Chemistry 217, Problem Set 9

Recommended Problems: 7.25-7.33, 7.36-7.37, 7.39-7.40, 7.59—7.65, 7.67-7.70, 7.72-7.75, 8.1-8.22, 8.25-8.26, 8.28, 8.31, 8.33-8.35, 8.37-8.45

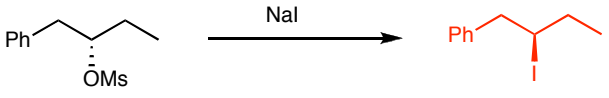
(1st ed.: 7.20-7.33, 7.36, 7.38-7.39, 7.58-7.64, 7.66-7.69, 7.72-7.75, 8.1-8.21, 8.24-8.25, 8.27, 8.30, 8.32-8.34, 8.36-8.43)

Supplemental Problems: Elimination reactions: Klein, Ch. 10

1. Determine the mechanism (S_N1 or S_N2) and predict the products of the following reactions. Be sure to indicate the stereochemistry where relevant.

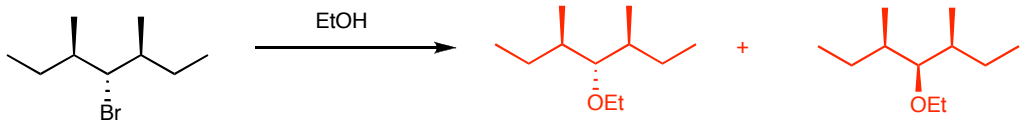
Note: Based on what you now know, there will also be elimination products. For this problem, only the substution products are given, even though they may be accompanied by E1 or E2 products.

(a)



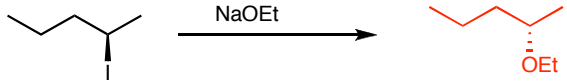
mechanism=S_N2
2° iodide: no S_N1

(b)



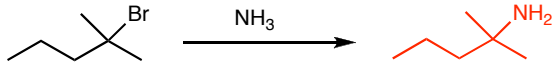
mechanism: S_N1
EtOH not strong enough nucleophile (or base) for a 2° bromide: no S_N2

(c)



with a stronger nucleophile than in part c, the rate of S_N2 is faster, so S_N2 is the mechanism.

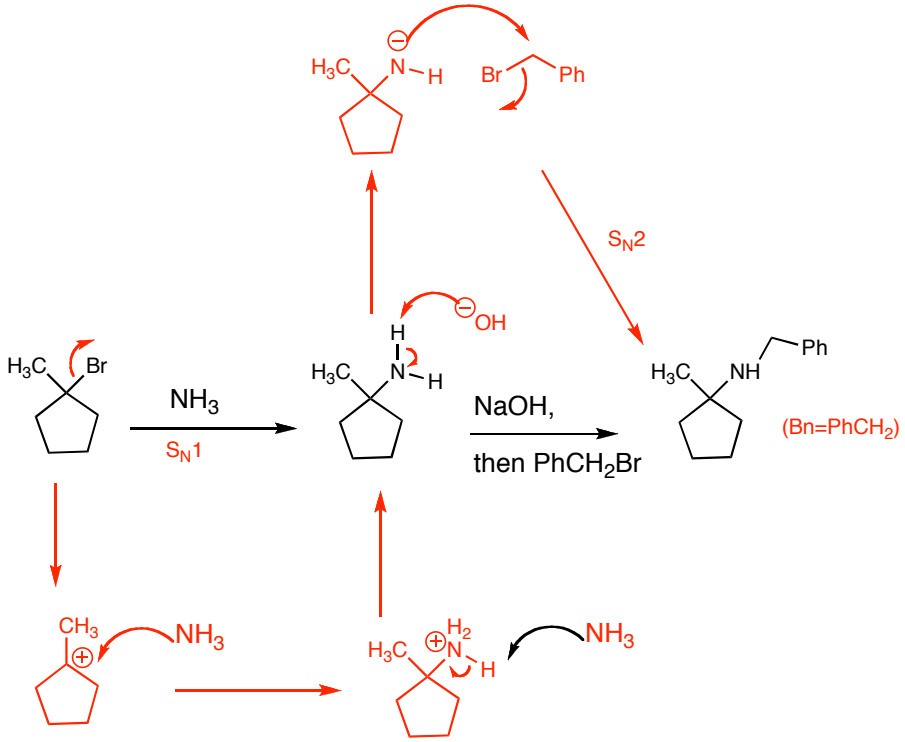
(d)



