CHEMISTRY 112A FALL 2013

EXAM 2

Answer Key

NOVEMBER 14, 2013

NAME- WRITE BIG ______________________________

STUDENT ID: ________________

SECTION AND/OR TA IF YOU ARE IN THE LABORATORY COURSE: ______________________

- **You will have 75 minutes in which to work.**
- **BE NEAT! Non-legible structure drawings will not be graded.**
- **Only answers in the answer boxes will be graded – you can write in other places, but we only grade the answers in the boxes.**
- **All pages of the exam must be turned in.**
- **No calculators**
- **Molecular models may be used**

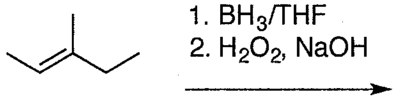
Problem	Points (Maximum)	Points (Obtained)
1	20	
2	16	
3	10	
4	10	
5	14	
6	19	
7	17	
8	19	
Total	*125*	

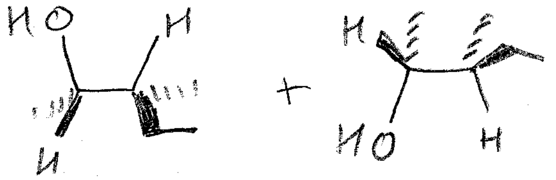
1. (20 points) For each reaction:

(i) Draw the major and minor organic products, **including all stereoisomers**. Write NR if you think there will be no reaction.

(ii) Label each product you draw as major or minor.

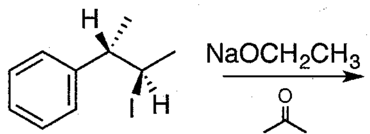
a.

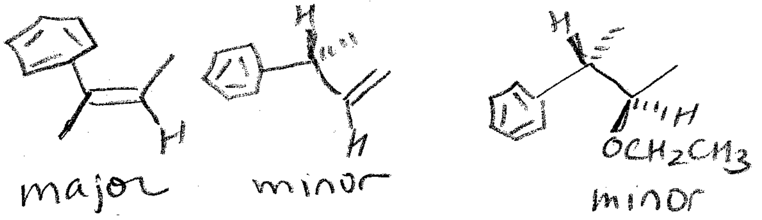




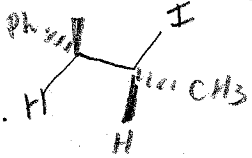
equal amounts of each

b.

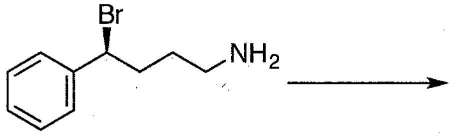


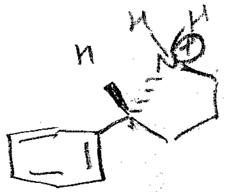


major minor minor

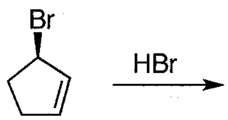


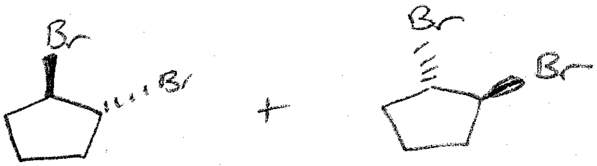
c.





d.

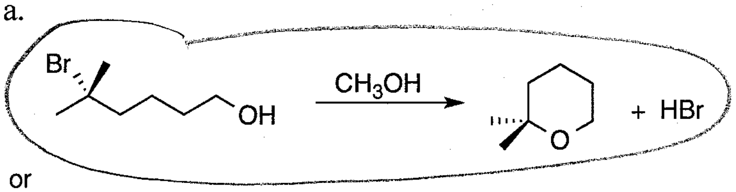




equal amounts of each

2. (16 points) Circle the reaction in the following pairs of reactions that you would expect to go faster. It is possible that both reactions have the same rate. Give brief explanations in the boxes provided.

a.



