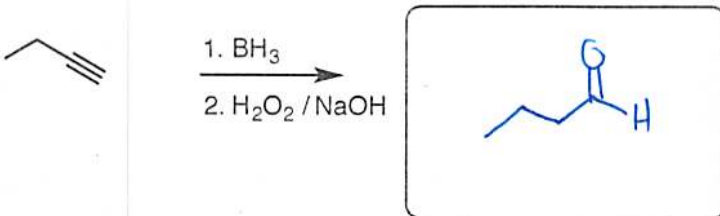
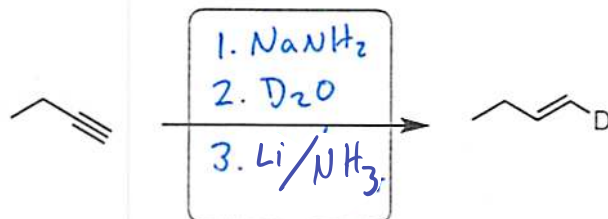
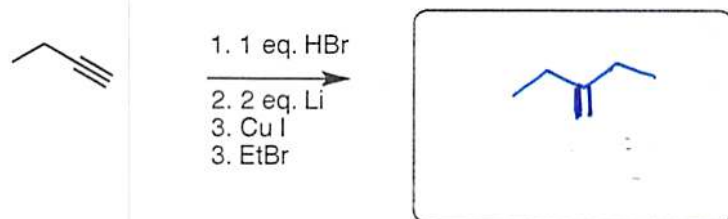
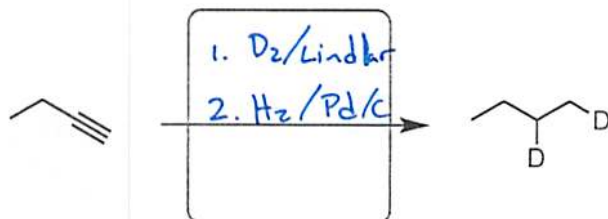
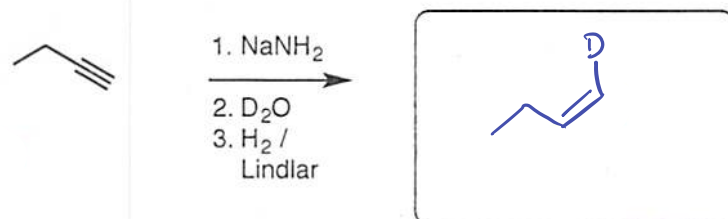
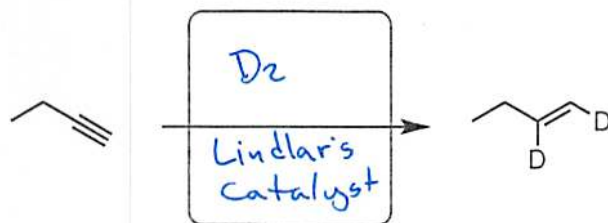


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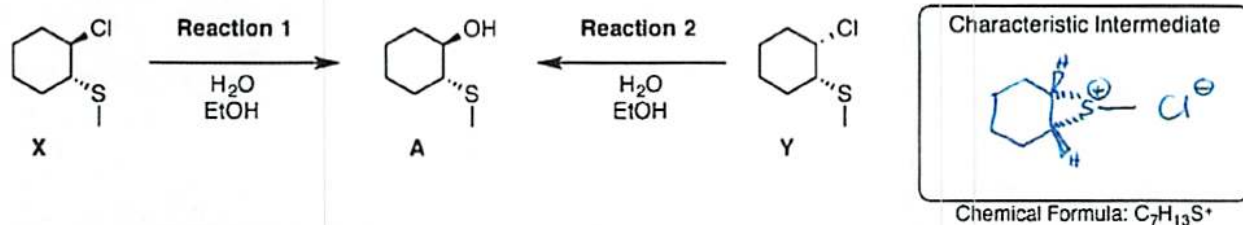
1. 24 pts. Fill in the appropriate products and reagents in the reactions below.



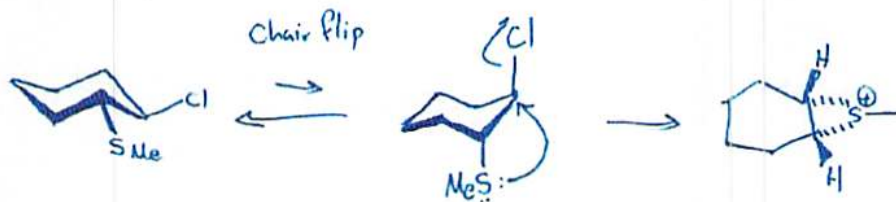
*useful to make the compound in problem 5a



