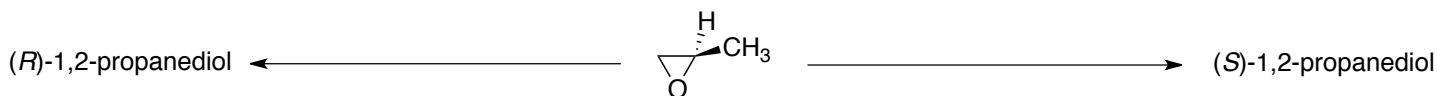


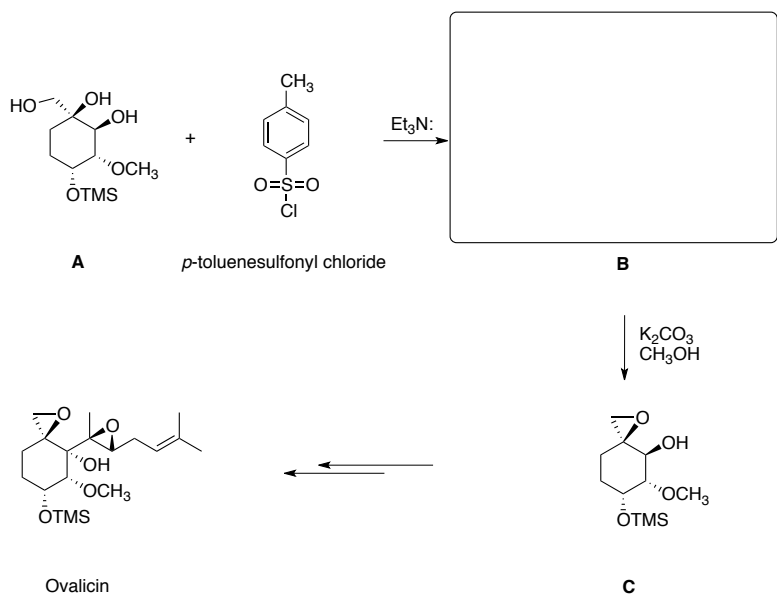
Completion (6 pts)		Name	
Random Sample(s) (4 pts)		BID	
Total (10 pts)		Section-CRN	
Additional Recommended Problems from McMurray (8 th Ed.)			

1. When (R)-(+)-2-phenyl-2-butanol is allowed to stand in methanol containing a few drops of sulfuric acid racemic 2-methoxy-2-phenylbutane is formed. Suggest a reasonable mechanism.

2. What reaction conditions would allow you to carry out each of the following stereospecific transformations?

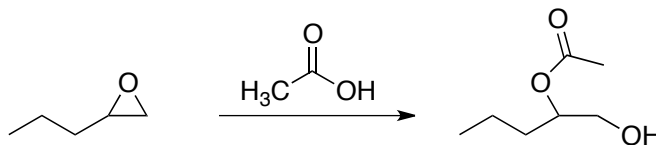


3. The growth of new blood vessels angiogenesis is a crucial embryonic development. Abnormal angiogenesis is associated with tumor growth, suggesting that inhibition of angiogenesis may be an approach for the treatment of cancer. The diepoxide, ovalicin, is an angiogenesis inhibitor that was synthesized from compound C, which was in turn prepared from compound A by a two-step sequence. **First**, draw the structure for compound B. **Second**, draw a mechanism for the conversion of B to C.



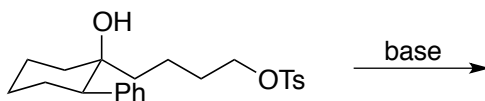
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4. The epoxide below can be opened with acetic acid. Draw the complete mechanism. Show all electron lone-pairs, formal charges and curved arrow notation.



