Part A (1-12) True or False (Put **T** or **F** on the line at the left.) (12 pts)

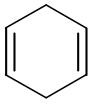
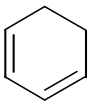
T_____1) Epoxides are more reactive than normal ethers.

T_____2) Epoxides have less ring strain than cyclopropane due the –O– bond angle being 104^{o}.

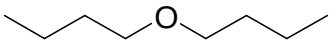
F_____3) The constructive interference of two molecular orbitals results in a molecular orbital with one more node.

T_____4) Normal ethers are reactive to non-nucleophilic acids.

F_____5)

 is more stable than 

T_____6) The oxygen atom in this ether is sp^3 hybridized

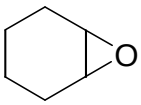


F_____7) When ethers are stored in the presence of air, they become explosive due the formation of peroxides compounds from the H_2O_2 in air.

F_____8) The S_N2 reaction leads to retention of configuration.

F_____9) The plus and minus signs in p orbitals represent the charge in each lobe.

T____10) The oxygen atom in this epoxide is sp^3 hybridized



F____11) Cyclopentene plus acetylene is a thermally, symmetry allowed reaction.

T____12) Cyclopentene plus butadiene is a thermally, symmetry allowed reaction.

_____/12

Part B

1. What is an orbital?(3pts)

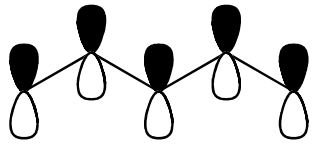
An orbital is a **mathematical function** that describes the **wave-like behavior** of **an electron.**

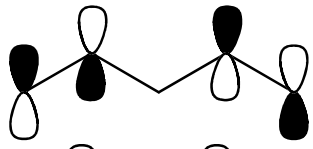
2. The following diagrams are for three of the π MOs in the pentadienyl radical.
   (# π MOs = # π AOs = # π C atoms)
   a)What is the total number of π MOs in the pentadienyl radical **anion**? 5_____2pt

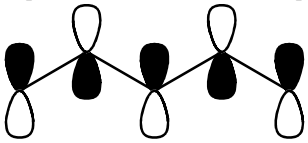
   b)What is the total number of π MOs in the pentadienyl radical **cation**? _5_____2pt

   c)What is the total number of π electrons in the pentadienyl radical **anion**?_____6_____ **$_2$HC=CH-CH=CH-CH$_2$ $^-$** **(2 +2 + 2 π** electrons) 3pt

   d) Identify the number that each π MO is. (Put the number on the line, π___).(10 pt.)

(a)  π___

(b)  π___

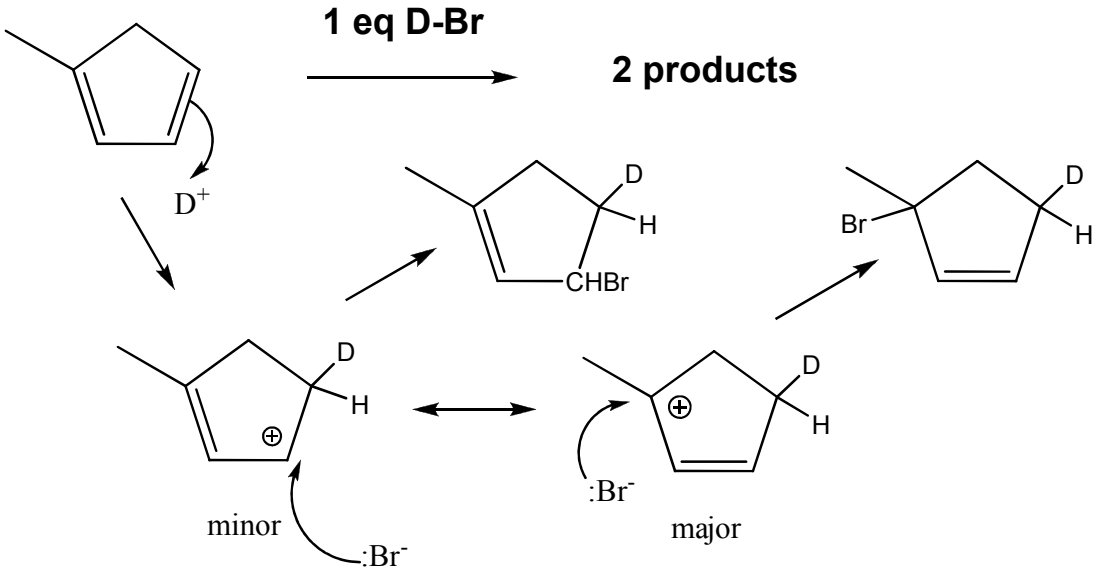
(c)  π___

a) 1 b) 4 c) 5 (1 pt each)