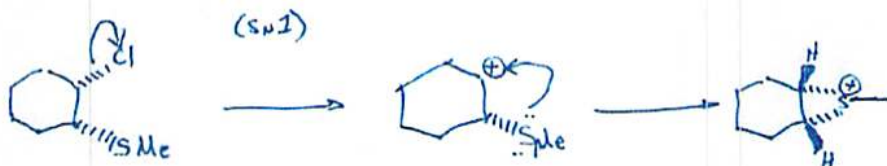
2a. The reactions below yield the same product A (only *trans* enantiomers, no *cis*), however, at *extremely different rates*. Reaction 1 is faster than reaction 2 by a factor of 1,000,000! This clearly shows that **different mechanisms** are involved. Interestingly, the rate-limiting step does not depend on the concentration of water (EtOH is the solvent) AND both mechanisms yield one *strained* intermediate that is similar in both processes. Draw the structure of such characteristic intermediate below, including dashes and wedges (2pts).



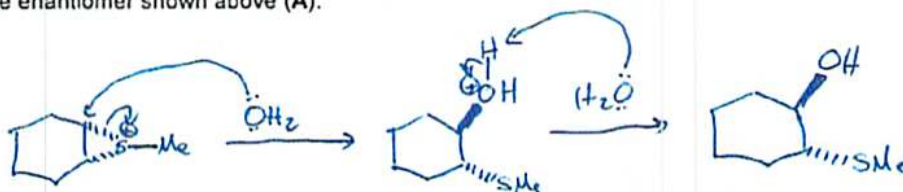
2b. 3 pts. Considering the two possible chair conformations, draw the mechanism for **Reaction 1** that accounts for the formation of the *characteristic intermediate*.



2c. 3 pts. Considering the representation of Y shown above, draw the mechanism for **Reaction 2** that accounts for the formation of the *characteristic intermediate*.



2d. 2 pts. Starting from the *characteristic intermediate*, show how it accounts for the formation of A. Note: you only need to show the formation of the enantiomer shown above (A).

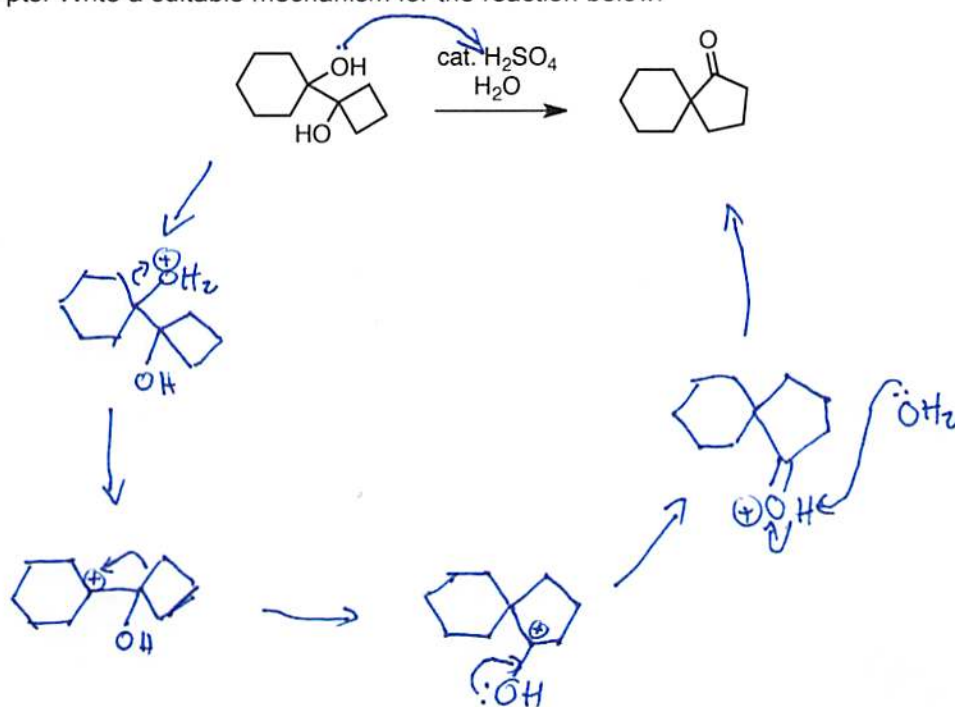


2e. 2 pts. Briefly explain why Reaction 1 is faster than Reaction 2:

Rxn 1 undergoes a fast intramolecular $\text{S}_{\text{N}}2$ rxn to displace chloride anion. Rxn 2 is slower because it involves an $\text{S}_{\text{N}}1$ process to yield a 2° carbocation, without the participation of the neighboring -SMe group. Thus, the RLS in Rxn 2 is much slower than the RLS of Rxn 1

Name: _____

4. 15 pts. Write a suitable mechanism for the reaction below.

