CHEMISTRY 12A FALL 2019

EXAM 3

Answers Final

NOVEMBER 26, 2019

NAME- WRITE BIG _____

STUDENT ID: _____

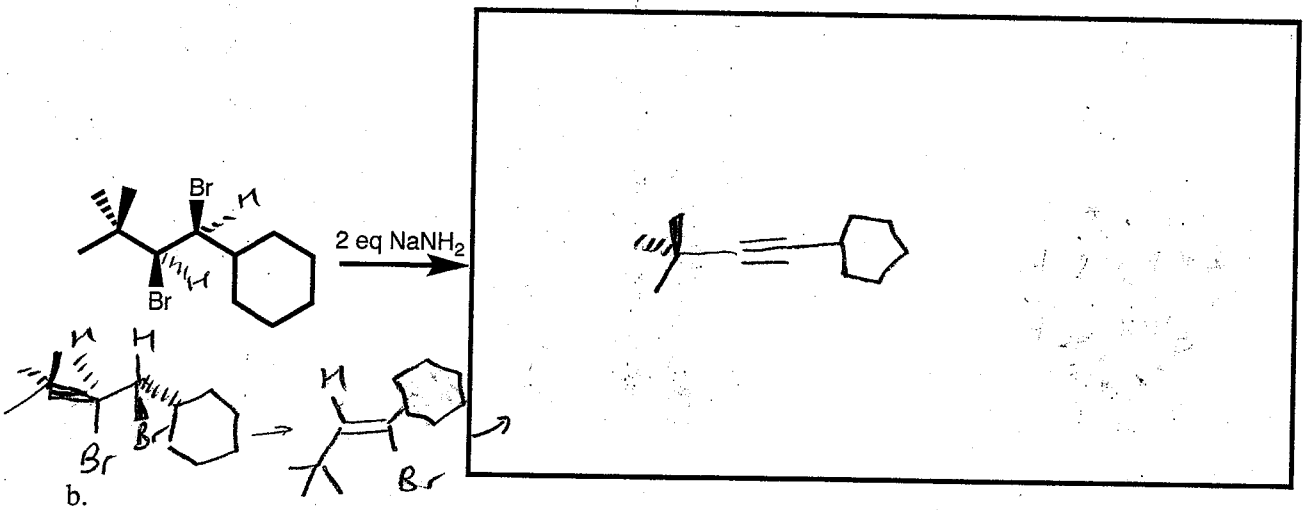
SECTION AND/OR GSI IF YOU ARE IN THE LABORATORY COURSE: _____

- **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**
- **No stencils**
- **Molecular models may be used**

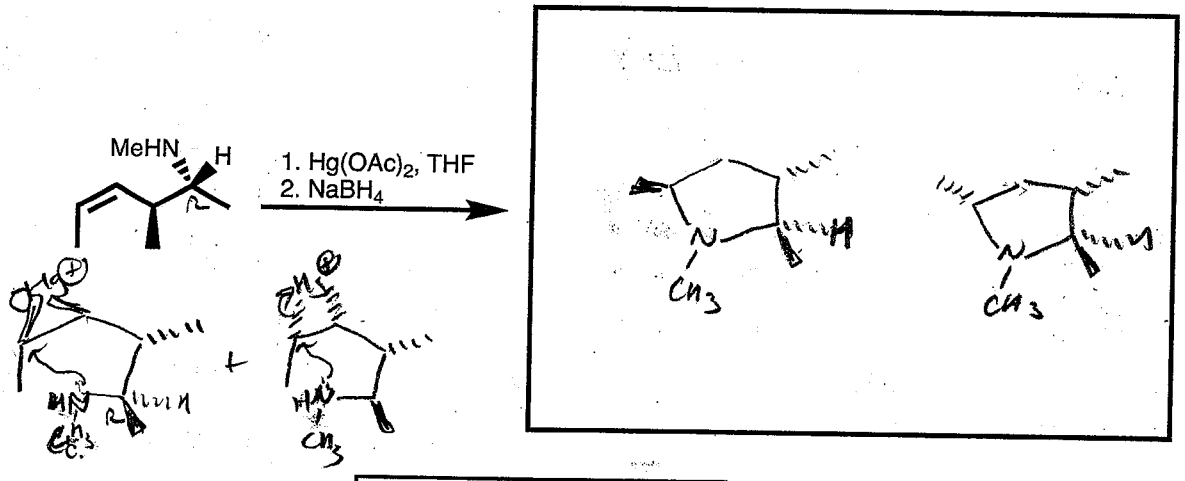
Problem	Points (Maximum)
1	23
2	12
3	24
4	23
5	24
6	14
Total	*120*