_____/13 _____/25

3. The addition of 1 equivalent of DBr to methylcyclopentadiene generates a mixture of products. (D is an isotope of hydrogen, ^2H)

a) Draw the products, and mechanistically account for the mixture of products. Curved arrows must follow IUPAC convention.
a) 10 pts (See 2008)



In class on Thursday, we went the 1,2 and 1,4 additions to dienes. We *mechanistically accounted for the mixture*s of two products whose ratios were controlled kinetically and thermodynamically. We *mechanistically accounted for the mixture of products* again on Tuesday for the question above, just before the test.

The above example accounts for the kinetically controlled 1,4 product (and for the reason why the D^+ adds on the right of the diene rather than the left). The intermediate has two resonance structures. The tertiary cation structure is more stable compared to the secondary cation resonance structure. So, the Br^- anion will preferentially attack the intermediate at the 4 position. When the temperature is low enough, there will be very few cases where the Br^- anion has enough energy to attack at the 2 position. The higher 1,2 TS makes the reaction "kinetically" controlled so that there is more 1,4 product. It is *crucial* that you show major and minor structures to explain this (-2pts if you didn't).

When the T is high enough so that there are enough high energy Br^- anions to get over both TSs, then it is the relative stability of the products that determines the product ratio. Equilibrium ratios are determined by thermodynamics (ΔG^o=-RTlnK). The double bond in the 1,2 product has 3 C atoms around it and only two in the 1,4 product. So, the 1,2 product is thermodynamically controlled.
(10pts)

b) Draw the structure of the product you would expect to dominate as the temperature of the reaction is raised:

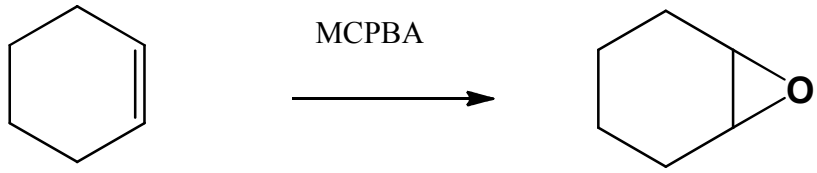
1,2 (but 1,4 was the correct answer for butadiene, the example in class) So, no pts added or taken off for part b.

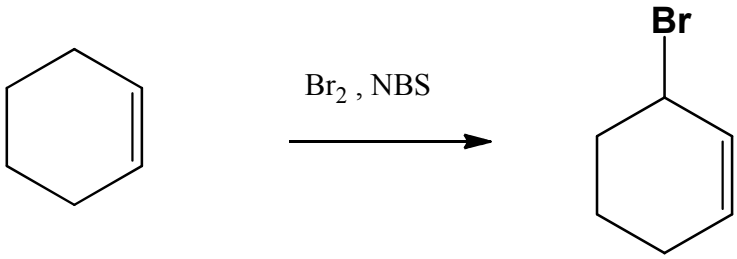
c) Is this the kinetically or **thermodynamically** controlled product (circle correct word.
2pts (12 pts, total)

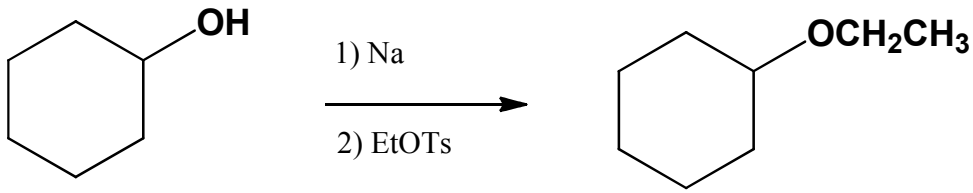
_____/12 _____/37

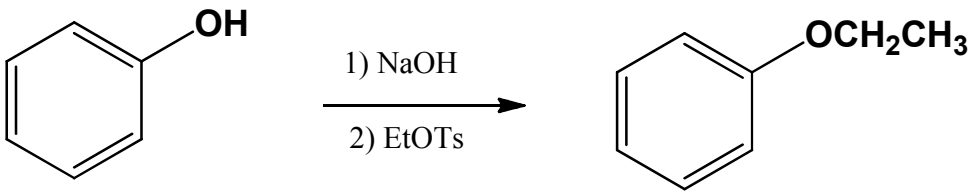
4. Give reagents and conditions to accomplish the following transformations. (24 pts)

Remarks:
-There is a huge difference between Na and Na^+.
-Allylic bromination under light can lead to di- and tribromo products. NBS is used to control the reaction. No points were taken off if you used hν, this time.