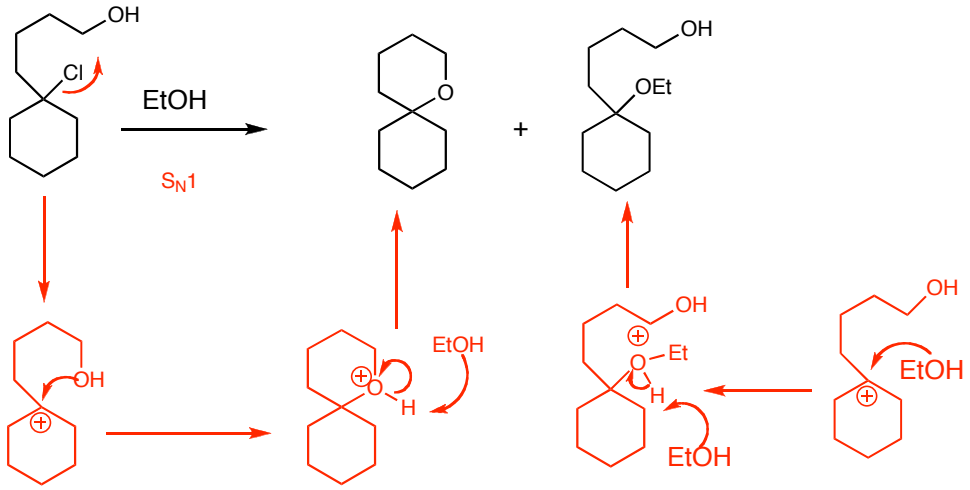
3°: too sterically hindered for S_N2, and 3° cation stabilized, so S_N1 is the mechanism.

2. Propose a mechanism for each of the following reactions. If more than one product is given, draw the mechanism for each product.

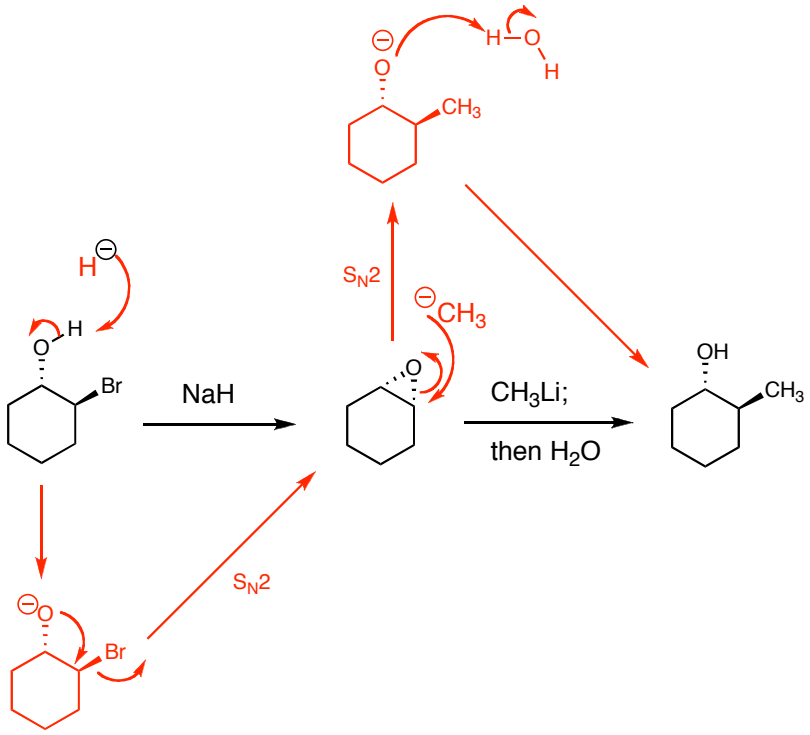
(a)