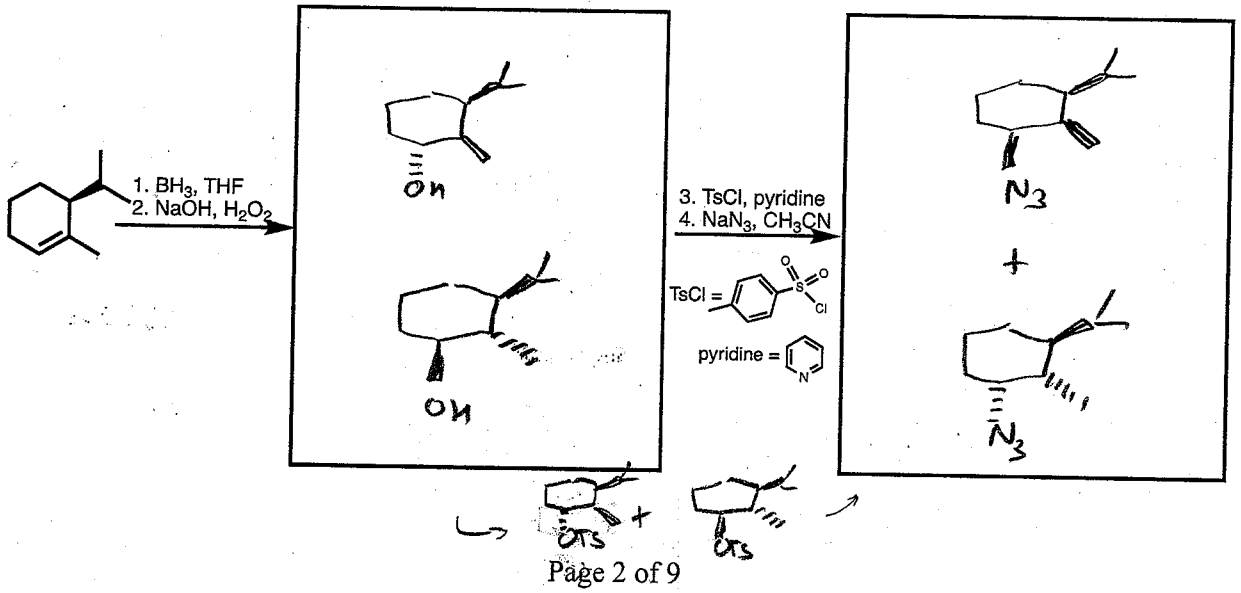
1. (23 points) For each reaction draw the major organic products, **including all stereoisomers**. Write NR if you think there will be no reaction.

a.

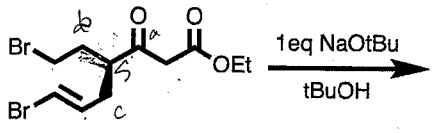


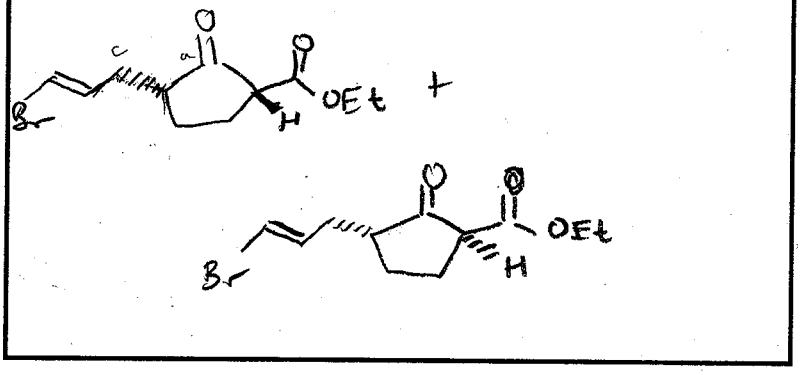
b.

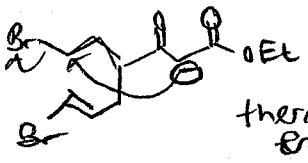




d.



