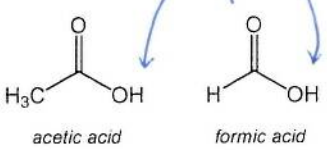
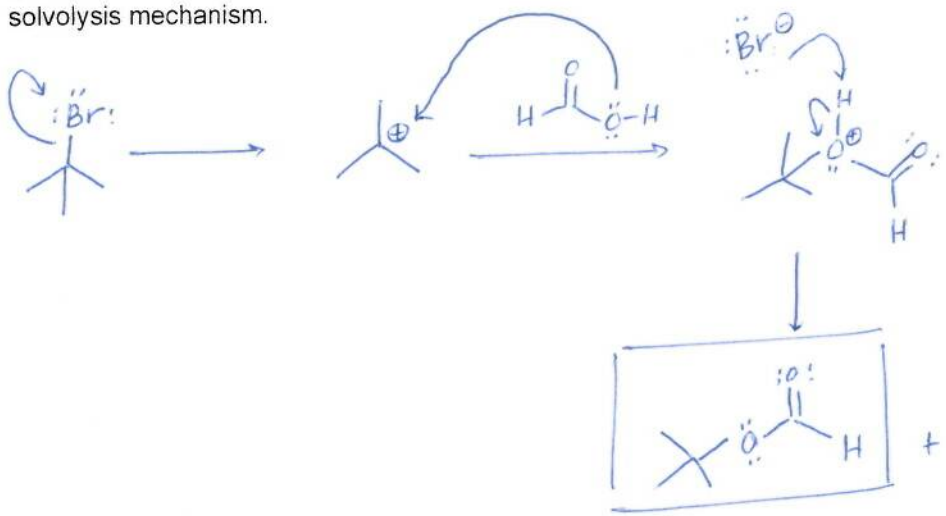
1. (12 pts) 2-bromo-2-methylpropane undergoes solvolysis in either acetic acid or formic acid. (a) In one solvent the SN1 reaction is 5000 times faster than it is in the other. In which solvent is the reaction more rapid? Briefly explain. (b) Write a mechanism for the faster reaction. Draw a box around the product of the solvolysis mechanism.

both protic

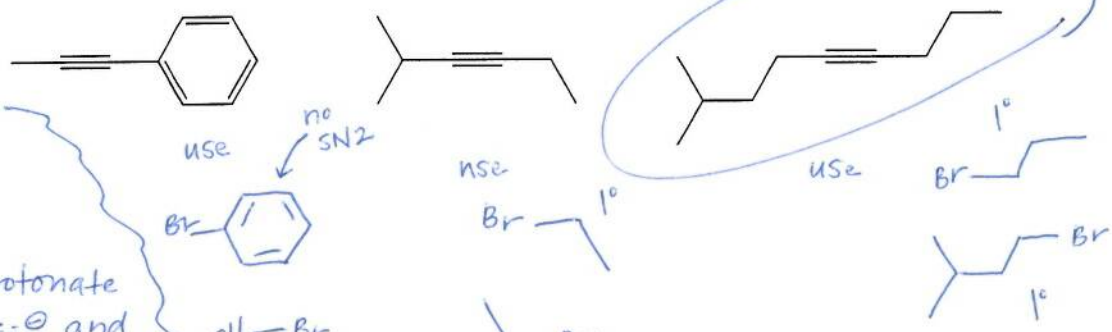


acetic acid formic acid



faster; this solvent is more polar than acetic acid (both are protic) SN1 will be faster in the more polar/protic solvent b/c the C⊕ + LG are stabilized by the dipole of the solvent + H bonding

2. (10 pts) Of the alkynes shown below, which can be synthesized in the highest yield starting from ethyne. Clearly explain.



ethyne

need to deprotonate to make $\equiv:^{\ominus}$ and do SN2 (avoid E2)

use

no SN2

CH_3-Br

use

2°

use

1°

both electrophiles would be 1°. SN2 would be successful.

3. (4 pts each) For each pair of reactions, circle which reaction (if either) should have faster rate of reaction. In all cases you can assume that the reactions occur. Explain your choice in 7 words or less.

a. reaction of cyanide anion with bromoethane in methanol or acetone

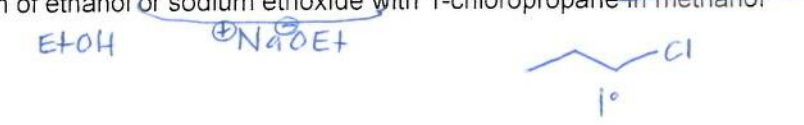
SN2 faster in aprotic

b. reaction of 3-methyl-2-butanol or 2,3-dimethyl-2-butanol in aqueous acid

3° C⊕ made faster

c. reaction of ethanol or sodium ethoxide with 1-chloropropane ~~in methanol~~

SN2 faster with stronger Nu (stronger base)



