An Introduction to Reaction Stereoelectronics 2016-2017 EXAM QUESTION

Answer part (a) and EITHER part (b) OR part (c) of this question.

(a) The cis-diol shown below reacts in aqueous acid to give two products, as shown:

\[
\begin{align*}
\text{Me} & \quad \text{OH} \\
\text{Me} & \quad \text{OH}
\end{align*}
\hspace{1cm}
\stackrel{\text{HClO}_4 (\text{aq.})}{\rightarrow}
\begin{align*}
\text{Me} & \quad \text{OH} \\
\text{Me} & \quad \text{O}
\end{align*}
\hspace{1cm}
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

i) Draw mechanisms for the formation of each product.  
\hspace{20em} (4 marks)

ii) Highlight the key bonds that are involved in each reaction. Explicitly indicate which orbitals are involved and their relative orientations.  
\hspace{20em} (5 marks)

iii) Provide possible reasons as to why the cyclopentane is the major product. 
\hspace{20em} (3 marks)

iv) Would you expect the isomeric trans-1,2-diol substrate to give the same products? Explain.  
\hspace{20em} (4 marks)

(b) Consider the following reaction which is a key step in Harmata’s approach to tricyclolavulone.

\[
\text{Br} \quad \text{O}
\hspace{1cm}
\stackrel{\text{Li}}{\rightarrow}
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me}
\end{align*}
\hspace{1cm}
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

i) Draw a mechanism for the formation of the product.  
\hspace{20em} (4 marks)

ii) Highlight the key bonds that are involved in this reaction and explicitly indicate which orbitals are involved and their relative orientations.  
\hspace{20em} (5 marks)

(c) Consider the following reaction which is a key step in Baran’s synthesis of ingenol.

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me}
\end{align*}
\hspace{1cm}
\stackrel{\text{BF}_3 \cdot \text{Et}_2 \text{O}}{\longrightarrow}
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

i) Draw a mechanism for the formation of the product. HINT: The Lewis acid initiates this reaction by interacting with the allylic alcohol.  
\hspace{20em} (5 marks)
ii) Highlight the key bonds that are involved in this reaction. Explicitly indicate which orbitals are involved in the reaction and their relative orientations.

(4 marks)

(5 marks)