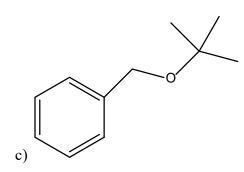
Organic II

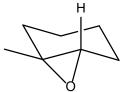
Assignment # 6 Spring 2021

1) The heats of combustion of 1,2-epoxybutane and tetrahydrofuran have been measured: one is 2499 kJ/mol; the other is 2546. Match the heats of combustion with the respective compounds.

2) Only one combination of alkyl halide and alkoxide is appropriate for the preparation of each of the following ethers by the Williamson ether synthesis. What is the correct combination in each case? Also, show the other combination and explain why it would not work as well.



3) The epoxide shown below gives a mixture of two azido alcohols on reaction with sodium azide in aqueous acid and in base. A) Write a structural formula for the major product formed at pH 9.5.



- b) A different isomer predominates at pH 4.2. What is the structure of this isomer? The pKa of HN_3 is 4.2
- 4) Ethers, like alcohols, lose an alkyl radical from the molecular ion to give an oxygen stabilized cation. For sec-butyl ethyl ether, a) give the structure for TWO ions of m/z of 87.

B) Give the structure for the m/z ion of 73.

5) Suggest an explanation for the fact that the most stable conformation of cis-3-hydroxythiane 1-oxide (shown below) is the chair form in which both substituents are AXIAL.

6) Predict the principal organic product(s) of each of the following reactions. Specify stereochemistry if important.

7) The growth of new blood vessels, angiogenesis, is crucial to wound healing and 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. Can you suggest structures for compound B and C?

$$K_2CO_3$$

methanol

8) The following reaction has been reported in the chemical literature. Suggest a reasonable mechanism.

9) Suggest short, efficient reaction sequences suitable for preparing each of the following compounds from the given starting materials and any necessary organic or inorganic reagents:

from bromobenzene and cyclohexanol

from bromobenzene and isopropyl alcohol

from benzyl alcohol and ethanol

10) A compound CE is a cyclic ether of molecular formula $C_9H_{10}O$. Its ^{13}C NMR has 6 different aromatic carbons, and 3 CH_2 . Oxidation of the compound with sodium dichromate and sulfuric acid gave the molecule below. What is the structure of CE?

$$\begin{array}{c} \text{Na}_2\text{Cr}_2\text{O}_7 \\ \text{H}_2\text{SO}_4/\text{H}_2\text{O} \end{array} \\ \begin{array}{c} \text{OH} \\ \end{array}$$