(b)



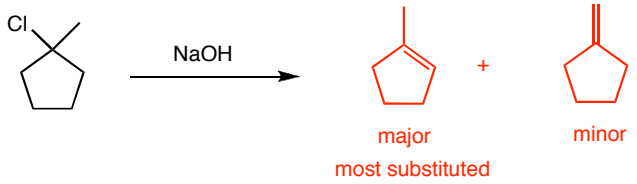
(c)



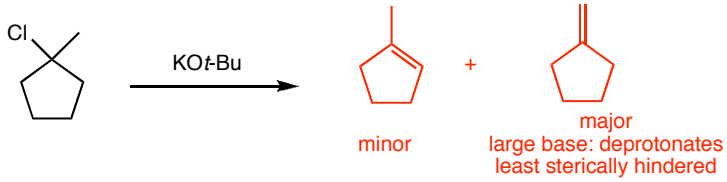
3. If the reaction from part c above were performed on a compound in which the hydroxyl group and the bromide are cis rather than trans, there is no reaction. Explain why. The reaction is an S_N2 reaction, which must proceed by backside attack. If the hydroxyl group and the bromide are cis, the oxygen cannot approach from the backside.

4. Give the major and minor products of the following E2 reactions:

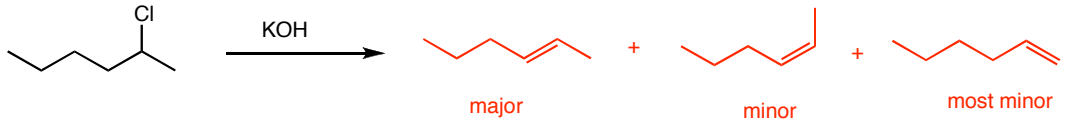
(a)



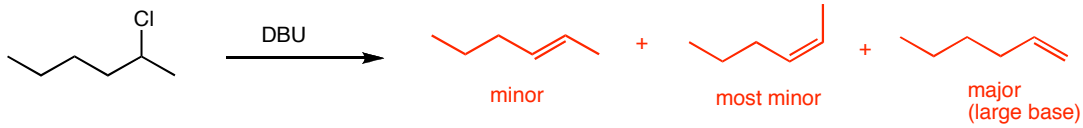
(b)



(c)



(d)

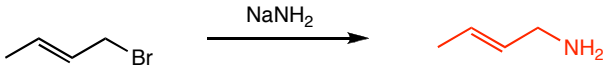


5. Fill in as many blanks in the table below as you can with the mechanism most likely to occur for that set of conditions and give an example for each. See your class notes.

Nucleophile	3° R-X	2° R-X	1° R-X	Me R-X
Weakly-basic and charged Cl^-, Br^-, CN^-				
Weakly-basic and neutral (H_2O, ROH)				
Basic, charged, small (HO^-, MeO^-, EtO^-)				
Basic, charged, large (KO*t*-Bu)				

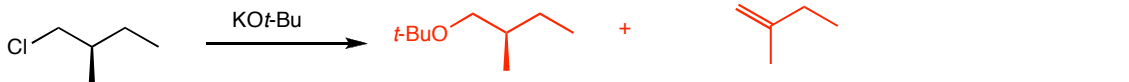
5. Determine whether the following reactions will follow an S_N2 or an E2 mechanism, and draw the major product for each. In some cases there may be no reaction.

(a)



(no β-hydrogens: all S_N2)

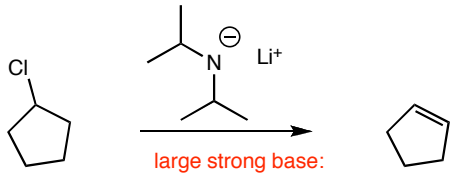
(b)



minor

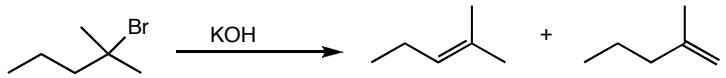
major (large base reduces rate of S_N2, so E2 becomes major product)