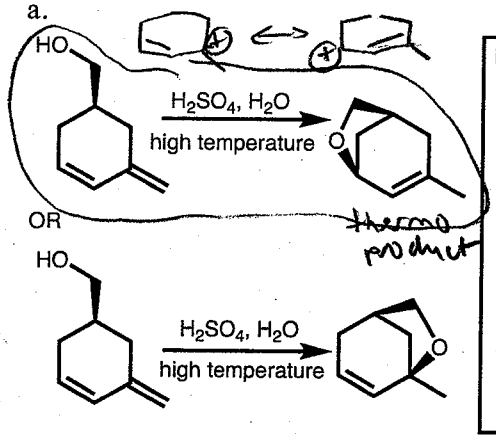




thermodynamic enolate

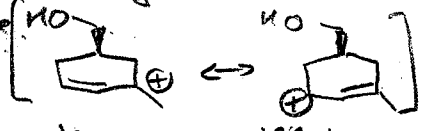
2. (12 points) **Circle** the reaction in the following pairs of reactions that shows the formation of the major products you would expect to observe. You may disregard any other products besides the ones pictured that may form under the reaction conditions. Give explanations in the boxes provided.

a.



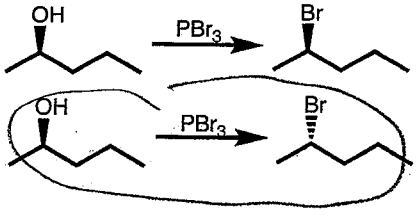
Explanation for your choice :

This is addition to a 1,3 diene w/ a resonance stabilized carbocation intermediate



At high temp the rxn will be reversible & the most stable (most substituted) alkene will be the major product

b.

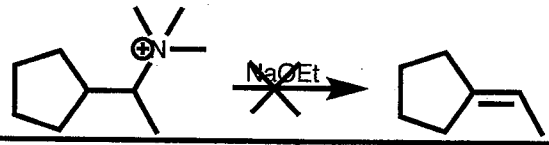


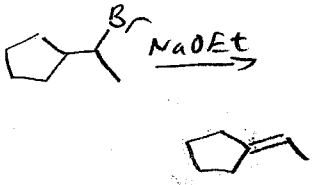
Explanation for your choice :

Reaction proceeds via an SN2 substitution & therefore there is inversion of stereochem

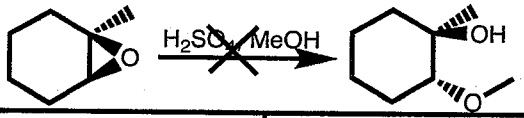
3. (24 points) The following reactions would not occur as written. i. What product would actually be made? ii. Why was the desired product not formed? iii. How could you change either the substrate **or** reaction conditions to give the desired product?

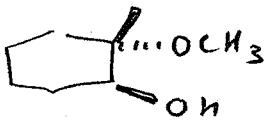
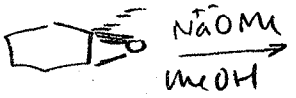
a.



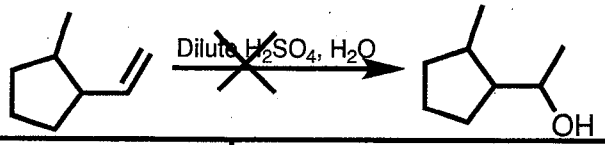
What product is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Explain in 1 sentence and include drawings of any relevant structures)	How could substrate OR reaction be changed to give desired product? Draw your revised reaction.
	Hoffmann elimination Large leaving group favors cracks Steric hindrance so that less substituted alkene is favored	Use a smaller L.G. 

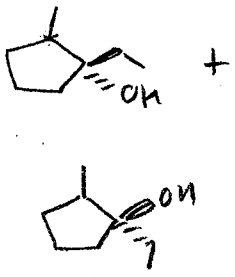
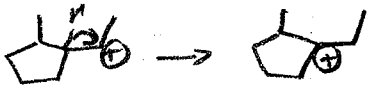
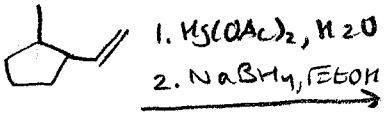
b.



What product is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Explain in 1 sentence and include drawings of any relevant structures)	How could substrate OR reaction be changed to give desired product? Draw your revised reaction.
	Protonated epoxide will open at more substituted carbon because this carbon has more partial positive charge.	Use OCH_3 to give SN2 mechanism. 

