusions

This section should include the following:

1. Were the goals of the experiment achieved? Explain your answer.
2. What was the identity of your product and did it agree with your prediction? Explain how the nmr supports your conclusion.
3. Does the product structure support a carbocation mechanism? Does the product structure refute any other possible mechanisms? Did Markovnikov's rule apply and when is the rule applicable?

