1. (4 pts) Bumbling Igor and his lab wizard wife Elvira, recovering from Halloween and the even scarier Tuesday that followed, are now thinking ahead to Thanksgiving. Yum, turkey, gravy, fat, etc. But their fridge has died, due to a Freon leak, so (among other messes) their margarine has gone rancid. Freon’s destruction of ozone in the upper atmosphere, and fat going rancid seem pretty far apart, but they both involve the radical chemistry of oxygen (more on this in another test/quiz). Ingesting halocarbons (Freons are in this category) is undesirable, and Igor & Elvira wonder if the leaked Freon could have actually gotten into the margarine. Wishing to test the idea, they look in the lab fridge (no food allowed!), but find only some 3-hexyne $A$, so they decide to make Z- and E-3-hexenes $B$ and $C$ as simple alkene models for the unsaturated fats in their margarine. Provide reagents in the boxes below to enable them to convert $A$ into separate samples of $B$ and of $C$.

![Chemical structures]

2. (10 pts) In part 1 of this story our laboratory team didn’t make any mistakes. They successfully made $B$ and $C$ from $A$. Now it’s time for the Freon study, but they don’t have any of the old fashioned “Freon 12” ($\text{CF}_2\text{Cl}_2$) that leaked. Instead, they decide to make their own $\text{CCl}_4$ (carbon tetrachloride) via radical chlorination of $\text{CH}_4$ (natural gas, available from their lab gas taps). So…they combine $\text{CH}_4$ and $\text{Cl}_2$ in a cooled chamber, turn on the light, and stand back (remember, light absorbed by the pale green $\text{Cl}_2$ gas can break it into $2\text{Cl}$•).

   a) (2 pts) Why cool the chamber? Is this an exothermic reaction? Here are some heats of formation in kcal/mol: $\text{Cl}_2$: 0.0; $\text{CH}_4$: -17.9; $\text{CH}_3\text{Cl}$: -20.0; $\text{CH}_2\text{Cl}_2$: -22.8; $\text{CHCl}_3$: -24.7; $\text{CCl}_4$: -22.9; $\text{HCl}$: -22.1. Write the overall reaction equation for conversion of $\text{CH}_4$ to $\text{CCl}_4$, and compute its energy change. Don’t forget that $\text{HCl}$ is a byproduct; your reaction equation must be balanced for you to calculate the energy change correctly.

   $\text{CH}_4 + 4 \text{Cl}_2 \rightarrow \text{CCl}_4 + 4 \text{HCl}$

   $\Delta H_{\text{rxn}} = -111.3 - (-17.9) = -93.4$ kcal/mol (i.e. quite exothermic!)

   b) (2 pts) Why is it reasonable for them to specifically target $\text{CCl}_4$, when in class we said that partial chlorination gives complicated mixtures? Which reagent, $\text{Cl}_2$ or $\text{CH}_4$, should be in excess to maximize the yield of $\text{CCl}_4$? Note that $\text{CCl}_4$ doesn’t react with $\text{CH}_4$, $\text{Cl}_2$, or $\text{HCl}$ in any significant way. Also note, it’s easy to separate $\text{CCl}_4$ (a liquid) from the other components in the final mixture (mostly gases).

   If you use a large excess of $\text{Cl}_2$, and just let the reaction go as far as it can, $\text{CCl}_4$ is the endpoint, since it doesn’t react further with $\text{Cl}_2$ or other species present.
c) (6 pts) Now consider the last step in the reaction. Write a full reaction scheme for radical chlorination of CHCl₃ to form CCl₄. You should include the three parts: Initiation (1 reaction, already mentioned), Propagation, and Termination steps for a total of 6 reactions.

Initiation step (1 reaction):

\[
\text{Cl-Cl} \xrightarrow{\text{h\textsuperscript{\textbullet}}\text{r} \text{or} \Delta} 2 \text{Cl}\cdot
\]

Chain propagation steps (2 reactions)

\[
\begin{align*}
\text{Cl}\cdot + \overset{\text{h\textsuperscript{\textbullet}}\text{r}}{\text{ClCCl}}_3 & \rightarrow \text{HCl} + \text{Cl}_3\text{C}\cdot \\
\text{Cl}_3\text{C}\cdot + \overset{\text{h\textsuperscript{\textbullet}}\text{r}}{\text{Cl}\text{Cl}} & \rightarrow \text{CCl}_4 + \text{Cl}\cdot
\end{align*}
\]

Termination steps (3 reactions)

\[
\begin{align*}
2 \text{Cl}\cdot & \rightarrow \text{Cl}_2 \\
\text{Cl}\cdot + \cdot\text{CCl}_3 & \rightarrow \text{CCl}_4 \\
2 \cdot\text{CCl}_3 & \rightarrow \text{Cl}_3\text{C}-\text{CCl}_3
\end{align*}
\]

3. (6 pts) Igor is burned out, but Elvira explores the radical addition of the CCl₄ to their alkene.

(a) (4 pts) Addition of the Cl₃C-Cl bond across the two alkenes B and C from problem (1) gives mixtures of C₇H₁₂Cl₄ products (look in the book’s index under Carbon Tetrahalides). Full analysis reveals four stereoisomers. Draw these four compounds (including enantiomeric forms). (Hint—it wouldn’t hurt you to practice checking R and S configurations).

(b) (2 pts) To Igor’s surprise, the product mixtures from B and from C are essentially identical. But Elvira laughs knowingly and says “Of course they’re the same! It’s a stepwise radical addition.” Explain how her insight makes sense of the sameness of the two product mixtures (hint—think of the intermediates).

Because of free rotation after the first radical addition step, the radical intermediates that are formed from either cis or trans compound are the same, as shown for the case where the Cl₃C• has come from above.