Hw4: Alkyl Halides, Substitutions on Saturated Carbons

1. Explain the following terms:

(a) Free radical reaction

(b) Ionic reaction

(c) Synergistic reaction

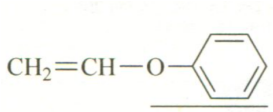
(d) Nucleophile

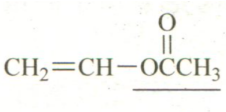
(e) Electrophile

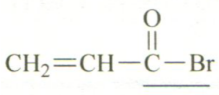
(f) Transition state

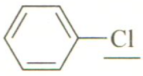
(g) Intermediate

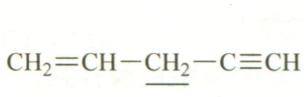
2. Analyze electron effects of the underline groups:

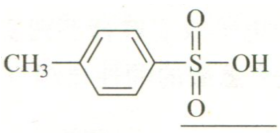




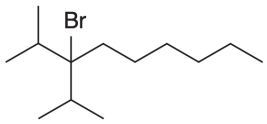


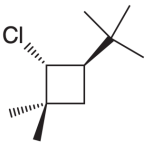


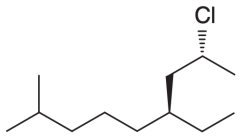


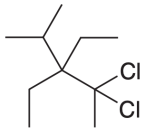


3. Assign a systematic name for each of the following compounds:

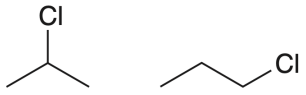
(e) 

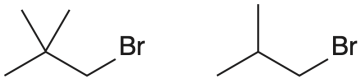
(f) 

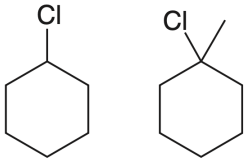
(g) 

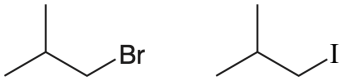
(h) 

4. For each of the following pairs of compounds, identify which compound would react more rapidly in an S_N2 reaction. Explain your choice in each case.

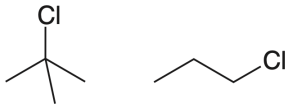
(a) 

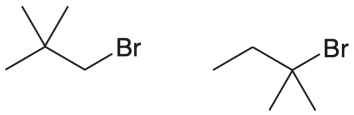
(b) 

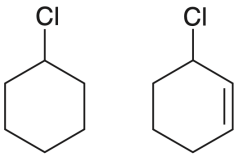
(c) 

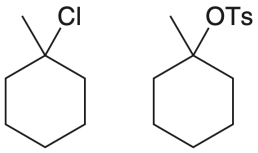
(d) 

5. For each pair of the following compounds, identify which compound would react more rapidly in an S_N1 reaction. Explain your choice in each case.

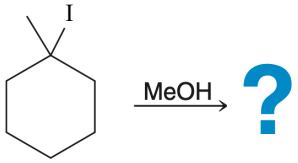
(a) 

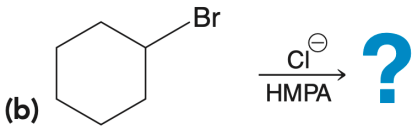
(b) 

(c) 

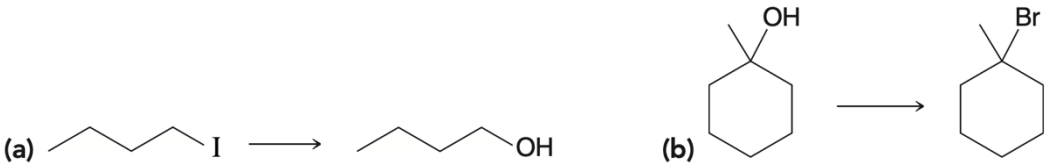
(d) 

