Problem Set 3

<u>Chem 220</u>

1. Draw each structure and classify each hydrogen as primary, secondary, or tertiary.

- (a) methylcyclopentane
- (b) 2,3-dimethylbutane
- (c) 3-methyloctane
- (d) 2,2-dimethylpentane

2. The chlorination of 2-methylbutane gives a mixture of four monochlorinated products.

- (a) Draw 2-methylbutane and label the four possible sites for cholrination.
- (b) If the combined yield of the two primary halide products 41%, the secondary halide is formed in 36%, and the tertiary halide in 23%, compute the relative reactivity. (*Relative reactivity primary:secondary:tertiary*)

3. For each of the following compounds, predict (draw) the major product of free-radical bromination.

- (a) methylcyclopentane
- (b) 2,3-dimethylbutane
- (c) 3-methyloctane
- (d) 2,2-dimethylpentane
- 4. Calculate ΔH^0 values for the following reactions from bond energies in your book:
 - (a) $H_2 + F_2 \rightarrow 2HF$ (b) $H_2 + I_2 \rightarrow 2HI$ (c) $(CH_3)_3CH + Br_2 \rightarrow (CH_3)_3CBr + HBr$ (d) $(CH_3)_3CH + Cl_2 \rightarrow (CH_3)_3CCl + HCl$

5. Write a mechanism for the radical bromination of benzene (C_6H_6) (Label the initiation and propagation steps). Calculate ΔH° values for each step and for the overall reaction. How does this reaction compare thermodynamically with the bromination of other hydrocarbons? (Bond dissociation energies: C_6H_5 -H 111 kcal/mol, C_6H_5 -Br 81 kcal/mol)

6. Calculate the ΔG° at 25°C for the following reaction:

 $CH_3CH_2CH_2CH=CH_2 \rightarrow CH_2=CH_2 + CH_3CH=CH_2 \qquad \Delta H^\circ = 22.4 \text{ kcal/mol} \qquad \Delta S^\circ = 33.3 \text{ e.u.}$

What is the effect of raising temperature on ΔG° ? What is the temperature at which the reaction becomes favorable? Show units.

7. Draw a reaction profile (potential energy diagram) to represent each of the following situations: Label reactants, products, and activation energy.

- (a) an exothermic reaction with a small activation barrier
- (b) an exothermic reaction with a large activation barrier
- (c) an endothermic reaction with a small activation barrier