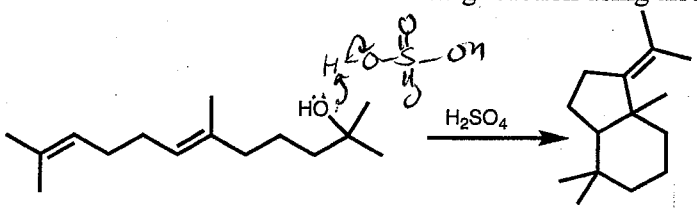
c.

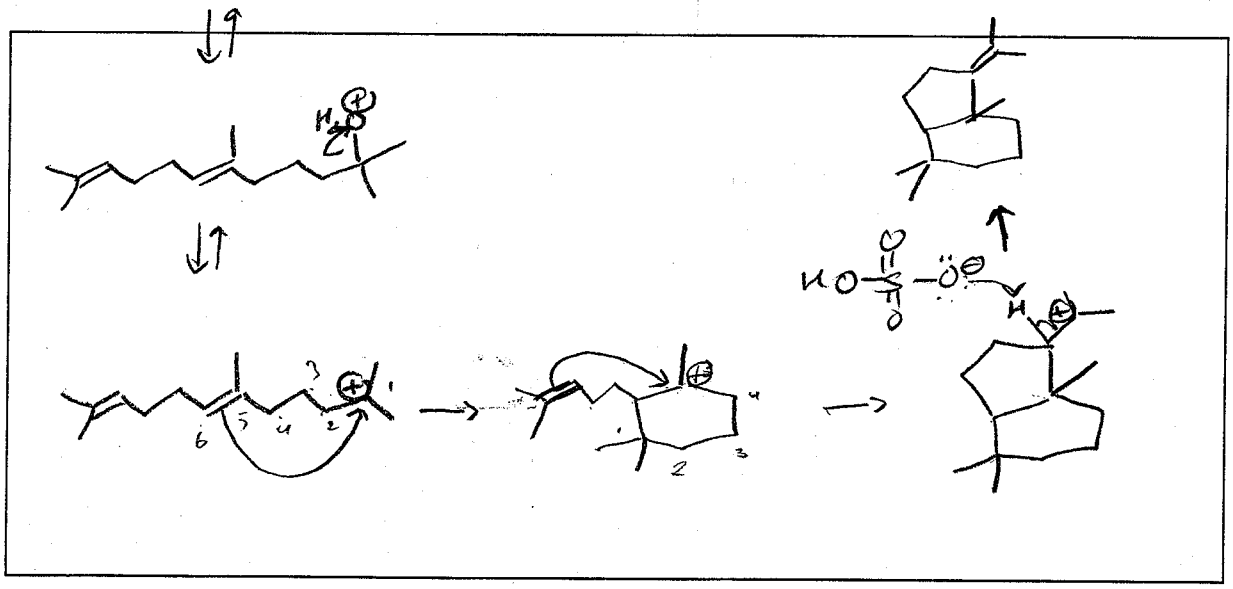


What product is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Explain in 1 sentence and include drawings of any relevant structures)	How could substrate OR reaction be changed to give desired product? Draw your revised reaction.
	2° carbocation will undergo a $H^{\ominus}$ shift to form more stable 3° carbocation 	Use $Hg(OAc)_2$, H_2O - Markovnikov addition w/ no carbocation rearrangements 

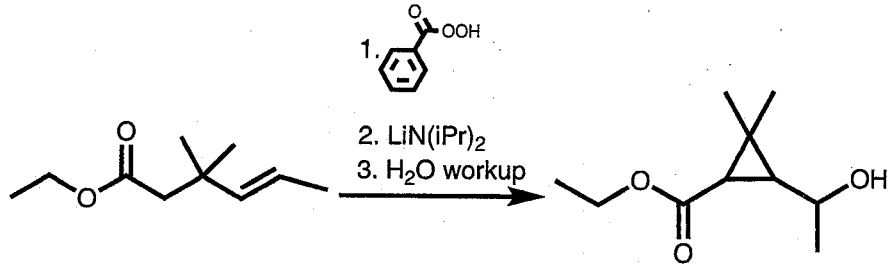
4. (23 points) Mechanisms

a. Draw the mechanism of the following reaction using arrows to indicate the flow of electrons.