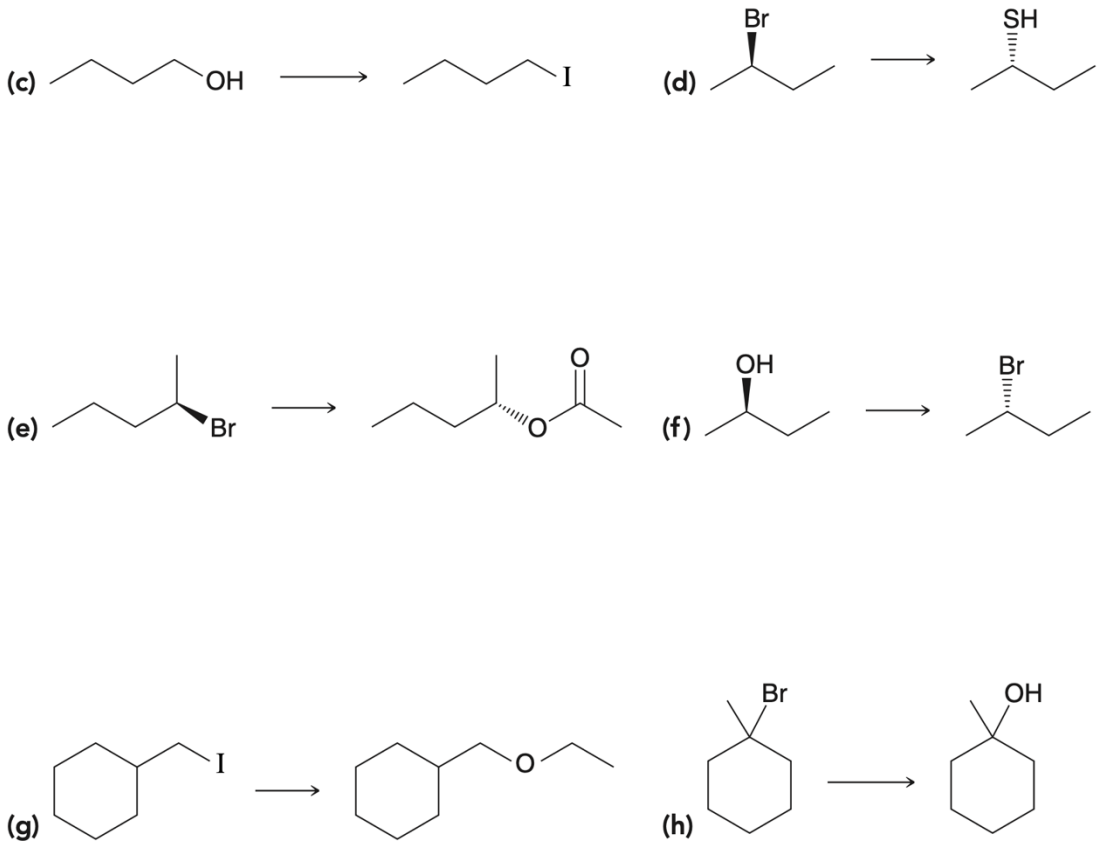
6. Determine whether each of the following reactions proceeds via an S_N1 or S_N2 mechanism and then draw the product(s) of the reaction:

(a) 

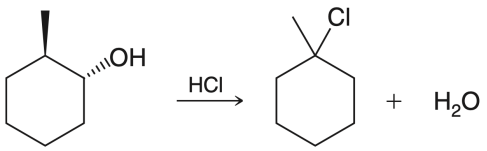
(b) 

7. Determine whether each of the following reactions proceeds via an S_N1 or S_N2 mechanism, and identify the reagents you would use to accomplish each of the following transformations:

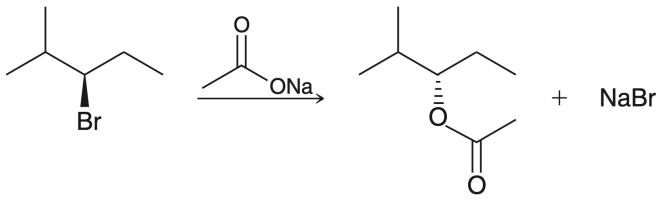




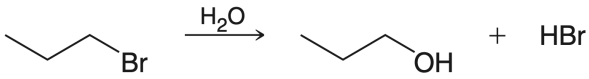
8. Propose a mechanism for the following transformation:



9. Draw the mechanism of the following reaction:



10. The following reaction is very slow:

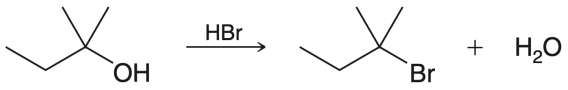


(a) Identify (but don't draw) the mechanism.

