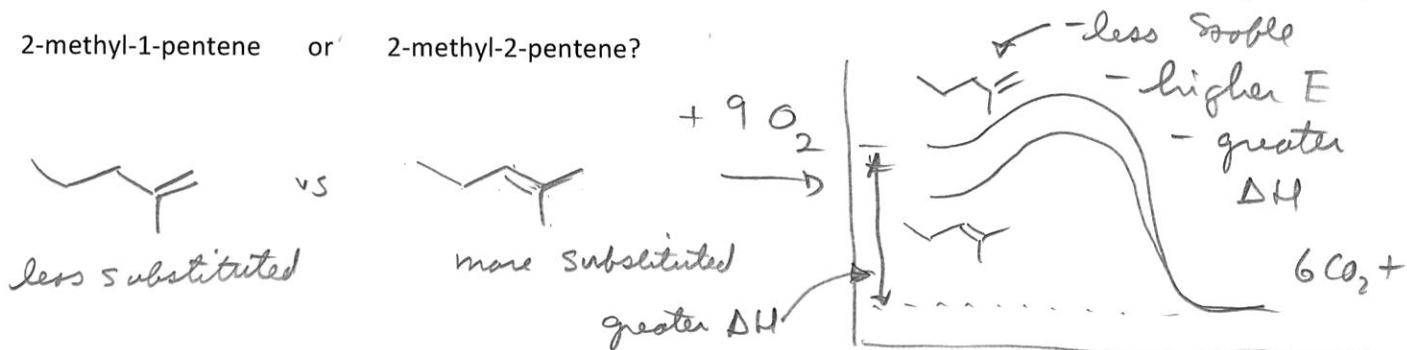


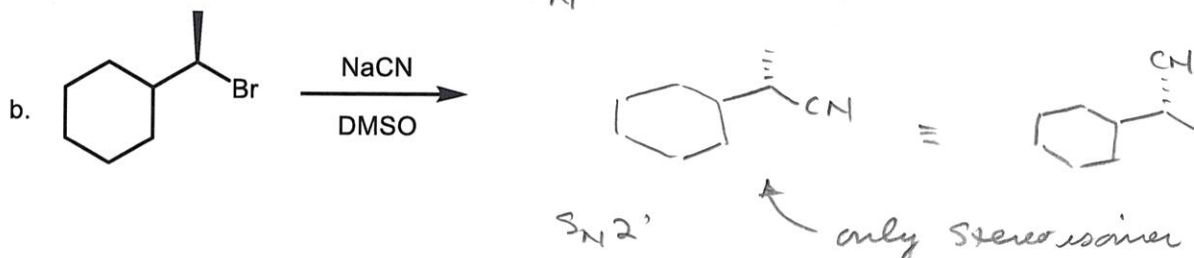
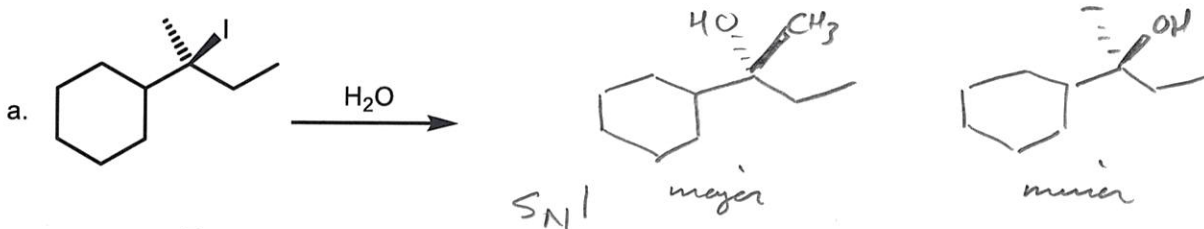
Key