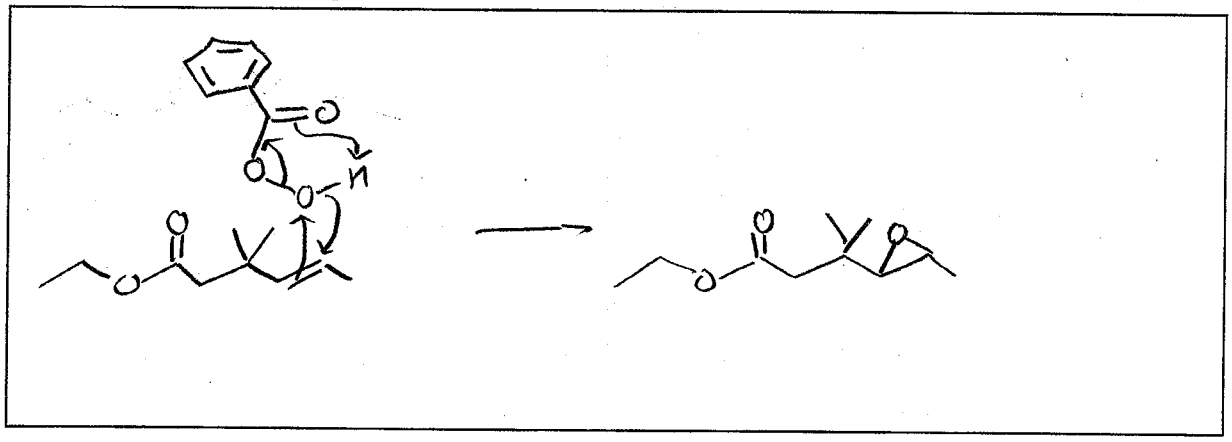




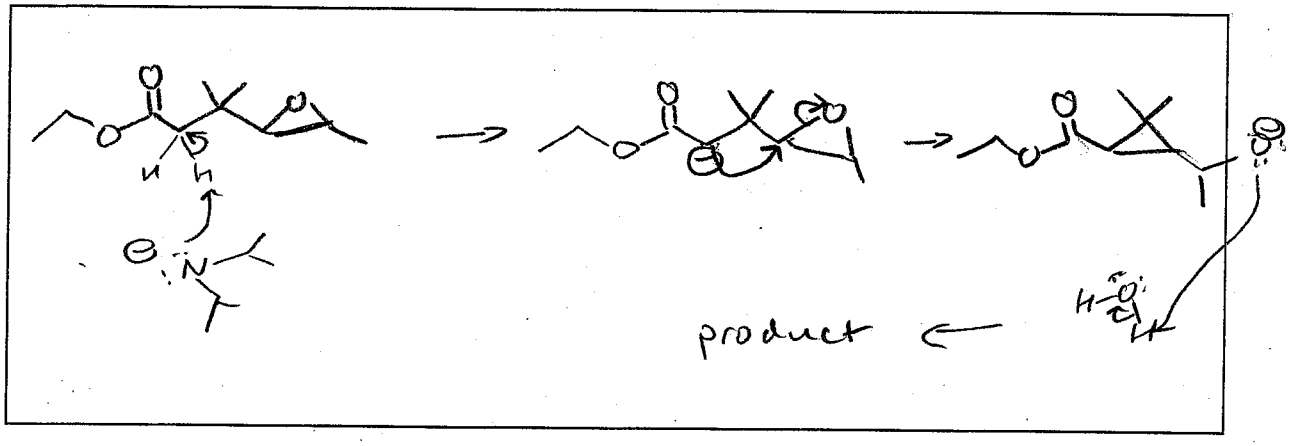
b. Draw the mechanism of the following reaction using arrows to indicate the flow of electrons.



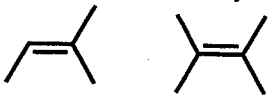
i. Reaction indicated in step 1.



ii. Reaction indicated in steps 2 and 3.

