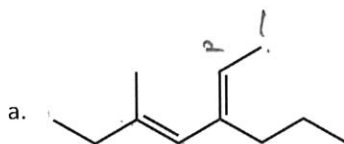
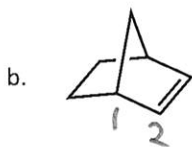


1. Name the following compounds. Don't forget to assign any stereochemistry using the correct notation. (15 points)

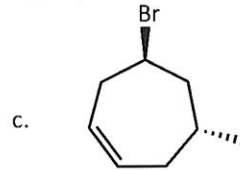


(2E,4E)-5-methyl-3-propylhepta-2,4-diene



bicyclo[2.2.1]hept-2-ene

(4S,6R)-4-bromo-6-methylcycloheptane

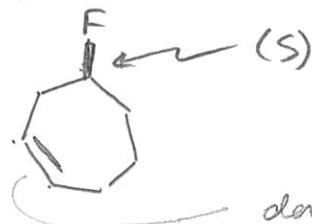


2. Draw the structure of the following compounds. (10 points)

- a. (4E)-4-(2,2-dimethylpropyl)octa-1,4-diene

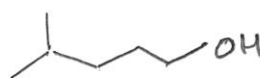
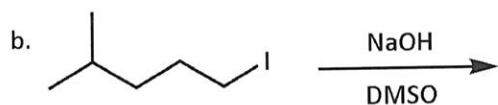
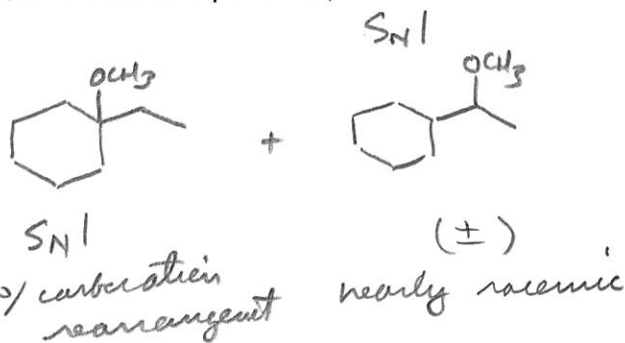
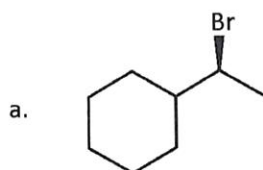


- b. (S)-4-fluorocycloheptene



don't need to indicate (Z) in < 8-membered rings

3. For the following substitution reactions show the product (or products). Indicate whether the reaction proceeds by the S_N1 or S_N2 mechanism. (only show substitution products) (20 points)



S_N2

4. Consider the following reaction:

(30 points)



a. Indicate whether this reaction proceeds via an S_N1 or S_N2 process. Explain.

the inversion suggest backside attach

b. Draw the mechanism of this reaction.



c. What is the rate equation of this reaction?

$$\text{Rate} = k [\text{R-Br}] [\text{CN}^-]$$

d. Would the reaction occur at a faster rate if the concentration of sodium cyanide (NaCN) were doubled? Explain.

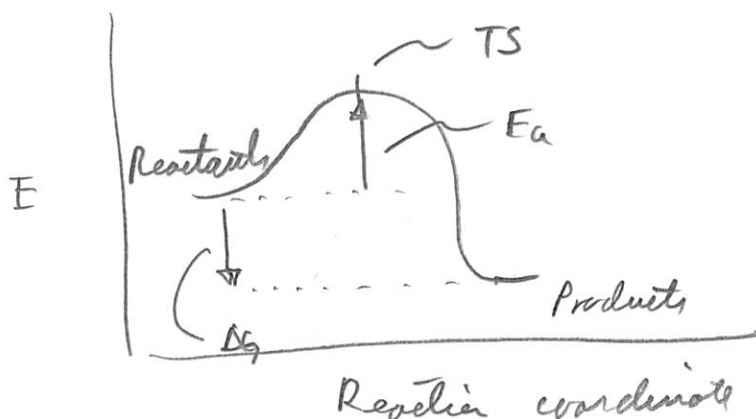
Yes, because it is present in the rate equation and the TS

e. If the solvent was changed to ethanol (EtOH), how would this effect the reaction rate? Explain.

the rate limiting step depends on the concentration of CN^-

f. Draw an energy diagram of the reaction above.

the rate would decrease since the nucleophile will be more solvated in a polar protic solvent such as EtOH and therefore will be less nucleophilic



5. Consider the table below (Table 9.5) regarding the S_N2 reaction of select nucleophiles from Group 6A and 7A with methyl iodide (CH_3I). (40 points)

- a. Which data in the table indicate the trend in nucleophile strength for Group 6A elements – which one is the “stronger” nucleophile? Explain your answer.

the rate constant, the larger the rate constant, the faster the reaction, the stronger the Nu

- b. What does the pK_a of the conjugate acid indicate about the nucleophile strength for the Group 7A nucleophiles? Explain your answer.