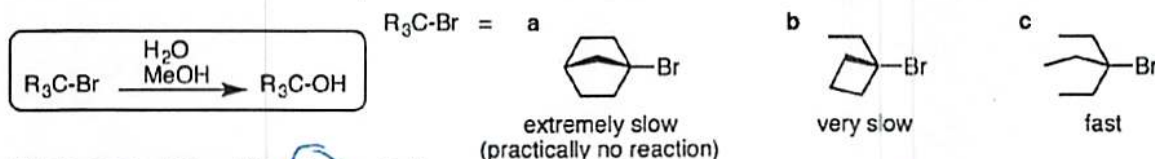


pts. this pg.



Name: _____



2a. 8 pts. Consider the generic reaction in the box. When three alkyl bromides, a, b, and c, are reacted under those conditions, drastically different rates of reactivity are observed: compound c reacts much faster than b and a. BRIEFLY explain the trend. Specify the type of mechanism: E1, E2, S_N1, or S_N2.



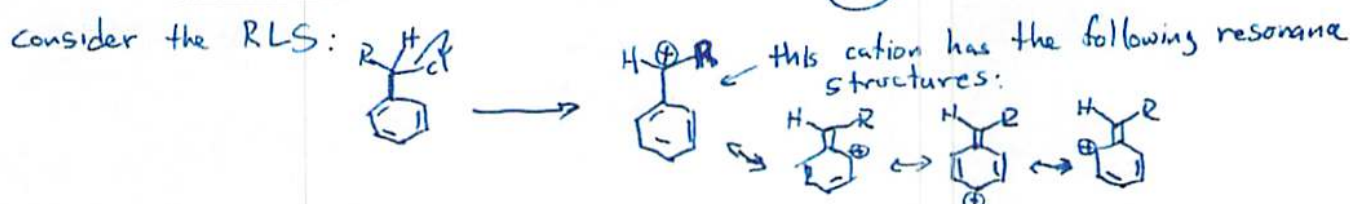
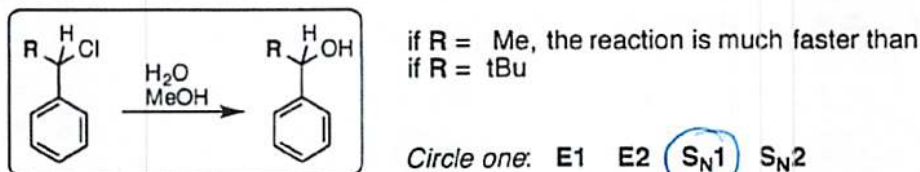
Circle one: E1 E2 **S_N1** S_N2



The rxn involves the formation of an sp³ carbocation that wants to be planar. The fastest rxn would enable the formation of a stable cation.

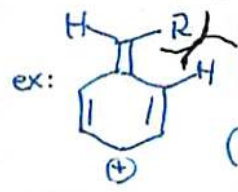
- compound a would form a highly strained cation  ← not planar!
- Similarly, compound b would form a strained cation, susceptible to rearrangements  ← strained in 4-membered ring.
- However, compound c can form a 3°, flat cation stabilized by hyperconjug.

2b. 8 pts. Now consider the generic reaction in the box below, where R can be methyl (Me) or *tert*-butyl (tBu). When R = Me, the reaction proceeds 500 times faster than when R = tBu. BRIEFLY explain the trend. Specify the type of mechanism: E1, E2, S_N1, or S_N2.



Considering the resonance structures, the compound that yields a "planar" alkene-like resonance structure will proceed faster.

if R = Me, it is less bulky than tBu, therefore there is less steric hindrance and allows for the formation of the resonance-stabilized benzylic cation

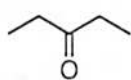
ex:  ← steric hindrance between R & H.
(better if R is smaller)

pts. this pg.