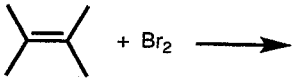


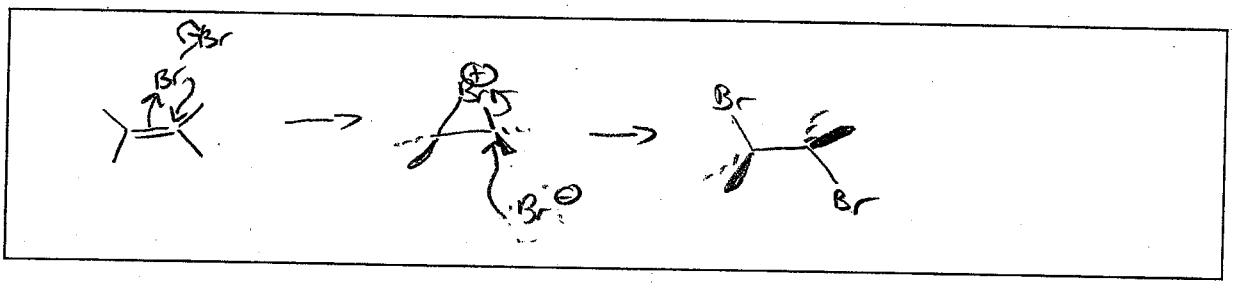
5. (24 points) The rate of addition of Br_2 to the two alkenes below are different. The more substituted alkene proceeds at approximately 10 times greater rate.



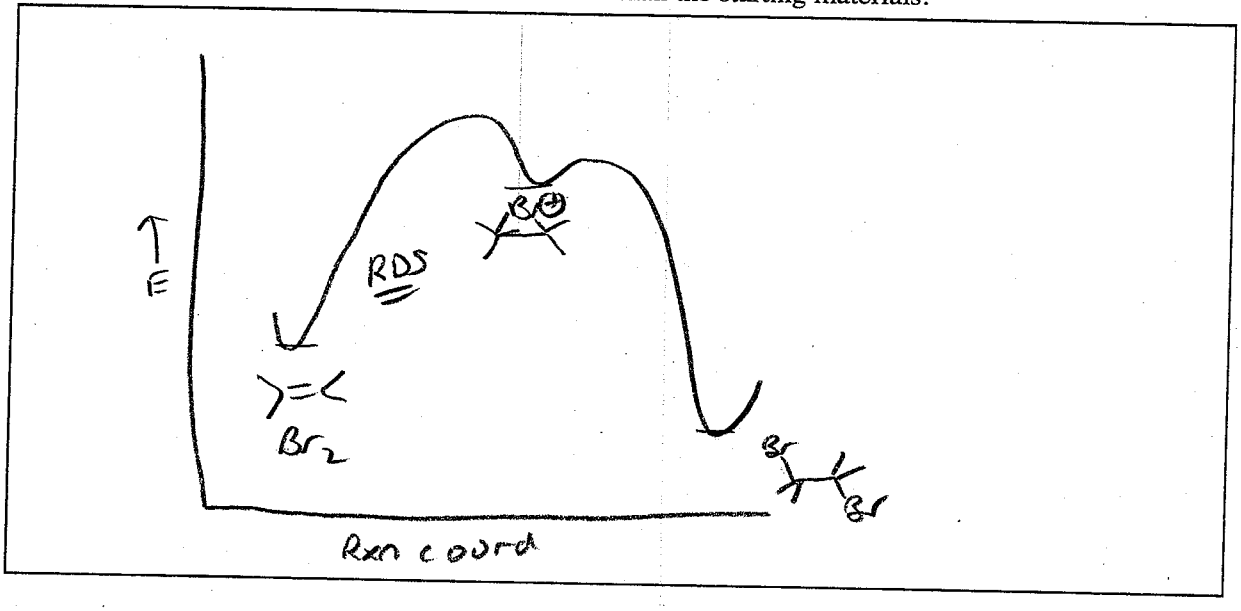
Relative rate 1 14

a. Using the tetramethylethylene as the substrate. Draw the mechanism of the bromination reaction using arrows to show the flow of electrons.

