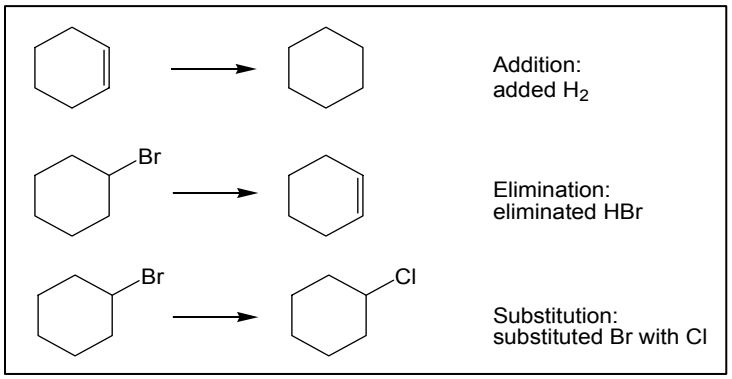
Chem 221 F08 Sect 01 Dr. C. Rogers **NAME:**

INTRODUCTORY ORGANIC CHEMISTRY I --- **PROBLEM SET #2**

INSTRUCTIONS: ANSWER ALL QUESTIONS ON THESE PAGES. HAND IN (stapled, with no extra pages please) **AT THE BEGINNING OF CLASS on Tuesday Nov.25th.** LATE SUBMISSIONS WILL **NOT** BE ACCEPTED (EARLY IS FINE). ALL MATERIAL CAN ALL BE FOUND IN THE CLASS NOTES, PREVIOUS TERMS' PROBLEM SETS & BRUICE CH. 1-9 & 11.

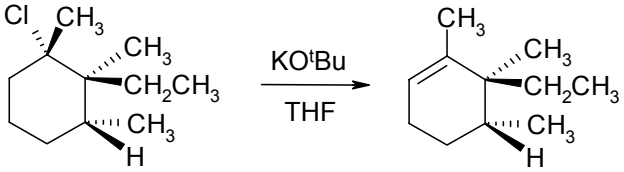
#1. Shown in the box at the right are examples of three reaction types we study in this course:
addition, elimination & substitution.



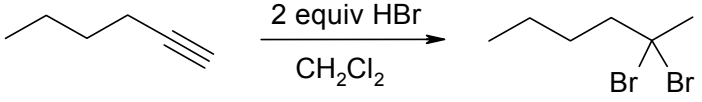
For reactions a-c shown below, identify the reaction type and net change that occurred during the reaction (as shown for examples).

Hint: drawing implied H-atoms & lone pairs will help.

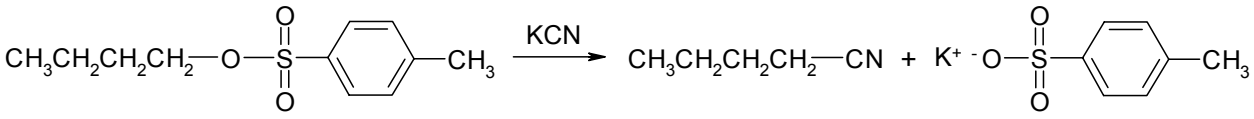
a)



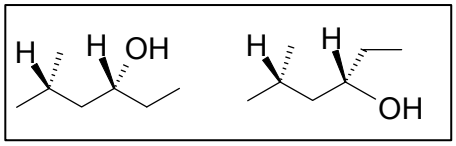
b)



c)



#2. For each statement below, circle the word(s) in the parentheses that correctly **describes the molecules shown** here at the right.



a) They are (IDENTICAL / ENANTIOMERS / DIASTEREOMERS).

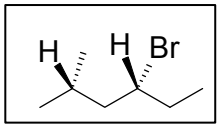
b) They each have (ONE / TWO) chiral centres, *i.e.*, asymmetric carbon atoms.

c) A 50 : 50 mixture of them (WOULD / WOULD NOT) exhibit optical rotation.

d) A pure sample of one of them (WOULD / WOULD NOT) exhibit optical rotation.

e) They have (IDENTICAL / DIFFERENT) physical properties in an achiral environment.

f) A 50:50 mixture of them could form via an (S_N1 / S_N2) reaction between NaOH & the alkyl bromide shown here.



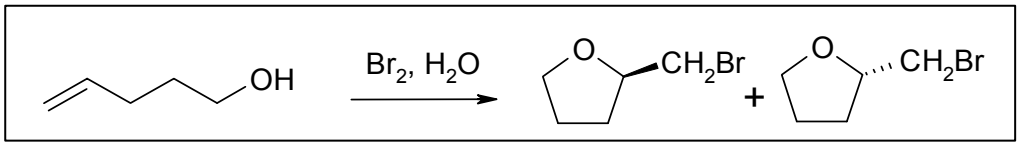
#3. *Diethylamine and ethanol are technically both "amphiprotic". However, both are considered "protic" solvents, but only one of them is commonly used as a weak base.*

Your tasks here:

a) **Explain** the meaning of both of these statements (include definitions of terms, structures & pK_as).

b) **Identify** which substance is a commonly used weak base and explain why the other substance is not.

#4. When 4-penten-1-ol is treated with aqueous Br_2 (at neutral pH), a cyclic bromo ether is formed, rather than the expected halohydrin. **Propose a mechanism** for this result (note: "mechanism" means show arrow pushing for each elementary step and complete structures of intermediates).



#5. For each pair of molecules shown, **circle the one** that best fits the description.