1. Which of the two alkenes has the greater heat of combustion ( $\Delta H_{\text{comb}}$ ) Explain. (10 points)

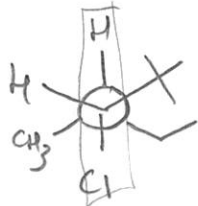
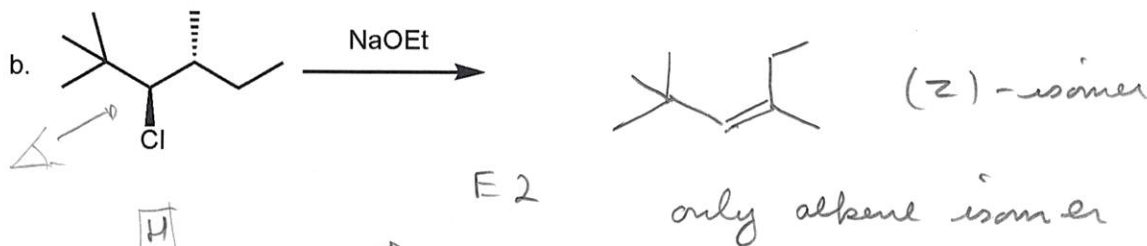
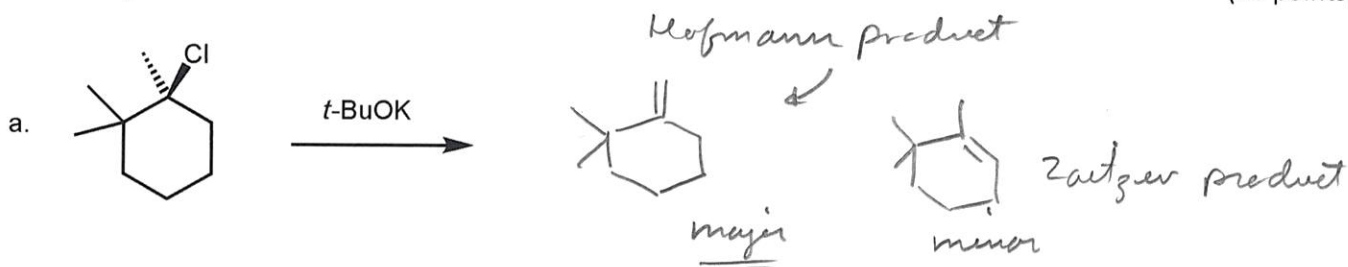
2-methyl-1-pentene or 2-methyl-2-pentene?



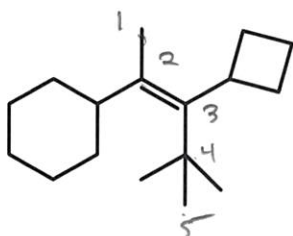
2. For the following substitution reactions show the product (or products). Indicate whether the reaction proceeds by the  $S_N1$  or  $S_N2$  mechanism. (Be very clear about any stereochemistry outcomes) (10 points)



3. For the following elimination reactions show the product (or products). Be very clear about any stereochemistry outcomes). (10 points)



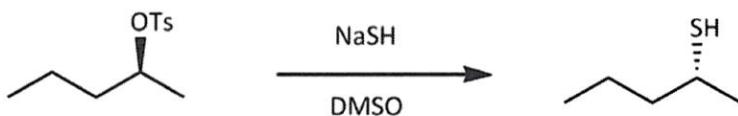
4. Name the following compound. Assign stereochemistry where appropriate. (10 points)



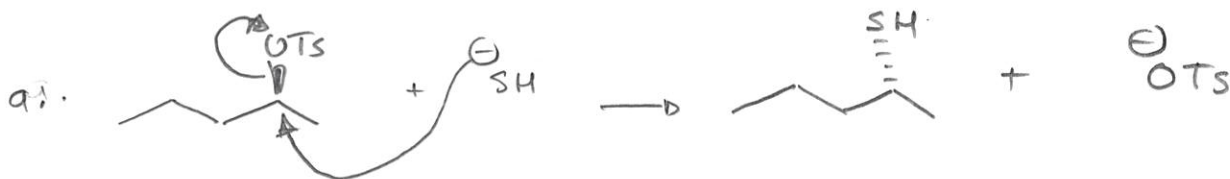
parent chain  
↓  
pent-2-ene  
↑  
unsaturation