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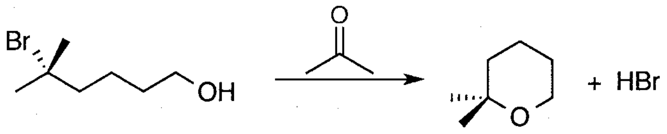
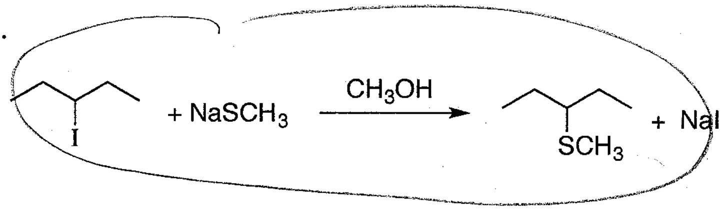


Reason
S_N1 rxn faster in polar protic solvent. T.S. is more charged than starting materials

b.



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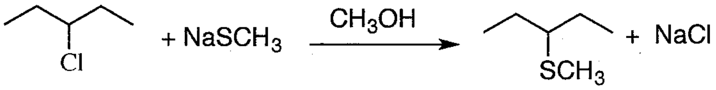
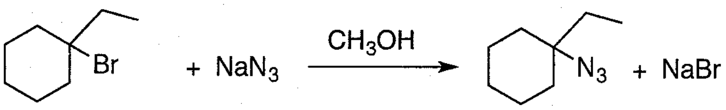
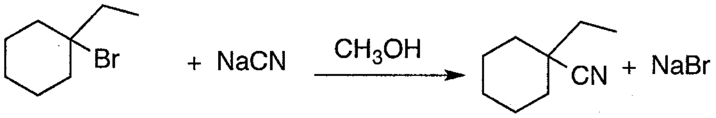


Reason
I^- is a better leaving group than Cl^- because it is a weaker base

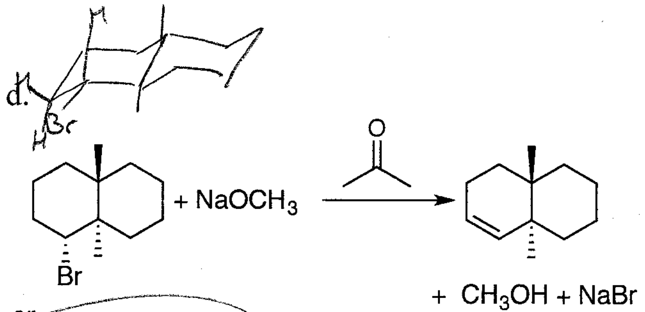
c.





Reason
Same rate. S_N1 reaction, no effect of Nu on rate.

d.



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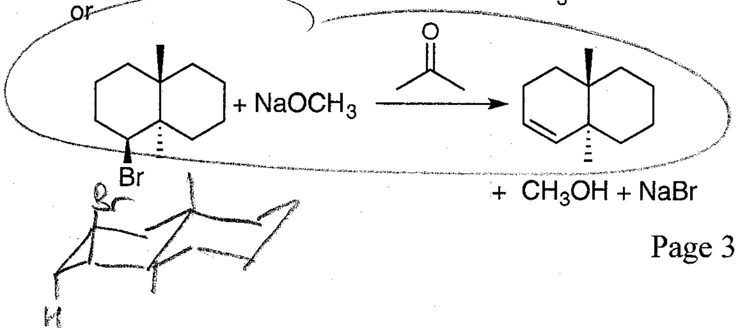
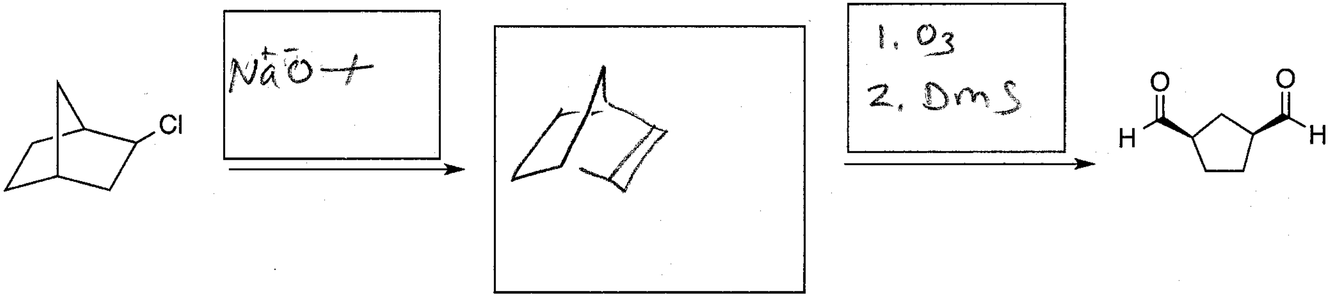