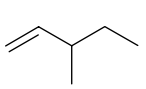
a) The solvent that is described as polar & aprotic: tetrahydrofuran (THF) *vs.* methanol

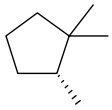
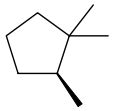
b) The substance with the better leaving group: $CH_3CH_2CH_2OH$ *vs.* CH_3CH_2Br

c) The substance that will react faster via S_N2: $(CH_3)_3CI$ *vs.* CH_3CH_2I

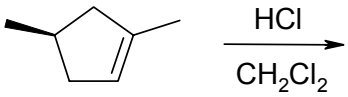
d) The substance that yields a racemic mixture via S_N1: EtMeHCBr *vs.* $(CH_3)_3CBr$

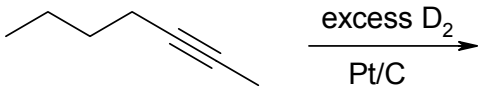
e) The alkene that reacts faster with HCl: $H_2C{=}CHCH_2CH_3$ vs. $CH_3CH{=}CHCH_3$

f) The alkene that yields enantiomers via hydroboration:  *vs.* 

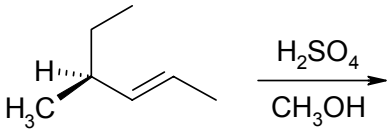
g) The molecule with "R" configuration:  *vs.* 

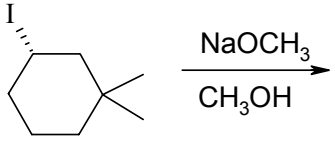
#6. Draw the **major products** of the following reactions (include stereochemistry). Label each reaction with keywords about its **mechanism** (*e.g.*, E+ addition via C+/radical intermediate or concerted mechanism, or S_N1/S_N2, *etc.*). Label each product as **chiral or achiral**, and if stereoisomers are formed, specify their **relationship** (*i.e.,* enantiomers *vs.* diastereomers).

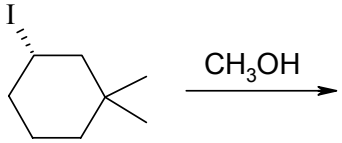
a) 

b) 

note: D is deuterium (isotope of hydrogen)

c) 

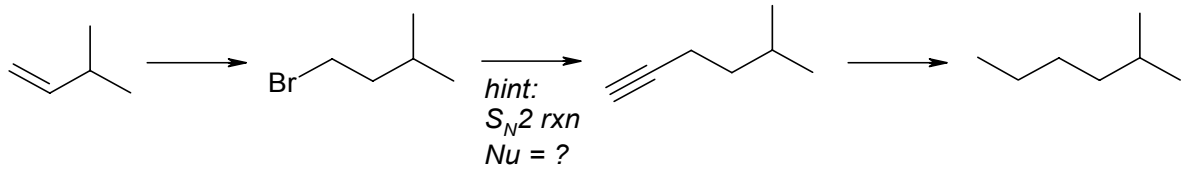
d) 

e) 

#7. Organic synthesis (see Bruice 4.12, 6.12 & 9.11) involves two types of thinking:
(1) **Backwards:** What building blocks (*e.g.,* E^+ & Nu…) might the target molecule be built from?
What types of rxns yield the target's functional groups? regiochem.? stereochem.?
(2) **Forwards:** Which specific reagents would take us step-by-step from starting material to target?

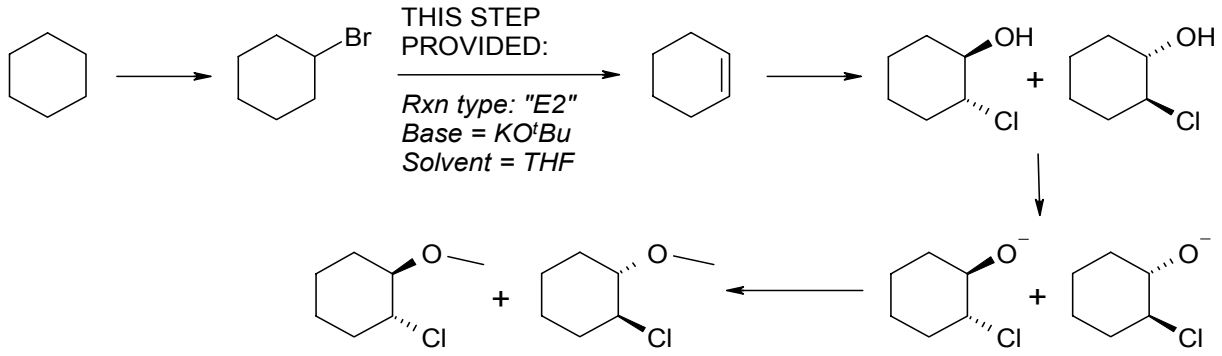
Your tasks here: consider the two synthetic routes shown below. First practice thinking forwards, and **specify exactly which reagents would be required** to perform each step (*i.e.,* each separate reaction run in lab; not mechanistic step) with a high yield of the desired product. Then, practice thinking backwards, and **write a *retrosynthetic analysis* for each pathway** (CRITICAL: read Bruice section 6.12 first). In your retrosynthetic analyses, use an "⇒" arrow for each "disconnection" (breaking up the target into building blocks for each step). To help learn retrosynthetic thinking for devising future synthetic routes, you should also indicate the reaction type (not reagents) needed to go forward at each disconnection, as well as which building block will be E+ versus Nu in that reaction.

a) Synthetic route: (fill in the missing reagents/solvent/conditions around each step's arrow)



Retrosynthetic analysis: (start at target; provide rxn type & E+ vs Nu for each "⇒" step)

b) Synthetic route: (fill in the missing reagents/solvent/conditions around each step's arrow)



Retrosynthetic analysis: (start at target; provide rxn type & E+ vs Nu for each "⇒" step)