In this case appears, the data suggest the larger the value, the weaker nucleophile – more acidic implies better (stronger) Nu

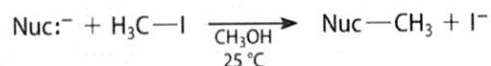
- c. What effect would switching the solvent of the reaction to DMSO have on the rate of reaction of the nucleophiles in Group 7A with methyl iodide?

Fluoride would become the stronger Nu – Iodide the weaker Nu

- d. Where would the nucleophile PhSe^- be placed in the Table?

above PhS^-

TABLE 9.5 Dependence of S_N2 Reaction Rate on the Basicity of Nucleophiles from Different Periods of the Periodic Table in Methanol



Nucleophile	pK_a of conjugate acid*	k (second-order rate constant, $\text{M}^{-1} \text{s}^{-1}$)	$\log k$
Group 6A Nucleophiles			
PhS^-	6.52	1.1	+0.03
PhO^-	9.95	7.9×10^{-5}	-4.1
Group 7A Nucleophiles			
I^-	-10	3.4×10^{-3}	-2.5
Br^-	-8	8.0×10^{-5}	-4.1
Cl^-	-6	3.0×10^{-6}	-5.5
F^-	3.2	5.0×10^{-8}	-7.3

* pK_a values in water

(Source: Marc Loudon *Organic Chemistry* 6th edition, Roberts and Co., 2016, p. 399)

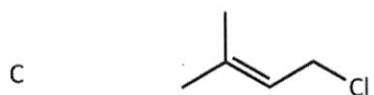
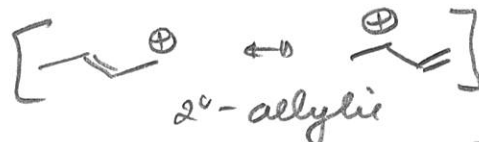
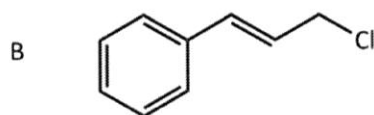
6. The three compounds below undergo rapid reaction with water (H_2O) with increasing rates as noted by the relative rates. In terms of the mechanism, explain the trend in two parts: (20 points)

- a. Explain why B reacts faster than A
 b. Explain why C reacts faster than B

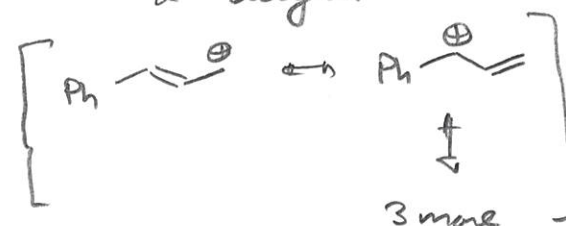
Entry alkyl halide Relative rate



The reaction proceeds through an S_N1 mechanism. So the more stable carbocation means faster reaction w/ H_2O



1430

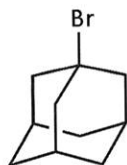


benzylic + allylic

3° allylic most stable of all

Going from A to B, then to C, each cation intermediate is more stable than the previous

7. Adamantyl bromide is completely unreactive toward nucleophiles in either the S_N1 or the S_N2 reaction. Suggest an explanation for this lack of reactivity. (10 points)



adamantyl bromide

S_N2 reaction is impossible since

3° and ultra-buried from the backside which is "inside" the ring.