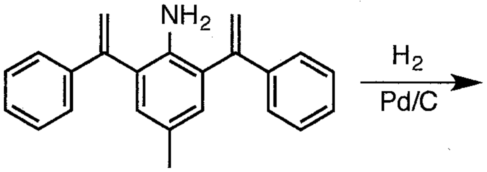
Reason E2
Need anti orientation of H & Br. Trans decalin cannot undergo ring flip. In the bottom structure there is a H anti to Br. In top structure there is no H anti to Br. Therefore, bottom rxn goes faster

3. (10 points) Fill in the boxes in the following reactions to produce the indicated products in the highest yield with the fewest number of steps. Note that only the organic products have been drawn.

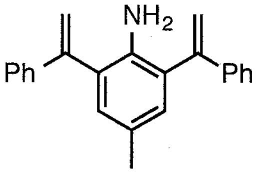


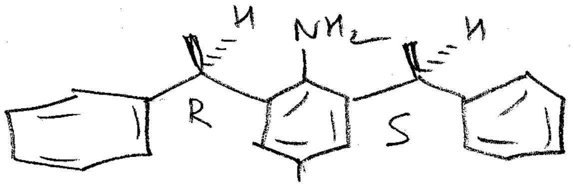
4. (10 points) Consider the hydrogenation reaction shown below.
i) Draw all of the stereoisomeric products.
ii) Assign R and S configuration to each asymmetric carbon.
iii) Label any meso isomers.

Remember that  is not reactive

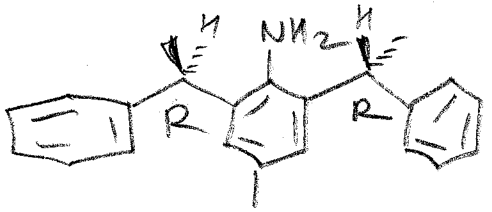


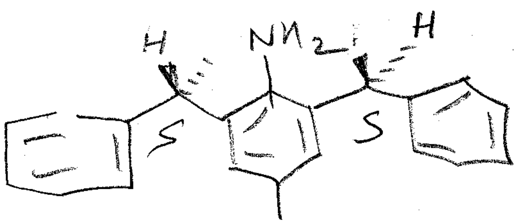
You may use the abbreviation Ph in your structures. For example, the starting material can be drawn:



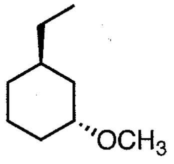


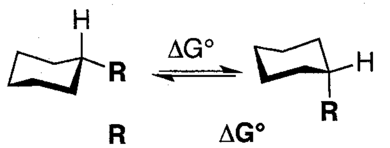
meso





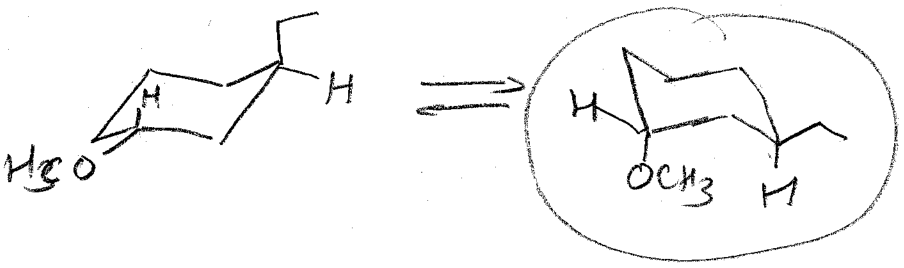
5. (14 points) Consider the substituted cyclohexane drawn below and the table of information:





R	ΔG°
OCH_3	0.75 kcal/mol
CH_2CH_3	1.70 kcal/mol

a. Draw both conformations of the substituted cyclohexane.

