Answers to Ch2 Problems

• Please only use these to check your answers – there is no better way to get good at organic problems that trying to do them yourself.

• The struggle to figure out the right answer is training you to be able to answer the questions on examinations.

• Being lazy and cheating yourself by not attempting these problems yourself will cause you to do horrifically on my quizzes and exams.

• BEAR IN MIND, the problems are VERY relevant to the text they follow.

• E.g. if we cover the Stevens’ rearrangement, the problems directly after that in the text *MAY* involve some sort of similar mechanistic process.

• (If you are stuck, read the section in the notes directly before that problem).

• For the mechanisms I did not write out all possible resonance structures, I just put a resonance arrow to indicate that you can (and should) write other resonance structures.
For this transformation, \( \text{CH}_2=\text{CHC}_6\text{H}_5 + \text{CBr}_4 \xrightarrow{\Delta} \text{PhCCH}_3\text{CHBrC}_6\text{H}_3 \)

(a) Draw in the (single bold) arrows for each step:

\[
\begin{align*}
\text{(I)} & \quad \text{Ph} - \text{C} - \text{O} - \text{C} - \text{Ph} \quad \rightarrow \quad 2\times \text{Ph} - \text{C} - \text{O}.
\text{(II)} & \quad \text{Ph} - \text{C} - \text{O} \rightarrow \text{Br} - \text{CBr}_3 \quad \rightarrow \quad \text{Ph} - \text{C} - \text{O} - \text{Br} \cdot \text{CBr}_3
\text{(III)} & \quad \text{CBr}_3 + \text{CH}_2 = \text{CHC}_6\text{H}_3 \quad \rightarrow \quad \text{Br}_3\text{CCH}_2\text{CHC}_6\text{H}_3
\text{(IV)} & \quad \text{Br}_3\text{CCH}_2\text{CHC}_6\text{H}_3 + \text{Br} - \text{CBr}_3 \quad \rightarrow \quad \text{Br}_3\text{CCH}_2 - \text{C} - \text{CHC}_6\text{H}_3 \cdot \text{CBr}_3
\end{align*}
\]

(b) What are initiation and propagation steps?

(c) Why is (III) regioselective? More highly substituted alkyl formed.
For the following reaction:

\[
\begin{align*}
\text{CN} & \xrightarrow{N=N \cdot H \cdot} 2x \\
\text{CN} & \xrightarrow{N=CN \cdot H} \text{Y} \\
\text{Bu}_3\text{Sn}=H
\end{align*}
\]

...can write the mechanism (identify initiation & propagation steps).

(b) This side product is a minor product. Show how it might be formed:

\[
\begin{align*}
\text{Bu}_3\text{Sn}-H
\end{align*}
\]
Write initiation & propagation mechanisms for R₂Sn-H → R₂Sn-R

Propose a mechanism for:

(Barton Nitrite Photolysis: Steroid functionalization in hand to reach places.)
Write mechanism for:

(a) \( \text{Ph}_3\text{CHCH}_2\text{COAg} + \text{Br}_2 \)
Write mechanisms for both processes below, and explain why they occur.
Write a complete mechanism for...

$$\text{CN} \xrightarrow{\text{H}_2\text{N}-\text{N}} \text{CN} \quad \xrightarrow{\text{Bu}_3\text{SnH}} \quad \text{CN} \quad \xrightarrow{\text{S} \cdot \text{R}_3} \quad \text{CN}$$

Write mechanisms for the following:

(a) $$\text{Br} \xrightarrow{\text{Ph}_3\text{P}} \text{Cl} \xrightarrow{\text{hv} \text{DMF}} \text{Cl}$$

(b) $$\begin{align*}
\text{CF}_3 \quad \text{I} \\
\xrightarrow{\text{hv} \text{NMe}_3(\text{Cl})} \\
\text{CF}_3
\end{align*}$$
Write a mechanism which explains the formation of

\[ \text{OCH}_3 \rightarrow \text{OCH}_3 \rightarrow \text{OCH}_3 \]

Write a mechanism which explains all these products:

\[ \text{(PhCH}_2)_2\text{S} \rightarrow \text{PhCH}_2\text{CH}_2\text{Ph} \]

\[ \text{N}^+\text{Bu},\text{THF} \rightarrow \text{N}^+\text{Me} \]

\[ \text{Ph} \rightarrow \text{C} \rightarrow \text{Ph} \]

\[ \text{Ph} \rightarrow \text{C} \rightarrow \text{Ph} \]

\[ \text{Ph} \rightarrow \text{C} \rightarrow \text{Ph} \]

\[ \text{Ph} \rightarrow \text{C} \rightarrow \text{Ph} \]
Use the following experimental data to write mechanisms leading to the two products.

\[ \text{Experimental data:} \]
1. A was not formed in the presence of added \( \cdot \text{N}=\cdot \) (\( \Rightarrow \) Radical Process gives A)
2. B increased in yield if the reaction was performed in the dark. (\( \Rightarrow \) B from non-radical process)
3. A decreased in yield if the dark \( \Rightarrow \) (HONO gives A.)
4. A looks like it is formed from \( \text{S}_{n}2 \), B comes from Nuc. Aryl Attack & intramolecular amide formation

(See next page).