(Z)-3-cyclobutyl-2-cyclohexyl-4,4-dimethylpent-2-ene

5. Consider the following S<sub>N</sub>2 reaction: (50 points)



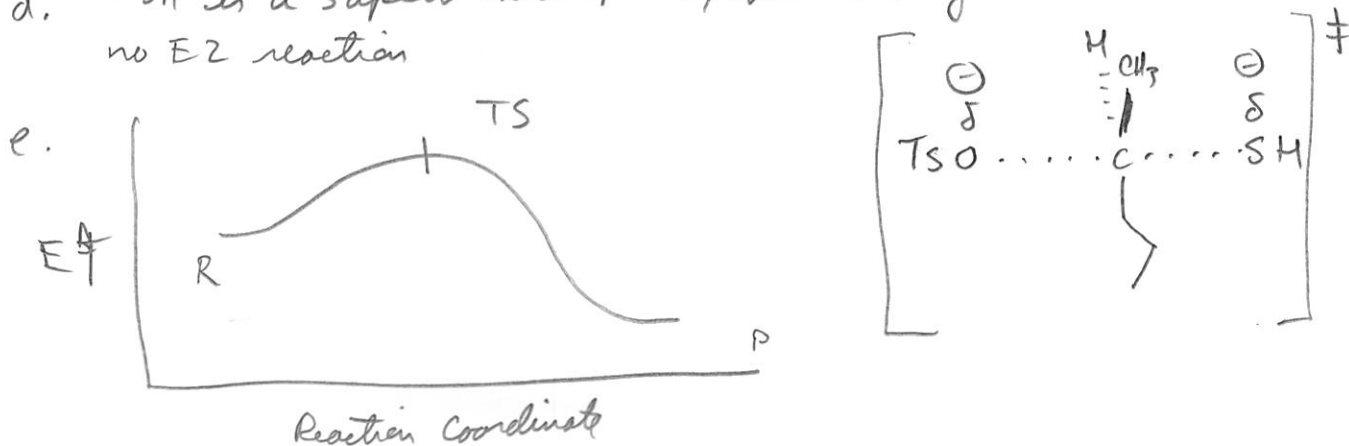
- Draw the mechanism for this reaction (electron pushing).
- Show the rate equation for this reaction?
- What would happen to the rate if the solvent is changed from DMSO to ethanol?
- Explain why there is no E2 reaction observed in this case.
- Draw an energy diagram for this reaction.
- Draw the transition state for this reaction.



b. Rate =  $k [R-OTs][^{\ominus}SH]$

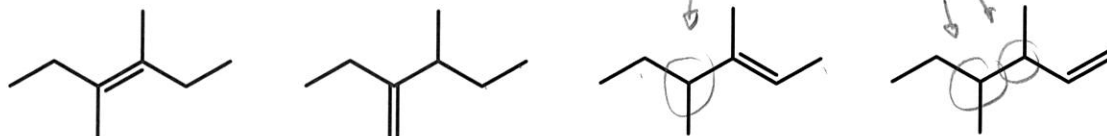
c. the rate would increase dramatically (~1000-fold)

d.  $^{\ominus}SH$  is a superb nucleophile, but a very weak base, so no E2 reaction



6. Consider the following series of alkenes. (30 points)

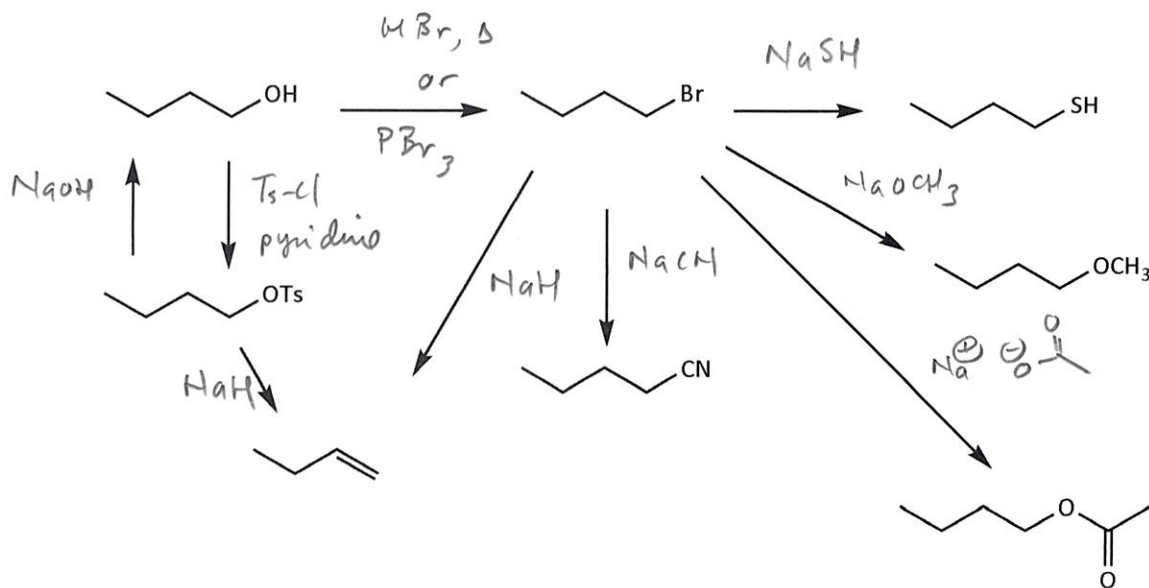
- Rank each of them from most stable (1) to least stable (4).
- Name each alkene (use E/Z notation if necessary)
- Predict which alkene will have the most exothermic heat of hydrogenation ( $\Delta H_{\text{hydrog.}}$ )  
(hint: remember, hydrogenation is alkene +  $\text{H}_2 \rightarrow$  alkane)



