Assignment

1. Ireland et al., *J. Org. Chem.*, 1991, 56, 3572 reports selective preparation of $E$ and $Z$ silyl ketene acetals. Warming these compounds to 20-30 °C for a short time and subjecting them to an aqueous work-up (to cleave OSi bonds) yields a mixture of carboxylic acids (see below).

- Draw the $E$ and $Z$ silyl ketene acetals

Assume a Claisen rearrangement converts the silyl ketene acetals into silyl esters.

- Which product would each acetal yield if the rearrangement proceeded solely by way of a *chair* transition state?
- Which product would each acetal yield if the rearrangement proceeded solely by way of a *boat* transition state?

(Hint: Stereochemical problems like this can be handled easily using the transition state model → product model technique developed in-class.)

![Diagram of Claisen rearrangement](image)

2. Potential one-step sigmatropic rearrangements are shown below and on the next page. For each reaction, say

- the $[m, n]$ label
- how many electrons participate in the reaction
- whether the rearrangement is *suprafacial* or *antarafacial* with respect to each participating pi system
- whether the rearrangement can be viewed as a *migration* reaction, and if it can, whether the migration occurs with *retention* or *inversion* at the migrating group
- whether the transition state is Hückel or Möbius
- whether the rearrangement is allowed or forbidden

![Diagram of rearrangements](image)
3. Draw plausible mechanisms for the reactions shown below. *Hint:* Every mechanism is believed to involve at least one thermally allowed sigmatropic rearrangement. Wherever these rearrangements appear in your mechanism, include an \([m, n]\) label.

\[
\begin{align*}
\text{PhCH}_3 & \quad \text{CH}_3H \\
\text{Ph} & \quad \text{CD}_3 \quad \text{OH} \\
\text{N} \quad \text{H} & \quad \text{ClH} \\
\text{N} & \quad \text{+} \quad \text{CH}_3 \\
\end{align*}
\]

4. Sulfoxides are chiral molecules that do not invert configuration \((E_a \sim 40 \text{ kcal/mol})\). Allyl sulfoxides racemize relatively easily. Suggest a mechanism that accounts for this behavior.

\[
\begin{align*}
\text{S} & \quad \text{+} \quad \text{O} \\
\text{R} & \quad \text{S} \quad \text{O} \\
\text{E}_a \sim 20 & \quad \text{R} \quad \text{S} \quad \text{O} \\
\end{align*}
\]