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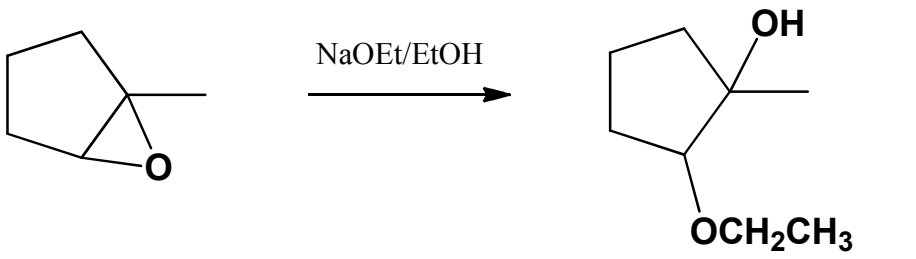
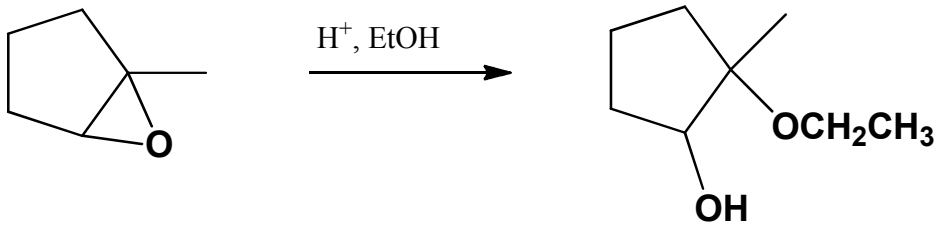
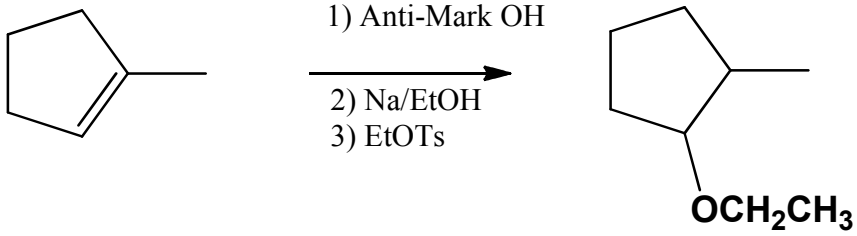
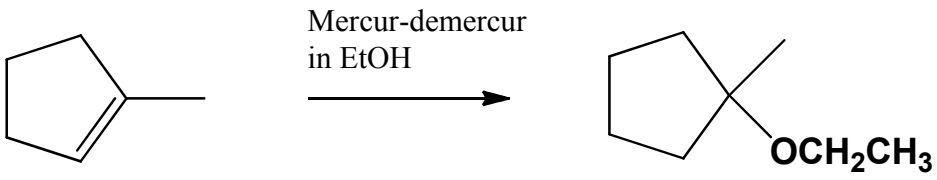

