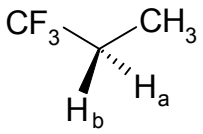
CHEM221 Section 02 Dr. C. Rogers **NAME:**

INTRODUCTORY ORGANIC CHEMISTRY I --- **PROBLEM SET #4**

INSTRUCTIONS: HAND IN STAPLED, COMPLETED ASSIGNMENT **AT THE BEGINNING OF CLASS on Thurs. April 7th.** LATE SUBMISSIONS WILL **NOT** BE ACCEPTED (EARLY IS OK). ANSWER ALL QUESTIONS, BUT ONLY 3 WILL BE MARKED. ALL MATERIAL WILL BE COVERED BEFORE THE DUE DATE (nothing is post-Ch.11; but recall already did 4.2 & 4.6).

NOTE: Only show "arrow-pushing" mechanisms and reaction intermediates for question #7. For the other questions, please show only the products or reagents/conditions requested.

#1. Imagine we treat the compound shown with one molar equivalent of a base that is sufficiently strong to remove the most acidic proton: H_a or H_b, adjacent to the strongly electron-withdrawing CF_3 group. H_a and H_b are chemically equivalent, so the resulting anions will be equally basic, but they will not be identical.



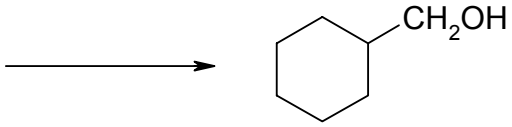
a) What is the stereochemical relationship between the anion formed if H_a is removed and the anion formed if H_b is removed?

b) If these two anions are used as nucleophiles in an S_N2 displacement of bromide from 1-bromobutane, what will be the relationship between the two products? (Draw them.)

c) If these two anions are used as nucleophiles in an S_N2 displacement of bromide from (R)-2-bromobutane, what will be the relationship between the two products? (Draw them.)

#2. Each of the following compounds can be synthesized via an S_N2 displacement of an alkyl halide. For each compound, provide reaction conditions (reagents: alkyl halide, nucleophile; and conditions: relative concentrations, solvent) that would yield the desired compound as a major product.

a)



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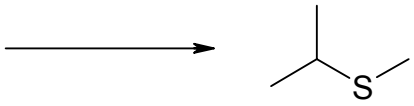
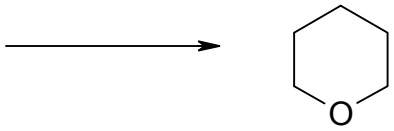


c)

d)



#3. A student wanted to synthesize methyl *t*-butyl ether, $CH_3OC(CH_3)_3$. He attempted the synthesis by adding sodium methoxide $NaOCH_3$ to a solution of *t*-butyl chloride $Cl-C(CH_3)_3$ in methanol, but he obtained none of the desired product.

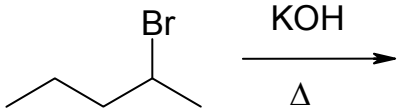
a) Why did the desired reaction not occur?

b) What product DID the student obtain?

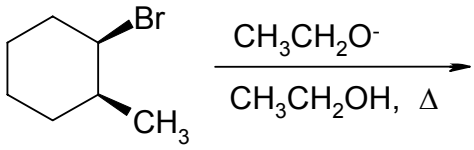
c) Suggest a better synthetic route to methyl *t*-butyl ether.

#4. Predict the products of E2 elimination of the following compounds. If more than one product is expected, label the products as *major* versus *minor*. Include stereochemistry as appropriate.

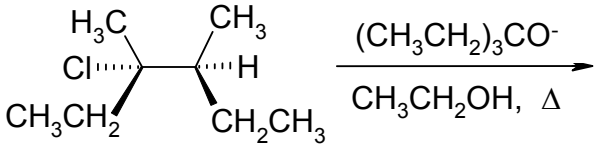
a)



b)

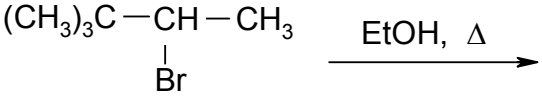


c)



#5. Predict the products of E1 elimination reactions for the following compounds. If more than one product is expected, label the products as *major* versus *minor*. Include stereochemistry as appropriate.

a)



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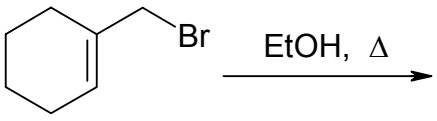

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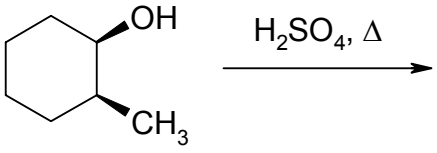
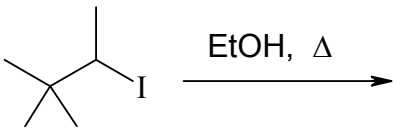


#6. Substitution and elimination can both occur by different mechanisms and are generally in competition with each other. However, careful choice of reaction conditions can help control product distributions. With this in mind, predict the products (label major/minor) of the following reactions. Remember to consider the effects of:

- Substrate: degree of substitution; leaving group ability
- Nucleophile / Base: inherent basicity *vs.* steric demand
- Solvent: polarity; protic *vs.* aprotic
- Temperature: higher temperatures drive entropically-favoured reactions…

a)



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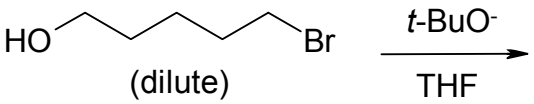

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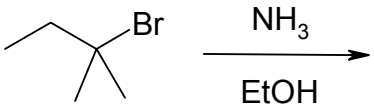
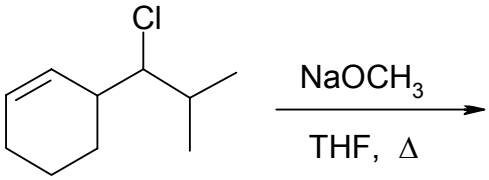


d)



#7. Solvolysis of bromomethylcyclopentane in hot methanol gives a complex product mixture, as shown below. Propose mechanisms (show full, step-by-step, "arrow-pushing" mechanisms) to account for <u>each</u> of the five products. (FOR THIS QUESTION: YOU'LL HAVE TO ATTACH SEPARATE PAGES OF PAPER….)