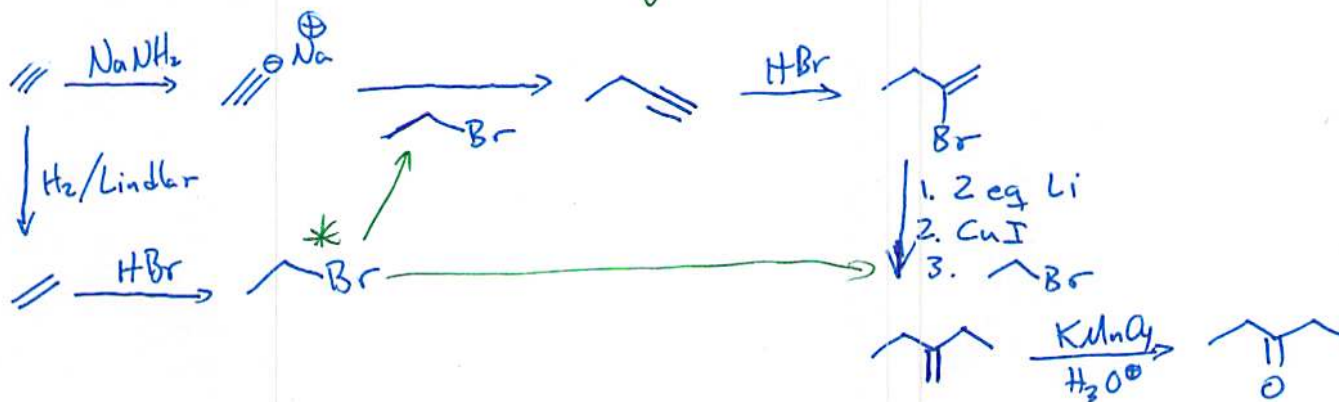


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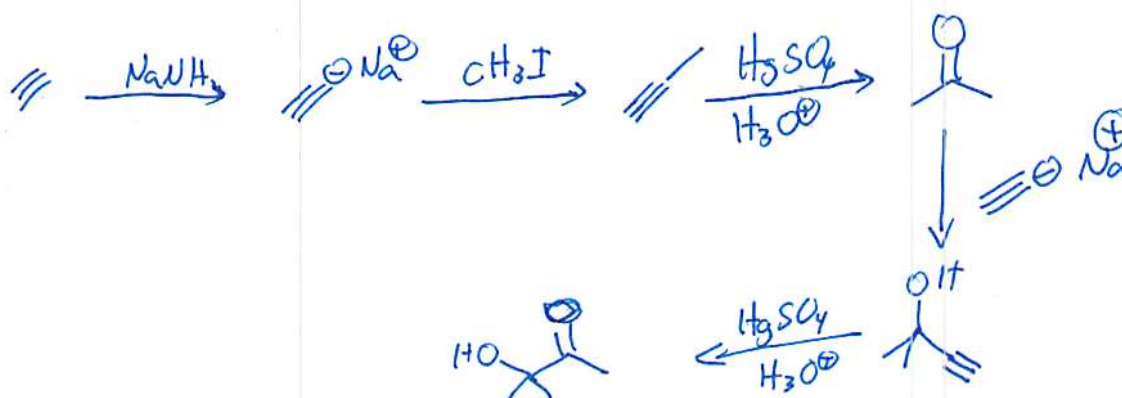
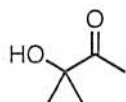
5a. 10 pts. Synthesize the product shown below. You can only use **acetylene** as your only sources of carbon to make the product. If you need any Gilman or Grignard reagents, you will have to synthesize them from sources of carbon noted. Note: this product is formed exclusively, not as a mixture of products.



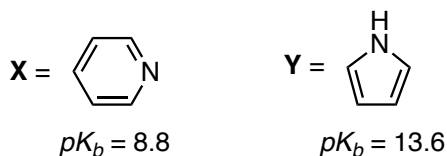
see page 2 to make



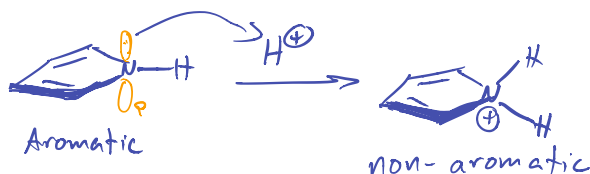
5b. 10 pts. Using **any alkyl halides containing only one carbon** and **acetylene** (C_2H_2) as your only sources of carbon, propose the synthesis of the products below. You can use acetylene to make any compounds you may need.



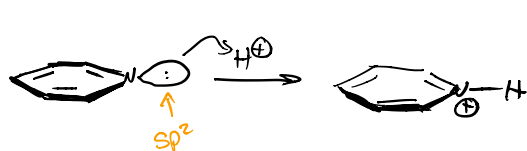
7 pts. 5a. The pK_b is shown for the Brønsted bases below **X** and **Y**. Explain the differences in basicity.



Compound Y is less basic because upon protonation of the nitrogen, the conjugate acid is no longer aromatic:



However, protonating N in compound **X** maintains aromaticity:



since aromaticity is maintained, this reaction is more favorable than the one above

7 pts. 5b. Are both compounds **A** and **B** aromatic? Explain your answer.



Compound **A** is aromatic because it has 10 π electrons ($4n+2$) in a cyclic fashion, delocalized in p-orbitals, and it is FLAT.

The π -electrons in **B** are similar than in **A** ($4n+2$), but the molecule is not flat. The middle hydrogens "collide" with each other, puckering the molecule out of plane. Therefore, it is non-aromatic.