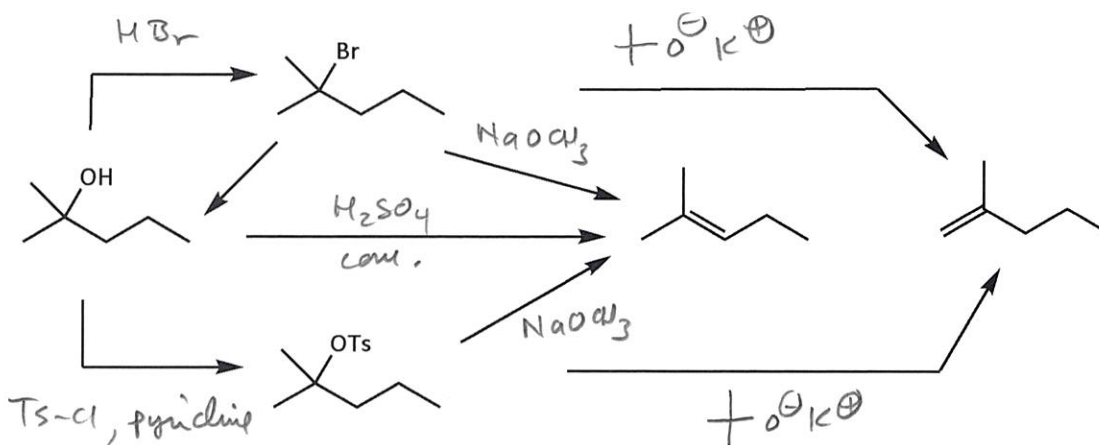
Rank	1	3	2	4
Name	(E)-3,4-dimethylhex-3-ene	2-ethyl-3-methylpent-1-ene	(E)-3,4-dimethylhex-2-ene	3,4-dimethylhex-1-ene
$\Delta H_{\text{hydrog}}$				✓

7. Explain why fluoride ( $\text{F}^-$ ) is a better nucleophile in DMSO than in ethanol. (10 points)

8. Show how to accomplish all of the following transformations, i.e., fill in the reagents over each arrow. (The problem continues on the next page) (85 points)

