CHEM95002: Orbitals in Organic Chemistry - Stereoelectronics

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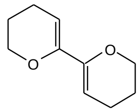
1. On heating bis-dihydropyran **1**, 1,2-ethanediol and a catalytic quantity of *para*-toluene sulfonic acid in toluene just one of the three possible diastereomeric products **2**, **3** and **4** is formed.

(i) Which is it?

(ii) Why is the reaction so selective?



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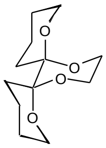

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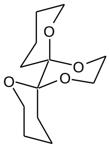

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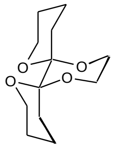

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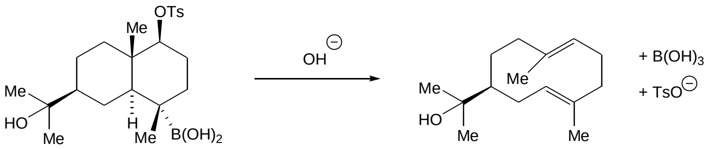
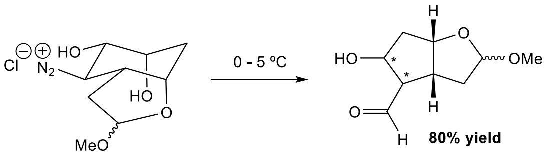
2. The following base induced fragmentation reaction was reported in 1972 by Wharton:



(i) Draw a mechanism for this transformation.

(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.

3. The reaction drawn below is a key step in R.B. Woodward's classic synthesis of prostaglandin F2α and can be considered to be a Tiffeneau-Demjanov rearrangement.



(i) Draw a mechanism for this transformation.

(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.