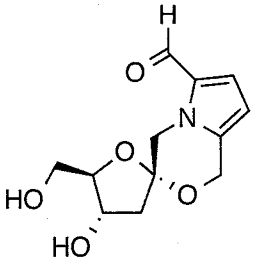


b. Circle the most stable conformation that you drew in part a.

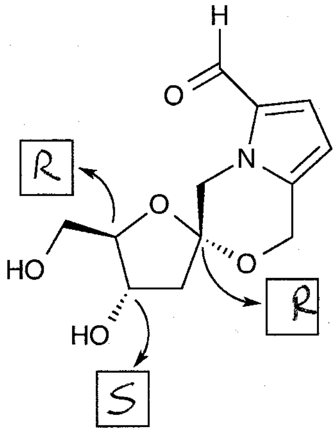
c. What is ΔG° of the equilibrium between the two conformations you drew? Make sure to have the correct sign for ΔG° considering the equilibrium you drew in part a. Show your work.

$\Delta G^\circ = -1.70 + 0.75 = -0.95$ kcal/mol

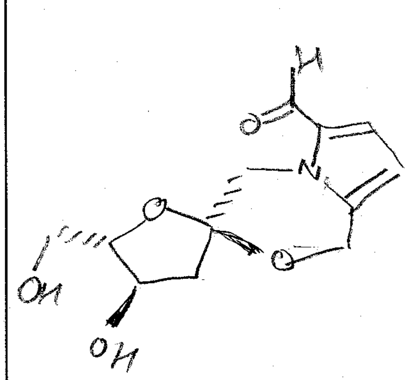
6. (19 points) The structure of acortatarin A, a possible lead for the development of new diabetes treatments, is shown below:



a. Assign all asymmetric carbons in acortatarin A as R or S. Write your assignments next to the structure.



b. Draw the enantiomer of acortatarin A.



c. The [α] of pure acortatarin A is 200°. If a chemist synthesizes acortatarin A and determines the [α] of the product mixture to be 180°, how much acortatarin A and how much of the enantiomer is present in the product mixture? Show your work.

