1) Suggest reasonable ways to encouraging the formation of either CH₃Cl or CCl₄ from methane in a photochemical chlorination reaction.

In order to form reasonably good amounts of methyl chloride (CH₃Cl) in a photochemical chlorination, one needs to have the ratio of methane to chlorine be very, very large. This high ratio nearly assures that, statistically, a chlorine molecule will only encounter a methyl radical, and that the concentration of methyl chloride (relative to Cl₂) never gets very high.

In the other case, the ratio needs to be the reverse: chlorine to methane needs to be high. In that way, a chlorine atom will, statistically, encounter only chlorinated products until all the hydrogen atoms have been replaced.

2) Sulfuryl chloride, SO₂Cl₂, is a commonly used reagent for the chlorination of alkanes. These reactions require the presence of a free-radical initiator, such as benzoyl peroxide or simply ultraviolet light. Suggest a mechanism for the monochlorination of neopentane in the presence of ultraviolet light by sulfuryl chloride. (show initiation and propagation steps only):

Initiation:  
\[ \text{Cl} \rightarrow \text{SO}_2\text{Cl} \rightarrow \hat{\text{Cl}} + \hat{\text{SO}_2\text{Cl}} \rightarrow \text{SO}_2 + \hat{\text{Cl}} \]

Propagation:  
\[ \hat{\text{Cl}} + \hat{\text{H}} \rightarrow \hat{\text{Cl}} + \hat{\text{H}} \rightarrow \hat{\text{Cl}} + \hat{\text{HCl}} \]

\[ \text{Cl} \rightarrow \text{SO}_2\text{Cl} \rightarrow \hat{\text{Cl}} + \hat{\text{SO}_2\text{Cl}} \rightarrow \text{SO}_2 + \hat{\text{Cl}} \]
3) Give the expected product(s) for the following reactions. Be careful of both stereo- and regiochemistry:

a) ![Image](image1.png)

Two equivalents of bromine → two replacements. There are two 3° hydrogens, so they both get replaced:

b) ![Image](image2.png)

Assuming only one equivalent of NBS (N-bromosuccinimide), we should see only one replacement. Radicals display the same stability order as carbocations, so we might predict a 3° bromide. Offsetting this consideration is the consideration that more substituted double bonds are more stable than less substituted double bonds. Here we are comparing a tetrasubstituted double bond and a secondary bromide with a trisubstituted double bond and a tertiary bromide. It seems to me that the tetrasubstituted double bond wins the day, and therefore, here is our product:

![Image](image3.png)

4) Consider the photohalogenation of 2,3-dimethylbutane using Br₂ and Cl₂.

a) Draw the possible monohalogenated (C₆H₁₃X) products when X = Cl or Br.

I’ll use X to represent the halogen, with the understanding that X = Cl or Br.
b) Given that $3^\circ$ hydrogens are 5.2 times more reactive than $1^\circ$ hydrogens towards abstraction by chlorine atoms, calculate the expected ratio of monochlorinated products formed.

Here we have 2 $3^\circ$ hydrogens and 12 $1^\circ$ hydrogens; our mathematics looks like this:

$$\left( \frac{2_{tertiary}}{12_{primary}} \right) \left( \frac{5.2}{1} \right) = \frac{10.4}{12} = 0.87.$$  
This is our ratio of $3^\circ/1^\circ$ products. Let $x = \% 3^\circ$ products; then $100 - x = \% 1^\circ$ products. Now we can say: $0.87 = \frac{x}{100 - x}$. Solving for $x$, we get: $x = 46.5\%$, which is our $3^\circ$ product, and $53.5\% 1^\circ$ product.

c) Given that $3^\circ$ hydrogens are 1640 times more reactive than $1^\circ$ hydrogens towards abstraction by bromine atoms, calculate the expected ratio of monobrominated products formed.

We can use the same type of analysis here, as we have the same distribution of hydrogens.

$$\left( \frac{2_{tertiary}}{12_{primary}} \right) \left( \frac{1640}{1} \right) = \frac{3280}{12} = 273.33.$$  
This is our ratio of $3^\circ/1^\circ$ products. Let $x = \% 3^\circ$ products; then $100 - x = \% 1^\circ$ products. Now we can say: $273.33 = \frac{x}{100 - x}$. Solving for $x$, we get: $x = 99.64\%$, which is our $3^\circ$ product, and $0.36\% 1^\circ$ product.

5) To determine whether radicals would undergo rearrangements analogous to those found with carbocations (equation below), deuterated isobutene was subjected to photochemical chlorination.
It was found that the DCl/HCl ratio was equal to the \((\text{CH}_3)_3\text{CCl}/(\text{CH}_3)_2\text{CDCH}_2\text{Cl}\) ratio, within experimental error. How could this experiment be used to demonstrate whether or not rearrangements did occur? What is your conclusion? Explain.

\[
\begin{align*}
\text{H}_3\text{C} &\quad \text{C} &\quad \text{CH}_3 \\
&\quad \text{D} &\quad \text{Cl}_2 &\quad \text{hv} &\quad \rightarrow &\quad \text{H}_3\text{C} &\quad \text{C} &\quad \text{CH}_3 \\
&\quad \text{Cl} &\quad &\quad &\quad &\quad &\quad &\quad \text{H}_3\text{C} &\quad \text{C} &\quad \text{CH}_2\text{Cl} \\
&\quad \text{D} &\quad &\quad &\quad &\quad &\quad &\quad + &\quad \text{HCl} &\quad \text{DCl}
\end{align*}
\]

Every abstraction of a D yields DCl, and every abstraction of H yields HCl. Another way to put it is that the only way to get non-deuterated product is by loss of deuterium. If the deuterium could shift from the tertiary to the primary site after loss of a primary H, then the amount of \textit{tert}-butyl chloride would not match the amount of DCl. In other words, every abstraction of D yields \textit{tert}-butyl chloride, and every abstraction of H yields isobutyl chloride. No radical rearrangement takes place.

6) Provide a reasonable synthesis for the following compound from the indicated starting material.

Hmmmm. A methyl ketone on one end, and an acid on the other—both are carbonyl compounds, so I’m thinking…ozonolysis! But how? Need a double bond for that. We can make one. Here’s how:
OH
O
Br
2
hν
Br
(CH₃)₃CO⁻K⁺
(CH₃)₂COH

1) O₃
2) H₂O₂/HOAc

O
O