S_N1 relies on forming a carbocation, and normally 3° substrates are best, but in this case the α -carbon cannot attain the plane sp^2 geometry need for a carbocation -

So unreactive under either set of conditions

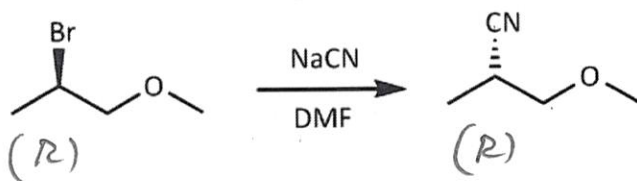
8. The Finkelstein reaction is a widely used reaction to prepare alkyl iodides (R-I). The reaction converts alkyl chlorides (R-Cl) and bromides (R-Br) to their corresponding iodides in excellent yield. Given the "normal" order of nucleophilic strength of the halides in protic vs. aprotic solvents and noting that the only alkali metal salt that is soluble in acetone is NaI, suggest an explanation for the success of this popular reaction. (20 points)



R = methyl, primary, or secondary
X = Cl or Br

Normally, Br^- and Cl^- are stronger nucleophiles than I^- in aprotic solvents, but in this case the sodium iodide is soluble in acetone, so when it displaces a bromide or chloride it's uphill, but the product NaX precipitates from the reaction and "draws" the reaction forward - Le Chatelier's principle

9. Consider the following $\text{S}_{\text{N}}2$ reaction: (15 points)

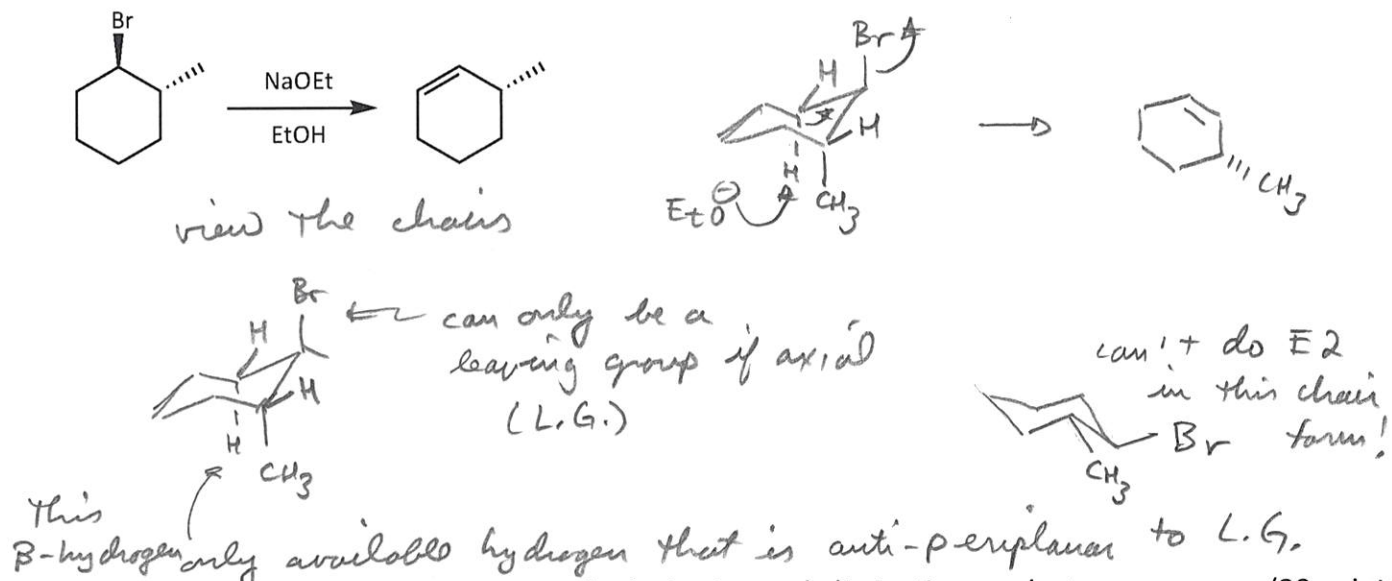


- Assign the configuration of the chirality center in the substrate. (R)
- Assign the configuration of the chirality center in the product. (R)
- Does this $\text{S}_{\text{N}}2$ process occur with *inversion* of configuration? Explain.

The carbon is inverted 100% but the priority of groups result in the configuration being the same as in the substrate.

The answer is yes or no depending on how you answer the question - strictly speaking the "configuration" is preserved and not inverted. However the carbon is "inverted" in the process!

10. Explain why the alkyl bromide shown below undergoes E2 reaction and only results in the Hofmann product shown below (none of the Zaitzev product is formed). (10 points)



11. The following reaction gives a mixture of substitution and elimination products. (20 points)

Answer the following:

- Show all of the possible products from this reaction. (10)
- Indicate whether the products are formed from S_N1 , S_N2 , E1, or E2 mechanisms. (5)
- Indicate the major and minor product, where appropriate (or possible). (5)