NaOEt/EtOH
O
OH
OCH2CH3


H+, EtOH
O
OCH2CH3
OH


1) Anti-Mark OH
2) Na/EtOH
3) EtOTs
OCH2CH3

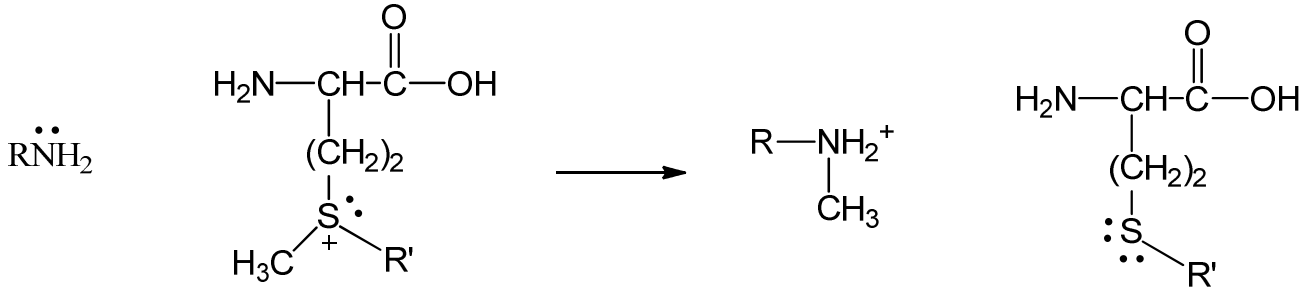

Mercur-demercur
in EtOH
OCH2CH3

_____/24 _____/61

5. Show **clearly** how you would synthesize butyl isopropyl sulfide using 1-butanol, 2-propanol, and any solvents and reagents you need. (6 pts)

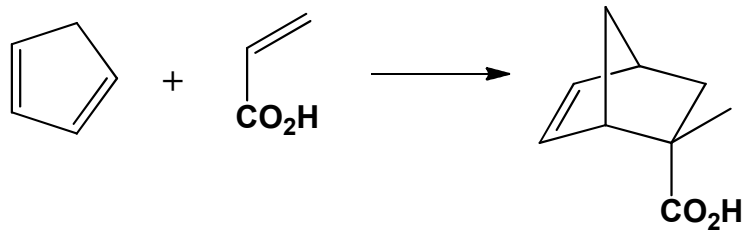
   See class notes

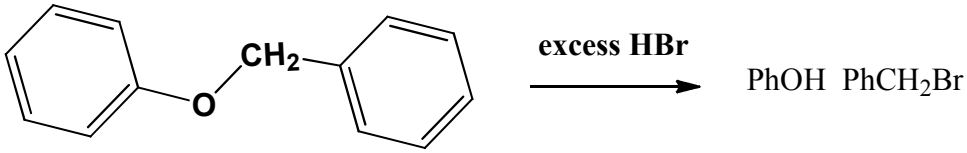
6. Draw the mechanism (by drawing the "curly arrows") for this biochemical methylation reaction and write the name of the mechanism over the reaction arrow. (3 pts)
   See class notes

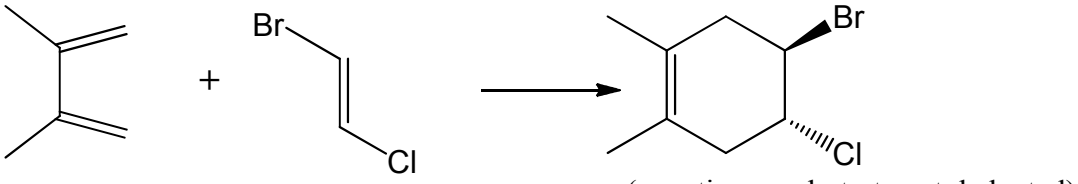


_____/9 _____/70

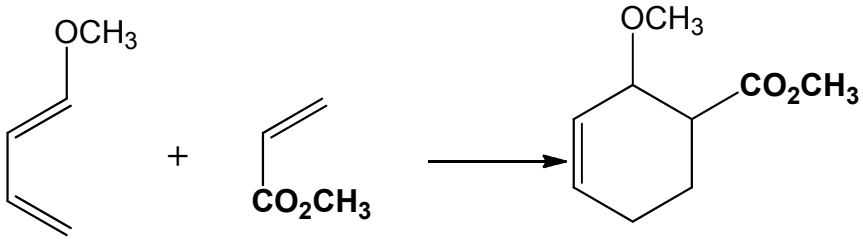
7. Predict *all* products in reaction. (If you believe no reaction will occur, write NR). Write all regio/stereochemical products where applicable. In cases of two or more isomeric products, indicate the *major* isomer or if *equal* amounts.(18 pts)