(b) Explain why the reaction is so slow.

(c) When hydroxide is used instead of water, the reaction is very rapid. Draw the mechanism of this reaction and explain why it is so fast.

11. Consider the following substitution reaction:



(a) Determine whether this reaction proceeds via an S_N1 or S_N2 process.

(b) Draw the mechanism of this reaction.

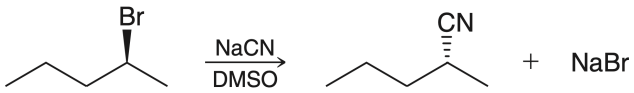
(c) What is the rate equation of this reaction?

(d) Would the reaction occur at a faster rate if sodium bromide were added to the reaction mixture?

(e) Draw an energy diagram of this reaction.

You can use the space below to write your answer.

12. Consider the following substitution reaction:



(a) Determine whether this reaction proceeds via an S_N1 or S_N2 process.

(b) Draw the mechanism of this reaction.

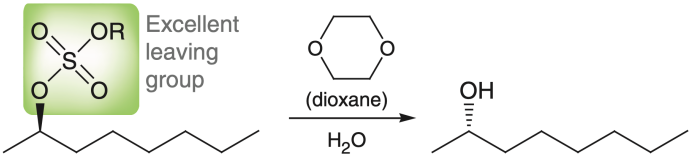
(c) What is the rate equation of this reaction?

(d) Would the reaction occur at a faster rate if the concentration of cyanide (CN^-) were doubled?

(e) Draw an energy diagram of the reaction above.

You can use the space below to write your answer.

13. (hard) Optically pure 2-octyl sulfonate was treated with varying mixtures of water and dioxane, and the optical purity of the resulting product (2-octanol) was found to vary with the ratio of water to dioxane, as shown in the following table (*J. Am. Chem. Soc.* **1965**, 87, **287–291**).

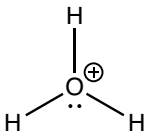


(*R*)-2-Octyl sulfonate (optically pure) → **(*S*)-2-Octanol**

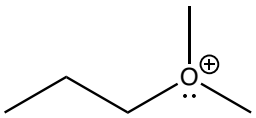
Solvent ratio (water : dioxane)	Optical purity of (*S*)-2-octanol
25 : 75	77%
50 : 50	88%
75 : 25	95%
100 : 0	100%

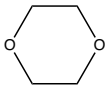
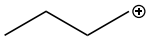
(a) Propose a mechanism for the transformation when the solvent is **100% water**.

(b) An *oxonium* is a kind of ion formed by oxygen that losses an electron (which means the oxygen contains a positive charge). A typical oxonium H_3O^+ (alternatively called hydronium) is shown below:



Also, for organic compounds, oxonium can exist in a form that an oxygen linked to three different groups, like this:



Draw an oxonium that formed by dioxane  and butan-1-ylium  (only one oxygen in dioxane forms oxonium).

(c) The oxygen in dioxane is a nucleophilic center, which means dioxane can function as a nucleophile to complete substitution reactions. Propose and draw a mechanism that dioxane reacts with 2-octyl sulfonate to form an oxonium-containing intermediate.

(d) Given that dioxane possesses fairly nucleophilic oxygen atoms, provide a complete mechanism that explains the variation in the product's optical purity due to changes in solvent composition. (*Hint: consider the reaction between water and the oxonium-containing intermediate drawn in part c – the oxonium is a better leaving group than water*)