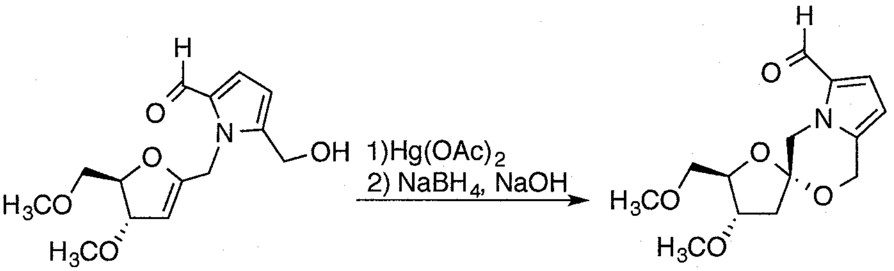
$\frac{180}{200}$ = 90% ee

95% acortarin

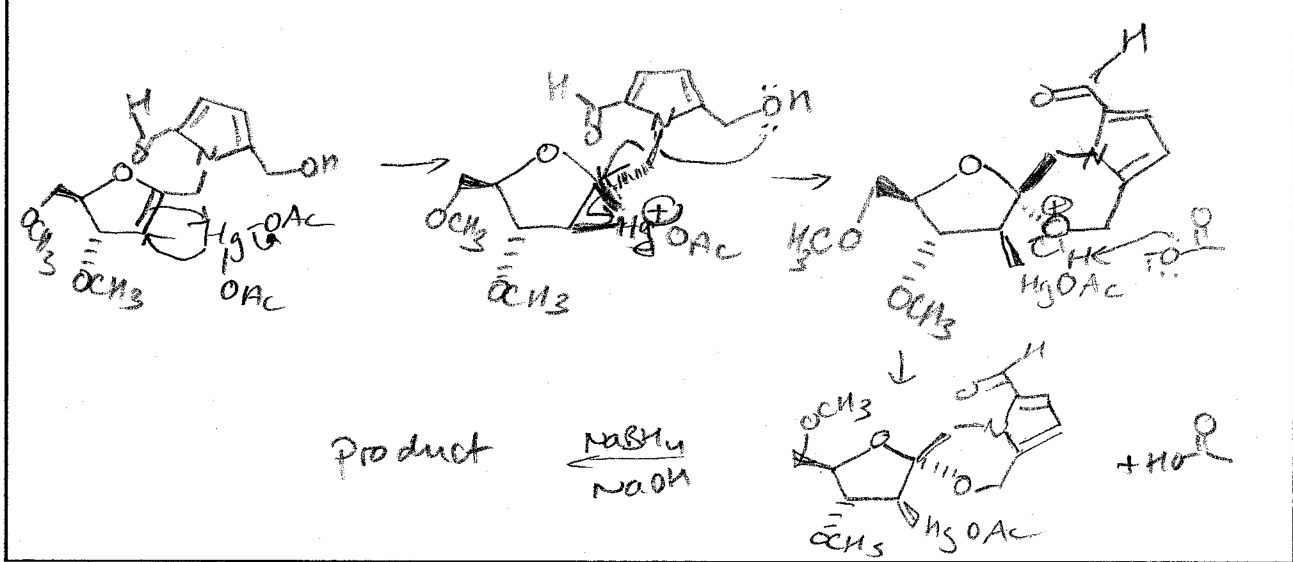
5% enantiomer

$\frac{95-5}{100} = 90$

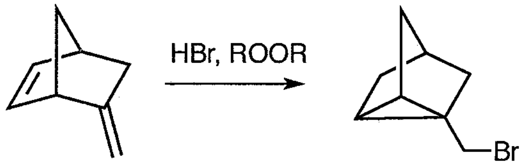
d. A key step in the synthesis of acortatarin A is shown below:



Draw the mechanism of the first step of this reaction using arrows to show the flow of electrons. Make sure that your mechanism clearly shows the formation of the observed stereoisomer. You do not need to show the mechanism for the NaBH4 step.



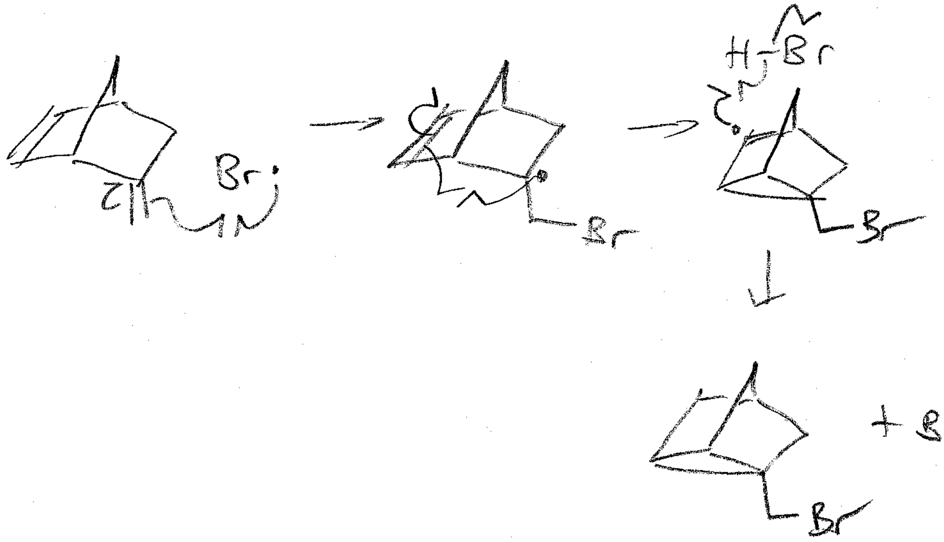
7. (17 points) Draw the mechanism of the reaction shown below, using arrows to indicate the flow of electrons. Include initiation, propagation, and termination (one example) steps.