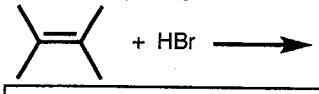


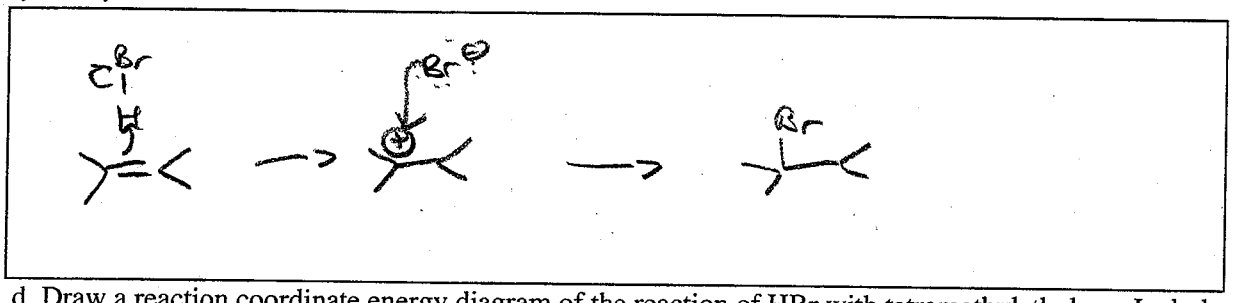


b. Draw a reaction coordinate energy diagram of the reaction of bromine with tetramethylethylene. Include sketches of the starting materials, products, and intermediates. Label the rate-determining step. You can assume the products are a bit more stable than the starting materials.

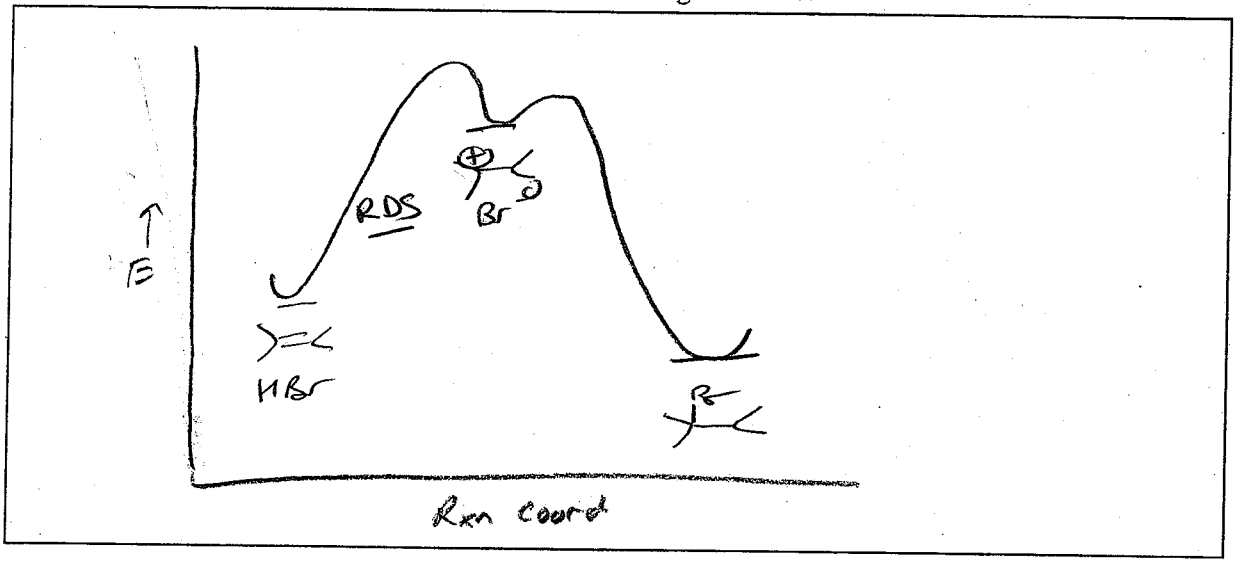


c. In contrast to the addition of Br_2, the addition reactions of H-Br to tetramethylethylene and trimethylethylene proceed at similar rates. Draw the mechanism for the addition of H-Br to tetramethylethylene below.





d. Draw a reaction coordinate energy diagram of the reaction of HBr with tetramethylethylene. Include sketches of the starting materials, products, and intermediates. Label the rate-determining step. You can assume the products are a bit more stable than the starting materials.



e. Explain why the rates of reaction of tetramethylethylene and trimethylethylene with Br_2 are different, while their rates of reaction with HBr are similar.

For both, the rate determining step forms an unstable intermediate. The transition state of the R.D.S. resembles this intermediate by Hammond's postulate.
In  the charge will be stabilized by alkyl groups on either carbon. In  the ⊕ is localized on one carbon and will (therefore,) only be stabilized by alkyl groups on this carbon.

6. (14 points) Synthesize the indicated product from the indicated starting material. All of the carbons in the product should come from the indicated starting material. You can use any other reagents. In your synthesis, show each product formed by each set of reagents you use.