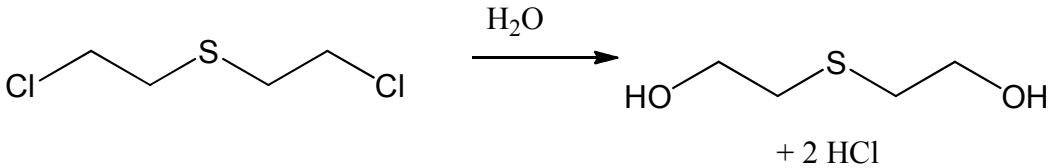




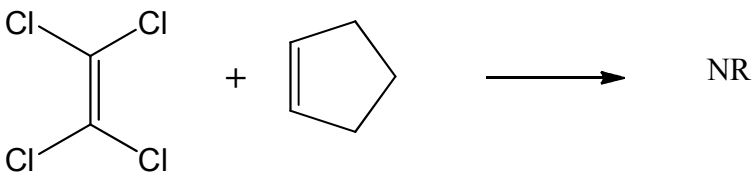


(enantiomers, but pts not deducted)



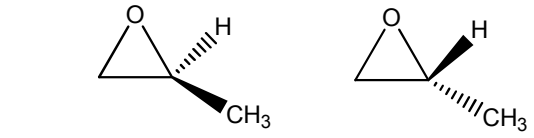


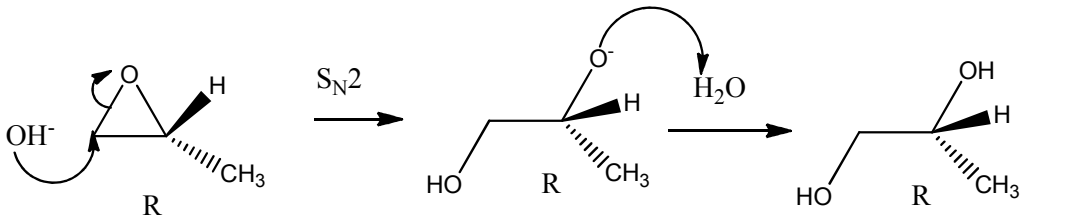
+ 2 HCl

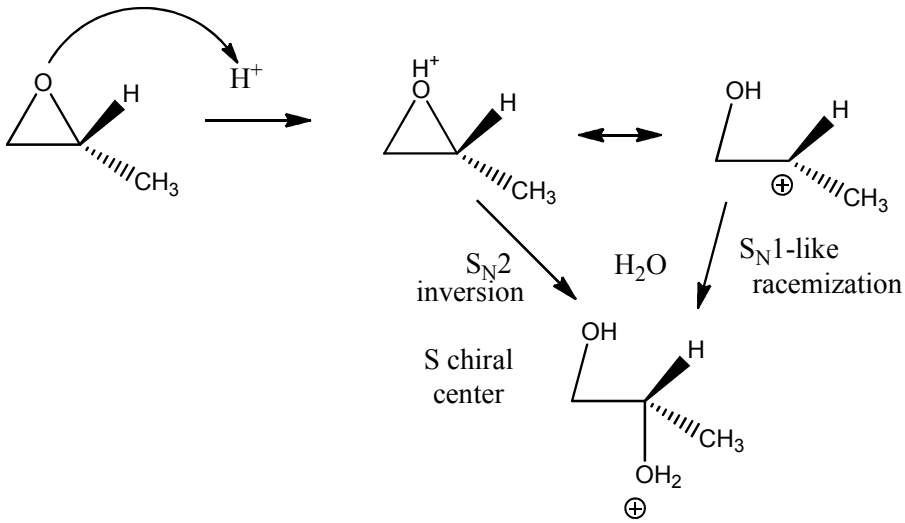


_____/18 _____/88

8. (3 pts) 1,2-epoxypropene is a chiral molecule. Hydrolysis of this epoxide gives another chiral molecule, propane-1,2-diol. (6 pts)
(a) Draw the enantiomers of 1,2-epoxypropane.
(b) Draw the mechanism for the base-catalyzed hydrolysis of (*R*)-1,2-epoxypropene, draw the chiral product, mark whether the chiral center is *R* or *S*.
(c) Propose a mechanism for the acid-catalyzed hydrolysis of (*R*)-1,2-epoxypropene and explain *in a few words* why the acid-catalyzed hydrolysis is less stereospecific than the base-catalyzed.

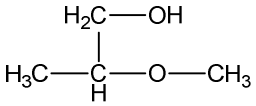


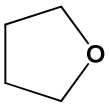


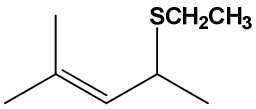


9. Name the following compounds using IUPAC rules. (6pts)

a) b) c)







a) 2-methoxypropan-1-ol

b) tetrahydrofuran

c) 4-ethylthio-2-methylpent-2-ene

_____/12 _____