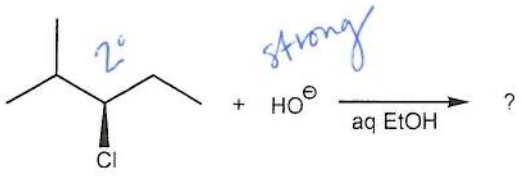
d. reaction of 2-chloro-2-methylbutane with iodide anion or bromide anion in ethanol

3°

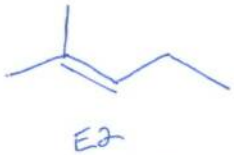
$I^{\ominus}$ $Br^{\ominus}$ EtOH protic

Same rate Same RDS Nu doesn't matter

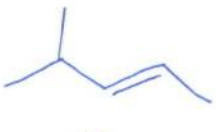
4. (16 pts) Consider the reaction of (*R*)-3-chloro-2-methylpentane, as shown to the right.



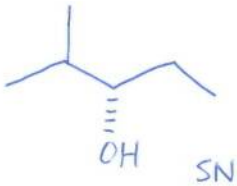
a. Show the structures of all possible products, both major and minor, assuming second order kinetics. Under each product, label it as major or minor and give the name of the mechanism that produces the product.



E2 major

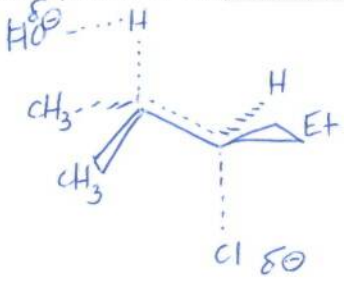


E2 minor



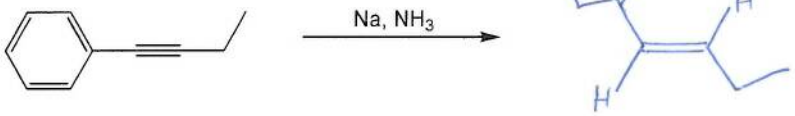
SN2 minor

b. Draw a three-dimensional picture of the transition state that leads to the formation of the major product identified in Part 4a.



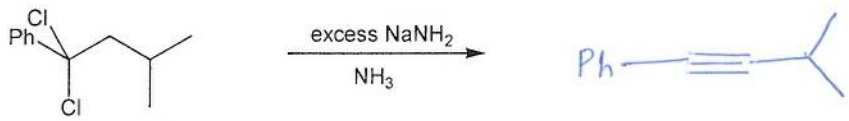
5. (3 pts each) Draw products of the following reactions.

a.

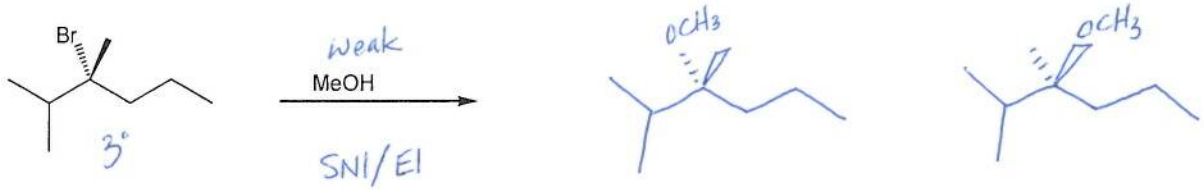


b.

c.

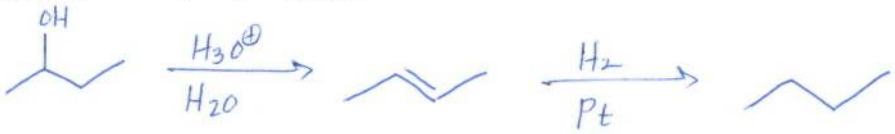


d.

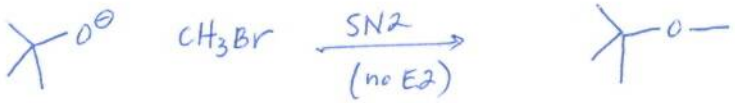


6. (16 pts) For parts a through c, outline a synthesis starting from the given reactant. You may use any other needed reagents. More than one reaction may be necessary. Mechanisms are not required.

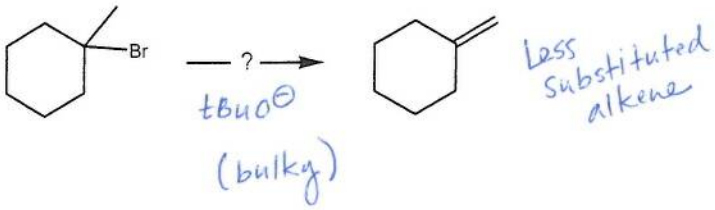
a. 2-butanol —— ? ⟶ butane



b. alkyl halide of your choosing —— ? ⟶ $tBuOCH_3$



c.



7. (18 pts) (a) Draw a reasonable mechanism for the reaction shown below. (b) Draw a reaction coordinate for the mechanism that you propose. Briefly annotate your diagram to indicate how you arrived at your answer.