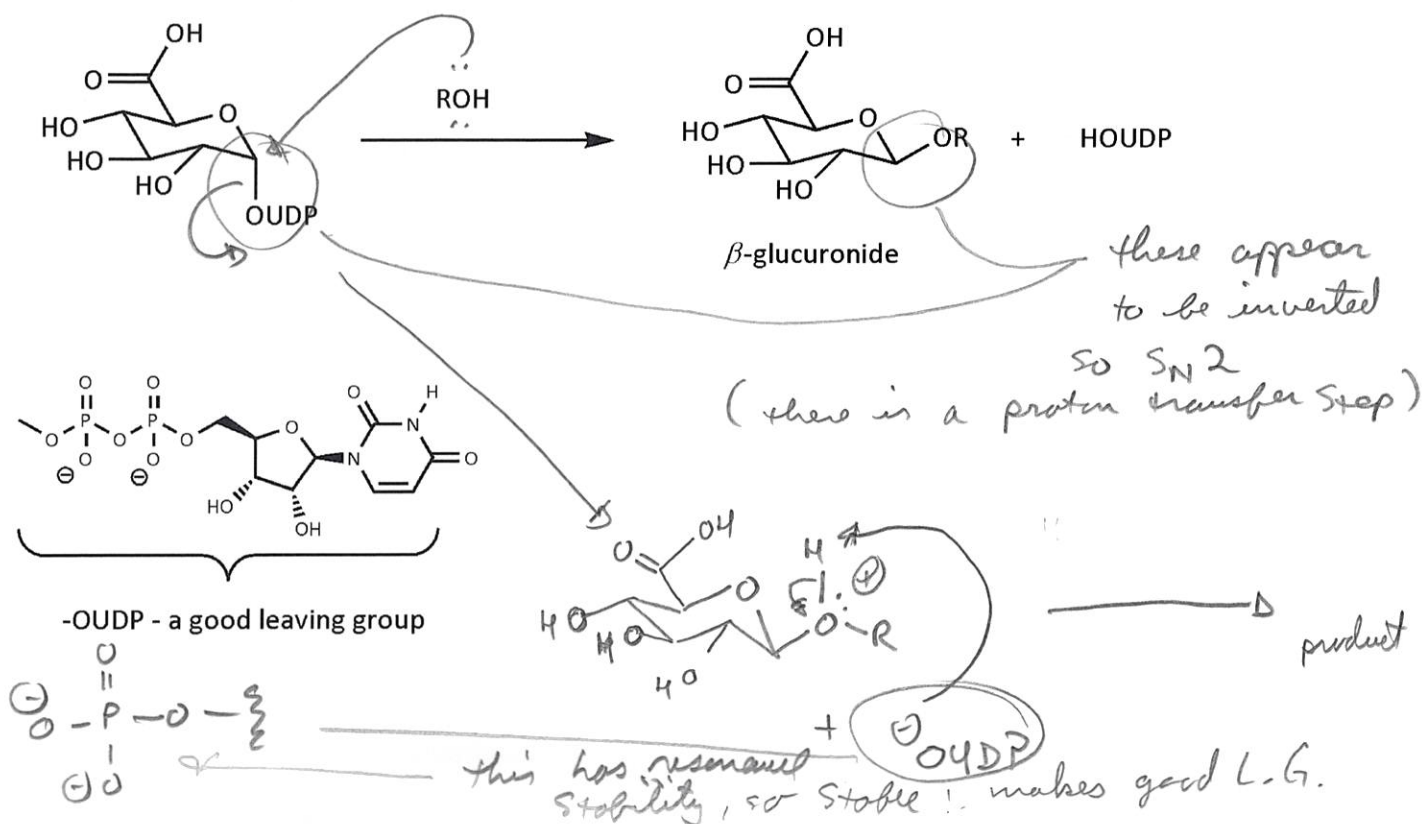


8. Cont'd



9. One of Nature's biochemical mechanisms of dealing with toxic substances, if it has an alcohol functional group (ROH), is to convert it to the  $\beta$ -glucuronide shown below. (30 points)

- What is the reaction mechanism for this transformation?
- What makes the  $-OUDP$  group a good leaving group?
- Show the mechanism with electron pushing (note any proton transfers).





10. Consider the table (next page) regarding the  $S_N2$  reaction of select nucleophiles from Group 6A and 7A with methyl iodide ( $\text{CH}_3\text{I}$ ). Note that this question requires complete explanations for each part (not just one or two word answers) (50 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 constants tell the “strength” – the larger the value, the faster the reaction – this shows a nucleophile is ranked in terms of strength. Therefore  $\ominus\text{SPh}$  is  $\sim 10^4$  times stronger (faster)

b. For the Group 7A nucleophiles, given the trend in the  $\text{p}K_a$  of the conjugate acid, is acidity a factor in predicting how strong the nucleophile is? Explain your answer.

The acidity trend would suggest that  $\text{F}^\ominus$  than  $\ominus\text{OPh}$  should be a stronger nucleophile than  $\text{I}^\ominus$ , since  $\text{F}^\ominus$  is by definition a stronger base. So in this series the acidity alone doesn't account for the observed trend.

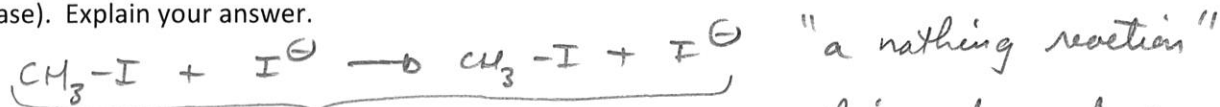
c. What effect would switching the solvent of the reaction to DMSO have on the rate of reaction of the nucleophiles in Group 7A with methyl iodide? Explain your answer.

Changing to an aprotic solvent, the nucleophile receives less stabilization due to lack of H-bonding; the most concentrated change is  $\text{F}^\ominus$  using DMSO so the trend reverses –  $\text{F}^\ominus$  is strongest,  $\text{I}^\ominus$  is weakest  $\text{N}_q$

d. Where would the nucleophile  $\text{PhSe}^\ominus$  be placed in the Table? Explain your answer.

Would be an entry above  $\text{PhS}^\ominus$  in the table and  $k$  would be greater than 1.1. Selenium is actually below sulfur in the periodic table, so the trend would be same as observed w/ the 7A element (in  $\text{CH}_3\text{OH}$  solvent)

e. For the “nothing” reaction in the table – the reaction of methyl iodide with iodide – how would you measure the rate constant for the reaction if “nothing” seems to happen (note the leaving group in this case). Explain your answer.



as shown, can't tell anything changed, so how to measure rate? Use a radioisotope of iodine (e.g.  $^{131}\text{I}$ ). Follow the rate to form 50% mixture