(c)



large strong base: S_N2 too slow

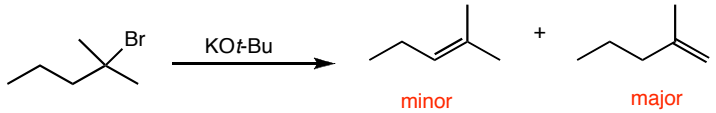
(d)



major minor

3°: too sterically hindered for S_N2, E2 only product, with most substituted product as major

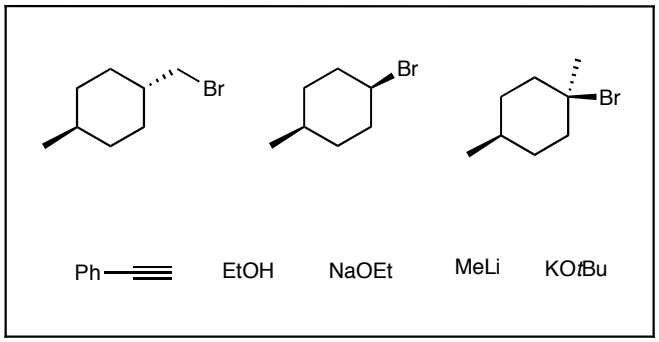
(e)



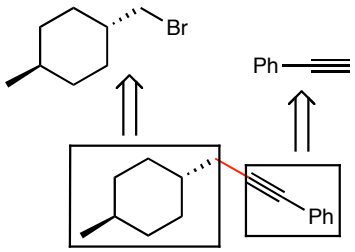
minor major

3°: too sterically hindered for S_N2, E2 only product, big base: least substituted alkene formed

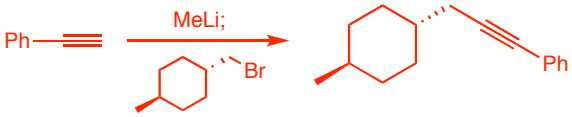
6. Given the compounds shown in the box, propose a method for preparing the following compounds.



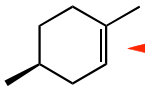
(a)



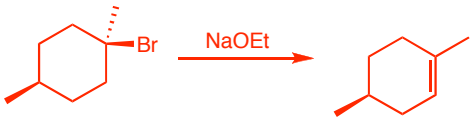
To make this molecule, the red bond above will be formed by S_N2 of an alkyl halide and the negatively charged alkyne. The first step, then, is to deprotonate the alkyne to make it a nucleophile.



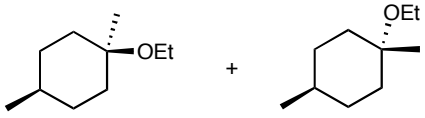
(b)



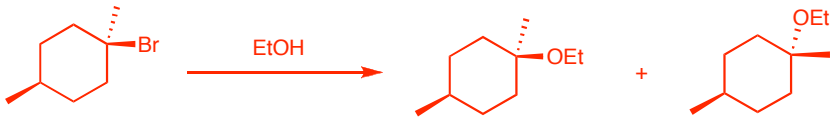
form this bond by E2



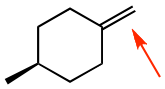
(c)



These are the product of substitution on a 3° carbon, so the mechanism had to be S_N1 with EtOH as the nucleophile (if NaOEt were used, it would give E2)

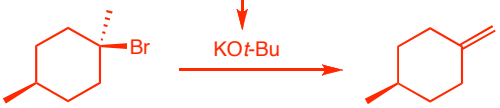


(d)



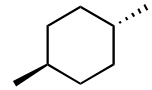
form this bond by elimination. Elimination of the 1° or 3° bromides above would give this alkene. However, the 1° would give S_N2, not E2. So, the 3° bromide must be used.

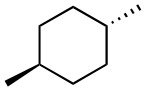
use big base, to get least subst. product.



Note that this product would actually be the minor product with NaOEt. If we had access to KO*t*-Bu, this would be the major product.

(e)





This product does not contain any alkenes, so it must be the product of substitution.