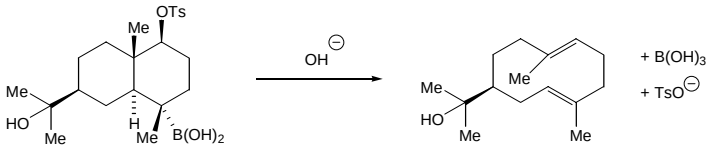
2ND YEAR ORGANIC TUTORIAL QUESTIONS 2003/2004
Dr Alan Spivey – Introduction to Stereoelectronics

1. (a) The following base induced fragmentation reaction was reported in 1972 by Wharton:



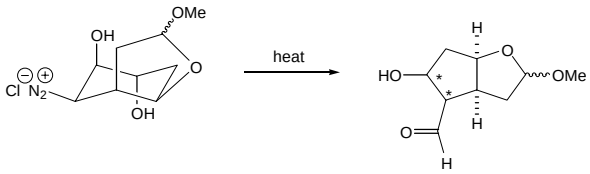
(i) Draw a mechanism for this transformation.

[2 marks]

(ii) Explain why the stereochemistry of the starting material is important for this transformation to occur. Include in your answer a diagram of the structure in its reactive conformation with the key bonds highlighted, and diagrams of the key orbitals which are involved in the fragmentation sequence.

[6 marks]

(b) The reaction drawn below is an example of what is known as a Tiffeneau-Demjanov rearrangement.



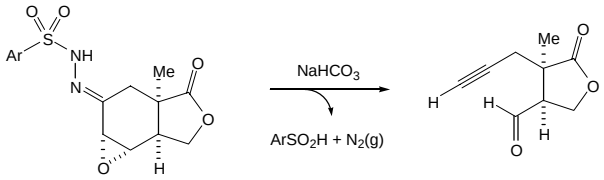
(i) Draw a mechanism for this transformation.

[2 marks]

(ii) Predict the stereochemistry of the chiral centres indicated in the product and rationalise your prediction on the basis of stereoelectronic control. Include in your answer a diagram of the diazonium intermediate with the key bonds highlighted, and show the key orbitals that are involved in the rearrangement.

[6 marks]

(c) The Eschenmoser fragmentation shown below was reported in 1975 by Corey.



(i) Draw a mechanism for this transformation.

[3 marks]

(ii) Draw diagrams of the fragmentation process with the key bonds highlighted, and show the orbitals that are involved.

[6 marks]

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