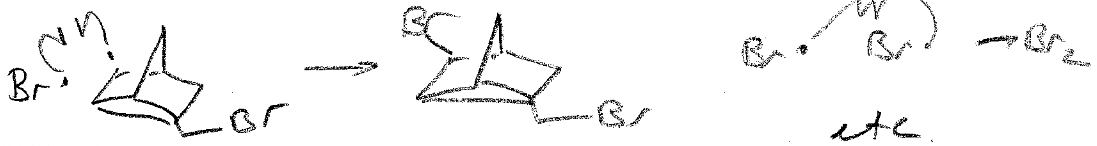
Initiation

RO–OR → 2 RO•   RO• H–Br → ROH + Br•

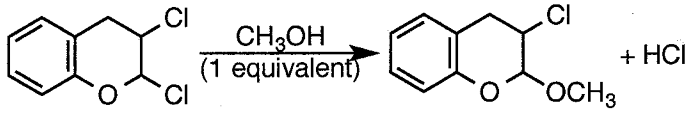
Propagation



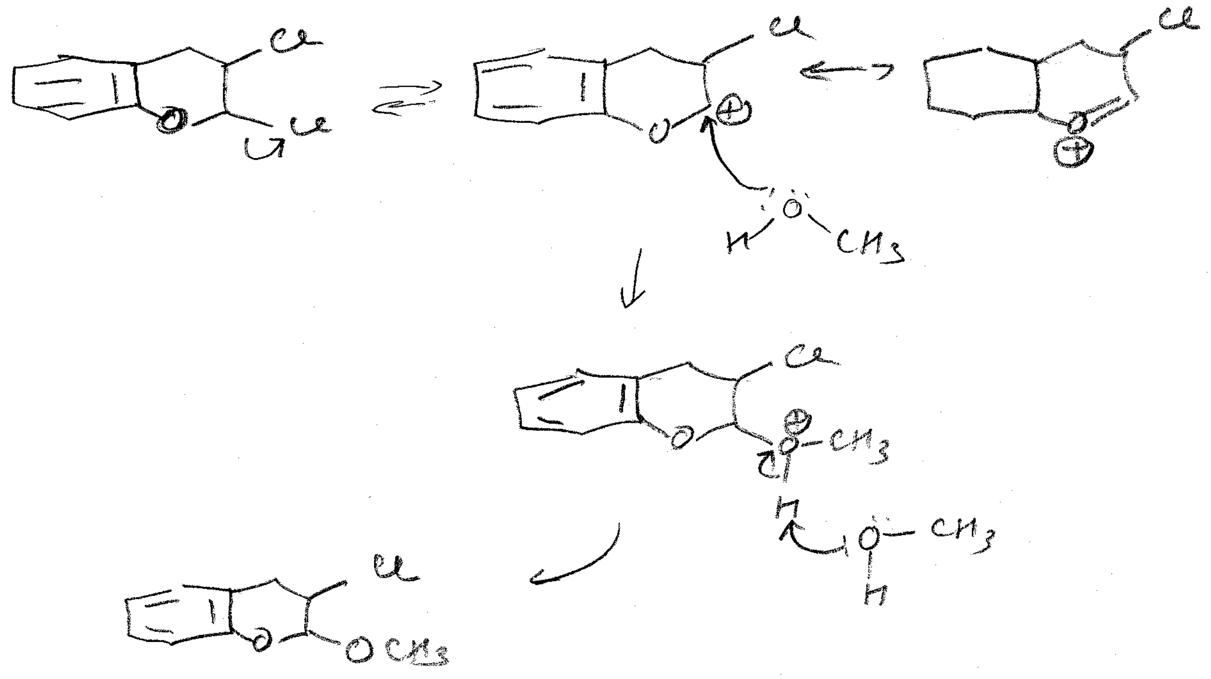
Termination (One example) Any rxn that does not produce a radical



8. (19 points) When the dichloride shown below is treated with methanol, substitution of only one Cl is observed in the product.

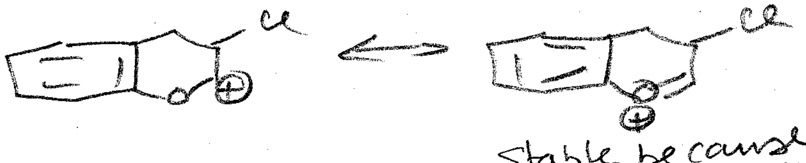


a. Draw the mechanism of this reaction using arrows to show the flow of electrons.



b. Explain why one Cl is much more reactive than the other Cl. Draw structures as part of your answer.

Intermediate carbocation is stabilized by resonance
T.S. resembles carbocation by Hammond's postulate
Therefore, T.S. also stabilized & rxn is faster



Stable because
all atoms have octet

c. Fill in the reaction coordinate diagram below to compare the reactions to substitute for each Cl. You can ignore the relative energies of the final products – they have nearly equal stability. Make sure to include all intermediates.