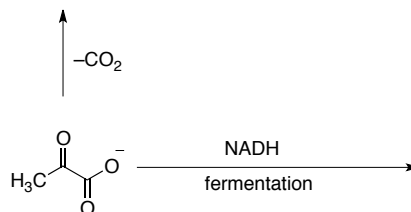
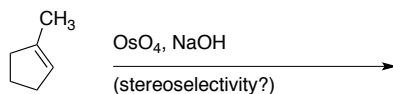
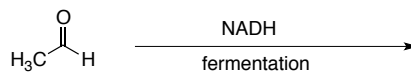
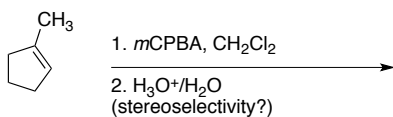
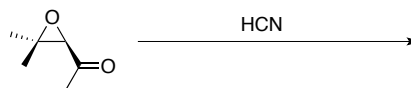
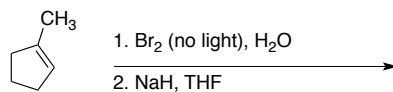
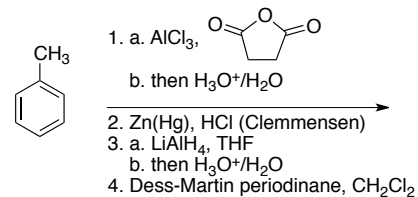
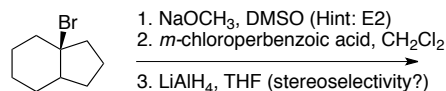
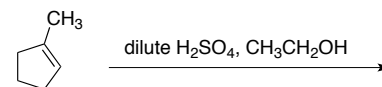
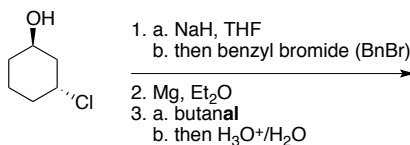
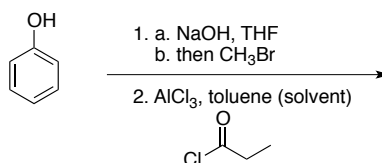
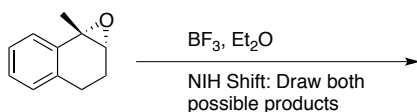
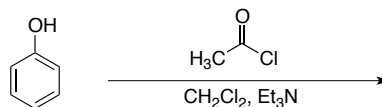
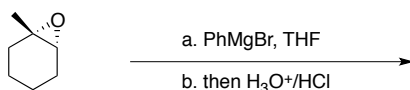
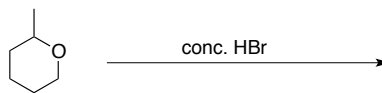
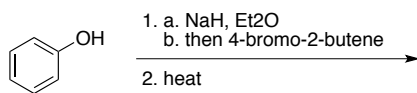
5. The reaction above is regioselective. Draw the transition state for the rate determining step above and then use that to explain why nucleophilic addition takes place at the most substituted carbon of the epoxide. Transition states should include partial charges and dashed lines (----) to indicate partial bond formation or cleavage.

6. The *p*-toluenesulfonate (OTs) undergoes intramolecular Williamson reaction on treatment with base to give a spirocyclic ether. Draw the structure of the product.



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7. Draw the major product. If more than one regioisomer or stereoisomer exists, draw the major.



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8. An A-value is the difference in free energy between axial and equatorial conformers. The larger the A-value, the larger the preference for the equatorial conformer.

$$\text{A-value} = \Delta G^\circ = (G^\circ_{\text{axial}} - G^\circ_{\text{equatorial}}) = -RT \ln K$$

	A-Value for 2-Methyl Substituent	A-Value for 3-Methyl Substituent
X		
S	1.42	1.40
CH ₂	1.74	1.74
O	2.86	1.43

- i. First, draw the axial conformation of methylcyclohexane and use this diagram to explain why axial conformers are generally higher in energy than equatorial conformers.

- ii. Explain the trend in A-values for **2**-methylsubstituted thiane (X = S), oxane (X = O) and cyclohexane (X = CH₂).

- iii. Explain the trend in A-values for the **3**-methylsubstituted thiane, oxane and cyclohexane. Why do 3-methylthiane and 3-methyloxane have almost identical and lower A-values compared to methylcyclohexane?

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9. Design a synthesis for each of the following molecules. Where stereochemistry is shown, your synthesis must be stereoselective.

